



SENSITIVITY OF SELECTED COLORADO SOILS TO FORM ETTRINGITE/THAUMASITE WHEN TREATED WITH CALCIUM-BASED STABILIZERS AND WHEN SOLUBLE SULFATES ARE AVAILABLE

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**COLORADO DEPARTMENT OF TRANSPORTATION
RESEARCH BRANCH**

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16. Abstract The sensitivity of five Colorado soils, which were selected to represent the variety of soils likely to be treated with calcium-based chemical stabilizers such as hydrated lime or Portland cement, to the formation of potentially expansive minerals are evaluated using thermodynamic principles based on Gibb's free energy and direct measurements. Phase diagrams are used to predict the threshold levels of soluble sulfates that favor the formation of the expansive mineral ettringite, which is most widely blamed for deleterious expansion in sulfate bearing soils treated with calcium-based stabilizers. The results of the thermodynamic, phase diagram evaluation are checked against direct measurement of ettringite using differential scanning calorimetry (DSC), and the results agree well. The conclusions derived from this research are that, as expected, mineralogical differences among the soils affect the threshold level of soluble sulfates that trigger the development of ettringite and that the presence of soluble silica and the form of alumina present have a dominant effect. The research validates previous research that a safe lower limit of soluble sulfates is approximately 3,000 ppm as long as additional soluble sulfates do not migrate into the soil. A methodology is presented for using the DSC to directly assess the threshold level of sulfates for a particular soil. However, refinement of the method is a key goal of on-going research. Implementation: The DSC method to assess the potential of a specific soil to react deleteriously with a calcium based stabilizer when sulfate content in the soil is above a threshold level should be implemented by CDOT. This will require the purchase of a Q-2000, TA Instruments or equivalent DSC by the CDOT Materials and Geotechnical Branch.			
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Sensitivity of Selected Colorado Soils to Form Ettringite/Thaumasite When Treated with Calcium-Based Stabilizers and When Soluble Sulfates Are Available

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EXECUTIVE SUMMARY

Sulfate induced heave in soils treated with calcium-based stabilizers such as lime, Portland cement and fly ash is a problem in many locations across the nation. Such distress has been noted in Colorado on a number of occasions. The heaving and pavement damage at the U.S. 287 by-pass around Berthoud, Colorado, is a case in point. Because of such distress potential in sulfate bearing soils when stabilized with calcium based additives, it is imperative that precise and accurate means are developed to measure the sulfate content of such soils. Furthermore, the reactivity of these soils varies depending on the specific mineralogy of the soil and its physical properties, including gradation. The Colorado Department of Transportation (CDOT) has developed and evaluated a colorimetric based protocol (CP-L 2103) for determining the sulfate content of soils. This report documents the development of a protocol for assessing the reactivity or potential for sulfate induced heave for specific soils.

Two methods were evaluated as a means to assess the sulfate induced heave potential: a thermodynamic stability model, and direct measurement of the expansive mineral ettringite using differential scanning calorimetry (DSC). Five Colorado soils were identified and supplied by CDOT for evaluation. The funding for chemical and DSC testing of these soils at Texas A&M University was provided by the Chemical Lime Company of Fort Worth, Texas. The stability model approach is based on the concept of Gibbs free energy and that the system with the lowest free energy will ultimately be stable in a certain soils environment. The stability model approach was able to determine the threshold sulfate content at which ettringite grows, that the threshold sulfate content varies from soil to soil, and that the amount of ettringite that grows varies among the five soils. These threshold levels for the five Colorado soils are reported within this document. Although the thermodynamic stability model is shown to be a useful tool for this type of evaluation, this type of analysis requires in-depth geochemical knowledge, which is typically beyond that of the practicing civil engineer.

The stability model-based findings were substantiated by direct measurement of ettringite as a function of time of curing using the DSC. These findings substantiated the hypothesis behind the research that both methods can be used to evaluate the reactivity (potential of sulfate-induced heave due to ettringite crystal growth) for soils of different mineralogies and geologies.

The researchers recommend an approach to assess soil reactivity. This approach is to prepare a soil slurry (1 part of blend of soil, calcium hydroxide and soluble-sulfate to 10 parts water). The sulfate content should vary (5,000, 10,000, and 20,000 ppm) by weight of the soil, and the calcium hydroxide content should be 5 percent by weight of soil. The soil fraction is comprised of only the fraction of the soil, which is smaller than 75 μm (silt and clay). Individual samples of slurry should be mixed in a centrifuge tube, cured for varying periods of time at 40°C and then centrifuged again to provide a paste from which 10 mg samples are collected for DSC testing. The amount of ettringite developed over time for various soils can then be used as an indicator or reactivity of a specific soil.

Implementation Summary

The DSC method to assess the potential of a specific soil to react deleteriously with a calcium based stabilizer when sulfate content in the soil is above a threshold level should be implemented by CDOT. This will require the purchase of a Q-2000, TA Instruments or equivalent DSC by the CDOT Materials and Geotechnical Branch. Soils from around the state representing the various mineralogical and geological conditions of the state should be tested using the recommended protocol. The reactivity of these various soils should be catalogued, and as more soils are tested, a correlation among soils properties including mineralogical properties and physical properties should be developed. As part of this evaluation step, the variability among these soils should be noted and the number of replicate samples required should be determined to provide an acceptable level of confidence.

Development of a catalogue of soil reactivity used in conjunction with CP-L 2103 to determine a reliable soluble sulfate content of the soil will provide a data base that can reduce the risk of sulfate-induced heave, and that will save the state considerably by avoiding such distress and the need for repair due to such distress. There is no quick fix to the problem of sulfate-induced heave in soils treated with calcium based stabilizers. A well thought out plan based on a sound test methodology and a sound hypothesis is required. We believe that the data base development is the most logical method and that with the development of the data base a considerable reduction in risk can be achieved

Although this method is proposed for implementation, the method will probably require additional refinement that can be gained during the process of evaluating various CDOT soils. Such refinement may include adjustments or changes in the step-by-step protocol as well as identification of the number of replicate test samples required to achieve the desired reliability or level of confidence.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
BACKGROUND	2
EVALUATION OF FIVE COLORADO SOILS	4
Classification of Soils	4
Sulfate Test Results Using TxDOT Colormetric Method.....	6
Thermodynamic Modeling of Potential for Ettringite Formation.....	7
Direct Measurement of Ettringite Mineral Phase	13
FINDINGS AND DISCUSSION.....	21
Sensitivity of Soils to Ettringite Based on DSC Testing	24
Comparison of Thermodynamic Model and DSC Results	28
Limitations of DSC	29
CONCLUSIONS.....	30
PROPOSED METHODOLOGY	31
Approach.....	31
Procedure	32
REFERENCES	37
APPENDIX A: COLORADO STATE MAP WITH THE LOCATIONS OF THE RESEARCH TEST SAMPLES IDENTIFIED.....	A-1
APPENDIX B: SUMMARY OF TEX-145E.....	B-1
APPENDIX C: SUPPORTING DATA	C-1

LIST OF FIGURES

Figure	Page
1	Thermodynamic phase diagrams for Halaquepts (C1) and Ildefonso (C2) soils when treated with 5 percent lime with natural sulfate contents.....9
2	Thermodynamic phase diagrams for Berthoud (C3) and Bloom clay (C4) soils when treated with 5 percent lime with natural sulfate contents.....10
3	Thermodynamic phase diagrams for Dwyer sand (C5) when treated with 5 percent lime with 2000 ppm soluble sulfate contents11
4	Sensitivity of Colorado soils to form ettringite with increasing amount of soluble sulfates identified using thermodynamic models12
5	Heat flow from DSC for pure ettringite synthesized in lab15
6	Ettringite quantification in soils based on comparison of heat signals with the control sample20
7	Highest observed ettringite concentration in all the soils for different sulfate content when reacted with 5 percent lime after 56 days curing21
8	Highest observed ettringite concentration in Berthoud soils with increasing sulfate contents when treated with 5 percent lime at different curing periods.....23
9	Sensitivity of soil C1 to form ettringite with time and increasing sulfate concentrations25
10	Sensitivity of soil C2 to form ettringite with time and increasing sulfate concentrations25
11	Sensitivity of soil C3 to form ettringite with time and increasing sulfate concentrations26
12	Comparison of thermodynamic model results (a) and DSC results (b) for Colorado soils treated with 5 percent lime and cured for 56 days.28

LIST OF TABLES

Table		Page
1	Soil classification based on USDA textural classification chart.....	4
2	Particle size fractions in soil identified by fractionation of soil	5
3	Semi-quantitative estimate of percentage mineral fractions in soil using x-ray diffraction	5
4	Water soluble sulfate concentration in soils identified by Tex-145E	6

INTRODUCTION

This research focuses on the development of a method to identify the potential of Colorado soils to react with soluble sulfates to form expansive, sulfate-containing minerals such as ettringite and thaumasite. These minerals are prone not only to expand when sufficient amounts of water are available, but the process may also result in a loss in the ability of the stabilized subgrade in question to support loads.

Little et al. (2005) demonstrated by using thermodynamic stability, or phase, diagrams that the mineralogy and chemistry of soils affect their reactivity with sulfates and therefore the potential for deleterious reactions. While phase diagrams are excellent tools, the user is required to make decisions in using these models that require a substantial familiarity with geochemistry and the ability to make such decisions as which minerals to include or exclude from the analysis based on reaction kinetics. The phase diagram approach is very useful, but since a high level of geochemical expertise is required to use it, the method is not amenable for most practicing engineers.

The differential scanning calorimeter (DSC) can be used to directly measure the amount of ettringite or thaumasite in a soil. Since these two minerals cause the swelling, heaving, and loss of strength normally associated with sulfate-induced damage in lime, cement, and sometimes fly ash treated soils, use of the DSC to measure the amount of these minerals that grow when a calcium-based stabilizer is added offers a direct method to assess risk.

This report focuses directly on the use of the DSC as a tool to assess the sensitivity of sulfate-bearing soils treated with calcium-based stabilizers to react deleteriously. The report also compares the predictive results of the thermodynamics-based phase diagram approach with direct analysis using the DSC to define the susceptibility of five Colorado soils to sulfate-induced expansion due to ettringite mineral growth. The report is divided into five sections.

Following this introductory section is a section that provides a general background description of the minerals that result due to the presence of sulfates in clay soils treated with calcium-based stabilizers. The third section describes the five Colorado soils evaluated in this study and the evaluation protocols used. Section four discusses findings from the study, and finally section five presents conclusions.

BACKGROUND

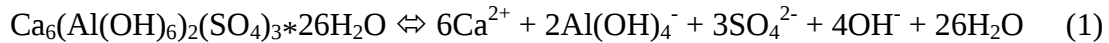
The hydrous sulfate mineral, ettringite ($\text{Ca}_6(\text{Al}(\text{OH})_6)_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), has been implicated in sulfate attack on cement and concrete, as well as stabilized soils (Jallad et al., 2003, Warren and Reardon, 1994, Crammond, 2002). Ettringite is a hydrous calcium aluminosulfate mineral that precipitates in environments with high pH and high sulfate activity (Perkins and Palmer, 1999). Activity is defined as the effective concentration. It is the product of activity coefficient and concentration. The activity of an ion represents the effective concentration available for reaction. Ettringite often forms when a calcium-based stabilizer is added to sulfate-bearing clay soils (Mitchell, 1986, Petry and Little, 1992), Petry, 1994, Harris et al., 2003). Ettringite, which tends to form very small (μm), fibrous crystals (Moore and Taylor, 1970) damages the soil structure through mineral expansion during precipitation. To make the matter even more complex a second mineral, thaumasite, may develop through the isostructural transformation of ettringite at temperatures below about 15°C in the presence of soluble silica and carbonate. The result of the formation of ettringite can be considerable expansion, while the formation of thaumasite will result in a loss of strength and is normally preceded by the formation of ettringite (Jallad et al., 2003, Crammond, 2002, Edge and Taylor, 1969, Crammond et al., 2001, Thaumasite Expert group, 1999, Jacobson et al., 2003).

The amount of damage due to ettringite formation depends on a number of factors including: (i) the thermodynamic favorability of ettringite precipitation in specific soils, (ii) the quantity of limiting reactants that stoichiometrically control the mass of ettringite formed, (iii) the migration of water, sulfate and other ions that support continued ettringite nucleation, (iv) the strength of the pozzolanic or cementitious matrix, and (v) the spatial arrangement of the

ettringite crystals in the soil matrix. It is possible for ettringite to grow in voids that can accommodate their growth without substantial expansion. It is also possible for ettringite crystals to grow within a dense matrix that will not accommodate their growth without expansion.

The ettringite mineral group has a general mineral formula of $(Ca_6(X(OH)_6)_2(Y)_3 \cdot 26H_2O)$, where X is a trivalent metal such as Al^{3+} , Fe^{3+} , or Cr^{3+} and Y is an oxyanion such as SO_4^{2-} , CO_3^{2-} , SeO_4^{2-} , or CrO_4^{2-} (Perkins and Palmer, 1999, Barnett et al., 2001, Crammond et al., 2001). Minerals with alternative substitutions of other ions, such as $B(OH)_4^-$ and AsO_4^{3-} , are possible but not common in most surface environments. The one exception is thaumasite $(Ca_3(Si(OH)_6)(CO_3)(SO_4) \cdot 12H_2O)$, a silicon-bearing member of the ettringite mineral group which can form a solid solution with ettringite (Barnett et al., 2002, Cripps et al., 2003).

Dissolution-precipitation reactions control the stability of ettringite in lime-treated soils. The solubility of ettringite can be written as a dissolution reaction:



Ettringite precipitates in highly alkaline solutions with high activities of Ca^{2+} , SO_4^{2-} and Al^{3+} . These reactants exhibit strong spatial variation at a variety of scales due to variation in their content with the geologic parent material and migration within the soil column (Myneni et al., 1998). Additional geochemical controls on ettringite stability include temperature and dissolved CO_2 and H_2O activities (Damidot and Glasser, 1993). The kinetics of ettringite precipitation-dissolution is fast, precipitation-dissolution achieves steady state in approximately 150 hours at pH 11.5 (Damidot and Glasser, 1993).

