ERDC TR-04-5

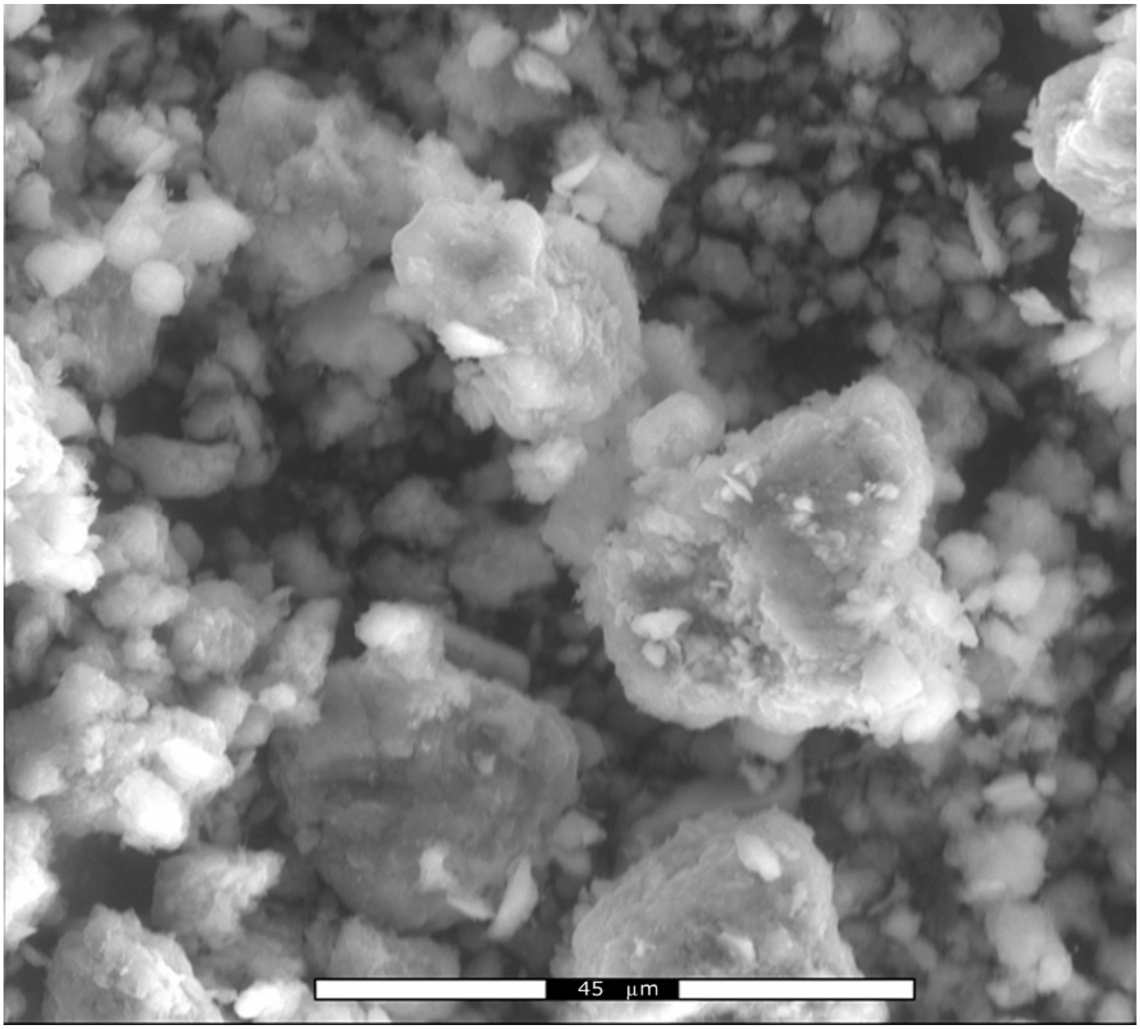
Engineer Research and Development Center

US Army Corps of Engineers ®

Constitutive Analyses of Nontraditional Stabilization Additives

Jeb S. Tingle, Steve L. Larson, Charles A. Weiss,
J. Kent Newman, John F. Peters, Barbara Tardy,
and Ernest S. Berney IV

November 2004



ERDC TR-04-5
November 2004

Constitutive Analyses of Nontraditional Stabilization Additives

Jeb S. Tingle, Charles A. Weiss, J. Kent Newman,
John F. Peters, and Ernest S. Berney IV

Geotechnical and Structures Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Steve L. Larson and Barbara Tardy

Environmental Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Final report

Approved for public release; distribution is unlimited

Prepared for Headquarters, U. S. Army Corps of Engineers
Washington, DC 20314-1000

ABSTRACT: Personnel of the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, conducted a series of laboratory experiments designed to characterize the constitutive properties of selected soil minerals and nontraditional stabilization additives. The results of these experiments were analyzed and included in this report to document the baseline characteristics prior to mixing the stabilizers and individual soil minerals. Analyses of the potential of individual stabilization products to reinforce specific soil types were conducted and reported. Additionally, an experimental modeling approach for describing the reinforcement mechanisms of individual stabilization agents was developed.

Contents

List of Figures

List of Tables

Preface

The purpose of this report is to describe the constitutive properties of new nontraditional stabilization additives and the potential of each additive for stabilizing specific soil types. This report provides data for the following:

a. Determining the constitutive properties of selected nontraditional stabilization additives.

b. Determining the fundamental properties of principal soil minerals and natural soils.

c. Evaluating the potential of selected additive types for stabilizing different categories of geotechnical materials.

d. Developing an innovative approach to modeling stabilized materials.

Users of information from this report include the U.S. military's engineer units charged with expedient road and airfield construction, the U.S. Army Maneuver Support Battle Lab, U.S. Army Engineer School, U.S. Army Force Projection Battle Lab Support Element, U.S. Army Deployment Modernization Office, U.S. Army Force Projection Center of Excellence, U.S. Army Force Projection Program Manager, U.S. Transportation Command, U.S. Army Corps of Engineers, Airfield Commanders, U.S. Army Aeronautical Services Agency, U.S. Air Force Civil Engineer Support Agency, U.S. Air Force Air Mobility Command, and agencies assigned operations planning responsibilities.

The project described in this report is part of the Pavements Research program, AT22 Work Package 238, currently sponsored by Headquarters, U.S. Army Corps of Engineers (CECW-EW).

This publication was prepared by personnel from the U.S. Army Engineer Research and Development Center (ERDC), Geotechnical and Structures Laboratory (GSL) and Environmental Laboratory (EL), Vicksburg, MS. The findings and recommendations presented in this report are based upon tests and analyses conducted at the Waterways Experiment Station. The research team consisted of Mr. Jeb S. Tingle, Dr. J. Kent Newman, and Dr. Ernest S. Berney IV, Airfield and Pavements Branch (APB); Dr. Charles A. Weiss, Concrete and Materials Branch; and Dr. John F. Peters, Research Group, all of GSL's Engineering Systems and Materials Division (ESMD); and Dr. Steve L. Larson and

Ms. Barbara Tardy, Inorganics Remediation Team, EL. Mr. Tingle and associates prepared this publication under the supervision of Mr. Don R. Alexander, Chief, APB, Dr. Albert J. Bush III, Chief, ESMD, and Dr. David W. Pittman, Acting Director, GSL.

COL James R. Rowan, EN, was Commander and Executive Director of ERDC and Dr. James R. Houston was Director.

Recommended changes for improving this publication in content and/or format should be submitted on DA Form 2028 (Recommended Changes to Publications and Blank Forms) and forwarded to Headquarters, U.S. Army Corps of Engineers, ATTN: CECW-EW, Kingman Bldg, Rm 321, 7701 Telegraph Road, Alexandria, VA 22315.

Executive Summary

Personnel of the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, conducted a series of laboratory experiments designed to characterize the constitutive properties of selected soil minerals and nontraditional stabilization additives. The results of these experiments were analyzed and are included in this report to document the baseline characteristics prior to mixing the stabilizers and individual soil minerals. Analyses of the potential of individual stabilization products to reinforce specific soil types were conducted and reported. Additionally, an experimental modeling approach for describing the reinforcement mechanisms of individual stabilization agents was developed.

The following conclusions were derived from the constitutive analyses of material characteristics and subsequent analyses of the potential effectiveness of each additive in different soil types:

a. Literature hypothesizes that the mechanism for soil stabilization using electrolytes or ionic stabilization additives consists of the additive serving as a catalyst to accelerate the weathering of the clay mineral structure. The ionic stabilizers alter the concentration of the electrolyte pore fluid resulting in cation exchange and flocculation of the clay minerals. As the clay minerals attract stronger cations from the pore fluid, the higher valence cations collapse the clay mineral structure into a more stable configuration exuding excess double-layer water in the process. Thus, based upon this mechanism, ionic additives would be suitable for soils that have a significant amount of clay material in order for the change in the clay structure to have a pronounced effect on the soil. In addition, the process of altering the properties of the electrolyte pore fluid, inducing the flocculation of clay minerals, and the collapse of the clay mineral structure would be expected to require a significant amount of time.

b. Research also speculates that the mechanism by which enzymes stabilize soils consists of bonding between the enzyme and large organic particles. The large organic particles are then attracted to the net negative surface charge of the clay minerals, and the organic molecule attraction eventually balances the net negative charge of the clay minerals. This reduces the clay's affinity for water. This mechanism suggests that the use of enzymes to stabilize soil requires that the soil composition include

a significant amount of organic molecules and clay minerals. This process is also expected to require significant time.

c. Historical experiments indicate that the stabilization mechanism of most polymer products is based upon physical bonding between individual soil particles. Thus, polymer-based additives are more suitable for the stabilization of granular soils. The actual chemistry of the particular additive may include other chemicals that could provide some secondary stabilization benefits.

d. Minerals such as quartz or calcite, which have no double-layer water, are more likely to perform better with stabilization additives whose primary reinforcement mechanism is physical bonding. Materials such as smectitic clays would probably work better with hydrophilic materials than hydrophobic materials because of the high water content of clays. Stabilizers that can produce a chemical bond between the stabilizer and the substrate should produce the best bonding characteristics. The high specific surface area of clay minerals also suggests that additives that rely on physical bonding may be difficult to adequately disperse in fine-grained clay materials.

e. The soil analyses conducted on the clayey silty-sand (SM-SC) indicate that it is a granular material with some plasticity characteristics due to significant fines content. Thus, additives that rely upon a physical bonding mechanism will be more effective with this soil than those with a chemical reaction mechanism, because of the lack of a significant amount of clay minerals, exchangeable cations, or bound water.

f. The analyses conducted on the low-plasticity clay (CL) suggest that both physical bonding and chemical reaction mechanisms may be beneficial in improving the strength properties of the material. The magnitude of the strength improvement due to physical bonding additives will be less than a similar quantity used in a granular material. This is because of the high specific surface area of the clay minerals, the reduced individual grain size, and the inability to adequately mix the additive into fine-grained soils. Chemical additives may be successful in altering the properties of the CL soil, as a result of the soil possessing a significant amount of clay minerals and bound double-layer water.

g. The soil tests conducted on the high-plasticity clay (CH) demonstrated only minor changes in the soil when combined with additives that rely upon physical bonding mechanisms due to high specific surface area minerals, reduced grain size, and the inability to adequately coat individual particles. Stabilization additives that rely upon chemical reactions with the clay minerals should be successful in altering the properties of the CH soil through cation exchange, flocculation, and reduction of the double-layer water within the mineral structure.

h. Ven-Set 950 appears to be an ionic stabilization additive and, as such, its ability to effectively alter the properties of a soil are dependent upon the soil's mineralogy. Ven-Set 950 would be expected to behave as a surfactant and adsorb onto particles, and has the potential to develop ionic bonds with cations present in clay soils.

i. The reinforcement mechanism of Enviroseal 2001, a polymer emulsion, is a physical bond generated by a cementation between particles. The amount of product required to effectively stabilize a soil will be dependent upon the soil's grain size distribution and ability to adequately mix the material into the soil.

j. Soil-Sement is a polymer emulsion that will provide a physical bond between soil particles. Soil-Sement's effectiveness will also be dependent upon the soil's gradation and will be more effective in granular materials.

k. PolyPavement is also a polymer emulsion that will physically bind soil particles together similar to Soil-Sement and Enviroseal 2001. Thus, PolyPavement would be expected to be more effective in granular materials than fine-grained soil.

l. Dustac 100 is a lignosulfonate that may act as an ionic surfactant capable of forming ionic bonds with cations present in clay soils with minor physical bonding attributes. As a lignin, this product may be susceptible to leaching from the soil with moderate precipitation.

m. Road Bond EN1 is an acid that is expected to act as an ionic stabilizer by altering the properties of the electrolyte fluid in the clay mineral structure. Thus, its stabilization mechanism is a chemical reaction and may require time to produce significant changes in the soil's engineering properties.

n. Road Oyl is a natural resin that would produce a physical bond between soil particles similar to Soil-Sement, Enviroseal 2001, and PolyPavement. However, since Road Oyl is a by-product, it may not be as efficient in generating the physical bonds as engineered bonding agents for the same percent solids.

o. Soil stabilization additives directly influence the void ratio, hydrostatic stress state, and the free energy resulting from changes in water content. These factors affect the limiting state of the soil and influence the ability to model the behavior of stabilized soil within a pavement system.

p. The ability of an additive to increase soil strength is derived from its enhancement of the stability of the interparticle contacts. This increase in soil strength is often attributed to increased internal friction or cohesion, but may be more generally described as the change in surface tension between particles and/or the additive.

1 Introduction

Military engineers are continually faced with maintaining and developing pavement infrastructure with limited financial resources. Traditional pavement design and construction practices require high-quality materials for fulfillment of minimum construction standards. In many areas of the world, quality materials are unavailable or in short supply. Because of these constraints, engineers are often forced to seek alternative designs using substandard materials, commercial construction aids, alternative pavement materials, and innovative design practices. One category of pavement materials receiving increased attention is soil stabilization additives. Soil stabilization additives can be divided into two broad categories, traditional stabilizers and nontraditional additives. Traditional stabilization products include the use of cement, lime, fly ash, and bituminous products. Traditional stabilization products have been intensely researched, and their fundamental stabilization mechanisms have been clearly identified. Nontraditional soil stabilization additives consist of a variety of commercially available chemical and liquid agents designed to enhance the engineering properties of geotechnical materials. These products are diverse in their composition and the manner in which they interact with the soil. Unfortunately, most of these products are relatively immature, and little is known regarding their interaction with geotechnical materials and their fundamental stabilization mechanisms. The research described herein represents the first phase of an effort to investigate the biological, physical, and chemical processes associated with new chemical/liquid soil stabilization technology.

Objective

The objective of the research was to develop a knowledge base of the chemical and physical bonding mechanisms associated with selected chemical and liquid stabilizers. The objective was accomplished by conducting laboratory experiments on selected stabilization products including acids, polymers, and tree resins. These experiments focused upon characterizing the biological, physical, and chemical processes relating to increased soil strength, reduced shrink/swell potential, and increased durability. Additional laboratory experiments will be conducted in a separate experiment phase to identify and characterize the composite stabilized material. Experiments will also be performed to evaluate the behavior of these stabilized materials when exposed to moisture-saturated conditions. Experts in the fields of chemistry, polymers, clay mineralogy, and soil stabilization will use the results of these experiments to develop the reaction equations and identify the primary bonding sources. Once the knowledge base is developed concerning the primary mechanical properties, the structural behavior will be investigated to determine how the stabilized materials behave as a pavement system. The development of a pavement systems model with stabilized layers will assist engineers in understanding how individual properties contribute to pavement performance. The model will also provide tools for predicting the suitability of a chemical stabilizer for a given set of environmental conditions based upon the predicted performance of the pavement. Therefore, the ultimate objective of the research program is to develop a knowledge base of the fundamental stabilization mechanisms of chemical/liquid stabilizers and a model of pavement performance capable of assessing stabilizer suitability.

Scope

This document describes the first phase of the research program including the characterization of the composition of selected stabilization agents and geotechnical materials. The composition of each stabilization additive is characterized using a battery of laboratory tests designed to fully identify the constitutive properties of the individual additives and geotechnical materials. These laboratory experiments included taxonomic identification, grain-size distribution, organic/ inorganic carbon determination, sequential extraction, gel permeation chromatography, pH tests, scanning electron microscope (SEM) imaging, X-ray diffraction (XRD) imaging, and other chemical analyses to determine the primary constituents of the mineral, soil, and the stabilizer. The results of the laboratory test program were used to characterize each material, and pertinent conclusions were drawn regarding the potential of each material to stabilize soils.

Literature Review

A detailed literature review was conducted to determine the state-of-the-art in soil stabilization. Numerous citations were identified that fully characterize the stabilization processes and reinforcement mechanisms of traditional stabilization additives (Transportation Research Board 1987, American Concrete Institute 1990, and American Coal Ash Association 1995). However, little independent research has been documented pertaining to the use of nontraditional stabilization additives. A large quantity of advertisements, pamphlets, and videos has been distributed testifying to the benefits of a particular stabilization additive. Unfortunately, most of the information disclosed in these media is subjective and traditional engineering properties are poorly documented. Because of the proprietary nature of the majority of these products, the mechanisms by which they interact with the soil are unknown. Another concern is the discontinuity of brand names resulting from frequent reformulations and changes in marketing strategies. Frequent brand changes result in a lack of product history and eventually poor user familiarity. One final barrier to the acceptance of nontraditional stabilization additives is the lack of standardized test procedures for evaluating product potential.

The variety of nontraditional stabilization additives has led to various attempts to categorize products according to their active components. Oldham et al. (1977) developed a synthesis of potential stabilizers identified by the Corps of Engineers and contract researchers from 1946 to 1977. Their report identified acids, asphalt, cement, lime, resins, salts, silicates, and other products as potential stabilizers demonstrating varying degrees of success. The results of their investigation divided performance by soil type and demonstrated that product performance differed for varying soil types. They also noted that the stabilization mechanisms for individual stabilizing agents, such as salts, were particularly suited for specific climates and environmental conditions. Unfortunately, most of the products evaluated under the research documented in this reference are no longer commercially available, have altered their formulas, or have changed trade names. Scholen (1992) categorized nontraditional stabilizers into five groups: electrolytes, enzymes, mineral pitches, clay fillers, and acrylic polymers. The proprietary nature of many of the products hinders the categorization process. The following paragraphs provide an overview of the available literature and pertinent conclusions. For organizational purposes, it was convenient to divide the stabilization into groups based upon their generically reported composition. The following stabilization groups were used: traditional additives, salts, acids, enzymes, ionic additives, polymers, lignins, silicates, and mineral pitches. The literature was also divided into two categories, stabilization of fine-grained soils and stabilization of granular soils.

Stabilization of fine-grained soils

Scholen (1992, 1995) attempted to describe the reinforcement mechanisms for stabilizing clay soils with ionic additives and enzymes. Scholen hypothesized that the electrolytes or ionic stabilizers served as catalysts to accelerate the weathering process of individual clay minerals. He proposed that the ionic stabilizers alter the electrolyte concentration of the pore fluid resulting in cation exchange and flocculation of the clay minerals. As the clay minerals attract stronger cations from the ionic electrolyte pore fluid, the higher valence cations collapse the clay structure into a more stable configuration exuding excess double-layer water in the process. The resulting clay material typically exhibits reduced plasticity, reduced swell potential, and reduced particle size. However, Scholen (1992) notes that a change in the quality of the environment from alkali to acidic or vice versa can result in a complete change in the material's molecular structure but usually over long periods of time. Scholen (1992) also hypothesized the mechanism by which enzymes could stabilize clay materials. He proposed that the enzymes could bond with large organic molecules that would be attracted to the clay minerals net negative surface charge. The large organic molecules would then surround the clay minerals neutralizing the negative charge and reducing the clay's affinity for moisture. The end result of both proposed mechanisms is a more stable clay lattice structure and a reduced affinity for moisture.

Numerous laboratory experiments have been conducted over the years with specific soil stabilizers. Although frequent brand changes and product reformulation have rendered specific product performance reports obsolete, performance trends and behavioral characteristics of individual product categories remain meaningful. Given this consideration, various research findings are presented focusing on the performance trends of individual product categories. For example, Scholen (1992, 1995) indicated that limited laboratory testing revealed only minor changes in grain size distribution and Atterberg limits for 10 clays gathered from construction projects stabilized with one of seven chemical stabilization additives including electrolytes, enzymes, mineral pitch, clay filler, and an acrylic polymer.

Ajayi-Majebi et al. (1991) conducted an experiment designed to determine the effects of stabilizing clay-silt soils with the combination of an epoxy resin (bisphenol A/epichlorohydrin) and a polyamide hardener. The additive mixture was composed of a 1:1 ratio of epoxy resin to polyamide hardener. Reported soil properties included a liquid limit ranging from 37 to 45 and a plasticity index ranging from 13 to 18. Ajayi-Majebi et al. concluded that admixing up to 4 percent stabilizer into a clay-silt material produced large increases in the load-bearing capacity of the material in terms of its unsoaked California Bearing Ratio (CBR). They observed that increases in the temperature of the curing environment led to increased strength formation. Cure times for the stabilization agent were reported as low as three hours.

Katz et al. (2001), Rauch et al. (2002), and Rauch (2002)[1] conducted a series of laboratory experiments designed to measure the engineering property effects and mechanisms of three liquid stabilizers on five clay soils. The three liquid stabilizers included an ionic stabilizer (electrolyte), an enzyme, and a polymer product. The clay materials consisted of three relatively "pure" clay minerals (kaolinite, illite, and sodium montmorillonite) and two high-plasticity clays. The liquid limits of the two natural clay soils ranged from 60 to 68, and the plasticity indices ranged from 37 to 48. Katz et al. (2001) performed various laboratory mineralogy tests on sodium montmorillonite clay samples stabilized with the ionic stabilizer at manufacturer recommended additive rates. Their results indicated only minor changes in the d-spacing between molecular layers and concluded that the application rates were much too low to effectively accelerate the clay's "weathering" process as proposed by Scholen (1992, 1995). A follow-on study was conducted by Rauch et al. (2002) to measure changes in commonly reported engineering properties for the three stabilizers and five clay materials. The study concluded that the only effective reduction in plasticity occurred with the ionic stabilizer in sodium montmorillonite. They reported no significant effect of any stabilizer on the compacted density or optimum moisture content. Also, among the three products evaluated, there was no consistent reduction in swell potential. Further unpublished testing by Rauch[1] including the same three stabilizers and five clay minerals indicated only minimal changes in X-ray diffraction results, specific surface area, and alumina-silica ratios for very high additive quantities of 50 percent by dry weight of clay. However, the

---

[1] Personal Communication, February 2002, A. F. Rauch, "Mechanisms of soil stabilization with liquid stabilizers," University of Texas at Austin.

researchers noted that the minor changes in the properties of the clay minerals did tend to support Scholen's hypothesized mechanisms for the ionic and enzyme stabilization additives.

Laboratory testing conducted by Scullion (2002)[1] on a clay soil stabilized with two acid (ionic) stabilizers revealed no significant reduction in shrink/swell potential or strength improvement for either product. A chemical analysis of treated and untreated samples failed to reveal any observable changes within the stabilized specimens using pH measurements, scanning electron microscope (SEM) imaging, and energy dispersive spectrometer (EDS) analyses.

Many manufacturers contend that common laboratory testing procedures do not provide adequate indicators of field performance. Scholen (1992) reported 34 abbreviated citations of successful field use of seven different nontraditional stabilization products. Unfortunately, these testimonials are poorly documented and do not include direct comparisons to untreated control sections. Indeed, the authors of this paper have found that a common tendency is to only report or publish successful projects making it difficult to discern the success rate of specific products. The authors have personal knowledge of at least two unsuccessful projects completed with the use of one of the ionic stabilizers reported by Scholen. Scullion[1] conducted field experiments during two highway construction projects in Texas to evaluate the potential for two ionic stabilizers and one polymer additive to stabilize an expansive clay subgrade. Scullion reported that none of the products provided an effective working platform. Dynamic cone penetrometer and falling-weight deflectometer results showed no substantial improvement in bearing strength or stiffness. It should be noted that the polymer experienced curing problems that resulted in exclusion from further testing.

In summary, various researchers have divided nontraditional stabilization additives into broad categories dependent upon the stabilizer's primary active components. Attempts to define the reinforcement mechanisms have been limited, but laboratory experimentation has provided minimal support for the hypothesized mechanisms for ionic stabilizers and enzymes. The benefit of many of the commercial stabilization additives for stabilization of clay soils has not been conclusively shown in the laboratory experiments cited. Well-documented field studies are lacking with limited testimonials indicating success. The approach of the research program presented in this paper is to screen commercial products to identify those demonstrating the greatest potential for success. Once specific products are identified, additional studies will be conducted to define the reinforcement mechanisms and evaluate their performance under field conditions.

---

[1] Personal Communication, February 2002, T. Scullion, "Identifying the benefits of nonstandard stabilizers in high-sulfate clay soils; Status report," Texas Transportation Institute, College Station, TX.

Stabilization of granular soils

A literature review of research on the stabilization of granular materials with nontraditional additives produced fewer documented efforts than for fine-grained soils. This should be expected since fine-grained soils tend to be more problematic during geotechnical construction. Oldham et al. (1977) concluded that polymer resins provided the greatest increase in unconfined compressive strength (UCS) for sand materials. A variety of polymer products were cited, but most of the products noted are no longer manufactured or have changed trade names.

Gopal et al. (1983) performed comparative studies using urea-formaldehyde (UF) and its copolymers to stabilize dune sand. Specimens were prepared at different combinations of UF ratios, pH levels, and acid catalysts. All specimens were cured for 6 hr at 60 °C. The results showed a maximum UCS of 16,182 kPa. Lowering the pH of the additive mixture using phosphoric acid catalysts improved the relative strength increase of the specimens. The optimum UF ratio for their experiment was 1:2.25 urea to formaldehyde by weight. Gopal et al. recommended using 9 percent resin and 0.3 percent acid catalyst for stabilizing dune sands.

Vvedenskaya et al. (1971) used copolymers to consolidate sands, silts, and clays. The copolymers used were guanidine acrylate (GA), methylene bisacrylamide (MBAM), and ethylene dimethacrylamide (EDMA). The additive formula consisted of a 24:1 ratio of vinyl monomer to diene. They reported increased strength due to increased hydrogen bonding, increased copolymer yield, and increased intermolecular bonding. The combination of GA and EDMA performed best in sands and loams followed by GA combined with MBAM. They reported an increase in UCS of 2,455 to 2,944 kPa for a 5 percent additive mixture in sand. Vvedenskaya et al. reported that the formation of the polymer-soil structure during soil consolidation was completed in less than 10 days. They recommended that the additive quantity should range between 5 and 10 percent.

Palmer et al. (1995) conducted experiments to evaluate the strength and density modification of unpaved roads using lignin sulfonate (lignin), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$). Additive concentrations ranged from 1.0 to 3.25 percent by dry weight. Laboratory results indicated that lignin was the only product of the three tested that increased specimen density. Laboratory tests on specimens subjected to four wet-dry cycles indicated reduced UCS with increasing additive content. The maximum reported UCS was 7,660 kPa for a 7-day air-dried silty-sand (SM) specimen stabilized with lignin at a concentration of 2.5 percent by dry weight. Dry UCS results for $CaCl_2$ and $MgCl_2$ stabilized soils were lower than control specimens. However, the field application of lignin performed poorly as the result of a combination of poor application methods and the high solubility of lignin sulfonate. Palmer et al. reported effective dust control of a lignin-modified unpaved road for a period of 28 days with nominal dust abatement for a total period of 69 days. Erosion and leaching of the lignin during exposure to moisture were identified as the primary source of strength degradation. These results suggest good performance with lignin in terms of increased strength, while poor performance in terms of moisture susceptibility.

2 Mineralogical Analyses

The minerals used in this study were characterized for particle size distribution, mineralogy, and morphology using laser scattering particle analysis, X-ray diffractometry, and scanning electron microscopy.

Methods

Particle size distribution analysis

Eight samples of soil were analyzed for particle size determination in the range of 0.02 to 1,020 µm using a Horiba LA-910 light scattering instrument (Figures 1 through 3). The samples were first sieved to remove particles larger than 1,000 µm, dispersed in water containing surfactant, and sonicated to break up agglomerates. A relative refractive index of 1.80 was used based on the default refractive index of inorganic materials dispersed in water.

X-ray diffraction analysis

The X-ray diffraction (XRD) samples were run as randomly oriented packed powders. A Philips PW1800 Automated Powder Diffractometer system was utilized to collect X-ray diffraction patterns employing standard techniques for phase identification. The run conditions included Cu K_α radiation and scanning from 2 to 65 °C with collection of the diffraction patterns accomplished using the PC-based, Windows-based version of Datascan, and analysis of the patterns using the Jade program from (both from Materials Data, Inc.). In preparation for XRD analysis, a portion of the sample was ground in a mortar and pestle to pass a 45-µm mesh sieve (No. 325). Bulk sample random powder mounts were analyzed using XRD to determine the mineral constituents present in each sample (Figures 4 through 13).

To determine the type of phyllosilicates present, oriented samples of the <2 µm size fraction of each sample were prepared and, XRD patterns were obtained. These samples were then placed in an ethylene glycol atmosphere overnight at room temperature, and an X-ray diffraction pattern was collected for each sample. Samples that show expansion of the crystal structure after exposure