EVALUATION OF FIVE COLORADO SOILS

Classification of Soils

Five soils were identified to have significant sulfate heave potential by the Colorado Department of Transportation (CDOT). These soils were evaluated using thermodynamic modeling and differential scanning calorimetry (DSC) techniques to determine their potential to form the mineral ettringite. The locations of these five soils are shown on a map of the state of Colorado in Appendix A.

Each soil supplied by CDOT for evaluation belonged to a different soil series. Mineralogical characteristics and the sulfate concentrations of these soils were determined in order to identify the reactivity of these soils when treated with lime. The soils were treated with increasing concentrations of soluble sulfates to determine sensitivity to ettringite formation with increasing sulfate content.

Table 1. Soil classification based on USDA textural classification chart.

Soil series	Typical pedon	Notation used
Halaquepts	Sandy loam	C1
Ildefonso	Sandy loam	C2
Berthoud	Clay loam	C3
Bloom clay	Silty clay loam	C4
Dwyer sand	Fine sand	C5

Our soil classifications were consistent with those of CDOT as shown in Table 1. Mineralogical characterization of soil samples was based on x-ray diffraction (XRD) analysis after fractionation. Sand, silt and clay fractions were analyzed separately in order to obtain a semi-quantitative estimate of the mineralogy of the soil. Identification of clay minerals was

facilitated by using oriented samples in order to enhance the basal reflections. These results are shown in Table 2.

Table 2. Particle size fractions in soil identified by fractionation of soils.

Soil Type	Sands (%)	Silts (%)	Clays (%)
Halaquepts (C1)	70	20	10
Ildefonso (C2)	58	27	15
Berthoud (C3)	37	28	35
Bloom Clay Loam (C4)	19	51	30
Dwyer Loamy Sand (C5)	76	17	7

As expected, the mineralogy varied considerably among the different soil size fractions. X-ray spectra for the clay fractions were determined after magnesium saturation, glycol solvation and various heat treatments in order to distinguish among clay minerals. Major mineral fractions identified in these soils are shown in Table 3. The clay content was lower in the Halaquepts and Dwyer sand soils than in the other three soils. Considering clays to be the major alumina releasing source in soils, these two soils would be expected to have the lowest reactivity among the five soils in terms of ettringite formation.

Table 3. Semi-quantitative estimate of percentage mineral fractions in soil using x-ray diffraction.

Minerals	C1	C2	C3	C4	C5
Quartz (sand and silt)	69	63	50.5	53	73
Feldspars (sand and silt)	10.5	5.5	6.5	6	12.5
Calcite (sand and silt)	5	12	2.7	5	1
Dolomite (sand and silt)	-	1	2	2.5	1.5
Mica (sand and silt)	2.5	0.5	1	1.5	1
Kaolinite	3	10	7	7.5	2.5
Illites	4	3	10.5	10	1.5
Smectites	2	1.5	15	9	2.5
Chlorite	0.5	1	2.5	3	1
Others	3.5	2.5	2.3	2.5	3.5

The major difference among the Ildefonso, Berthoud and Bloom clay is the concentration of smectitic clays. To determine the available aluminum and reactivity of these soils, the

solubility properties of other mineral phases must also be considered. Solubility information was not available at the time of this analysis; therefore assumptions were made based on established properties of the soils such as mineralogy and physical properties of the minerals. Among the different clays providing alumina for ettringite formation, the reactivity of kaolinites (one silica tetrahedral layer sharing a row of atoms with an aluminum octahedral layer or a one-to-one mineral) is probably greater (faster) than the 2:1 silica tetrahedral to aluminum octahedral layer minerals (Mitchell and Dermatas, 1992). Furthermore, the smaller surface area of kaolinite compared to smectite may result in less consumption of calcium ions from lime, and the hexagonal morphology of kaolinite may lead to more dissolution of alumina from edge sites. Ettringite formation during the early hydration period should be directly related to the consumption of calcium ions.

Sulfate Test Results Using TxDOT Colorimetric Method

Sulfate contents of the natural soils were determined by following test method TEX-145E, which is a colorimetric method and is very similar to CDOT method CP-L 2103 (See Appendix B). The results of TEX-145E summarized in Table 4 are for an average of three different samples selected from each soil. Sulfate levels in all but the Bloom clay were found to be below 3,000 ppm.

Table 4. Water soluble sulfate concentration in soils identified by Tex-145E.

Soil Type	Sulfate Content (ppm)
Halaquepts (C1)	1,680
Ildefonso (C2)	2,400
Berthoud (C3)	2,760
Bloom Clay (C4)	11,840
Dwyer loam (C5)	100

Soluble sulfate concentrations for Halaquepts and Dwyer loamy sand were below problematic levels based on TxDOT standards, 2,000 ppm, (Table 4). The observed concentrations for Ildefonso and Berthoud soils were just above 2,000 ppm, and the soils can be

considered to have a low level of risk for ettringite formation, based on soluble sulfate content alone. However, it is instructive to note that one of the Berthoud soil samples had a sulfate content of 6,520 ppm, indicating variability within the composite sample. The value was not included in the calculation shown in Table 4 as all the other tested samples were much closer to the value reported in Table 4. The variability in soluble sulfate contents for the soils used in sample preparation for DSC testing was small with a coefficient of variation of less than 10 percent.

Thermodynamic Modeling of Potential for Ettringite Formation

Thermodynamic models have been successfully used to predict dissolution and precipitation of the ettringite phase in complex systems (Warren and Reardon, 1994, Myneni et al., 1998, Damidot and Glasser, 1992, Mohamed et al., 1995). Models by utility are simplified representations of complex natural systems. In a geochemical model a soil is represented as a combination of minerals and ions. The stability field of minerals changes with the interacting environment, which is predicted by the model based on thermodynamic properties of the minerals (Little et al., 2005). Soils differ from each other due to the difference in phase composition, soil chemistry, and dissolved ion concentrations upon interaction with water. The predominance approach considers the aqueous chemistry of the system at a specified condition and determines the dominant species present at equilibrium. Soils are characterized in this model approach based on their soluble ion concentrations and mineralogy and are allowed to react with a known quantity of calcium hydroxide and sufficient water to form mineral phases. Soluble ions are identified through chemical analysis and soil composition is identified based on mineralogical analysis. The minerals present are subjected to speciation so that equilibrium based on mass and charge balance conditions is achieved. The stability fields are evaluated for the surrounding environment where a given mineral can exist in an unstable, stable or a metastable state. The metastable state, in most cases, is due to a slow reaction rate, which is dependent on the kinetics of the reaction (Othmer, 1976). Kinetics of mineral dissolution is not considered in the model and hence the accuracy of quantitative prediction within a model may not always precisely reflect performance in the field. Moreover the thermodynamic data set used in modeling consists of thermodynamic parameters for pure minerals, which are never

encountered in a natural system. Dissolution properties of minerals change with impurities and hence precipitation ratios observed in the field can vary from quantities predicted by the model.

Development of Phase Diagrams

A semi quantitative estimate of the mineralogy was obtained using x-ray diffraction. Sand, silt and clay particles were separated by soil fractionation and analyzed separately to identify the minerals present. These mineralogy data were used as the basis to define the available reactants in the soils when reacted with calcium hydroxide. The soil system was also characterized in the model in terms of its chemical composition. Concentrations of ions in solution were determined by chemical analysis at a soil to water dilution ratio of 1:10. The soil system containing dissolved ions and minerals was subjected to speciation at a pH of 12 in the presence of five percent calcium hydroxide by weight. The activities of ions present in the system were determined by speciation and used to develop phase diagrams to identify stable mineral phases in the system. The stability fields were based on thermodynamic properties of minerals and the net activity of ions present in the system.

Phase Diagrams for Five Colorado Soils

Thermodynamic models were developed for the five CDOT soils at their natural sulfate concentrations to identify the stability field of ettringite when the natural soil was allowed to react with lime. Soluble ion concentrations of these soils were determined by chemical analysis (Table 1-C). In developing the model, the sand fraction was considered non-reactive, and only 10 percent of the silt fraction of the soil was considered reactive. The latter is an assumption that was observed consistently for each soil. The kinetics of dissolution of minerals was not considered in the model. Mineral dissolution is dependent on the surface area of the minerals (Harris et al., 2003) and also on dissolution kinetics of the various minerals.

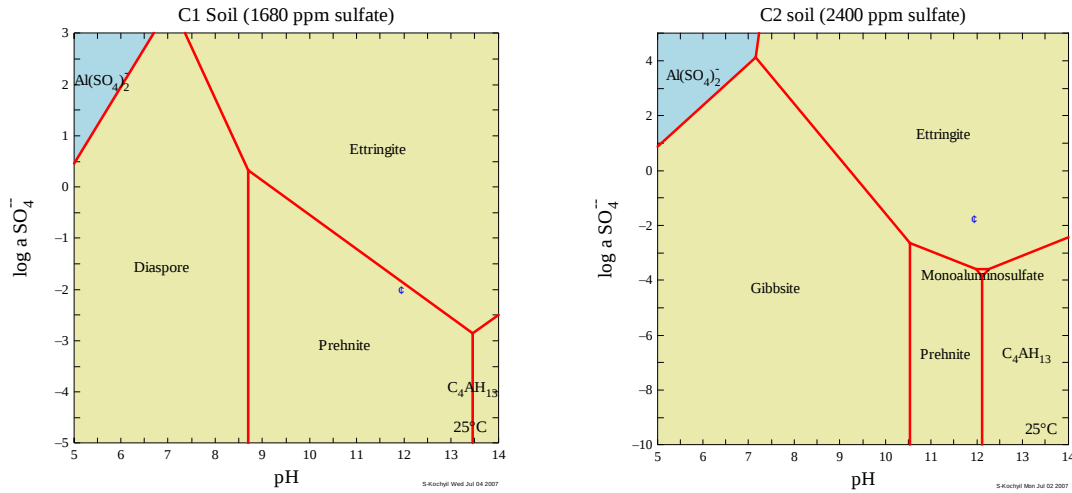


Figure 1. Thermodynamic phase diagrams for Halaquepts (C1) and Ildefonso (C2) soils when treated with 5 percent lime with natural sulfate contents.

The thermodynamic model results for the Halaquepts and Ildefonso soils when treated with calcium hydroxide are presented in Figure 1. In Figure 1 and in all subsequent phase diagram figures, the Y-axis represents the logarithm of the activity of the sulfate ion. Activity is effective concentration of ions in the system. In Figure 1, the Y-axis coordinate of the locus is the log of the activity of sulfate ions at natural sulfate contents in soil. Natural sulfate levels in both soils are nearly the same (Table 4). The Ildefonso soil has a higher concentration of clays and lower silt to clay ratio than the Halaquepts soil. The clay fraction of the Ildefonso soil is dominated by kaolinites with smectites and illites present in smaller concentrations. On the other hand, the clay content in the Halaquepts soil is lower overall with kaolinite, smectite and illite present in approximately equal proportions. The behavior of these soils when treated with calcium hydroxide is likely to be directly affected by mineralogy as the higher clay content can result in more available alumina for ettringite formation. This is evident in the phase diagrams where the locus of the pH of 12 (representing the alkaline condition that develops due to lime treatment) and the sulfate activity of the soil in question is in the polygon representing ettringite in the higher clay content Ildefonso soil but falls just outside the ettringite polygon for the Halaquepts soil. It is also important to note that the difference in solubility properties of minerals

in the silt fraction and their relative concentration in each soil contributes to the difference in behavior.

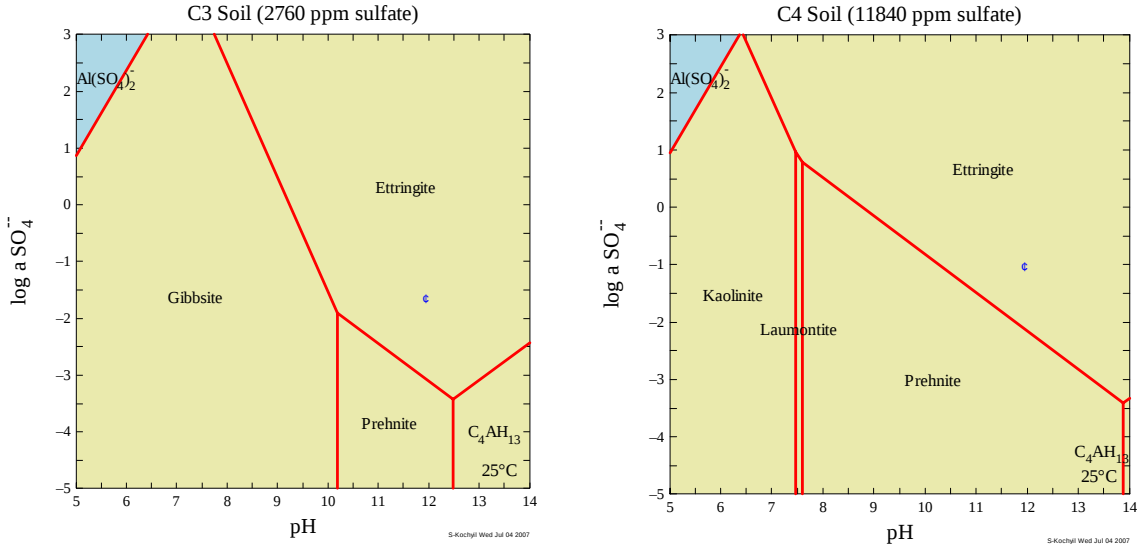


Figure 2. Thermodynamic phase diagrams for Berthoud (C3) and Bloom clay (C4) soils when treated with 5 percent lime with natural sulfate contents.

Considering Berthoud and Bloom clay soils at their natural sulfate content, ettringite appears to be the stable phase after the soil is allowed to react with calcium hydroxide (Figure 2). Both the mineralogy and the sulfate content of the two soils are considerably different and so are the shape and size of the stability fields. Although the total clay content and the relative distribution of different clay mineral fractions are similar for the two soils, the silt to clay ratio is different. Soil mineralogy tests confirm that Bloom clay has higher silt content than the Berthoud soil with silt to clay ratio of 1.45 for Bloom clay compared to only 0.8 for the Berthoud soil (Table 2). Silica bearing phases like feldspars and opal, when contained in the fine silt or even clay sized fraction, may provide the soluble silica to limit ettringite formation during lime treatment. This difference in mineralogy can determine the stability of ettringite precipitated in these systems during lime treatment and can also define the threshold level for ettringite formation in these soils.



For Dwyer loamy sand, the soluble sulfate content based on the TxDOT sulfate testing method was found to be about 100 ppm. Based on our current empirical assessment, soils with sulfate content below 2,000 ppm can be considered non-problematic in terms of ettringite formation. As a conservative approach, this soil was modeled with a soluble sulfate content of 2,000 ppm in lieu of 100 ppm in the development of the stability field of ettringite after treatment with calcium hydroxide (Figure 3). The model shows prehnite to be the stable phase in the system at a soluble sulfate content of 2,000 ppm.

In order to investigate the sensitivity of soils to ettringite formation, the soluble sulfate concentrations available to react within these soils were varied in the model. The natural sulfate contents of these soils were different and hence to compare their behavior the total available soluble sulfates reacting with these soils was varied from 2,000 to 20,000 ppm. The model considers a closed system for mass balance calculations and only considers the thermodynamic

stability of these minerals in the system. Kinetics of dissolution of minerals is not accounted for and hence a complete dissolution of minerals may over predict the concentrations that can form in these systems.

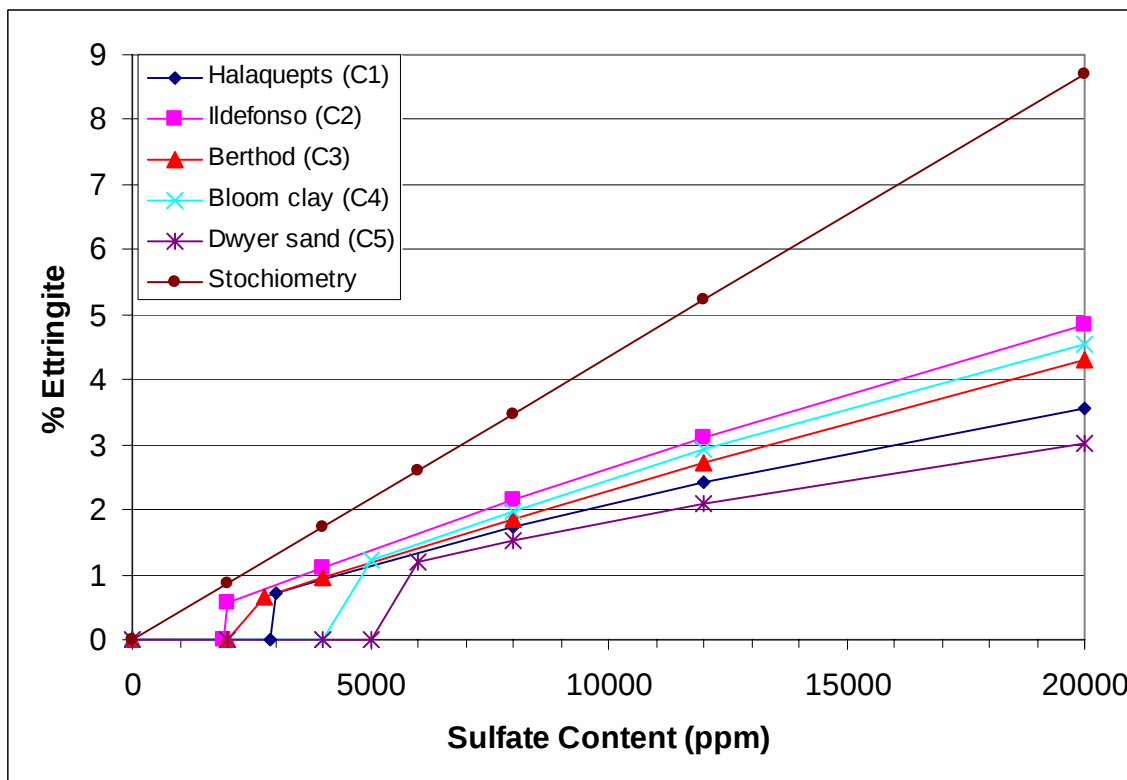


Figure 4. Sensitivity of Colorado soils to form ettringite with increasing amount of soluble sulfates identified using thermodynamic models.

The sensitivity of the five soils to form ettringite was evaluated using the thermodynamic model previously discussed and the results are presented in Figure 4. Phase diagrams for individual soils showing changes in the stability fields at different sulfate contents are presented in the Appendix (Figure 1-C, 2-C, and 3-C). Reactivity of soils for a given sulfate concentration is observed to vary based on the mineralogy of these soils. A linear correlation between increase in concentration of ettringite and increase in sulfate content is shown in Figure 4. The stability field for ettringite was found to be different for each soil type. Ettringite was found to be a stable phase for soils C1, C2 and C3 at lower sulfate concentrations (below about 2,000 to 3,000 ppm)

when compared to soils C4 and C5. Ettringite forms a stable phase in soil C4 at above about 4,000 ppm and for C5 at above about 5,000 ppm.

The line labeled “stoichiometry” in Figure 4 represents the maximum amount of ettringite that can theoretically develop when sulfate is the limiting reagent. The ettringite concentrations predicted to form in all soils were found to be less than the amount that can stoichiometrically form based on available sulfate ion concentrations. The amount of ettringite formed as a function of soluble sulfate content as predicted by the model is higher for soils C2, C3 and C4 than for soils C1 and C5. In other words, a higher concentration of ettringite is predicted in soils C2, C3 and C4 at a given sulfate content when compared to soils C1 and C5. Mineralogical analyses show that soils C2, C3 and C4 have higher clay concentrations than soils C1 and C5. Furthermore, the reactive silt fraction may vary among these soils, which can also affect the reactivity of these soils; but this was not established. Release of soluble silica can consume available calcium needed for ettringite formation and can limit the formation of ettringite during initial hydration periods (Wild et al., 1999).

Based on model results, the reactivity of soils C1 and C5 were found to be lower than the other three soils. Ettringite forms the stable phase for soil C1 in the system at a sulfate concentration of 3,000 ppm. Thereafter, the amount of ettringite formed with a further increase in sulfate content was found to be less than for soils C2, C3 and C4. The lower clay fraction in soil C1 and/or relatively higher silt to clay ratio in soil C1 may contribute to this behavior. Ettringite was found to be the stable phase in soil C5 at soluble sulfate concentrations above 5,000 ppm. The comparatively low clay content of these soils may be the reason for the lower ettringite formation potential.

Direct Measurement of Ettringite Mineral Phase

The efficacy of using differential scanning calorimetry (DSC) to identify concentrations of ettringite forming in lime-treated soils was investigated as a part of this research. In DSC the

difference in the amount of heat required to raise the temperature of a sample and a reference is measured as a function of temperature. When a sample undergoes physical transformation, depending on whether the process is endothermic or exothermic, the amount of heat flowing to or from the sample changes in comparison to the reference when both are maintained at the same temperature. A DSC measures the amount of heat absorbed or released during these transitions based on the heat flow between the sample and the reference. Many researchers have successfully used thermal analysis techniques to study ettringite formation in cement concrete (Ogawa and Roy, 1981, Shimada and Young, 2001, Odler and Abdul-Maula, 1984). Mehta, 1972, described the stability of ettringite under drying conditions and observed that part of ettringite decomposes at around 95°C. Ettringite has a characteristic endothermic peak in the DSC at around 110°C (Ogawa and Roy, 1981). This can be used for quantification purposes where the area of the dehydration peak is used to determine the quantity of ettringite in the system.

Structure of Ettringite

Ettringite and thaumasite minerals tend to form very small (µm), fibrous crystals that are present in aggregate masses (Moore and Taylor, 1970). Pure ettringite has a tubular structure with columns and channels running parallel to the c-axis. The columns are composed of $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}^{6+}$ where a chain of one alumina and three calcium polyhedrons repeat uniformly. $[Al(OH)_6]^{3-}$ is linked to its neighbors through groups of three Ca^{2+} ions. The coordination polyhedra are completed by water molecules. Each calcium polyhedron is shaped as a trigonal prism with water and OH ions occupying four apices each (Moore and Taylor, 1970). Oxygen in OH ions is shared between calcium and aluminum polyhedrons bridging the two continuous chains extending along the c-axis of the mineral. The channel in between columns consists of $[(SO_4)_3 \cdot 2H_2O]^{6-}$ ions.

Water is important to the stability of the mineral ettringite. Water molecules present in ettringite can be considered to be present in four distinct locations: in the inter column channel,

at the two main apices, at two additional apices of calcium polyhedra and as hydroxyl ions linking calcium and aluminum ions. Ettringite loses its structure with loss of water molecules from the channels and columns (Shimada and Young, 2001). Numerous studies have been conducted on the stability of ettringite and many differences of opinion exist on the structural changes occurring during dehydration. Many researchers agree that 20 – 24 molecules of water from the mineral are lost at around 70°C. This corresponds to water from inter column channels, from the main apices and half of the water from additional apices of calcium polyhedron (Moore and Taylor, 1970). Due to water loss, the coordination number of calcium changes resulting in a rearrangement of residual water molecules to retain charge balance of calcium polyhedra. Interaction between columns and sulfate ions changes distorting the parallel arrangement of columns and destroying the long range order of the molecule. Short range order is maintained until the bridging hydroxyl ions are removed from the structure. Ettringite maintains a short range order until the mineral loses 20 water molecules from the structure. A further loss is an overlapping process between removal of water from calcium polyhedra and the bridging hydroxyl ions, which disrupts the short range order of the mineral (Shimada and Young, 2001). Due to these differences the conditions of dehydration and the associated structural changes with dehydration will be different for each type of water molecules (Shimada and Young, 2001).

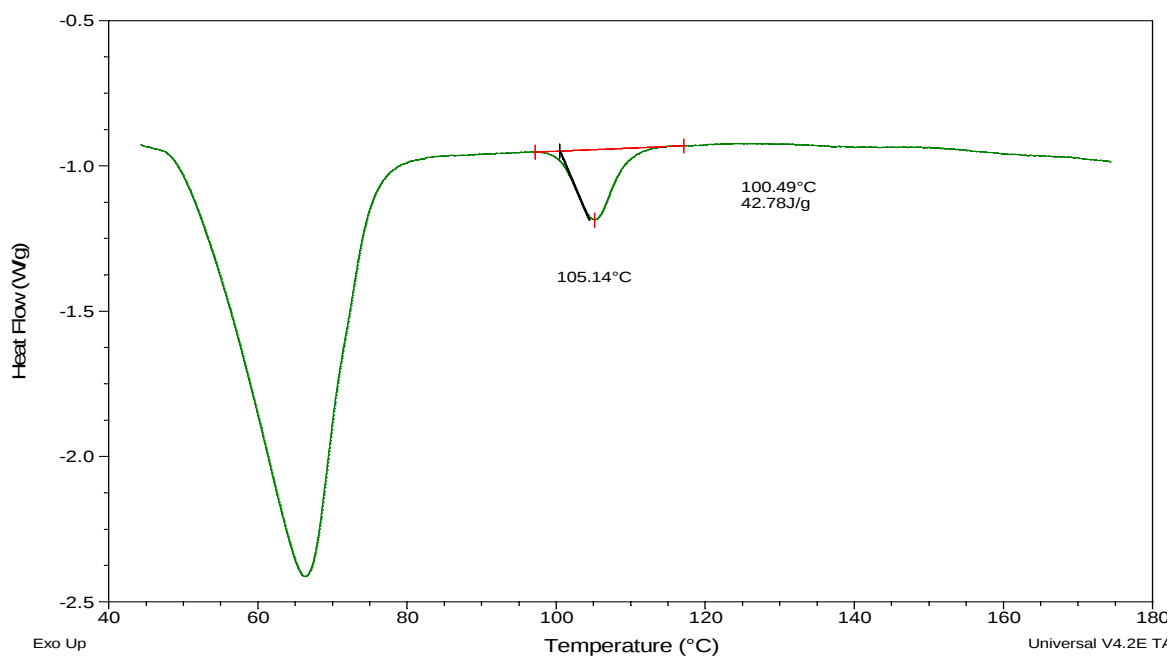


Figure 5. Heat flow from DSC for pure ettringite synthesized in lab.

Pure ettringite synthesized in our lab was tested to determine the properties and behavior inside the DSC, Figure 5. Samples were precipitated in our lab and stored under controlled conditions for 90 days. The mineral was found to lose water of crystallization with increasing temperature (Shimada and Young, 2001, Moore and Taylor, 1970). The larger endotherm for pure ettringite observed above 65°C cannot be used for identifying ettringite in soils as it overlaps with the dehydration endotherms of physical and chemically bound water in soils. Hence the peak located close to 105°C was selected as the characteristic peak for ettringite dissociation, Figure 5. This peak was used for quantitative analysis and the area of the peak was used to determine the amount of heat generated (in joules). Location of the peak for synthesized ettringite correlates well with observations of other researchers (Odler and Abdul Maula, 1984, Ogawa and Roy, 1981).