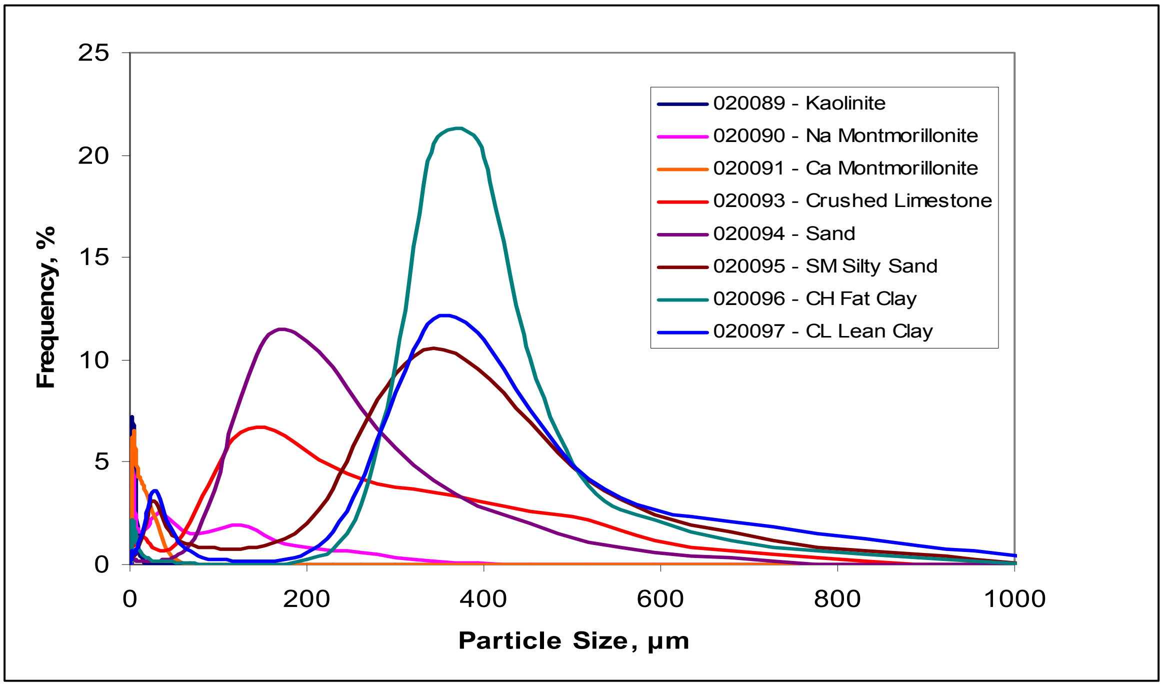


Figure 1. Particle size distribution analysis of minerals

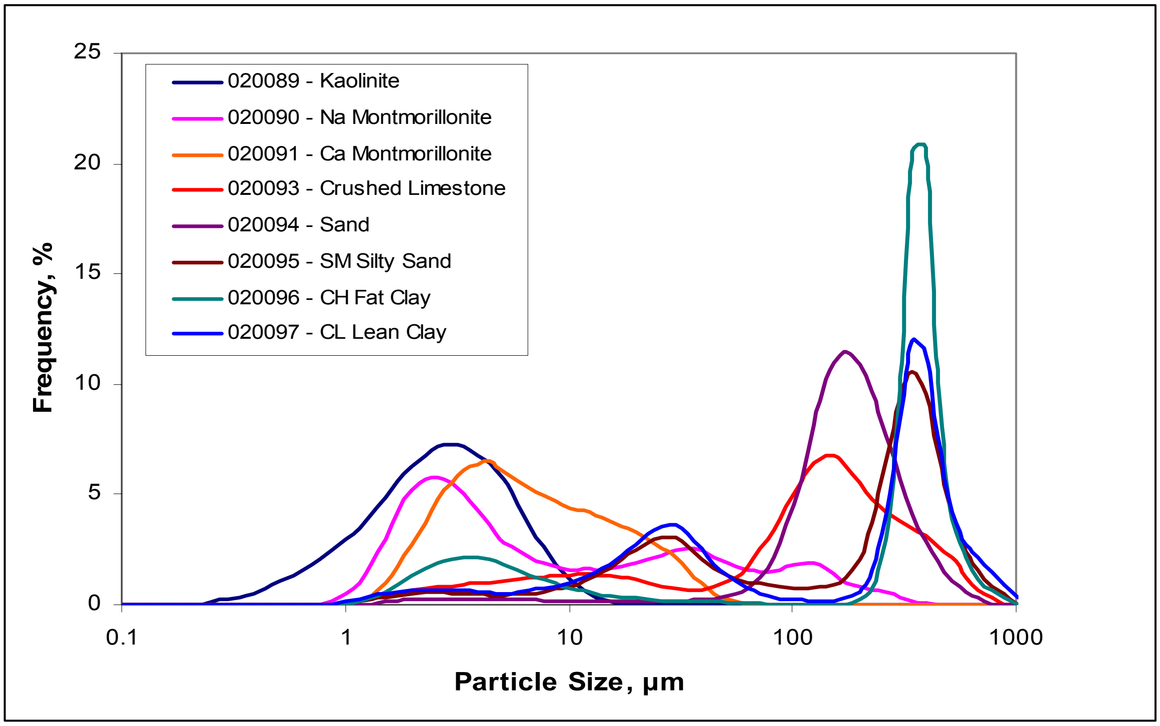


Figure 2. Log-scale particle size distribution analysis of minerals

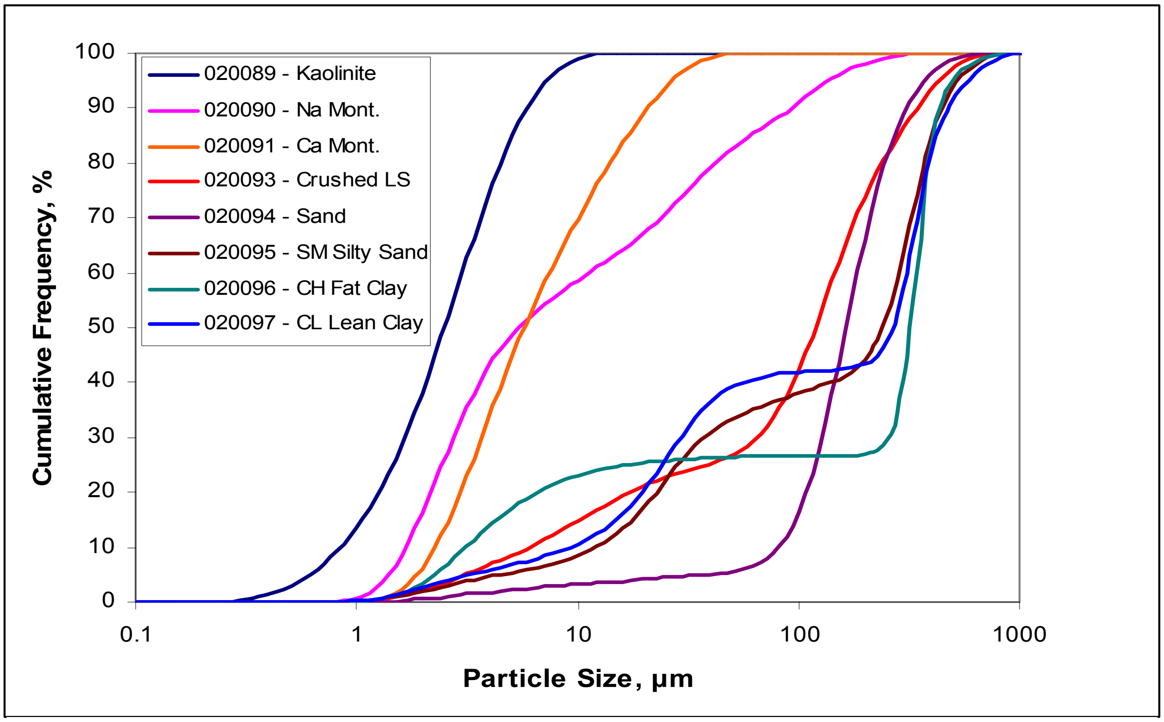


Figure 3. Cumulative log-scale particle size distribution analysis of minerals

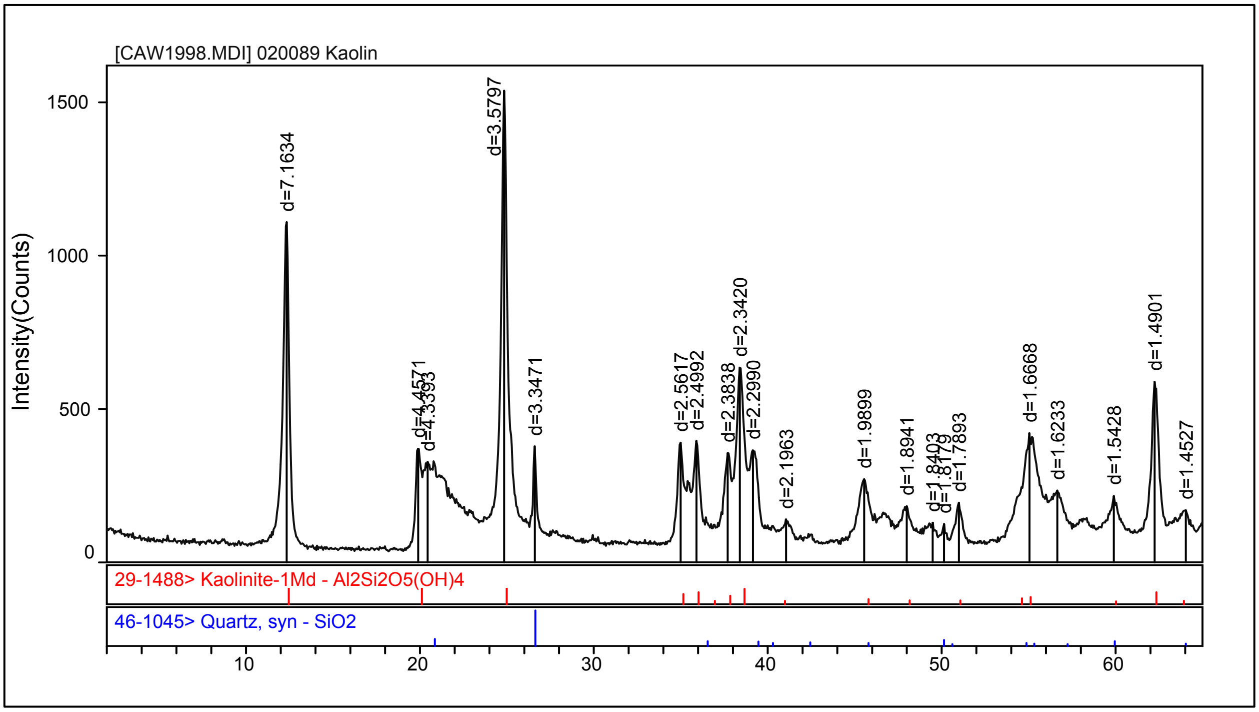


Figure 4. X-ray diffraction pattern of kaolinite

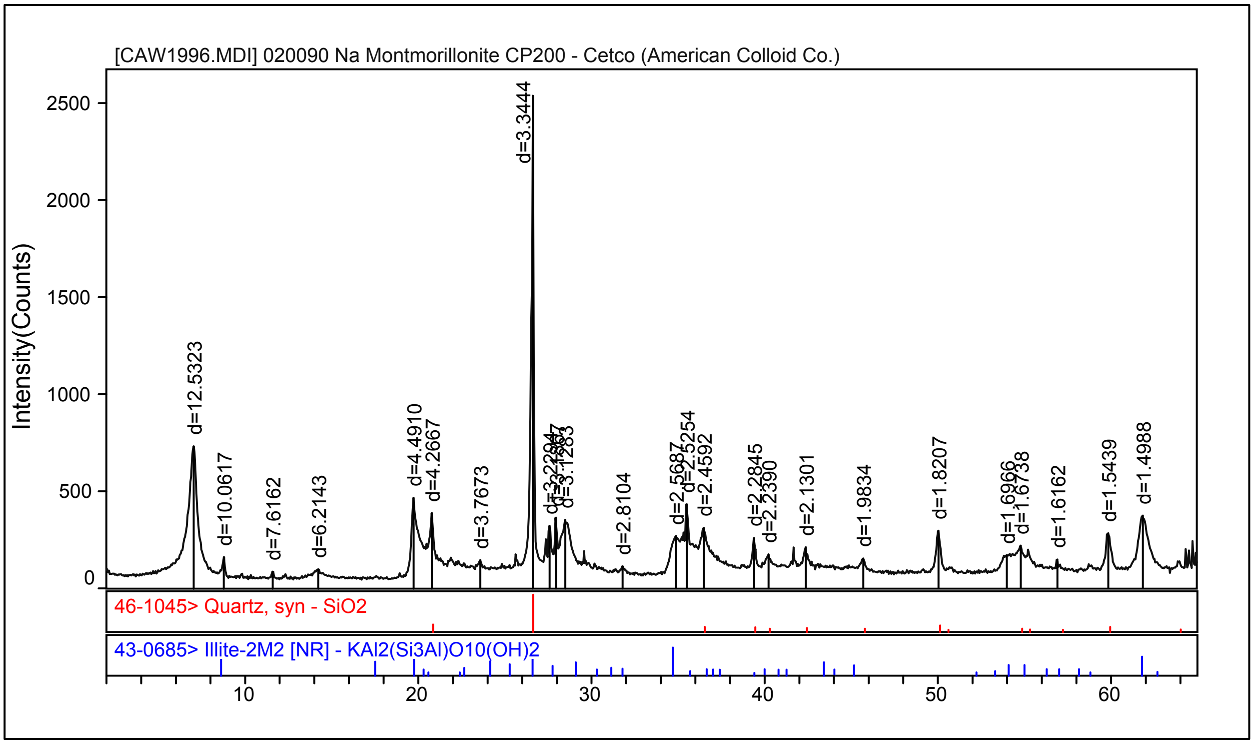


Figure 5. X-ray diffraction pattern of Na montmorillonite

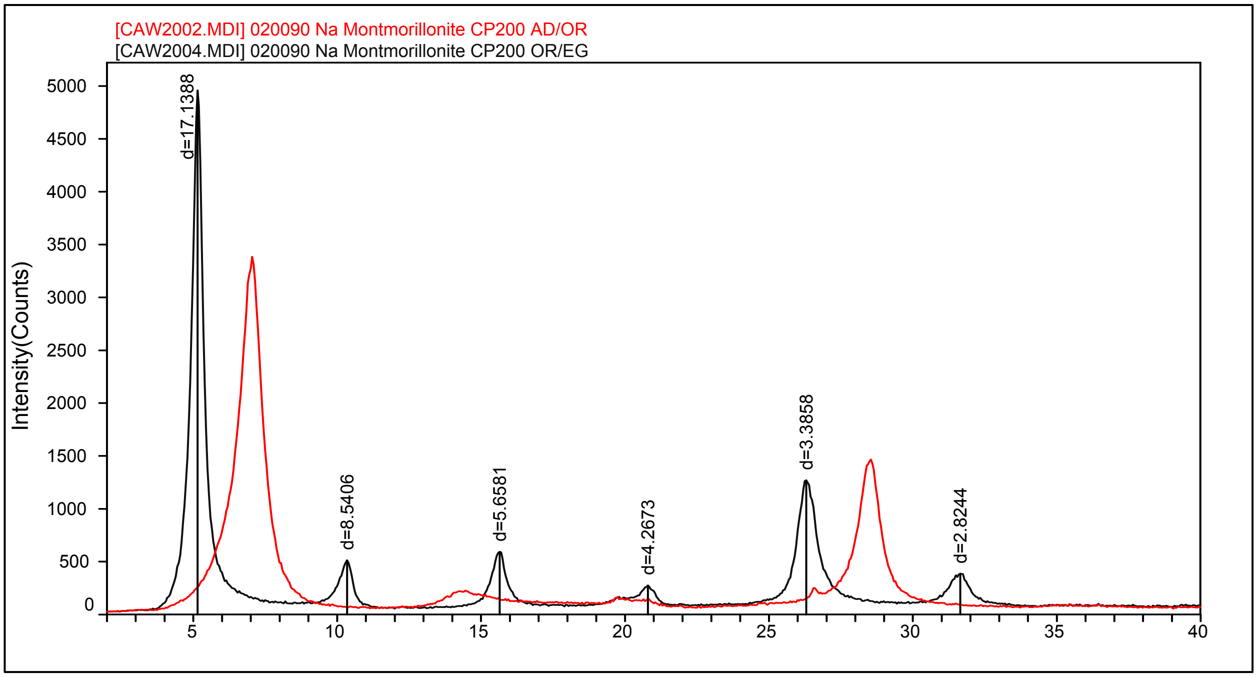


Figure 6. X-ray diffraction pattern of Na montmorillonite before and subsequent to exposure to ethylene glycol