Ettringite Synthesis

Pure ettringite was synthesized in our lab using a modified method (Perkins and Palmer, 1999, Cody et al., 2004) and was analyzed (with the DSC) to determine the properties and behavior. Each step within the protocol was conducted inside a glove box in which the atmosphere was continuously bubbled through 1 N NaOH to remove CO₂. Briefly stated, the protocol is as follows:

1. 25 ml of aluminum sulfate solution was mixed with 20 ml of saturated calcium hydroxide solution. The container was then capped and the solution is mixed thoroughly.
2. The final solutions were incubated for 24 hours.
3. The contents of the containers were transferred to a ceramic filter funnel and rapidly vacuum filtered through a 7 cm diameter, 1.6 µm filter to filter out precipitated ettringite.
4. The pH of the final supernatant solutions was determined.
5. Precipitates were dried and stored at room temperature inside a desiccator with a cup of saturated CaCl₂ solution to maintain a relative humidity of approximately 30 percent.

6. XRD and SEM analyses were conducted to analyze the properties of the precipitate.

Sample Preparation

Samples were prepared using 2.5 grams of selected soils with different sulfate levels and were treated with five percent calcium hydroxide. The samples were prepared in a centrifuge tube and then mixed with lime at optimum moisture content and cured at 40⁰C for different time periods. From the 2.5 gm soil samples, 10 mg samples are selected randomly and tested in the DSC. The steps are as follows:

1. Representative soil samples were selected from field collected samples and air dried to uniform moisture content.
2. Soil was tested for sulfate content following TEX-145E.
3. Remaining soil was pulverized to pass 75 μ sieve.
4. Five percent calcium hydroxide by weight was mixed with water using a vortex mixer to ensure uniform mixing.
5. Various concentrations of sodium sulfate were added to the lime solution to investigate the effect of increasing sulfate content on ettringite formation. The contents were thoroughly mixed to form suspensions.
6. 2.5 grams of soil were added to the appropriate suspension discussed in step 5 and was mixed thoroughly to ensure uniform mixing of lime, sulfates and soil.
7. Prepared samples were subjected to accelerated cure at 40⁰ C for the required time. Replicate samples were prepared for each soil type at different sulfate contents. Additional water was added to keep the sample moist during curing to ensure that water was not a limiting factor in ettringite formation.
8. At the end of curing period, soils were taken out of the centrifuge tubes and water in the sample was removed by drying the soil with acetone to stop further hydration (“freeze the hydration at that specific point”).

9. The sample was filtered using a frit sand filter and the residue was dried in oven at temperature below 45⁰C for 4 hrs.
10. Prepared samples were stored in desiccators to avoid re-adsorption of water.

The mineral ettringite starts to loose water at near 50⁰C and hence the oven temperature was maintained below 45⁰C. Acetone also helps remove some of the water from the calcium silicate hydrate phase and helps to remove its broad hydration peak in the DSC spectra at lower calcium-silicate-hydrate (CSH) levels (Hime et al., 2000).

Preparation of Control Samples

Control samples were used to identify the response of the soil with different quantities of ettringite added to the soil. The residue soil from sulfate testing based on TxDOT colorimetric testing (Tex 145-E) was used. Since all the natural sulfate content was removed from the soil no ettringite formation should occur in control samples during lime treatment. The steps are summarized as follows:

1. Control sample was prepared by removing the natural sulfates in soil by dissolution using deionized water at a 1:20 dilution ratio.
2. The soil was air dried and ground to pass 75 μ sieve and treated with five percent calcium hydroxide.
3. Pure ettringite synthesized in the lab was added to these soils to determine the intensity of heat signals for different concentrations of ettringite.
4. The quantity of ettringite formed after lime treatment was determined by comparing the heat signal from natural soil to the control sample.

Analysis

The formation of ettringite in soils is not uniform and hence the amount formed at different locations in a single sample may vary. The small sample size (10 mg) used in the DSC for testing may be one of the reasons for this variability. Due to the overlapping effect of the endothermic and exothermic peaks from cementitious and pozzolanic products formed in lime treated soils, differentiating the heat signals given by the DSC becomes difficult for low ettringite concentrations when hydration effects interfere. Hence, in some cases, ettringite signals need to be enhanced by adding a small known amount of synthesized ettringite in order to identify the end points of the endotherm signal. De-convolution software can also be used instead of adding ettringite to differentiate the signal. This was not available for the machine used in this study and hence the addition of ettringite was used during testing. The signals obtained were then compared with the control sample to identify the quantity of ettringite formed in the natural soils during lime treatment.

Ten (10) mgs of prepared sample were extracted from a random location in the treated soil, and was used in DSC testing. An ultra high purity N₂ gas environment was used in testing to limit the oxidation of organic matter in soils at temperatures above 100⁰C. A slow heating rate was selected to obtain higher resolution of the endotherm signals and also to reduce the effect of overlapping signals from other minerals, if any, that might disintegrate within the region of interest. The protocol steps involved here are as follows:

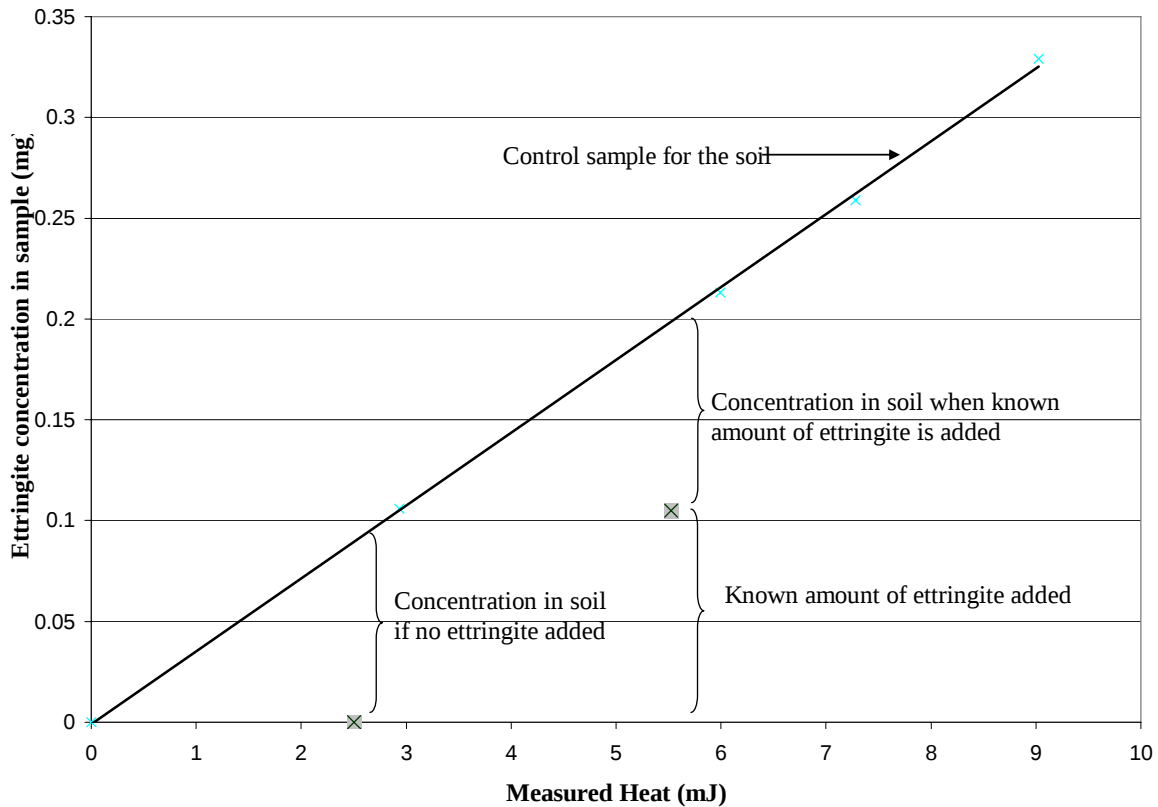


Figure 6. Ettringite quantification in soils based on comparison of heat signals with the control sample.

1. Capture a 10 mg sample.
2. Heat at a rate of $2.0^{\circ}\text{C}/\text{min}$.
3. Purge with N_2 gas at a flow rate of 10 ml/min.
4. Test over a temperature range 25°C to 175°C .
5. Determine the area of the measured heat flow signals from the sample at around 105°C by integrating with respect to time to determine the energy in Joules using the analysis software for the DSC.
6. Compare heat signals from the soils with values obtained for a control sample to determine the amount of ettringite formed. Details are given above (Figure 6).
7. The percentage ettringite obtained from analysis was plotted against sulfate concentration to determine the sensitivity of soil to sulfate concentration.

FINDINGS AND DISCUSSION

All samples showed progressively increasing ettringite concentrations with increasing sulfate contents for each period (up to 56 days). Sodium sulfate was used as the form of additional sulfates in the soils evaluated. The availability of alumina bearing phases from clay minerals can be considered a key, if not the limiting reagent, in ettringite formation. Although the trend for ettringite growth closely follows the available clay content in soils, the observed weight percentages of ettringite are not proportional to the clay concentration (Table 2). Soils are heterogeneous and complex systems, and this complexity affects reactivity significantly (Sverdrup, 1996, Gaans, 1998). This complexity makes it difficult to predict soil performance, and the synergy of interactions and processes can influence the precipitation of secondary minerals in the system. Concentrations shown in Figure 7 are based on weight percentages observed in 10 mg samples.

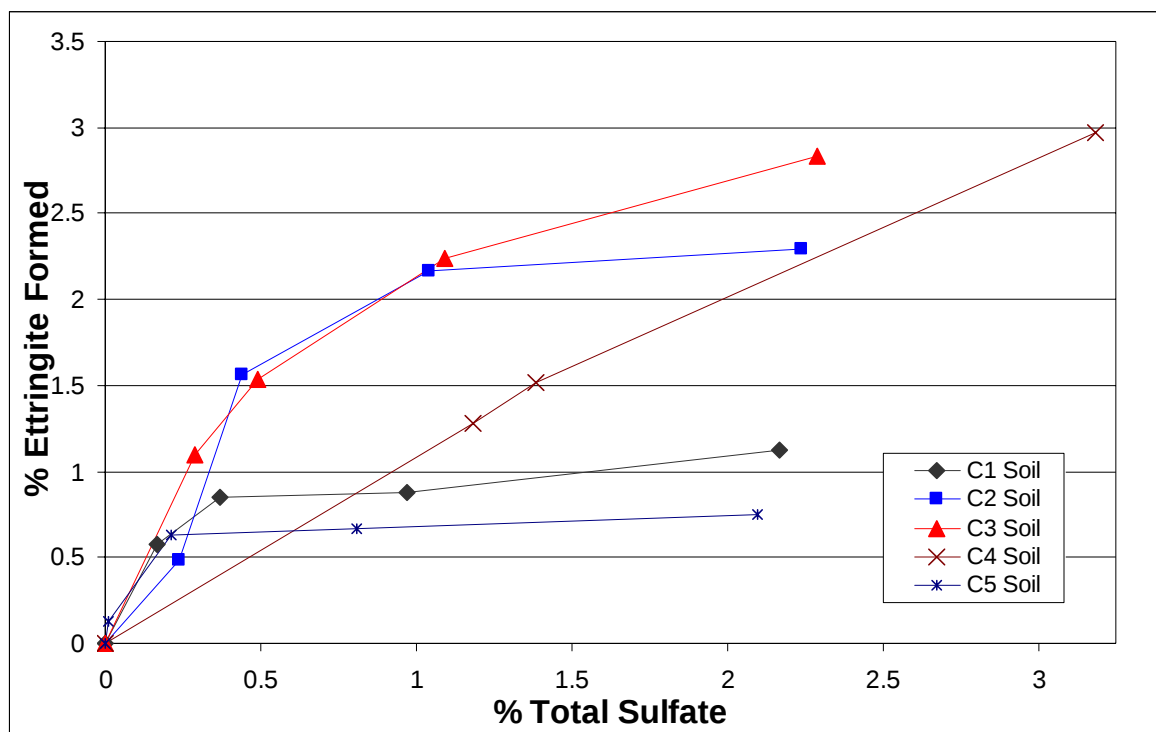


Figure 7. Highest observed ettringite concentration in all the soils for different sulfate content when reacted with 5 percent lime after 56 days curing.

Soils from Ildefonso (C2), Berthoud (C3) and Bloom clay (C4) series had higher clay concentrations when compared to the other two soils, and more ettringite formed in these soils over time. For all soils except C4 the amount of ettringite precipitated at sulfate concentrations below about 3,000 ppm was similar. This is in agreement with our current empirical assessment of soils, where sulfate concentrations below about 3,000 ppm can be considered non-problematic in terms of ettringite formation. This is probably applicable to soil C4 also, but this could not be tested as the natural sulfate content of this soil was above one percent, Table 4. The various soils respond somewhat differently with increasing sulfate content. This difference may be due to the difference in relative proportions of individual clay minerals and the total amount of reactive silt fraction in these soils (Table 3).

For the Bloom clay series (C4) the observed clay content was about 30 percent which was approximately the same level of clay content in the Berthoud soil, 35 percent (C3). But a comparatively small amount of ettringite was observed to form in these soils at sulfate contents up to and above one percent (Figure 7). This sulfate level corresponds to the natural sulfate content in this soil where gypsum is the major sulfate source. Considering the low solubility of gypsum when compared to sodium sulfate, a low rate of dissolution could limit the amount of available sulfates in the system. The soil is likely to behave differently in the field as water movement offers the possibility of continually activating sulfate ions as the sulfate laden water is replaced by fresh water with a low sulfate concentration. Hence the extent of ettringite formation in the Bloom clay soil, C4, can increase with time based on water movement and the dissolution properties of gypsum. In the Dwyer sand, C5, the maximum amount of ettringite formed was considerably lower than for C2, C3 and C4 soils, at about 0.75 percent. This is possibly due to lower clay content and the higher amount of soluble silica available in the silt fraction of these soils.

Observed ettringite concentrations in these soils can change with time due to progressive dissolution of minerals and available sulfate contents in solution. Considering a volume increase of 137 percent (based on the calculation of molar volume change between the product, ettringite, and the reactants, calcium sulfate and calcium aluminate) under ideal conditions upon formation

of ettringite, the volumetric increase in these soils can vary from about 1.0 percent for soil C5 to over 4.0 percent for soil C4.

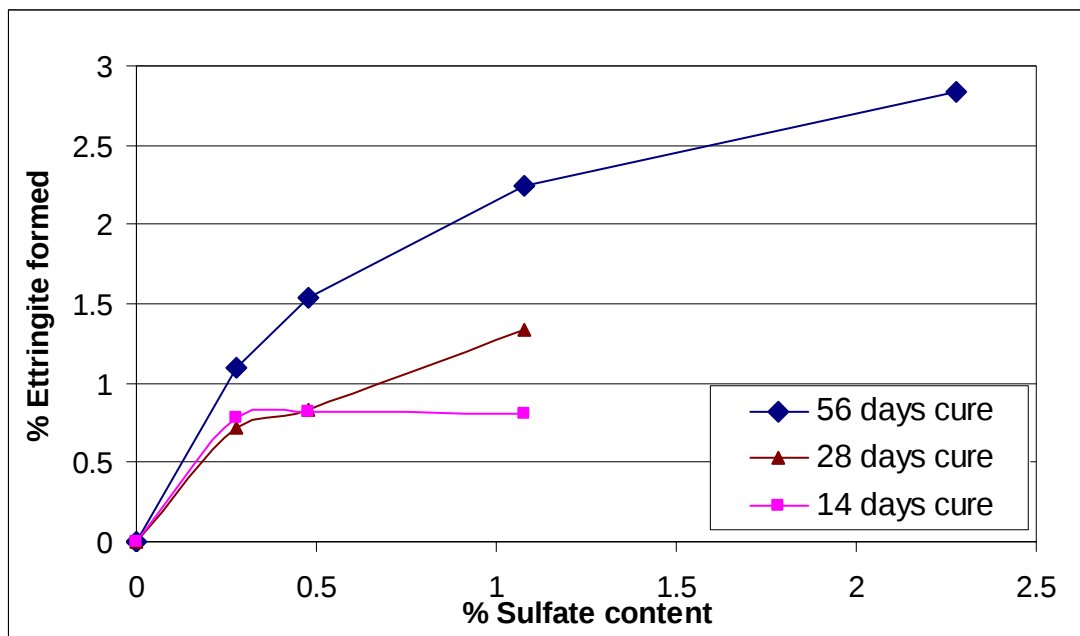


Figure 8. Highest observed ettringite concentration in Berthoud soils with increasing sulfate contents when treated with 5 percent lime at different curing periods.

The Berthoud soil, C3, which had a natural sulfate level of 2,760 ppm, was treated by adding additional sodium sulfate in order to assess the sensitivity to ettringite formation as a function of sulfate content (Figure 8). The ettringite concentration generally increased progressively with time and with increase in sulfate concentration. Scanning electron microscopic (SEM) images of samples cured for 14-days showed clusters of poorly crystallized ettringite. However SEM micrographs demonstrated that for 28-day cured samples ettringite rods were better crystallized but restricted and distributed randomly on the surfaces of clay particles (Figure 9-C, 10-C). The maximum amount of ettringite formed in the Berthoud soils was found to be nearly three times the concentrations found in Halaquepts soils, for example, under similar treatment and curing conditions. The reason for this difference is probably due to the fundamental difference in mineralogy between these soils. The clay content in the Berthoud soils based on x-ray diffraction was approximately 35 percent (compared to only about 10 percent for

the Halaquepts soil, Table 2) with both kaolinite and smectites being present in significant amounts. Considering the faster dissolution and easier release of aluminum from kaolinite when compared to smectites, the initial formation of ettringite is probably affected by the partial dissolution of kaolinites in these soils (Mitchell and Dermatas, 1993).

Sensitivity of Soils to Ettringite Formation Based on DSC Testing

The sensitivity of the Colorado soils to the formation of ettringite as a function of sulfate content was based on concentrations in 10mg samples quantified using the DSC. Samples were cured for a period of between 14 and 56 days. There was no significant increase in ettringite concentration with time for the Halaquepts soil (C1) for a sulfate content of 1,680 ppm. Although the observed concentrations are low, the rate of increase of ettringite growth with time is greater when the soluble sulfate content within soil C1 is increased to 3,680 ppm. The rate of increase in ettringite development versus time was about the same for sulfate levels of 3,680 ppm and 9,680 ppm. The lines indicating the formation of ettringite with time at 3,680 and 9,680 ppm sulfate are parallel and close to each other. However, the level of ettringite developed at any given time of reaction increased as the sulfate content increased, Figure 9. The maximum ettringite concentration observed in the 10 mg samples was only about 1.15 percent for an added sulfate content of two percent (Figure 7). Considering the sensitivity of ettringite formation to sulfate content as well as the observed scattered distribution of crystals in SEM images (Figure 5-C), it can be inferred that ion migration with diffusion of water carrying ions may lead to localized expansions in these soils.

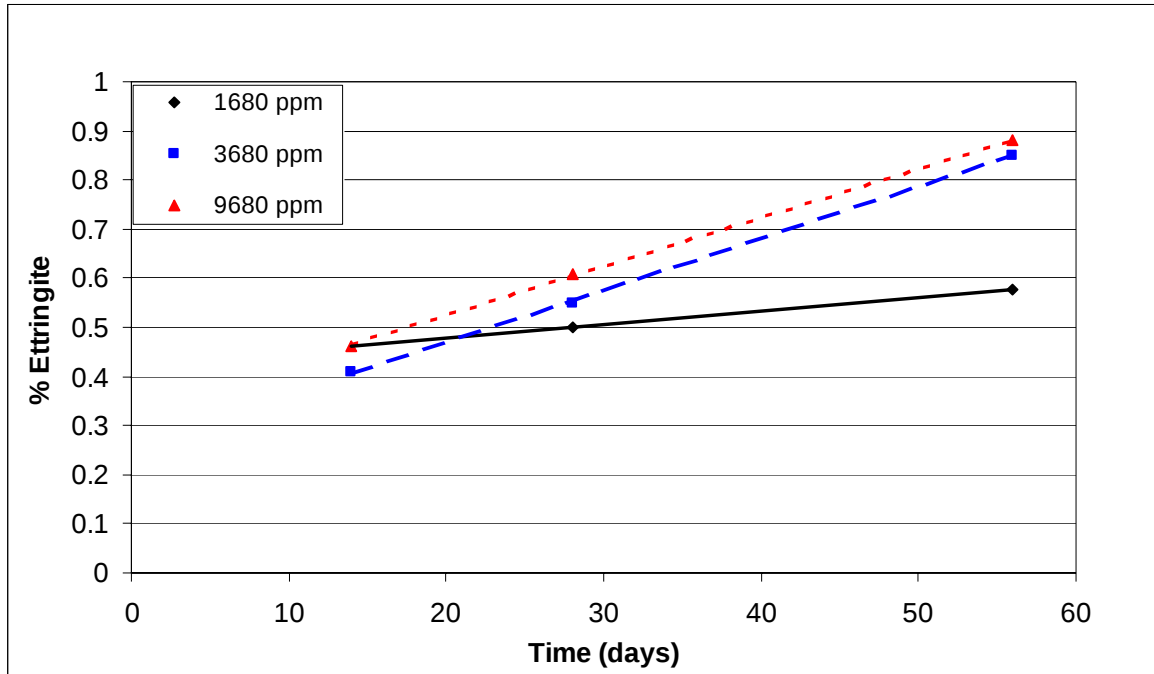


Figure 9. Sensitivity of soil C1 to form ettringite with time and increasing sulfate concentrations.

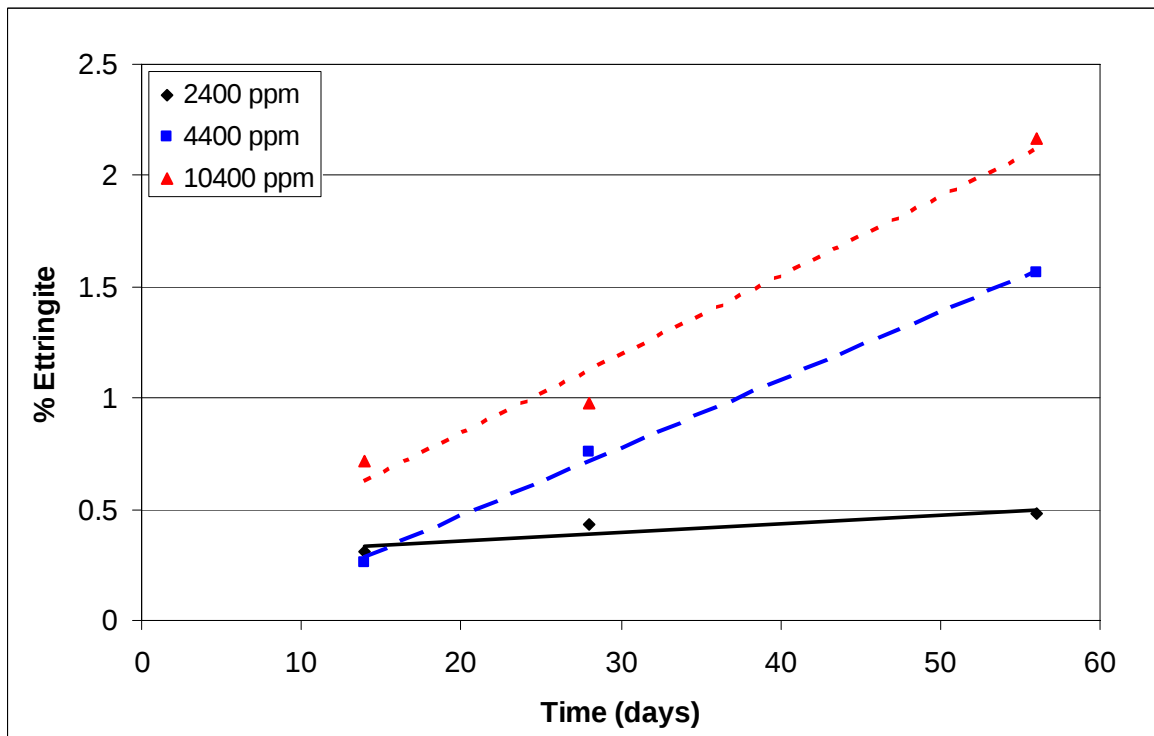


Figure 10. Sensitivity of soil C2 to form ettringite with time and increasing sulfate concentrations.

The Ildefonso soil (C2) showed a higher sensitivity to ettringite formation as a function of sulfate content than the Halaquept soil. For soil C2, the amount of ettringite formed in the soil at its natural sulfate content (2,400 ppm) remained essentially constant as a function of curing time. But the rate of formation increased considerably with an added sulfate content of 2,000 ppm to boost the total sulfate content to 4,400 ppm (Figure 10). This higher sensitivity for the Ildefonso soil may be due to the higher clay content, especially kaolinites, which provides a more readily available aluminum source for ettringite development than other minerals, including smectite clays. The greater reactivity of kaolinite is due to their lower cation exchange capacity and aluminum availability along the edge sites (Mitchel and Dermatas, 1992).

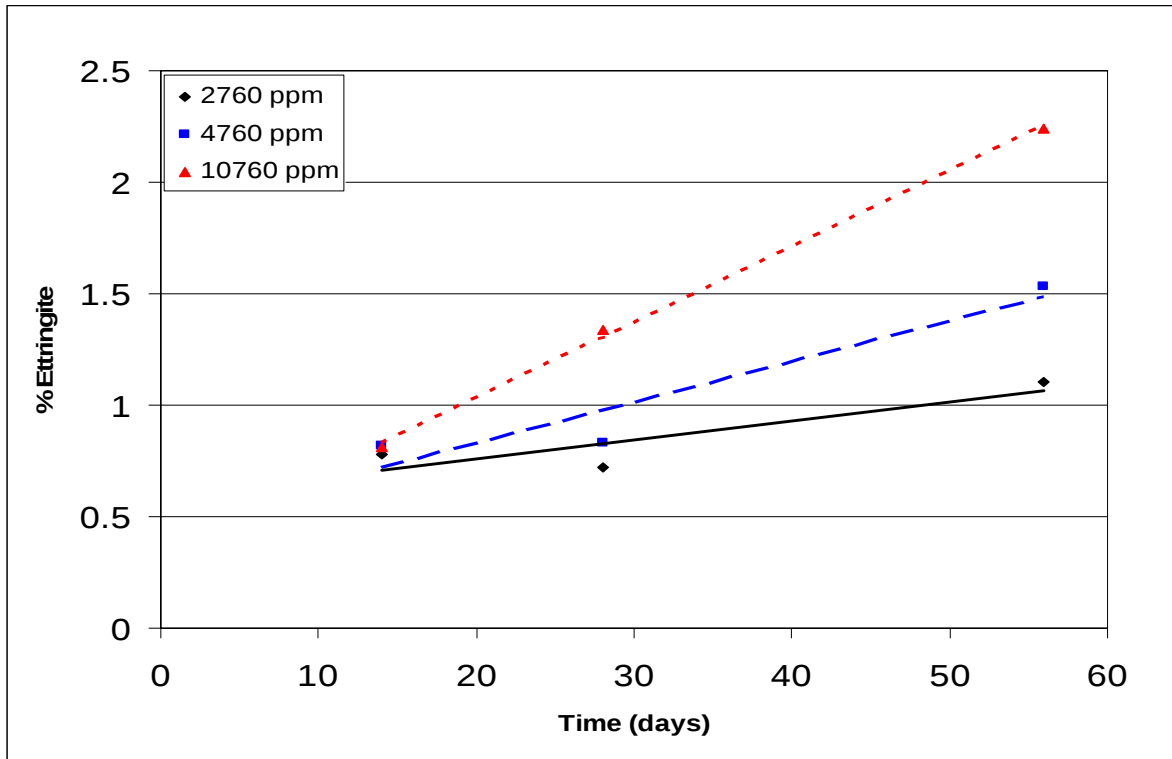


Figure 11: Sensitivity of soil C3 to form ettringite with time and increasing sulfate concentrations.