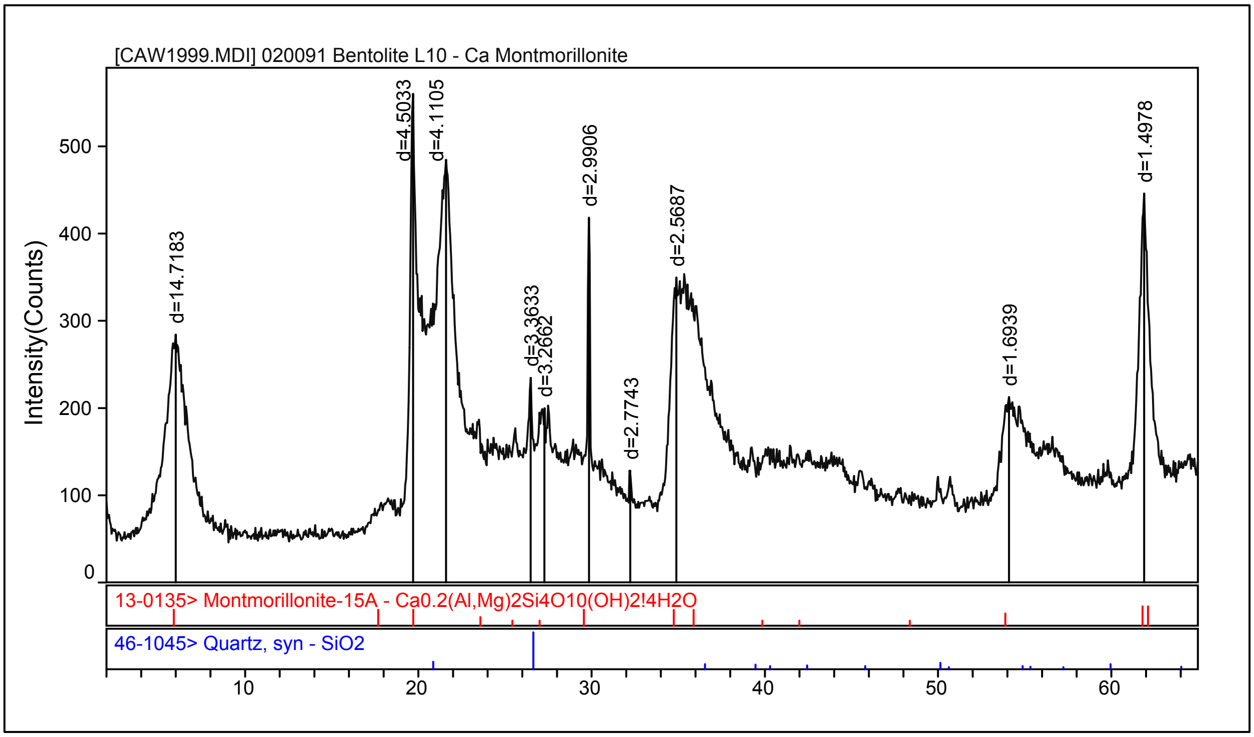


Figure 7. X-ray diffraction pattern of Ca montmorillonite

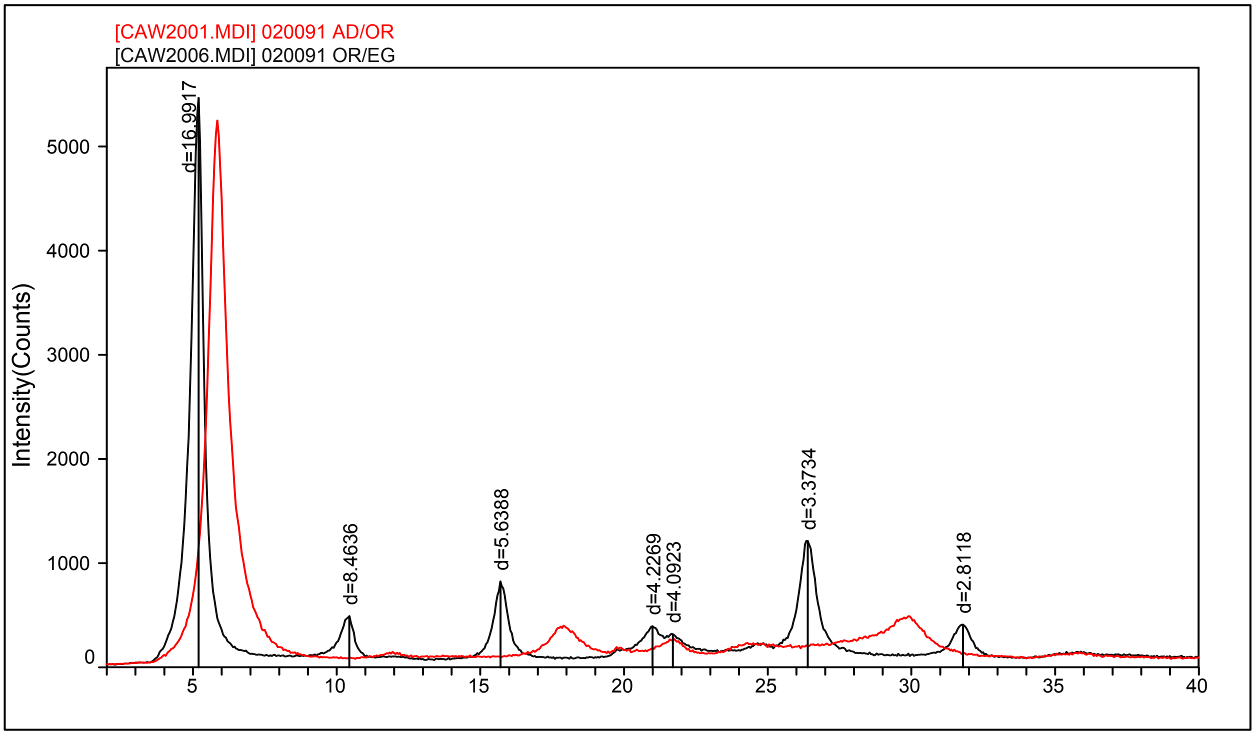


Figure 8. X-ray diffraction pattern of Ca montmorillonite before and subsequent to exposure to ethylene glycol

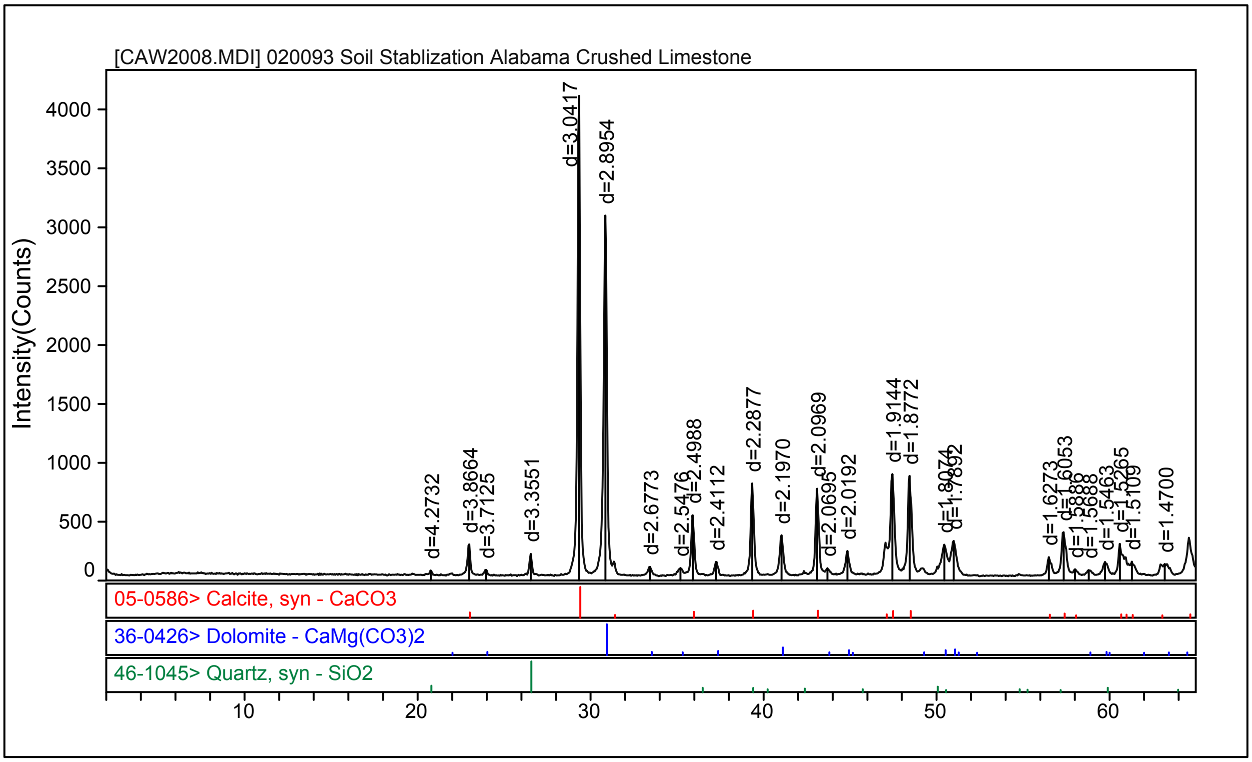


Figure 9. X-ray diffraction pattern of limestone dust

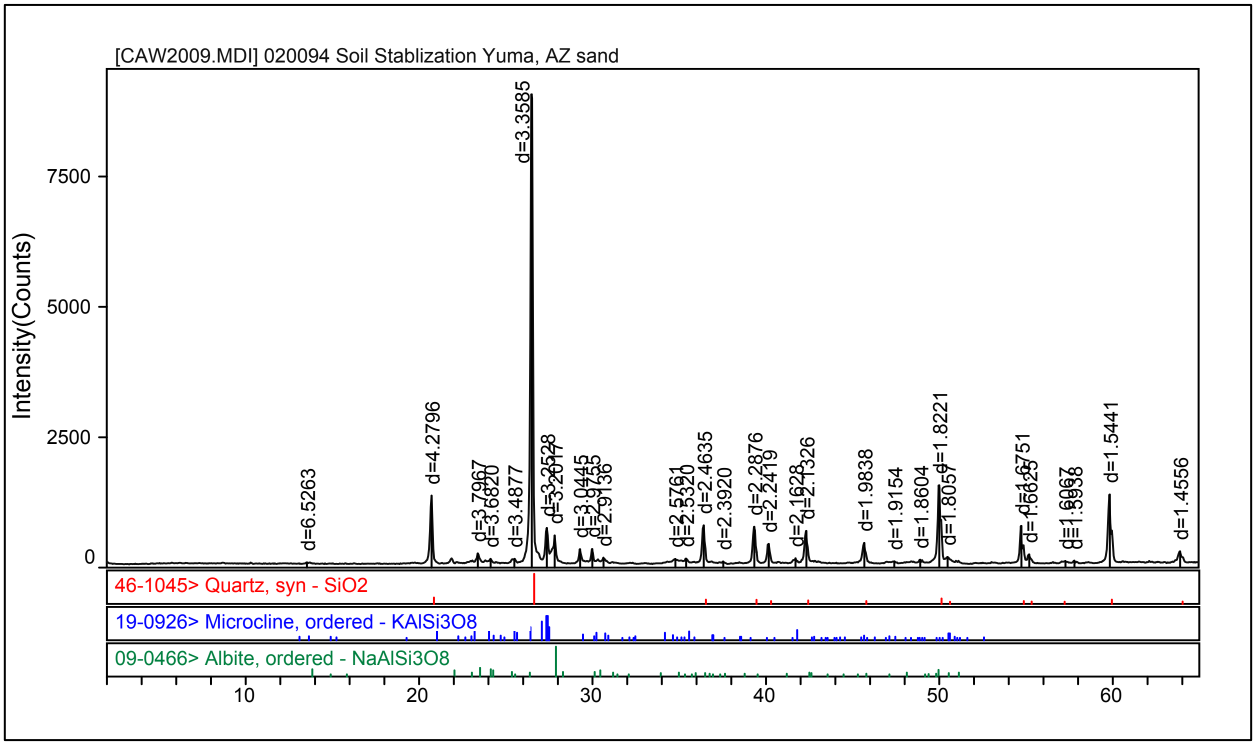


Figure 10. X-ray diffraction pattern of Yuma sand comprised primarily of quartz and feldspar

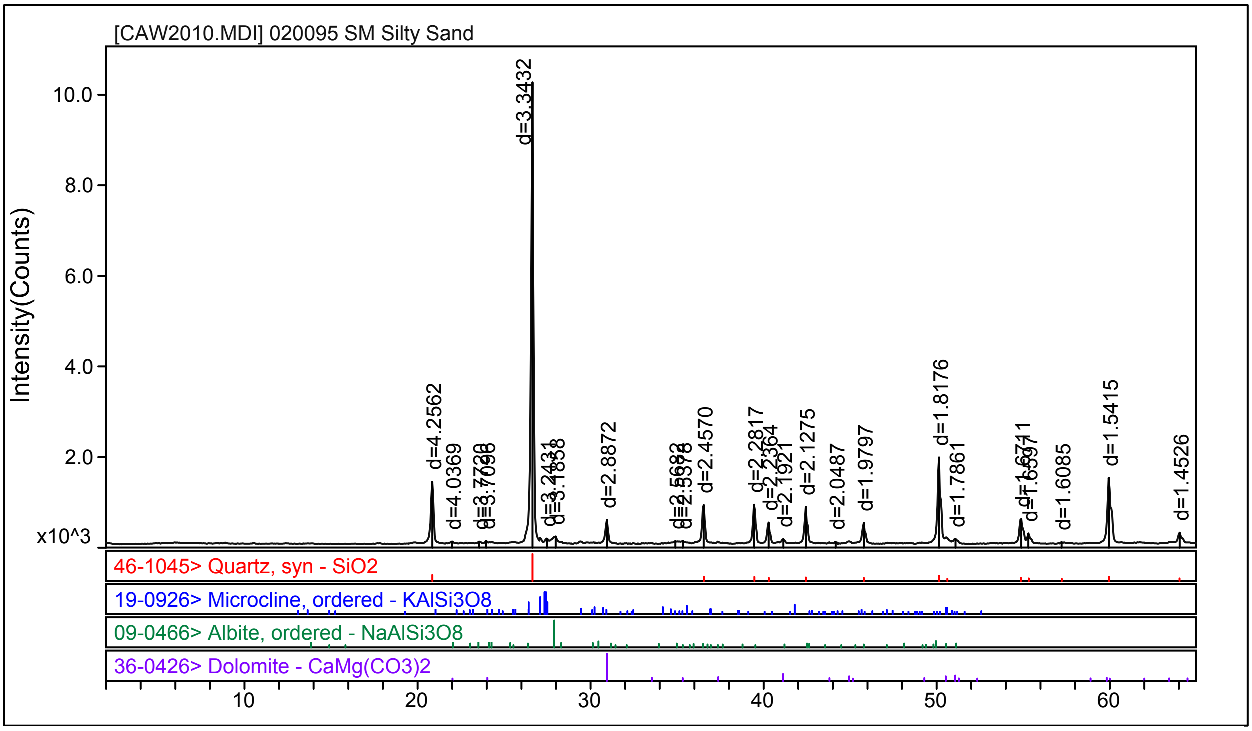


Figure 11. X-ray diffraction pattern of SM-SC (a sand consisting primarily of quartz, dolomite, and feldspar (microcline))

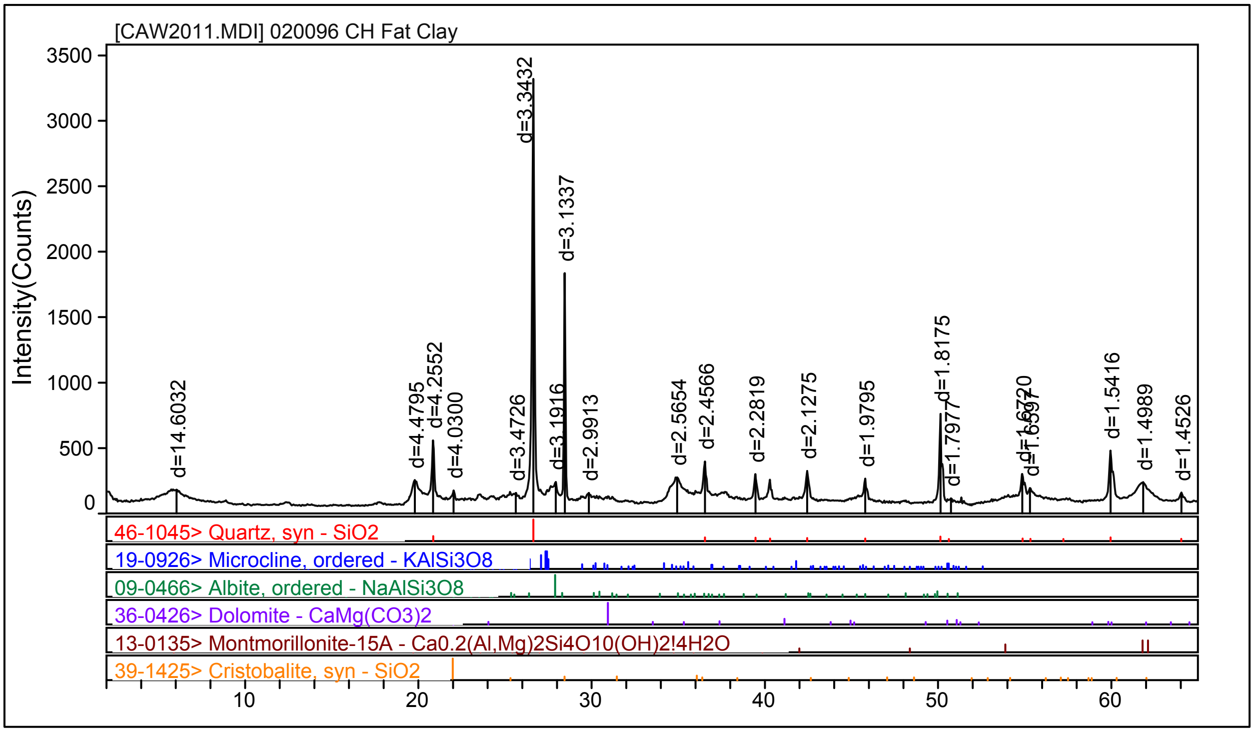


Figure 12. X-ray diffraction pattern of CH (fat clay)

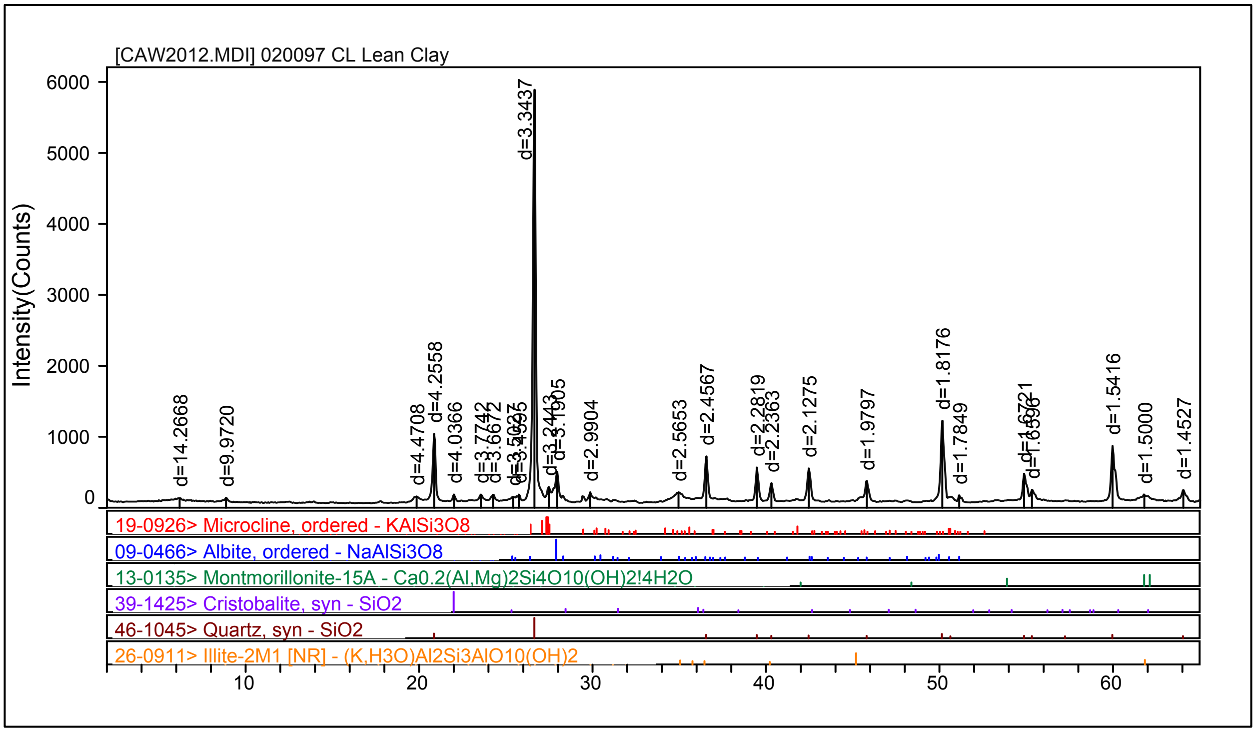


Figure 13. X-ray diffraction pattern of CL (lean clay)

to an ethylene glycol atmosphere compared to air-dried pattern indicate expandable smectitic clays. Comparisons of patterns obtained before and after exposure to glycol were used to determine the amount of expandable clay present.