The Berthoud soil (C3) has higher clay content than the Ildefonso soil and the form of clay mineral is predominately smectite (Table 3). The soil shows a gradual increase in ettringite formation with increasing sulfate concentrations (Figure 11). The higher initial concentration of

ettringite may be due to kaolinite, and the steady increase with time is probably due to increased aluminum supply from kaolinite and smectite in the presence of water and sulfates (Mitchell and Dermatas, 1992). As with soils C1 and C2, the general trend is that the rate of ettringite formation below about 2,000 to 3,000 ppm is significantly smaller than for higher sulfate contents. This trend continues to validate the empirical evidence from the field (Little et al., 1995) that a threshold soluble sulfate level of about 2,000 to 3,000 ppm might differentiate soils with little or no risk from those of notable risk. This trend was further verified by Harris et al., 2004. These data also appear to verify the impact of extended mellowing on reducing the potential for sulfate induced heave due to the formation of ettringite before compaction. The hypothesis here is that if sufficient water can be applied to solubilize sulfates and form ettringite before compaction, then damaging post compaction heave can be averted. This trend was verified by Harris et al., 2004. However, since sulfate has a limited solubility, the ability of solubilize a sufficient proportion of sulfate in the mellowing period with water of construction is limited. It is possible that a level of soluble sulfates in the range of 3,000 ppm is linked to the upper limit of sulfates that can practically be dissolved during a mellowing period.

The natural sulfate content for the Bloom clay (C4) was almost 1.2 percent, well above the 2,000 to 3,000 ppm apparent threshold. The sensitivity of Bloom clay to sulfates was not investigated below the 1.2 percent sulfate level. However, the sensitivity to added sulfates above the 1.2 percent level was investigated and is presented in Figure 7.

For soil C5, variation in observed ettringite concentration as a function of sulfate content was very low after 56 days of curing (Figure 7). The maximum observed concentration with 2 percent added sulfates was below 0.75 percent. Observed ettringite formation in these soils agrees well with model predictions, which indicates that soil C5 has the lowest sensitivity ettringite formation potential.

Comparison of Thermodynamic Model and DSC Results

A comparison of results from the thermodynamic model and DSC is presented in Figure 12. The trend suggested by the model agrees relatively well with the trend measured using the DSC. The rate of ettringite formation as predicted by the model matches with observations in the DSC for soils C2 (Idefonso), C3 (Berthoud) and C4 (Bloom clay). These soils develop a higher concentration of ettringite with increasing sulfate content when compared to soils C1 (Halaquepts) and C5 (Dwyer sand). This is also predicted by the thermodynamic model.

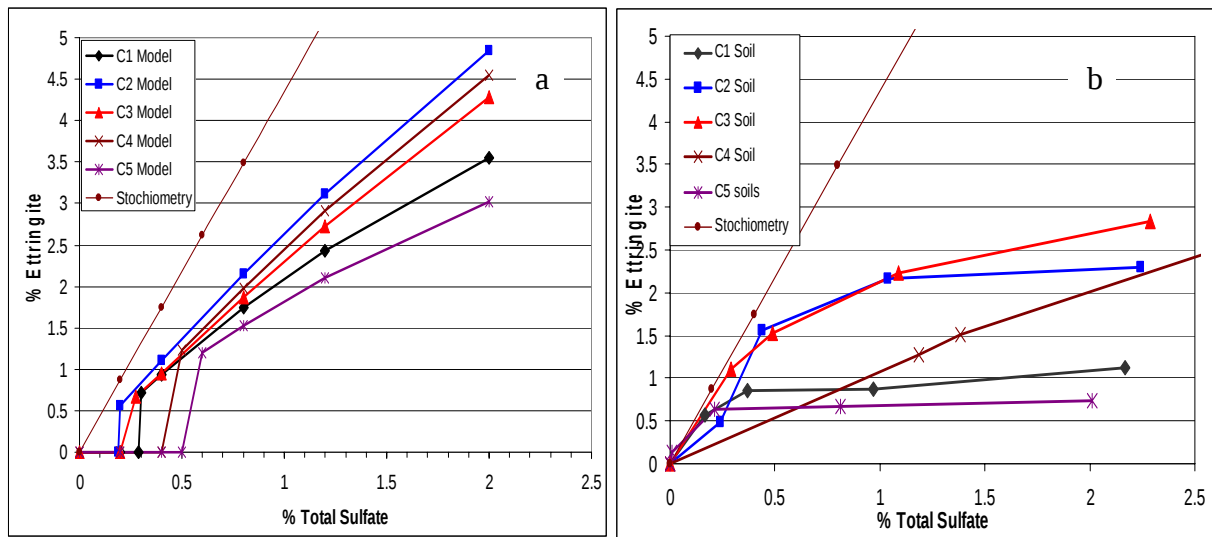


Figure 12. Comparison of thermodynamic model results (a) and DSC results (b) for Colorado soils treated with 5 percent lime and cured for 56 days.

Among the soils C2, C3 and C4; the thermodynamic model predicts soil C2 to be most reactive, but in DSC measurements, soil C3 was found to form the greatest amount of ettringite. The behavior of soil C4 (Bloom clay) as monitored with DSC measurements was completely different from the other soils. Even though the natural sulfate content in this soil was very high at 1.2 percent, a relatively small amount of ettringite developed even after 56 days of curing. The limited solubility of gypsum, which comprised the vast majority of the 1.2 percent natural sulfate

content, when compared to the much more soluble sodium sulfate, which was used in the other soils to increase the sulfate content, may help explain this behavior.

Soil mineralogical analysis and fractionation showed that soils C2, C3 and C4 have higher clay concentrations than soils C1 and C5 (Table 2). Ettringite concentrations formed in all soils as measured by the DSC and as predicted by thermodynamic modeling are well below stoichiometric proportions. This is as would be expected because the formation of ettringite is impacted by the formation of competing minerals with preferred energetics, reaction kinetics, interference of other ions present in the soil system and the amount of available reactants. However, the stoichiometric calculations provide a reasonable boundary for the predicted and measured ettringite levels. Furthermore, thermodynamic predictions are higher than the measured amounts of ettringite. This is also reasonable due to the effect of kinetics, which may be slow under some conditions, and kinetics is not accounted for in the thermodynamic model, where all reactions are assumed to proceed to equilibrium. The surface area of minerals, ionic concentrations in solution and solubility properties of minerals all decide the extent of mineral dissolution.

Limitations of DSC

The location of the ettringite endothermic peak can differ depending on the sensitivity of the machine and heating conditions used in measurement (Hime et al., 2000). In the current study, the sample of pure ettringite synthesized in the lab was used to identify the behavior of ettringite in the DSC. Determining the exact area within the ettringite peak becomes difficult with hydration due to the interference of other hydrated phase formed during lime reaction (Hime et al., 2000, Odler and Abdul-Maula, 1984). De-convolution software can be used to identify the start and end points of ettringite peaks. The sand fraction is essentially chemically inert and acts as filler in the soil matrix and hence creates variability. Also the amount of ettringite formed in soils during initial hydration is small when compared to the concentrations formed in cements. These factors along with the heterogeneity of formation within the sample can create variability in measurements. An alternative to reduce the variability in measurements is to use only silt and sand fractions in soils for analysis.

Volumetric expansion occurs with water absorption (Mehta and Wang, 1982) and hence the degree of crystallinity can also change with curing under moist conditions. By comparing the heat signals at different curing periods it is difficult to identify whether the increase is due to better crystallization of existing ettringite or due to additional formation.

CONCLUSIONS

1. The reactivities of the five Colorado soils with respect to ettringite formation are different when evaluated using either the thermodynamic model approach or DSC measurements.
2. Thermodynamic modeling of the soils indicates that the threshold sulfate content for reactivity is above about 2,000 to 3,000 ppm of soluble sulfates for each of the five soils tested. However, two of these soils have a threshold soluble sulfate content for reactivity that is substantially higher at about 4,000 to 5,000 ppm. This means that below this threshold, ettringite will not form at a significant level and will not be problematic. This agrees with previous empirical evidence and modeling efforts (Little et al., 2005). Even if ettringite is thermodynamically favored at sulfate levels as low as 2,000 ppm, the amount of ettringite that will form based on mass balance calculations is very low. Therefore, in keeping with field data, we believe that 3,000 ppm is a reasonable safe limit where risk is minimal.
3. If soluble sulfate contents are below about 3,000 ppm, an extended mellowing period during which sufficient water is added to allow ettringite formation prior to compaction is a reasonable approach. This substantiates previous work (Little et al., 1995 and Harris et al., 2003). The length of this extended mellowing period should probably be in the range of 72-hours based on Harris et al., 2004. However, this period must be validated through field experience.
4. The DSC can be used to not only assess the threshold sulfate level for various soils but also the rate and relative level of ettringite development with time.

5. DSC evaluation of ettringite development should be done on the fine fraction of the soil only. This fraction can be prepared by a combination of dry and wet sieving through the No. 200 sieve.
6. A recommended method for future work in assessing the potential for sulfate reactivity in a specific soil, based on this study, is presented in the Recommendations section below.

PROPOSED METHODOLOGY

Approach

The formation of ettringite in soils is not uniform and hence the amount formed at different locations may vary. As previously discussed, the sand fraction can be considered non-reactive and hence can be removed from the sample being analyzed. The sand fraction and coarser fractions become essentially non-reactive filler that affects the uniformity of mixing of the components (i.e., calcium hydroxide, sulfates and the reactive component of the soil). Thus when the random, small sub-sample (10 mg) is extracted from the sample prepared for DSC analysis, the results are affected by the uniformity of mixing. Hence for future work, we recommend that only the silt and clay fraction of the soil be used in the analysis. We suggest using a slurry phase of soil consisting of silt and clay alone at a 1:10 dilution ratio (soil:water) to react with calcium hydroxide and sulfate. The sand fraction can be removed by wet sieving the soil through the No. 200 sieve and washing the fraction retained on the sieve with deionized water to remove silt and clay particles adhering to sand.

We believe that a major goal should be to simply assess the reactivity of the soil as opposed to assessing the threshold sulfate level. The idea here is that if the soluble sulfate testing defines that a sulfate level above a target threshold of between 2,000 and 3,000 ppm exists, then sulfates have a reasonable probability of affecting the stabilization reactions and of causing a

deleterious reaction. Consequently, the fine soil fraction (less than about 75 μm) should be evaluated at three, intermediate sulfate levels (5,000, 10,000, and 20,000 ppm). This forces the limiting reagent to be something other than sulfates, i.e., calcium or aluminum. Since sufficient calcium hydroxide to achieve stabilization should be added to the soil, the calcium content should be sufficiently high to prevent calcium from being the limiting reagent. This leaves aluminum as the controlling factor. Two factors can limit the aluminum availability: the rate of release from the clay or the ability of aluminum to be solubilized in the presence of calcium hydroxide.

The slurry should consist of two parts. The solid part should consist of the clay and silt fraction blended with soluble sulfate (5,000, 10,000, and 20,000 ppm by mass of dry soil) and 5 percent calcium hydroxide by dry mass of the soil. The second part of the slurry is deionized water. The two components should be thoroughly mixed in a centrifuge tube. Individual samples of the slurry should be allowed to cure for different curing periods at 40°C. Following the cure the sample will be centrifuged to provide a “paste” from which 10 mg samples will be collected for DSC testing. The number of replicate samples required will depend on the variability among the samples. In future work, the number of replicate samples required to assess the risk with a defined level of reliability will be determined. Once this is done, this analysis can be used to catalog the reactivity of various soils. Such a comparative study would be of great value in order to assess the relative reactivity of the fine fractions of the various soil series of Colorado. The relative reactivity of the total soil, considering the coarser fraction, could then be considered by using the “law of mixtures” to additively blend the fine and coarser fraction. At this point a relative comparison is all that is possible. After a database is populated, it may be possible to establish more specific criteria.

Procedure

The objective of the method is to separate out the fine soil fraction (less than about 75 μm) without affecting the mineralogy of the soil. Based on our testing and analysis, we believe that the sand fraction is essentially inert and does not significantly contribute to reactivity. Use of strong chemicals to separate silt and clay fractions by removing organics and cementing agents

in soil can affect soil mineralogy and result in loss of reactive fractions from soil. Hence sonication is suggested to separate out the sand fraction. The amount of soil and the number of samples to be tested is not included in this outline.

I. Sample Fractionation – Protocol designed to determine the soluble sulfate content of the soil sample and determine the relative proportions of coarse-grained and fine-grained soil particles.

i. Determine sulfate content in soil.

1. Follow CP-L2103.

ii. Determine dry weight of sample (X gm).

1. Dry the soil over night at 60⁰C.

2. Cool to atmospheric conditions and weigh.

iii. Sonication - This method uses sound energy to agitate particles and helps to separate silt and clay particles adhering to sand fraction in soil.

1. Use sample of the size determined in step ii.

2. Use one part soil to ten parts deionized water (1:10).

3. Sonicate the suspension. (Comment: Operation takes about 15 minutes.).

4. Leave the soil water suspension over night (at least 12 hrs) to facilitate dissolution of gypsum.

iv. Filtration

1. Use a 75 μ sieve (No. 200 sieve) to filter out silt and clay.

2. Use soil retained on the sieve and wash repeatedly with water used in sonication to separate silt and clay particles from sand.

v. Determine weight percentage of sand.

1. Use the fraction retained on 75 μ sieve.
 - a. Dry over night at 105 $^{\circ}$ C.
 - b. Cool inside a desiccator.
2. Weigh the sample (Y gm).

vi. Clay and silt content measurement.

1. Determine the concentration of clay and silt in water.
 - a. Weigh a dry ceramic crucible.
 - b. Mix the suspension thoroughly and extract 10-20 ml for weight measurement.
 - c. Transfer the suspension to the ceramic crucible and weigh.
 - d. Dry sample and crucible over night at 105 $^{\circ}$ C and allow for cooling inside a desiccator.
 - e. Determine final weight.
 - f. Determine weight (Z gm) of clay and silt per ml of water.

II. Sample Preparation - This method describes the protocol for preparing samples using silt and clay fractions separated from the soil. Samples are made into slurry form with one part soil (clay and silt fraction only) and ten parts water. This slurry should be thoroughly mixed and allowed to cure for different curing periods at 40 $^{\circ}$ C.

- i. Prepare sample (clay and silt fraction only).
 1. Prepare slurry (10 parts water to one part silt and clay soil).
 2. Settle out solids using a high speed centrifuge.
 3. Decant supernatant solution to a 1 L bottle.
 4. Use the supernatant solution for sulfate testing following CP-L 2103.
 5. If soluble sulfate content is less than 500 ppm, continue to step 6. Otherwise, add another 10 parts water to the one part soil captured after centrifuging and repeat the soluble sulfate test. Repeat this

process until the soluble sulfate measured in the supernatant is less than 500 ppm. Recover all supernatant and move to step 6.

6. Prepare flocculent solution (0.5 M, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$).
7. Add 20-30 ml of flocculent to the supernatant solution.
8. Let sit for 2-3 hours and then centrifuge the supernatant solution one more time and check for additional settlement of clay particle. Add any residual clay to the fine-grained soil collected in step 2.
9. Add fresh DI water (equivalent to the amount removed by centrifuging) to the soil. The slurry should now have zero sulfate ions and a 1:10 soil to water ratio.

ii. ii. Prepare control sample.

1. Add five percent hydrated lime to the required volume of suspension and cure at 40°C for required curing periods.

iii. Prepare sulfate-bearing samples.

A high water to soil ratio will help ensure that sufficient sulfate ions are available in solution for ettringite formation.

1. Add varying amounts of soluble sulfate to the sample prepared in step 8: 5000 ppm, 10,000 ppm, and 20,000 ppm to ensure different sulfate contents in treated soil.
2. Add five percent lime to the suspension and cure at 40°C .

III. Curing and Sample Preparation for DSC Testing.

- i. Subject both control samples and sulfate-bearing samples to accelerated cure at 40°C for required time periods.

- ii. Centrifuge both control and soil samples using a high speed centrifuge at the end of curing period.
- iii. Filter the supernatant solution through 1.6 μm filter paper to capture any ettringite present in solution.
- iv. Test supernatant solution for pH and the residual sulfate content following CP-L 2103.
- v. Dry the precipitate with acetone (to stop further hydration).

IV. DSC Testing

- i. Test the samples with the DSC. For every sample tested, load 10 mg of the soil sample on the “sample cell”. Place an equal amount of control sample (by weight) cured for the same period as the sulfate-bearing soil in the “reference cell”. (Note: Using the reference sample may help limit the masking effect of hydrated phases forming in lime treated soil on ettringite signals.)

Note:-

The procedure outlined above is developed based on our current observations on the behavior of soil. Efficacy of the new method needs to be further tested and established before implementation.

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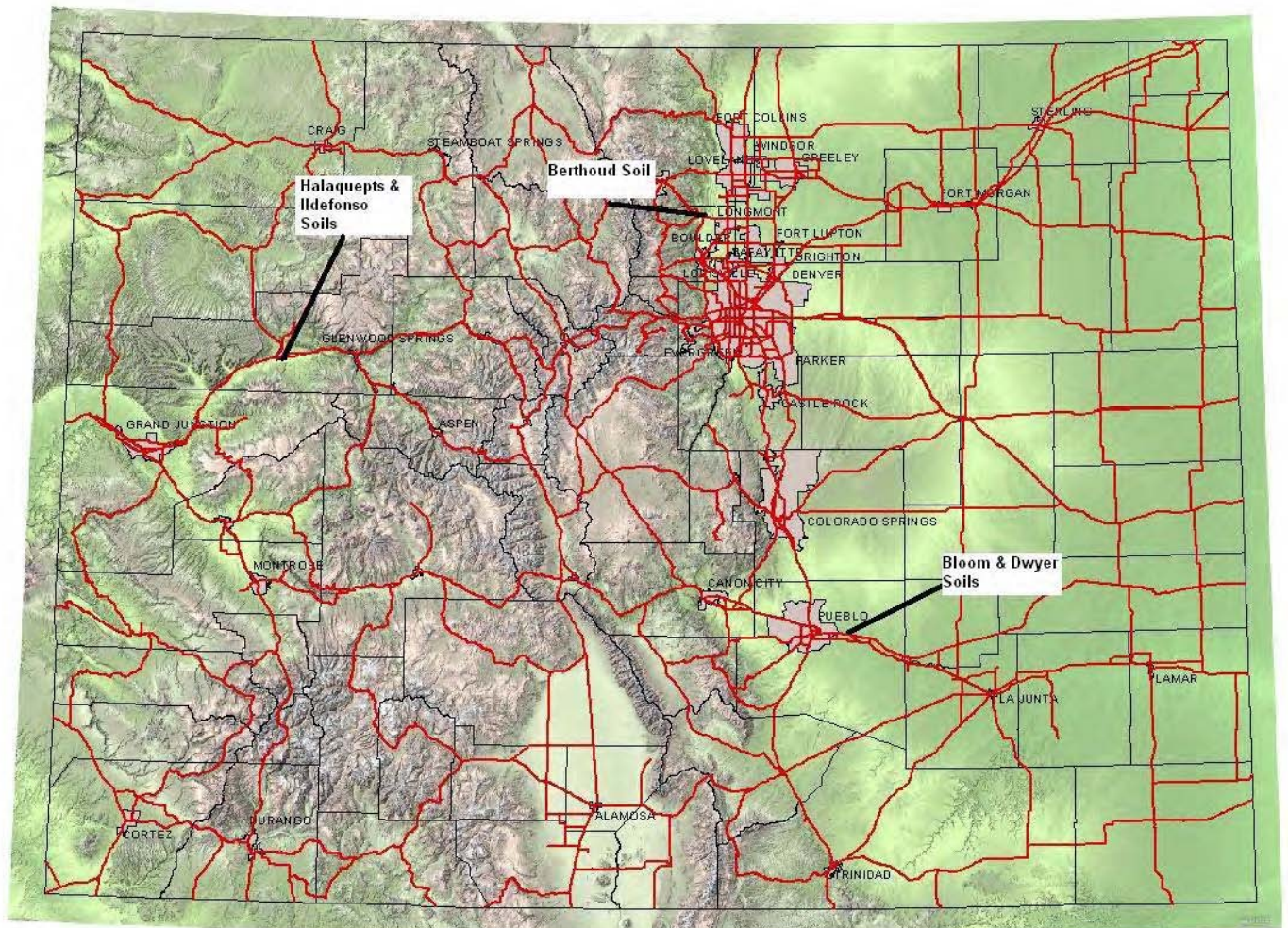
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APPENDIX A:

**COLORADO STATE MAP WITH THE LOCATIONS OF THE
RESEARCH TEST SAMPLES IDENTIFIED**

Appendix A: Colorado State Map with the Locations of the Research Test Samples Identified



The Colorado Department of Transportation (CDOT) selected the sites and soil types based on the information it received using the National Soil Conservations Service's web site. Using this site, CDOT was able to identify at or near surface probable high sulfate/gypsum soils and similar soils nearby that did not contain sulfates.

The sites in Rifle and East of Pueblo were selected by reviewing high sulfate content areas as per the National Conservation Soils Service's web site that contains national information on high sulfate content soils. These locations were picked in Colorado for their high probability of sulfates at or near the surface and their proximity to a major highway. An additional factor was the availability of nearby soils of approximately the same classification which did not have detectable sulfates.

The Berthoud site was a location where severe sulfate swelling had occurred and additional information in the form of more sophisticated testing was requested by the project engineer at this location.

APPENDIX B:
SUMMARY OF TEX-145E

Appendix B: Summary of Tex-145E

Preparing Sample

1. Sample soil within the depth of proposed stabilization.
2. Obtain a 300 g representative sample.
3. Air-dry the sample to constant weight.
4. Pulverize the 300 g to pass the No. 40 (425 μ m) sieve.
5. Split the sample and obtain 10 g of representative sample.
6. Weigh 10g to the nearest 0.1 g.

Measuring Sulfate Content

1. Place the 10 g soil sample in an 8 oz. (250 mL) HDPE bottle.
2. Add 200 mL of distilled or deionized water.
3. Vigorously shake the bottle of soil/water solution by hand for 1 minute (min.) and wait for 12 hours (hr).
4. After a minimum of 12 hrs. has elapsed, place one filter paper along the inside of the funnel and place the funnel into an 8 oz. (250 mL) beaker to capture the filtrate.
5. Shake the bottle of soil/water solution again for 1 min. and pour the solution into the funnel. Allow all the solution to filter and drain into the beaker.
6. Using a clean, 2 mL disposable pipette, fill the 10 mL graduated cylinder with the filtrate.
7. Take a minimum of three readings per sample and average the results.
8. Multiply the average result times the dilution.

A complete description of the Tx-DOT sulfate testing procedure is available at ftp://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/100-E_series/pdfs/soi145.pdf

APPENDIX C:
SUPPORTING DATA

APPENDIX C: SUPPORTING DATA

Table 1-C. Chemical analysis results for Colorado soils using a 1:10 soil to water extraction ratio.

Analyses (1:10 extraction)	Soils				
	Halaquepts	Ildefonso	Berthoud	Bloom clay	Dwyer sand
pH	8.6	8.1	8.3	8.7	7.8
Organic matter (%)	2.0	0.7	0.6	1.3	0.7
Aluminum (ppm)	7.0	4	2	1	23
Calcium (ppm)	165.0	612	1030	1980	43
Chloride (ppm)	44.0	770	32	381	61
Iron (ppm)	3.4	1.6	1.1	1	12.2
Potassium (ppm)	44.0	52	45	93	41
Silicon (ppm)	19.0	18	32	30	26
Sulfate (ppm) (1:20)	1680.0	2400	2760	11840	100

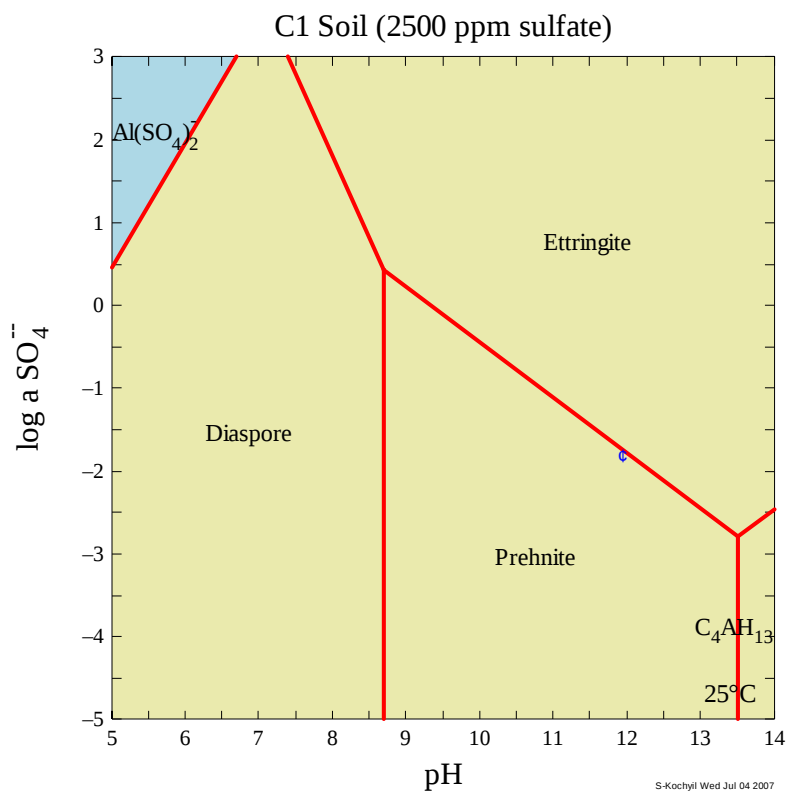


Figure 1-C. Thermodynamic phase diagrams for Halaquepts soil (C1) when treated with 5 percent lime with 2500 ppm total sulfate content.

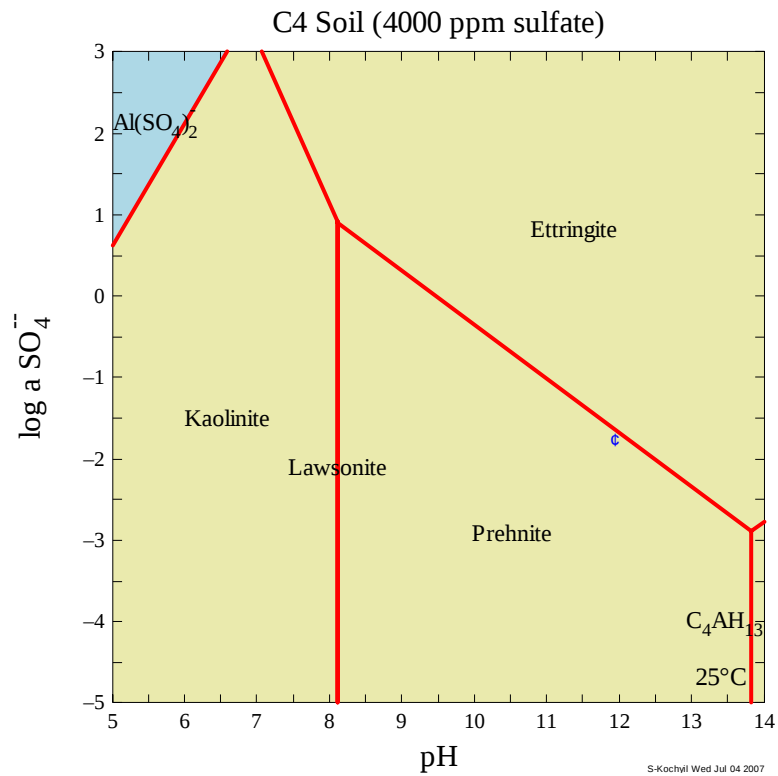


Figure 2-C. Thermodynamic phase diagrams for Bloom clay soil (C4) when treated with 5 percent lime with 4000 ppm total sulfate content.