Scanning electron microscopic analysis

Electron photomicrographs of selected uncoated samples (Figures 14 through 18) from this study were obtained using an ESEM Model 2020 with a lanthanum hexaboride (LaB_6) electron source and a gaseous secondary electron detector (GSED). The imaging conditions employed an accelerating voltage of 20 KeV and 1.81 mA and approximately 5 torr (665 Pa) water vapor in the sample chamber. The environmental gas was vaporized distilled water supplied via a digitally controlled needle valve assembly contained in a sealed Erlenmeyer flask located outside the sample chamber. Images of these samples were collected over a period of 30 sec, and stored as 1-MB TIF files.

Results and Discussion

Particle size distribution analysis

The particle size distributions for the soil materials to be used in the stabilization research are shown both in a linear scale (Figure 1), on a logarithmic scale

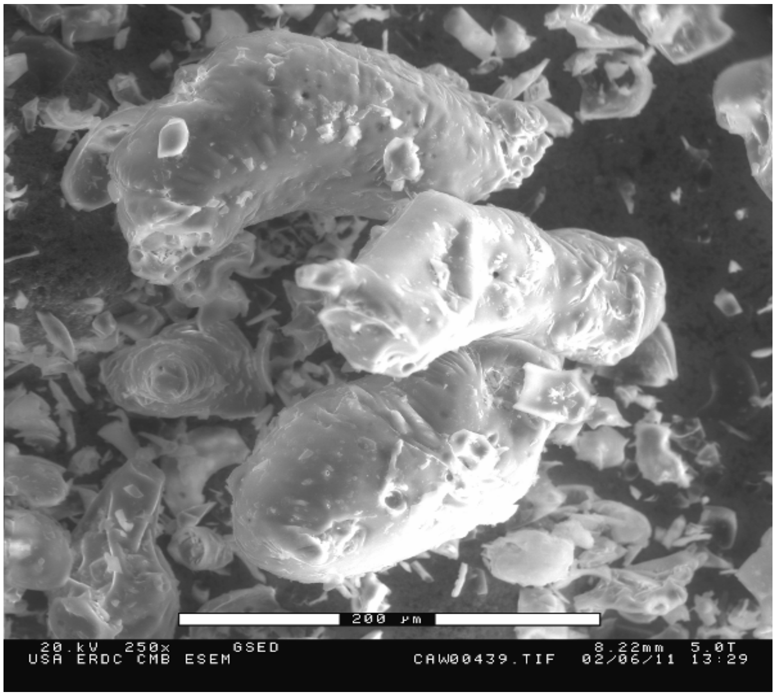


Figure 14. Scanning electron photomicrograph 1, Dustac 100

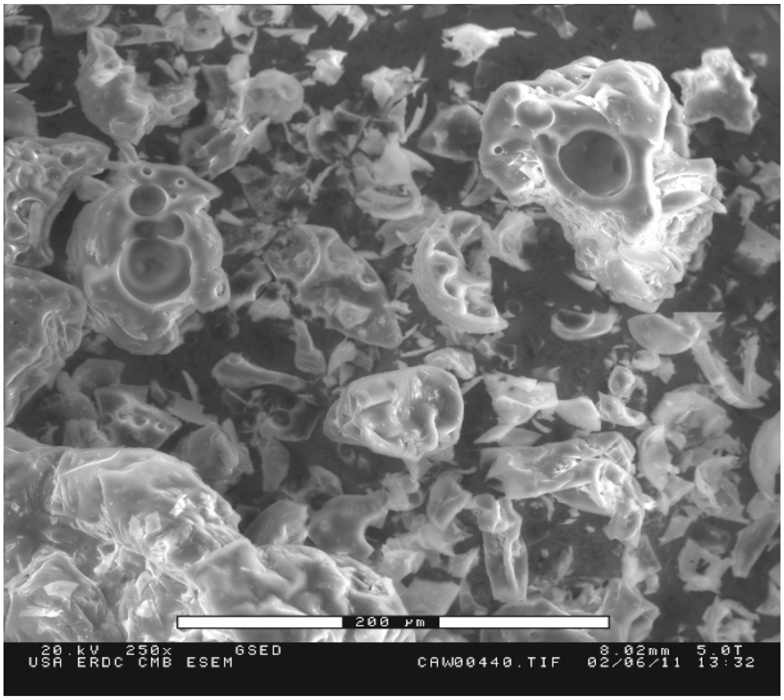


Figure 15. Scanning electron photomicrograph 2, Dustac 100

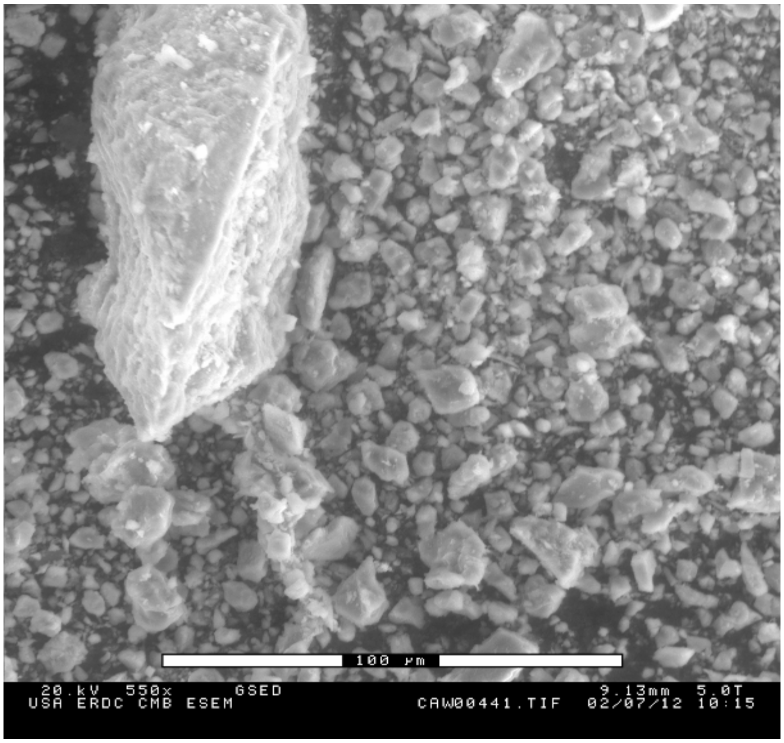


Figure 16. Scanning electron photomicrograph of limestone dust

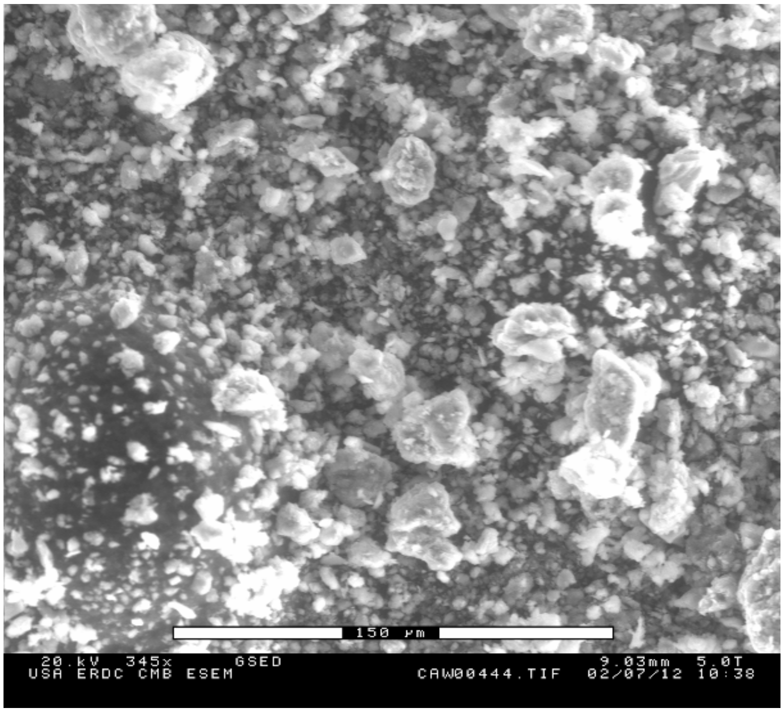


Figure 17. Scanning electron photomicrograph of Ca montmorillonite (CMB No. 020091)

Figure 18. Scanning electron photomicrograph of Yuma sand (CMB No. 020094)

(Figure 2), and a cumulative distribution on a logarithmic scale (Figure 3). Care must be taken when interpreting these data as particles larger than 1,000 µm were removed by sieving. The monomineralic clays (Na montmorillonite, Ca montmorillonite, and kaolinite) and the fat clay (CH) sample had the finest grain sizes with a large fraction of their material <10 µm in size, but had a large fraction of coarse material as indicated in Figure 3. The fat clay (CH) sample had a bimodal distribution of grain size with a fine fraction centering around 5 µm and the coarser fraction centered about 400 µm. Both the lean clay (CL) and the silty-sand (SM-SC) have similar size distributions fine fraction. The sand sample is fairly uniform in size centered about 200 µm.

XRD analysis

The mineralogy of each sample as each was received is given in Figures 4 through 11. This was done to determine a baseline for subsequent studies to determine if subsequent treatments to the materials affect the structures of the materials. In addition, these data permit the relevance of using certain stabilizers on selected soils based on mineralogy to be determined. A summary of the mineral phases found in each sample can be seen in Table 1.

Table 1
Qualitative Mineralogy of Samples with Locality, Source, and CMB No.

Sample Designation	Source Locality/Trade Name/Commercial Source	Phases Present	
		Major	Minor or Trace
Kaolinite	Dixie Clay Products, Bath, SC	Kaolinite (disordered)	Quartz
Na montmorillonite	CP 200, American Colloid, CO	Na montmorillonite, quartz	Illite, Na feldspar, K feldspar
Ca montmorillonite	Bentolite L-10, Southern Clay Products, Gonzales, TX	Ca montmorillonite	Quartz
Crushed limestone	Calera, AL	Calcite, dolomite	Quartz
Sand	Yuma, AZ	Quartz	Na feldspar, K feldspar
SM-SC silty-sand	Blended	Quartz	Dolomite, Na feldspar, K feldspar
CH fat clay	Yazoo City, MS	Quartz, montmorillonite	Na feldspar, K feldspar, cristobalite
CL lean clay	Vicksburg, MS	Quartz	Na feldspar, K feldspar, cristobalite, illite, montmorillonite

Scanning electron microscopic analysis

The SEM images were taken to assess the morphology of the particles of each sample. In particular, the size and shape of the particles were of interest. The only solid stabilizer to be used in the research, Dustac 100, was imaged (Figures 14 and 15). Note that there are a significant number of large particles (=300 µm) that are subrounded, as well as a large number of particles that are <50 µm in size. The limestone dust sample (Figure 16) is dominantly comprised of very small, angular particles (<10 µm) and a few which are much larger (=100 µm). The Ca Montmorillonite sample (CMB No. 200091) shown in Figure 17 is very fine-grained with all particles much smaller than 50 µm. The larger particles are actually agglomerations of many finer ones and not discrete particles of the individual minerals. The sand from Yuma, AZ (CMB No. 020094) is composed of subrounded to rounded grains variable in size. In Figure 18, one large particle at least 600 µm in size is shown.

Impact on stabilization alternatives

The rationale for our interest in obtaining the mineralogy (including the amount of clay minerals present), grain size, and angularity stems from the hypothesis that these factors determine how certain stabilizers will perform in the field. Minerals such as quartz or calcite, which have no double-layer water, are more likely to perform better with materials that rely on mechanical bonding. In these cases, the angularity of the particles would play a large role in the ability of the material to make a better mechanical bond. Because the surface area is less for larger particles, it is expected that larger particles would provide poorer surface area bonds compared with smaller particles. Materials such as expandable smectitic clays would probably work better with hydrophyllic materials compared to hydrophobic ones because of the high water content of the clay. Stabilizers that can cause a chemical bond between the stabilizer and the substrate should give the best bonding for large specific surface area characteristics.

3 Soil Analyses

Three natural soil types were selected for inclusion in this investigation: a clayey silty-sand (SM-SC), a low-plasticity clay (CL), and a high-plasticity clay (CH). The silty-sand was chosen because it represents the predominant surface soil type in the world (Robinson and Rabalais 1993). The two clay soils were chosen because clay materials are generally considered to be problematic materials, frequently requiring stabilization during geotechnical and transportation engineering projects. Each material was characterized using a battery of physical tests including: grain-size distribution, Atterberg limits, specific gravity, moisture-density relationships, and unconfined compressive strength.

Soil Characterization Tests

Grain-size distribution

Soils are frequently described by the particle size of their individual components. The grain size distribution for soils with the majority of particle sizes greater than 0.075 mm (No. 200 sieve) is determined by shaking the soil through a nest of sieves. The grain size distribution for soils with a significant percentage of particles less than 0.075 mm is determined by a sedimentation test using a hydrometer. All three soils were subjected to a sieve analysis according to ASTM D 422. The CL and CH soils were also subjected to a hydrometer analysis according to ASTM D 422. The grain size distribution results are shown in Table 2 and Figure 19.