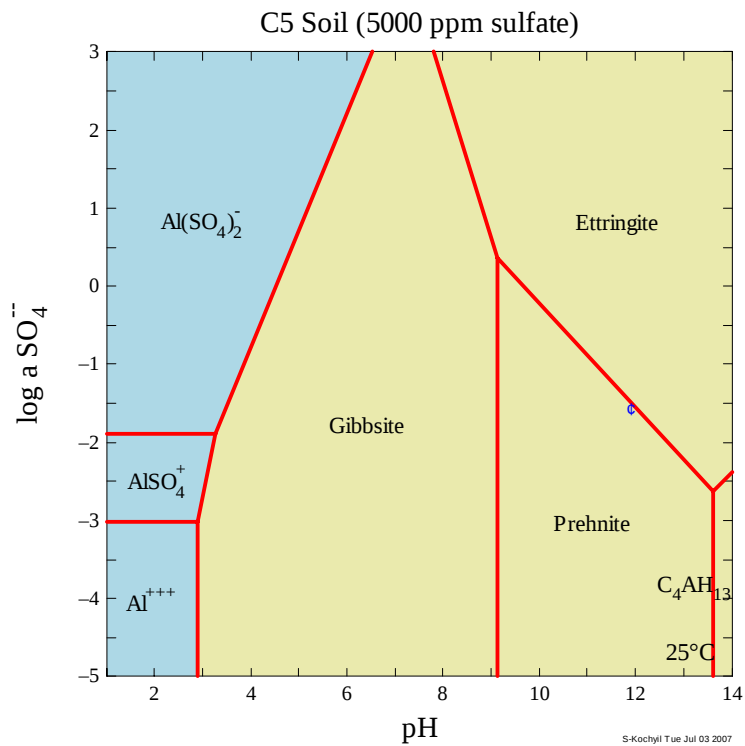


Figure 3-C. Thermodynamic phase diagrams for Dwyer sand (C5) when treated with 5 percent lime with 5000 ppm total sulfate content.

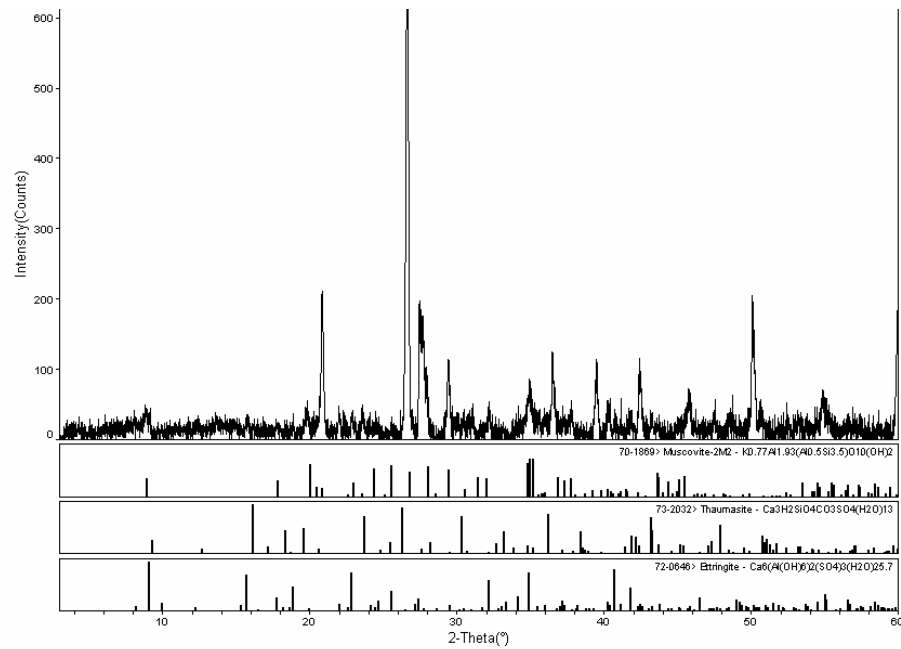


Figure 4-C. XRD of soil C4 soils with 2% sulfate after treating with 5% lime and 56 days cure.

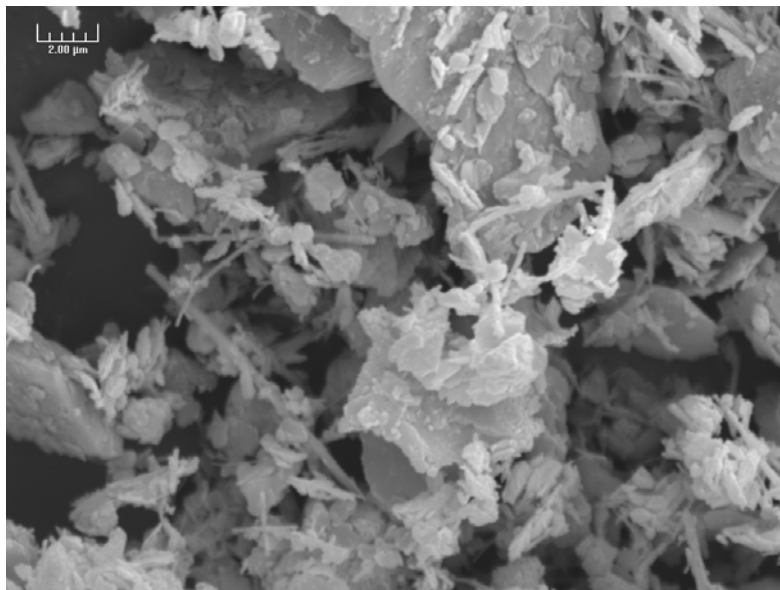


Figure 5-C. Scanning electron microscope image of ettringite distribution in soil C1 with 0.8 percent sulfates and after 28 days cure.

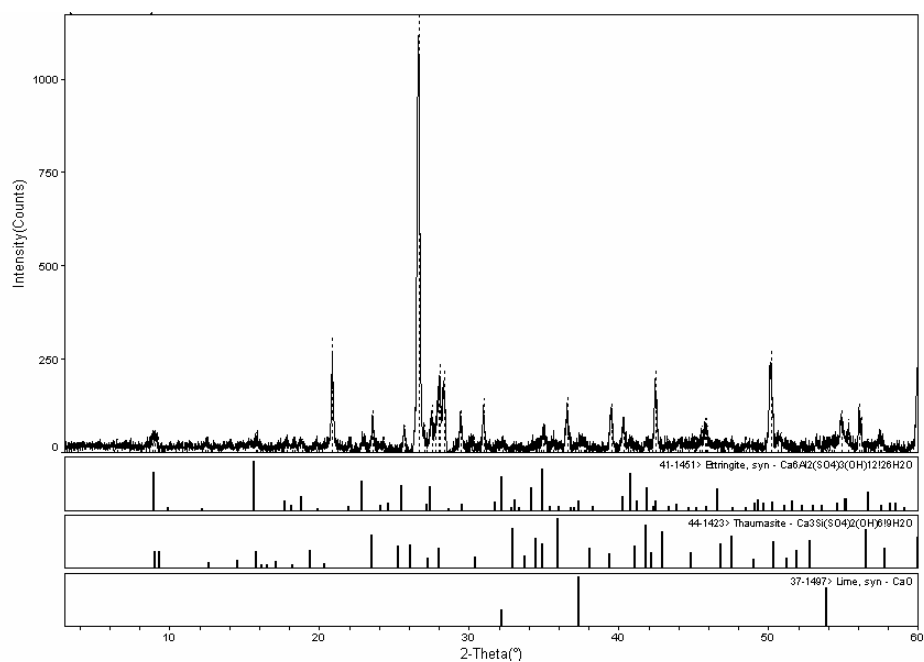


Figure 6-C. XRD of C1 soils with 2% sulfate after treating with 5% lime and 56 days cure.

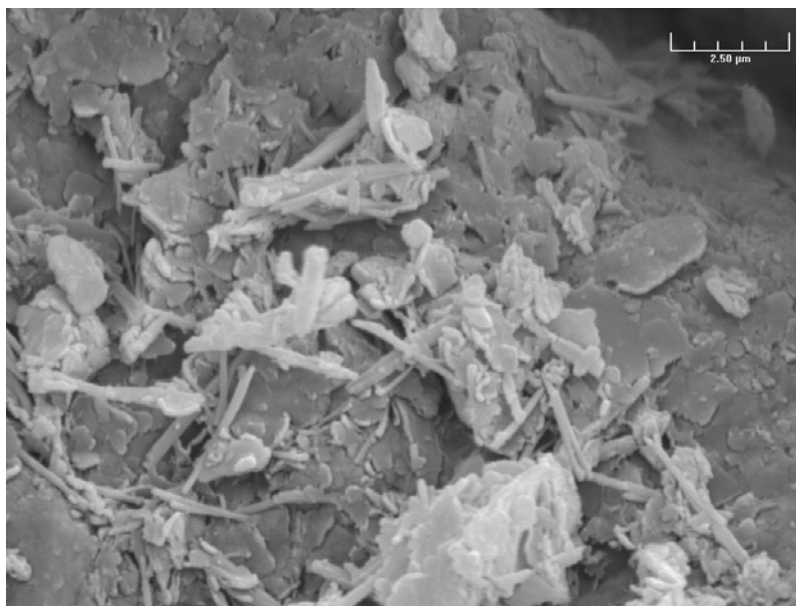


Figure 7-C. Scanning electron microscope image of ettringite distribution in soil C2 with 2 percent sulfates and after 28 days cure.



Figure 8-C. Scanning electron microscope image of ettringite distribution in soil C2 with 0.8 percent sulfates and after 28 days cure.

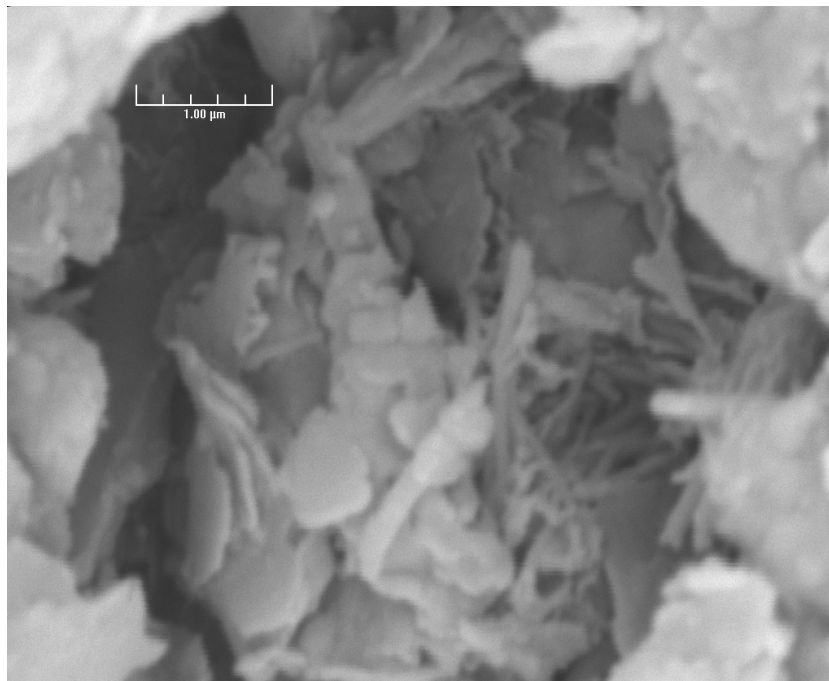


Figure 9-C. Scanning electron microscope image of ettringite distribution in soil C3 with 1.076 percent total sulfates and after 14 days cure.

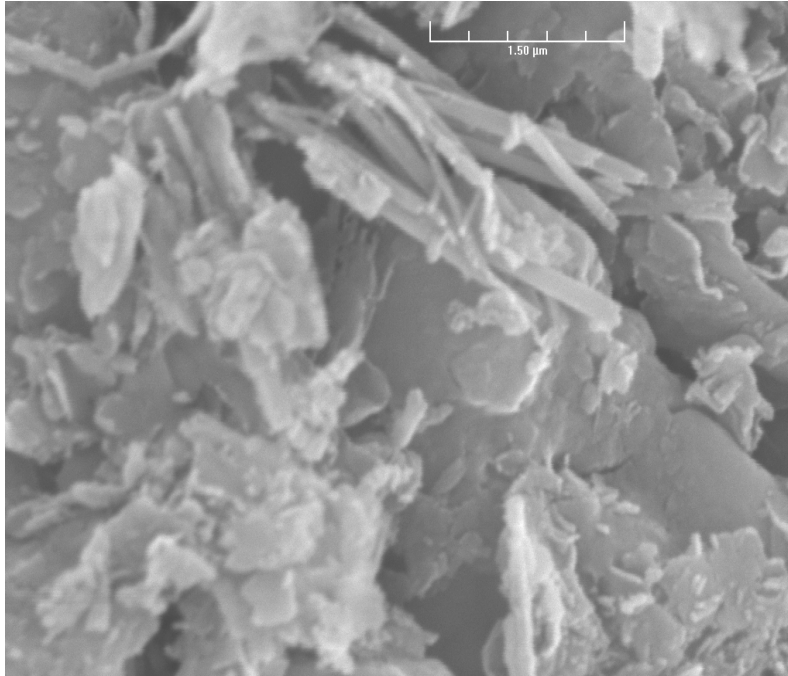


Figure 10-C. Scanning electron microscope image of ettringite distribution in soil C3 with 1.076 percent total sulfates and after 28 days cure.