Atterberg limits

The plastic behavior of soils is typically quantified by the material's Atterberg limits. The Atterberg limits consist of three rudimentary tests designed to characterize the soil's plastic behavior. The liquid limit (LL) is defined as the soil moisture content at which a standard groove cut in a pat of soil will close over the length of 12.7 mm when the cup containing the soil is dropped 25 times from a height of 1 cm onto a hard rubber pad. The plastic limit (PL) is defined as the soil moisture content at which the soil just begins to crumble when rolled into 3.2-mm-diam threads. The shrinkage limit (SL) is defined as the moisture

Table 2
Grain-Size Distribution Results for Natural Soils

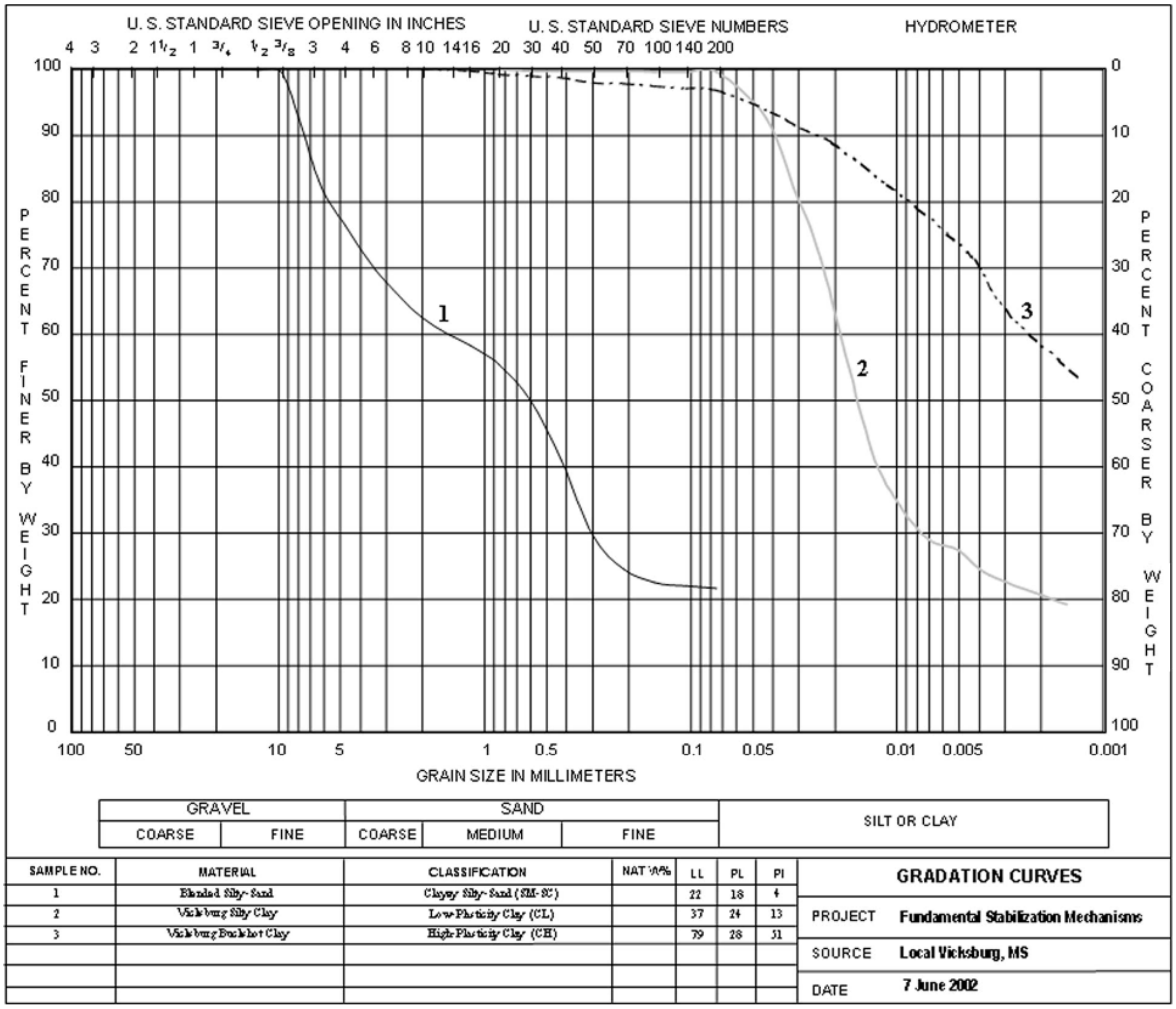
Sieve Size or Number	Opening Size mm	Percent Finer by Weight, %		
		SM-SC	CL	CH
1/2-in.	12.5	100	100	100
3/8-in.	9.5	99.2	100	100
3	6.35	83.2	100	100
4	4.75	76.5	100	100
6	3.35	69.6	100	100
10	2.0	62.5	100	100
16	1.18	58.3	100	99.7
20	0.85	55.5	100	99.3
30	0.60	50.0	99.8	99.0
40	0.425	41.0	99.8	98.7
50	0.30	29.6	99.8	98.0
70	0.212	24.6	99.8	97.8
100	0.150	22.5	99.6	97.5
140	0.106	22.0	99.6	97.1
200	0.075	21.7	99.6	96.8
Hydrometer	(CL)0.0432/(CH)0.0407	23.5	92.7	93.5
Hydrometer	0.0319/0.0292	54.7	82.1	91.1
Hydrometer	0.0235/0.0208	21.7	71.4	89.0
Hydrometer	0.0134/0.0111	--	42.7	82.6
Hydrometer	0.0097/0.0080	--	34.1	79.1
Hydrometer	0.0070/0.0057	--	29.0	75.2
Hydrometer	0.0050/0.0042	--	27.3	71.2
Hydrometer	0.0036/0.0030	--	23.7	63.7
Hydrometer	0.0015/0.0013	--	19.3	53.4

content at which further decreases in moisture content do not cause further shrinkage. The shrinkage limit is seldom used in the United States. Atterberg limits are only performed on the portion of the remolded sample passing the No. 40 sieve. The plasticity index (PI) of the soil is frequently used as an index of the material's plasticity. The PI of the soil is determined by subtracting the PL from the LL. The Atterberg limit results are shown in Table 3 for each soil type.

Table 3
Atterberg Limits and Specific Gravity Results for Natural Soils

Soil Property	SM-SC	CL	CH
Liquid limit (LL)	22	37	79
Plastic limit (PL)	18	24	28
Plasticity index (PI)[1]	4	13	51
Specific gravity	2.67	2.71	2.74

[1] Computed as LL-PL.



SAMPLE NO.	MATERIAL	CLASSIFICATION	NAT W%	LL	PL	PI
1	Blended Silty-Sand	Clayey Silty-Sand (SM-SC)		22	18	4
2	Vicksburg Silty Clay	Low-Plasticity Clay (CL)		37	24	13
3	Vicksburg Buckshot Clay	High-Plasticity Clay (CH)		79	28	51

GRADATION CURVES

PROJECT **Fundamental Stabilization Mechanisms**

SOURCE **Local Vicksburg, MS**

DATE **7 June 2002**

Figure 19. Natural soil gradations

Classification

Common engineering practice requires that engineers group soils into categories based upon their characteristics. The Unified Soil Classification System (USCS) provides a convenient procedure for grouping materials that is both systematic and repeatable. Each material was classified according to the USCS as required in ASTM D 2487 using the results of the grain size distribution and Atterberg limits analyses. The appropriate soil classification for each material is shown in both Tables 2 and 3.

Specific gravity

Specific gravity (G_s) is defined as the ratio of the weight in air of a given volume of soil to the weight in air of an equal volume of distilled water, at a given temperature. Typical values for specific gravity of solids are 2.65 for sands and 2.70 for clays. The specific gravity of clay materials can typically range from 2.50 to 2.90. The specific gravity of a soil is useful in characterizing the material's weight-volume relationships. The specific gravity values for the silty-sand and clay materials were determined in accordance with ASTMs C 128 and D 854, respectively. The specific gravity values are shown in Table 3.

Compaction

Compaction is the process of mechanically densifying a soil or aggregate. Compaction testing is usually accomplished to define the relationship between moisture and density for a given material at a given compaction effort designed to simulate field conditions. In this experiment, the moisture-density relationships were defined using a modified proctor compaction effort according to ASTM D 1557. Method A of ASTM D 1557 was used for the fine-grained soils and consists of a 101.6-mm soil mold, a 4.50-kg hammer weight, an 0.46-m drop height, five soil layers, and 25 blows per layer. Method C was used for the granular SM-SC soil and consists of a 152.4-mm mold, 4.5-kg hammer weight, a 0.46-m drop height, five soil layers, and 56 blows per layer. The modified proctor compaction curves for each material are shown in Figures 20 through 22. The optimum moisture content and dry density for the modified proctor compaction effort are noted on each figure.

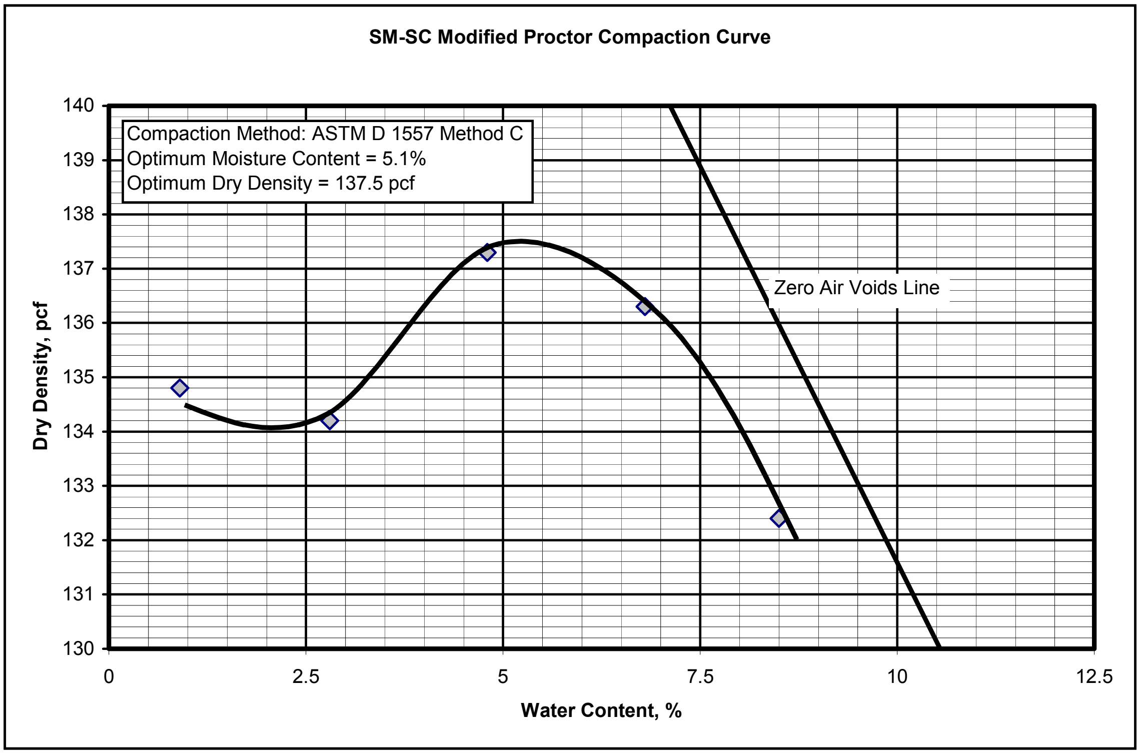


Figure 20. Modified proctor compaction curve for SM-S

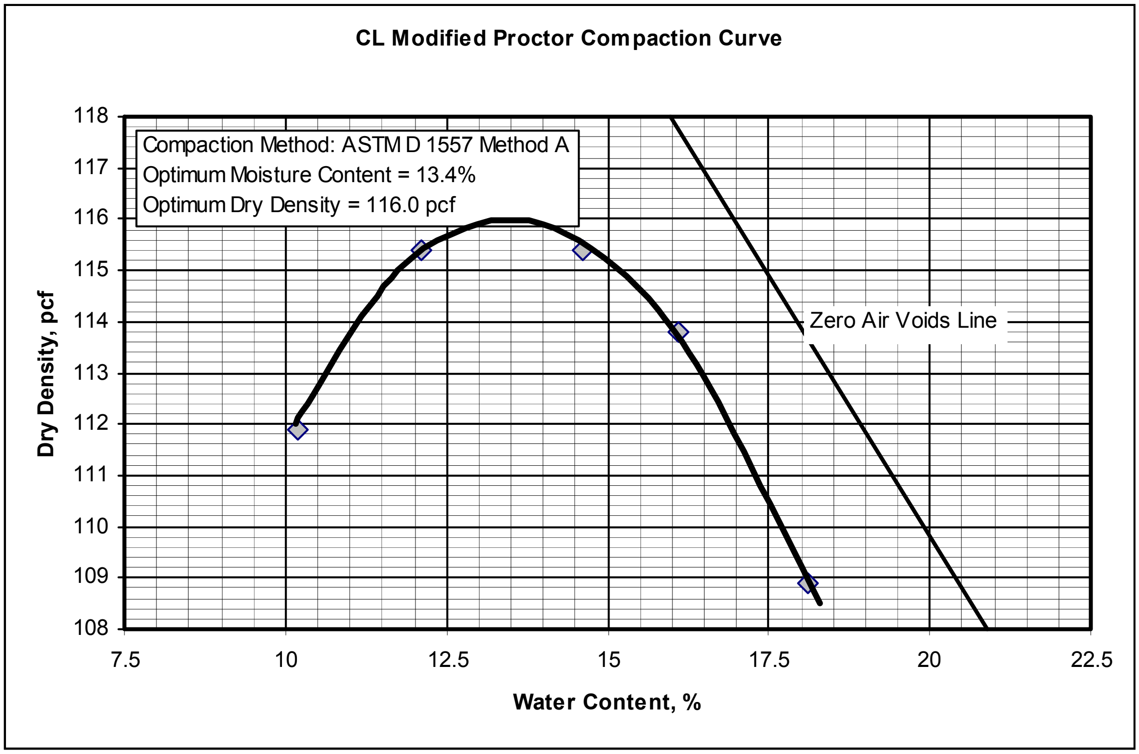


Figure 21. Modified proctor compaction curve for CL

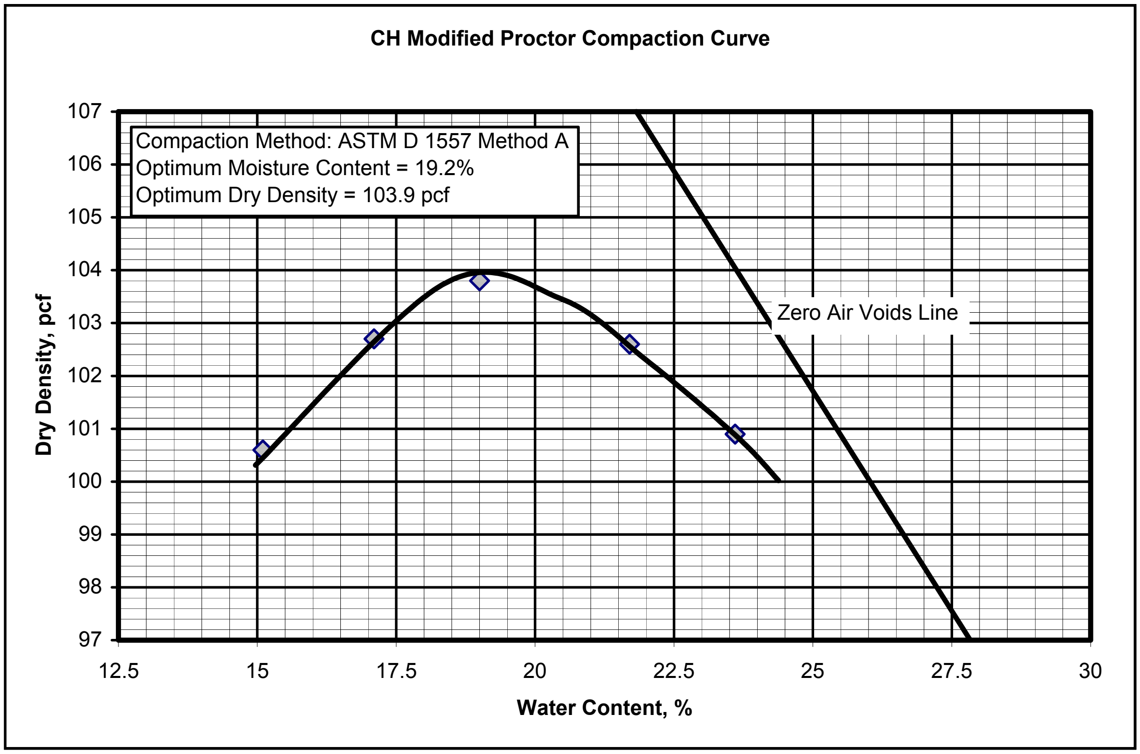


Figure 22. Modified proctor compaction curve for CH

Unconfined compression tests

The unconfined compression test is frequently used to approximate the compressive strength of a material. A cylindrical specimen is placed vertically in the test device, and a gradually increasing axial load is applied with no lateral support (unconfined). Unconfined compressive strength (UCS), q_u, is defined as either the maximum load sustained by the specimen divided by the specimen's loaded area or the load per unit area at a specified axial strain. The UCS is frequently assumed to be twice the undrained shear strength, s_u, of the material.

Prior to the start of the experiment, soil compaction curves were developed for 102-mm-diam by 152-mm-high cylindrical specimens of each material using a Pine® gyratory compaction machine. Previous gyratory compaction experiments demonstrated the ability to approximate modified proctor compaction by varying the gyration angle, ram pressure, and number of revolutions. The angle of gyration was set at 1.25 deg (0.022 rad) based upon the previous gyratory compaction experiments. The ram pressure and number of revolutions were varied to generate different compaction energies. A ram pressure of 870 kPa and 90 revolutions were selected to approximate the same compaction energy as ASTM D 1557 moisture-density compaction for the materials.

Specimen preparation consisted of four steps: soil preparation, molding, compaction, and curing. The soil was prepared by air-drying the material to a moisture content of 2 to 3 percent, pulverizing large clods of fines to pass the No. 4 sieve, determining the free water requirements to obtain the desired moisture, and mixing the soil-water to obtain the desired moisture content. Each material was sealed in a plastic container overnight to achieve equilibrium of the free moisture.

A sample of the material was taken to determine the initial moisture content of the material according to ASTM D 4643. An initial quantity of loose material was measured for each specimen that would produce a 152-mm-high compacted specimen. The quantity of material used to mold each specimen was altered slightly after compacting the previous specimen to improve the accuracy of the compacted specimen height. The material was molded using a 102-mm-diam by 254-mm-high gyratory compaction mold. The material was placed in five layers, and each layer was hand-rodded 25 times with steel rod to reduce the loose height of the material. This was necessary to ensure that all of the loose material would fit within the gyratory compaction mold. The top of the loose material was leveled using 10 blows of a rubber mallet on a 102-mm-diam steel plate. A 0.254-mm-thick circular polypropylene membrane was placed on each end of the specimen to prevent adherence to the top and bottom mold plates. Once placed in the mold, the specimens were inserted into the gyratory testing machine and compacted using the procedures described previously. The compacted specimens were extruded from the gyratory mold using the hydraulic jack extrusion device mounted on the machine. The height of the compacted sample was recorded by the gyratory machine's software, and the compacted sample was weighed to calculate the as-molded wet and dry densities. The compacted specimen was then placed in a temperature-controlled room where it was allowed to cure at 22.2 ^{o}C and 40 percent relative humidity for 28 days. The curing process could be considered an air-dried rather than a moist curing process. This method of curing was selected to represent field conditions during construction operations. The curing process primarily consisted of the evaporation of moisture from the specimens over time.

Six specimens of each material were prepared in the manner described. Note that the height-to-diameter ratio of the specimens was 1.5 rather than the traditionally recommended value of 2.0 for UC testing. This was due to the limitations of the size of the mold. However, correction factors are available in ASTM C 42 for alternative specimen sizes. The specimens used in this experiment were 101.6 mm in diameter and 152.4 mm tall. Thus, a correction factor of 0.96 (ASTM C 42) was multiplied by the resulting compressive strength to correct for the height-to-diameter ratio of 1.5.

Three of the six specimens were subjected to unconfined compression (UC) tests once the designated curing period was complete. These specimens were tested according to the “dry” test procedure. The remaining three specimens were tested according to the “wet” test procedure. Since the probability of exposure to moisture during the material’s performance life in a low-volume road is extremely high, a “wet” test procedure was developed to evaluate the material’s moisture susceptibility. A simplistic “wet” test procedure was developed in which the cured specimen was placed on its side in 25.4 mm of water for a period of 15 min. The specimen was then removed from the water and allowed to drain for five minutes. The specimen was then subjected to UCS testing. This “wet” procedure permitted a visual observation of the susceptibility to moisture, as well as, a physical evaluation of structural strength loss. The time for exposure to moisture was selected as 15 min, based upon the deterioration rate of the untreated control specimens. Full soaking of the specimens by complete immersion was not selected because of the complete disintegration of the control specimens. The unconfined compressive strength for each soil type is shown in Table 4 to withstand the test.

Table 4
Unconfined Compressive Stength[1] Results for Natural Soils

Specimen Mixture[2]	SM-SC			CL			CH		
	Dry	Wet	MC[3]	Dry	Wet	MC[3]	Dry	Wet	MC[3]
Untreated	4,619	1,538	4.9%	5,033	1,420	15.9%	4,737	1,158	23.3%
Cement – 7%	4,702	3,613	6.0%	5,006	3,123	16.9%	--	--	--
Cement – 9%	9,563	9,618	6.0%	5,633	4,447	17.5%	--	--	--
Lime – 3%	--	--	--	2,351	1,103	19.9%	283	0	23.0%
Lime – 5%	1,413	1,165	7.6%	2,999	1,848	18.5%	238	0	23.0%
Lime – 7%	--	--	--	3,440	1,986	19.0%	148	0	23.0%

[1] Unconfined compressive strength results reported in kPa and tested according to ASTM D 2166 or ASTM D 1633. All specimens were cured for 28 days at 22.2 °C and 40 percent humidity. The specimens were then tested according in either a “dry” or “wet” condition.
[2] Additive quantities are percent by dry weight of soil.
[3] Moisture content (MC) reflects the moisture content as molded. The moisture content at time of test was less than 0.5 percent for all specimens.

The UCS tests were conducted using an Instron® 4208 testing system. The Instron® system consists of the test loading instrument and a computer for recording results. The test specimen was positioned in the test instrument, and a seating load of 44.5 N was applied. This initial load was required to ensure satisfactory seating of the compression piston, and it was considered as the zero loads when determining the load-deformation relationship. The load was applied to each specimen at a constant rate of 0.042 mm per second. Each specimen was compressed until it reached a preset axial strain of 0.08 or until it collapsed.

California Bearing Ratio (CBR) tests

The California Bearing Ratio (CBR) test is both a laboratory and field test designed to provide an index of strength. The test involves pushing a 19.4-cm^2 piston into a soil specimen at a constant rate of 1.3 in./min. The unit load is recorded at 0.1-in. intervals up to a deformation of 12.7 mm. The loads at 2.5 and 5.1 mm of deformation are compared to loads required to cause equal penetrations in a standard well-graded crushed-stone specimen. Thus, the CBR values represent a percentage of the standard material's strength and typically range from 0.1 to 100 (the percentage sign is generally not used). The CBR value is commonly used in the design of flexible pavement systems. Characterization of materials using the CBR test is typically accomplished according to ASTM D 1883 at a given compaction effort (ASTM D 1557 in this case). Figures 23 through 25 show the CBR relationships developed for each of the soils used in this experiment.

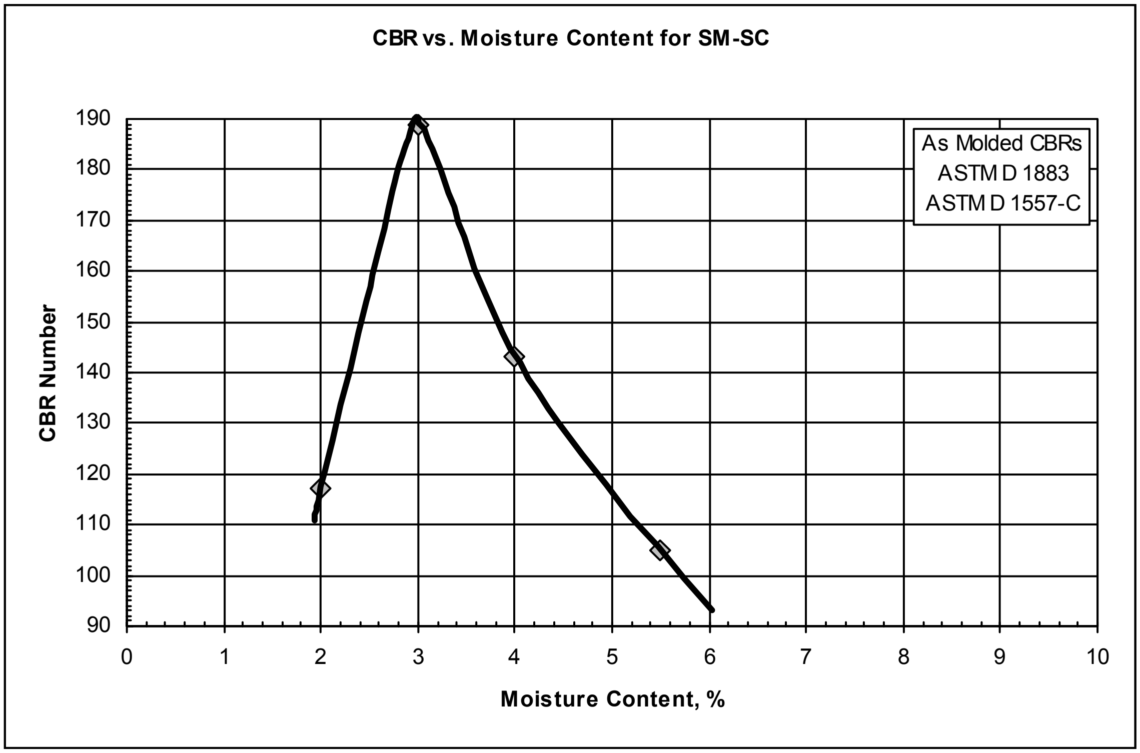


Figure 23. CBR versus moisture content curve for SM-SC

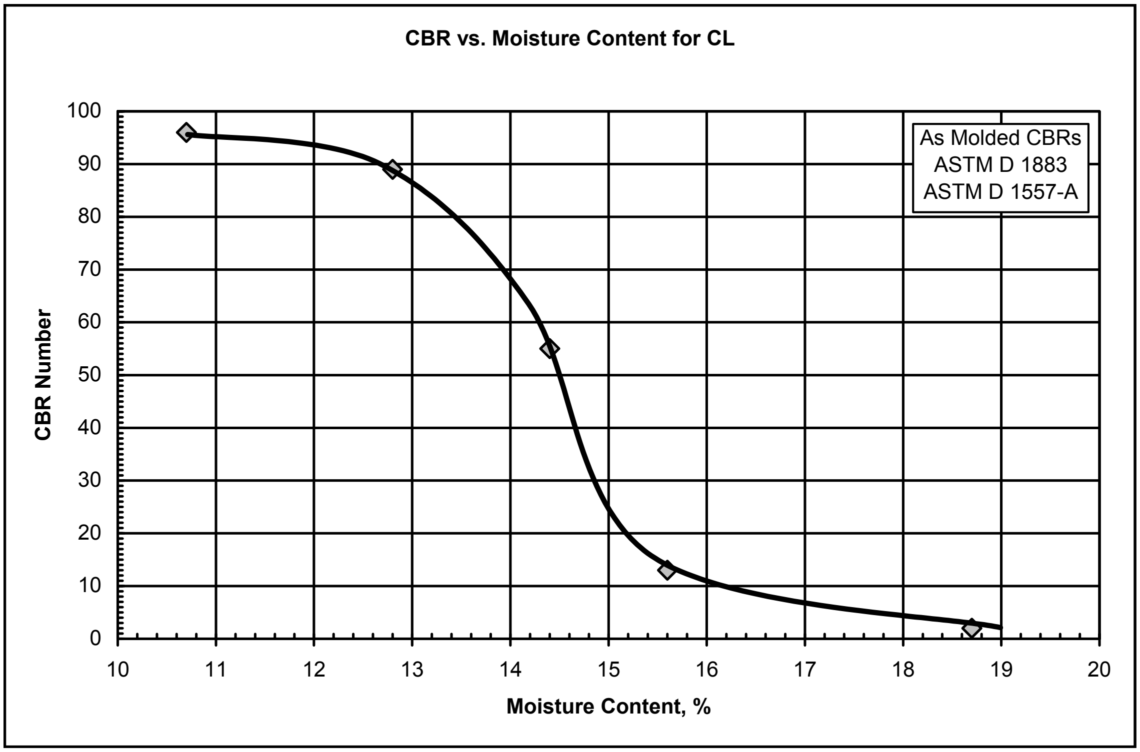


Figure 24. CBR versus moisture content for CL

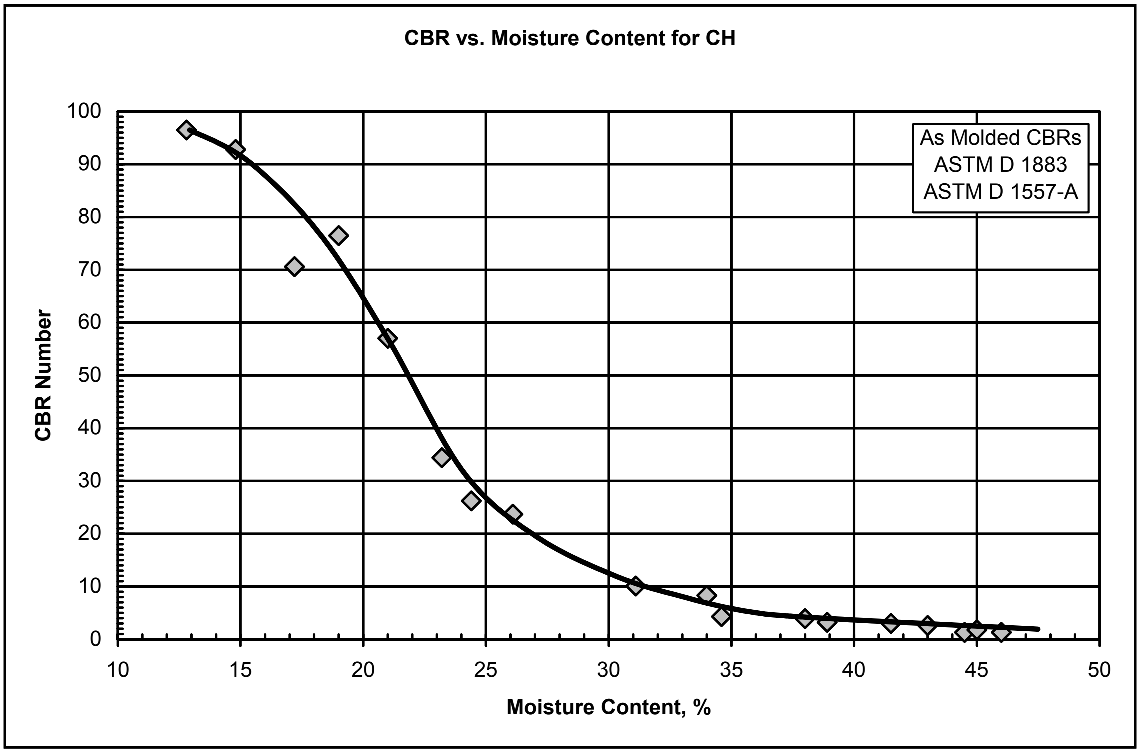


Figure 25. CBR versus moisture content curve for CH

Results and Discussion

Clayey silty-sand (SM-SC) properties

The clayey silty-sand material contained approximately 23.5 percent gravel, 54.7 percent sand, and 21.7 percent fines. The material had a specific gravity of 2.67, a LL of 22, a PL of 18, and a computed PI of 4. Thus, the material was classified according to the USCS as a clayey silty-sand, denoted by SM-SC. The material's moisture-density relationship was defined for a modified compaction effort resulting in an optimum moisture content for compaction of 5.1 percent and an optimum dry density of 2,203 kg/m^3 (137.5 pcf). The CBR value corresponding to the material's optimum moisture content was approximately 115, which is very high indicating excellent potential for use in pavement systems. However, typical design CBR values for this material range from 10 to 40. Finally, the unconfined compression strength of the material when molded and cured for 28 days was 4, 619 kPa for the dry tests and 1,538 kPa psi for the wet tests. Stabilization with two traditional additives, cement and lime, showed that 9-percent cement provided significant strength increase compared to the control tests. This was expected and is consistent with current guidance published in TM 5-814-5 for an SM-SC material. These results indicate that stabilization additives that provide significant physical bonding will be successful in modifying the properties of the SM-SC material. Additives that rely upon chemical reaction mechanisms may not be as successful due to the lack of adequate exchangeable cations or bound water. In summary, mechanical bonding may be more important for this material type than known chemical bonding processes.

Low-plasticity clay (CL) properties

The low-plasticity clay material contained approximately 0.0 percent gravel, 0.4 percent sand, and 99.6 percent fines. The material had a specific gravity of 2.71, a LL of 37, a PL of 24, and a computed PI of 13. Thus, the material was classified according to the USCS as a low-plasticity clay or CL. The material's moisture-density relationship was defined for a modified compaction effort resulting in an optimum moisture content for compaction of 13.4 percent and an optimum dry density of 1,858 kg/m^3 (1,16.0 pcf). The CBR value corresponding to the material's optimum moisture content was approximately 82, which is very high indicating excellent potential for use in pavement systems. Unfortunately, the material's in situ state is often far less competent, with CBR strengths typically less than 15. Finally, the unconfined compression strength of the material when molded and cured for 28 days was 5,033 kPa for the dry tests and 1,420 kPa for the wet tests. These unconfined compressive strengths should not be confused with as-molded strengths since the materials were "cured" allowing the moisture to evaporate. Stabilization with two traditional additives, cement and lime, showed that 9 percent cement provided some strength improvement compared to the control tests. The lime-treated specimens resulted in a strength reduction; however, the material was more friable, indicating a reduced plasticity.

These results indicate that stabilization additives that provide significant physical or chemical bonding might be successful in modifying the properties of the CL material. The material did indicate that cement was less effective than when used with the SM-SC material. The fact that the lime material modified some properties of the material other than strength demonstrates the potential for chemical alteration of the CL soil. In summary, both mechanical bonding and chemical alteration may change specific engineering properties of this material, and the additive selection should be consistent with the objectives of stabilization; reduced plasticity, reduced shrink-swell potential, increased strength, etc.

High-plasticity clay (CH) properties

The high-plasticity clay material or “buckshot” clay contained approximately 0 percent gravel, 3.2 percent sand, and 96.8 percent fines. The material had a specific gravity of 2.74, a LL of 79, a PL of 28, and a computed PI of 51. Thus, the material was classified according to the USCS as a high-plasticity clay or CH. The material’s moisture-density relationship was defined for a modified compaction effort resulting in an optimum moisture content for compaction of 19.2 percent and an optimum dry density of 1,664 kg/m^3 (1,03.9 pcf). The CBR value corresponding to the material’s optimum moisture content was approximately 70, which is very high. Unfortunately, the material’s in situ state is often far less competent with CBR strengths typically less than 15. Furthermore, the material’s high plasticity indicates significant shrink-swell potential. Finally, the unconfined compression strength of the material when molded and cured for 28 days was 4,737 kPa for the dry tests and 1,158 kPa for the wet tests. These unconfined compressive strengths should not be confused with as-molded strengths since the materials were “cured” allowing the moisture to evaporate. Stabilization with lime produced visible changes in the material’s plasticity but showed a net reduction in the unconfined compressive strength. No additional benefit was noted beyond 3 percent lime for this material. These results indicate that stabilization additives that rely upon chemical reactions with clay minerals and cations might be successful in modifying the properties of the CH material. The high plasticity of the clay material suggests significant double-layer moisture retention, indicating that additives that seek to reduce the double-layer moisture may be successful. In summary, chemical alteration may change specific engineering properties of this material, and the additive selection should be consistent with the objectives of stabilization: reduced plasticity, reduced shrink-swell potential, increased strength, etc.

4 Stabilizer Characterization

A primary focus of the project was to conduct a chemical analysis of the selected soil stabilization agents to determine the basic components present in each product. Once the primary components in a product have been identified, then the mechanism of action for that particular agent can be hypothesized. The purpose of the analysis is not to determine the exact chemical makeup of each product but to identify the components necessary to make an assessment of the mechanism of action.

Methods

A suite of analytical techniques was used to chemically characterize a group of commercially available soil stabilizers. Seven stabilizers were subjected to four analytical evaluations in order to determine the chemical descriptors for these compounds. The seven products and the specific evaluations used for each of the products are listed in Table 5. Figure 26 illustrates a flowchart for the steps followed in this study.

Table 5
Chemical Analyses Matrix

Stabilizer	FTIR	Comparative Solubility	GC/MS	ICP/MS	GPC
Enviroseal 2001	X	X	X	X	None
PolyPavement	X	X	X	X	X
Road Oyl	X	X	X	X	X
Road Bond EN1	--	X	X	X	X
Soil-Sement	X	X	X	X	X
Dustac 100	X	X	X	X	X
Ven-Set 950	X	X	--	--	--

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is routinely employed in many laboratories as an economical, rapid first-line chemical analysis technique and is well established as a forensic tool. A beam of infrared light is allowed to pass through a sample (solid, liquid, or gas). If the infrared frequency is in resonance with certain chemical bonds present in the sample, the light will be

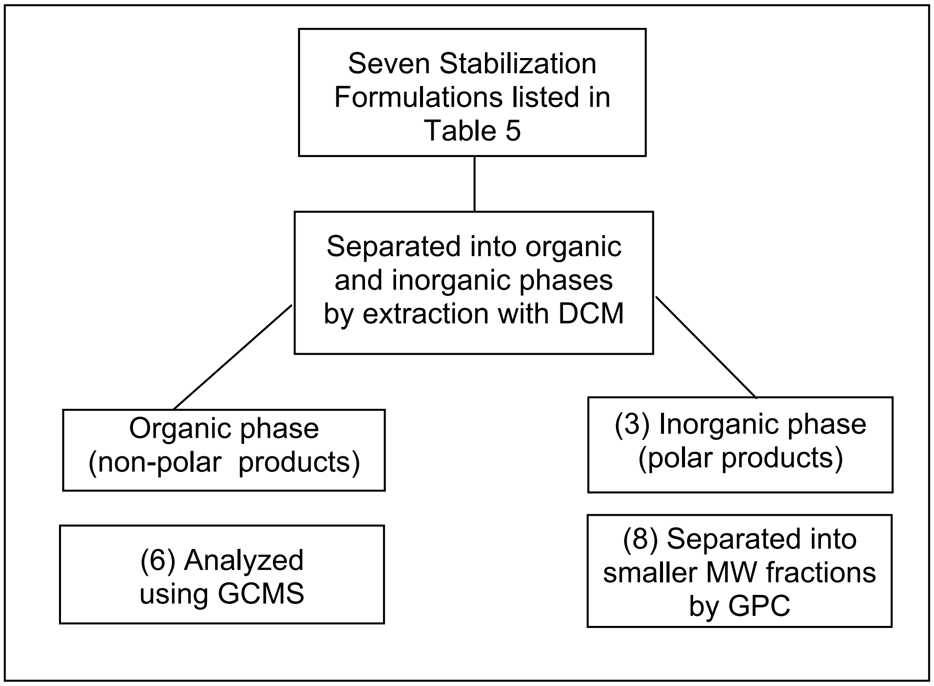


Figure 26. Chemical analyses flow chart

absorbed by the chemical bond and can be detected as a change in the intensity of the transmitted light. Different chemical bonds absorb different frequencies of infrared light such that many chemicals reveal a type of "fingerprint" specific to that chemical. Given that the intensity of the transmitted infrared light is proportional to the concentration of the chemical constituent, the concentration of a certain component can often be derived by careful analysis.

The analyses reported here were performed using a technique called Attenuated Total Reflectance (ATR). ATR can be employed on solid, semi-solid, and liquid samples. It was chosen for this analysis as a matter of convenience. All liquid samples were diluted to 100:1 and solid samples were prepared at 10 g/L with distilled, deionized (DDI) water. Samples were placed on the ATR crystal and dried at 95 °C for 2 hr minimum before testing. Samples were removed from the oven and placed in a nitrogen atmosphere for at least 2 hr before testing. FTIR spectra were collected from 400 to 4,000 cm^{-1}; 64 scans were collected at 4-cm^{-1} resolution.

Comparative solubility

Solvent/solvent extraction is a tool used to separate compounds based on their solubility (Brown 1997). Non-polar compounds dissolve in organic solvents and polar or ionic compounds dissolve in polar solvents. In this case, solvent extraction was used to determine the distribution of organic and inorganic compounds in the formulations gravimetrically.

The percent solid data was determined before performing the solubility test because many of the stabilizers were present as a water slurry. A known amount of each compound (≈1 gram) was placed in two-ounce glass jars. The samples were mixed with 10 mL of DDI water, dichloromethane, toluene, and acetonitrile. The solutions were shaken briefly and allowed to stand overnight. The solutions were then filtered using pre-weighed filter paper (GF/F 9.0-cm glass microfiber filter) and placed on watch glasses to dry. The filter paper/watch glass combination and the glass jars containing the remaining sample were placed in the oven at a temperature of 35 °C. The filter paper and glass jars were dried and weighed for a period of 4 days. Samples required longer drying time at low temperature due to high moisture content. It should be noted that samples were subject to an increase in temperature of 75 °C, which charred the samples. The final weights and percent solid data were complied in a table to produce solubility values.

Gas chromatography with mass spectroscopic detection (GC/MS). Gas chromatography with mass spectroscopic detection (GC/MS) is an analytical tool used for the separation and identification of semi-volatile organic compounds. The technique has been developed for environmental analysis of soils sediment and water samples. The technique is capable of elucidating the concentration of known compounds based on the detector response and a characteristic retention time from the gas chromatographic separation. The technique is also capable of determining the molecular structure of unknown, ionizable organic compounds. GC/MS is commonly used to determine product purity, to determine the presence and concentration of environmental contaminants, and to determine the concentrations of organic compounds in biological systems.

The Hewlett Packard GC/MS 5890 Series II with a quadrupole mass selective detector was used to analyze the organic fraction extractable from the stabilizers using dichloromethane. The samples were injected into gas chromatograph and the resulting peaks identified using the mass spectrometer.

Inductively coupled plasma with mass spectroscopic detection (ICP/MS). Inductively coupled plasma with mass spectroscopic detection (ICPGC/MS) is an analytical tool used for the identification and quantification of inorganic compounds such as rare earths and heavy metals. The technique has been developed for environmental analysis of soil sediment and water samples. The technique is capable of elucidating the concentration of a wide range of inorganic compounds based on the mass to charge ratio of atoms ionized during by the inductively coupled plasma sampler introduction system.

The Perkin-Elmer SCIEX ELAN 6000 Inductively Coupled Plasma Mass Spectrometer was used to analyze the water-soluble fraction extractable from the stabilizers. The samples were injected into inductively coupled plasma ion generator and the resulting mass spectral responses were used to identify the atomic inorganic species present.

Gel permeation chromatography (GPC). Gel permeation chromatography or Size Exclusion chromatography is an analytical tool developed for polymer classification and environmental sample preparation. Gel permeation chromatography, GPC, is utilized to determine the hydrodynamic radius of soluble polymer components present in specific formulations. The technique is capable of elucidating the hydrodynamic radius distribution that is comparable to the molecular weight distribution in complex mixtures and has been used in this study to determine the similarities and differences between the formulations for soil stabilizers. GPC is commonly used to determine molecular weight distributions during polymer characterization, to aid in separation of synthetic macromolecules, to aid in sample preparation prior to analysis of pesticides and/or polychlorobiphenyls in soils, sludges, animal fats, crops, feeds, and other environmental samples, and to calibrate the molar masses and sizes of plant products such as starches.

The Waters HPLC used was equipped with a Waters 600-M system controller, a Waters 991-MS photodiode array detector (PDA), and a Waters 7 Satellite WISP autosampler. The columns used to separate the organic phase were a Phenomenex 50 µ × 7.8-mm guard column, Phenolgel 5 µ × 103 A (300 × 7.8-mm), and Phenogel 5 µ × 50 A (300 × 7.8-mm) columns. The aqueous phase was separated on a Biosep 600 × 7.8-mm column (part number Biosep-sec-s-200). The molecular size standards were polystyrene polymers for the organic phase separations and polyethylene glycol for the aqueous phase separations. HPLC columns and both sets of molecular weight standards were purchased from Phenomenex, Torrance, CA.

Polyethylene glycol (PEG) molecular weight standards were used to calibrate the molecular weights in the inorganic samples and were made by dissolving 20 mg of each standard in 40 mL of water. Representative samples (20 µL) of each standard were injected onto the HPLC column. A flow rate of 1 mL/min was used with an aqueous mobile phase and the detector was set at 206 nM to observe aromatic components. Pump pressures averaged 6,895 kPa, which is normal for a long column and aqueous mobile phase in GPC. The run time was 40 min. Retention times were noted for the peak produced by each standard. Using the retention times of the PEG standards, a chart of sampling times was devised to collect the PEG equivalent molecular weight fractions of the sample. A representative sample (100 µL) of the inorganic phase was injected on the HPLC using the instrument protocol described above. PEG equivalent molecular weight fractions determined by comparison with retention times observed for known MW PEG standards.

Results and Discussion

Polystyrene molecular weight standards were used to calibrate the polystryene molecular weight ranges for the organic phase samples. A typical chromatogram of a polystyrene molecular standard is shown in Figure 27. Retention times of the polystyrene molecular weight standards were used to determine the collection times of the polystyrene equivalent molecular weight fractions of the samples. Figure 28 illustrates the standard curve for the

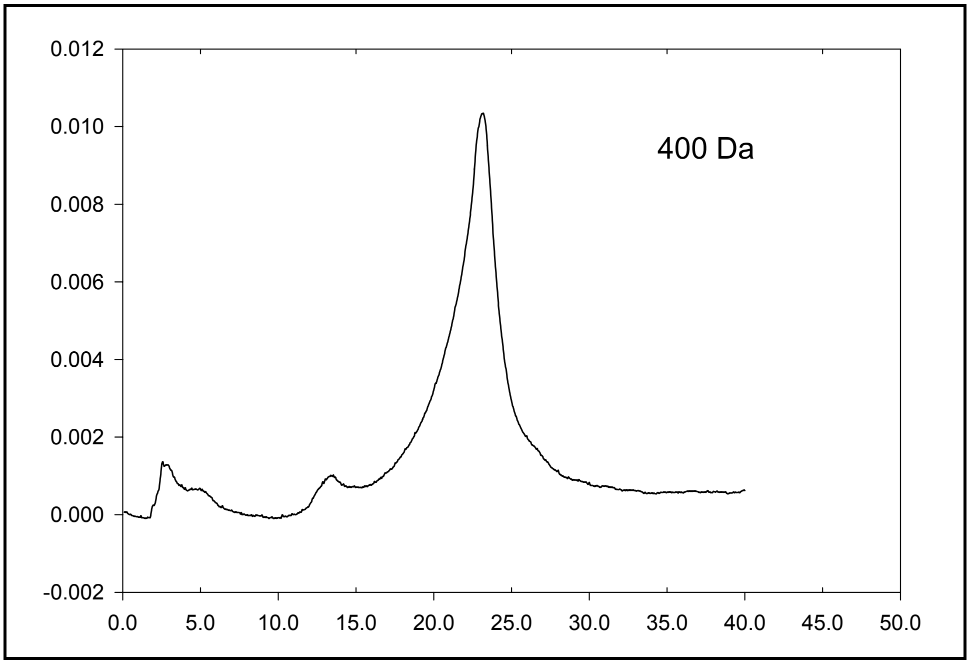


Figure 27. Chromatogram of the 400-Da polyethylene glycol molecular weight standar

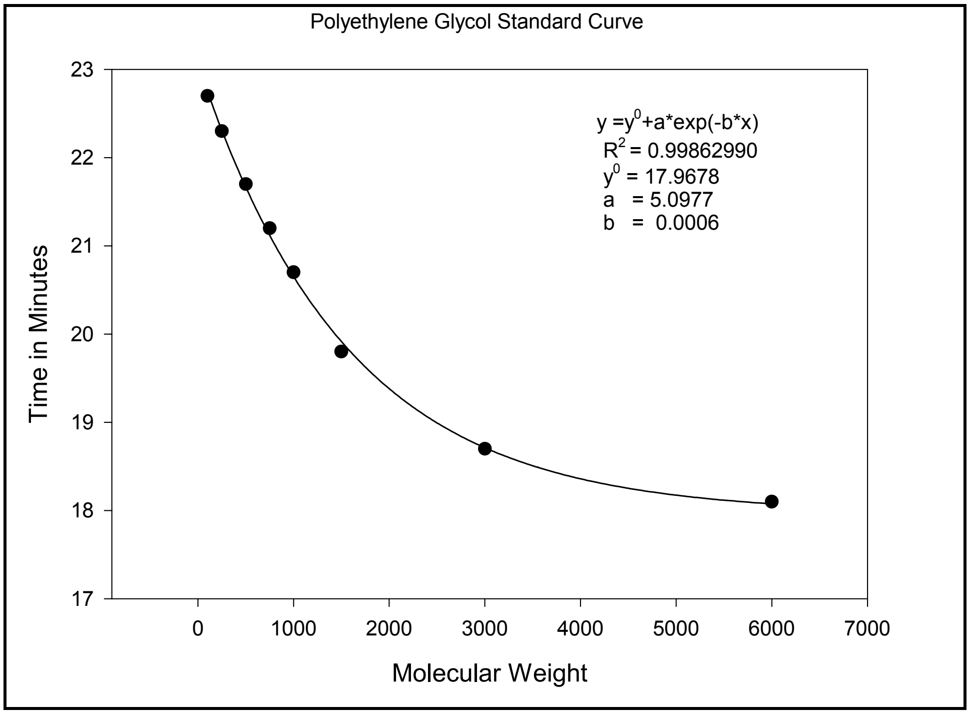


Figure 28. Standard curve for the polystyrene molecular weight standards

polystyrene molecular weight standards. The r^2 value of the regression was 0.9986 with slope of 5.098 and y-intercept of 17.9678.

FTIR results

Ven-Set 950. Ven-Set 950 is manufactured by Venture Chemicals. It is an amber, water-based liquid. The Material Safety Data Sheet states that Ven-Set 950 is a “blend of complex silicic acid salts, water-soluble polymers, and dispersants/ surfactants,” so it falls into the category of an ionic stabilizer. Venture Chemicals manufactures a wide range of air-oxidized oils and waxes. Ven-Set 950 is not listed as a product on their website. Based on the above knowledge and the FTIR spectra, Ven-Set 950 is most likely a mixture of organic acids reacted with silicic acid and titrated with base to obtain the silicate salts. The IR spectrum shows three broad areas of absorption: a strong absorption around 850 to 1,300 cm^{-1}, a weak area around 1,400 cm^{-1}, and a medium absorption around 1,630 cm^{-1} (see Figure 29).

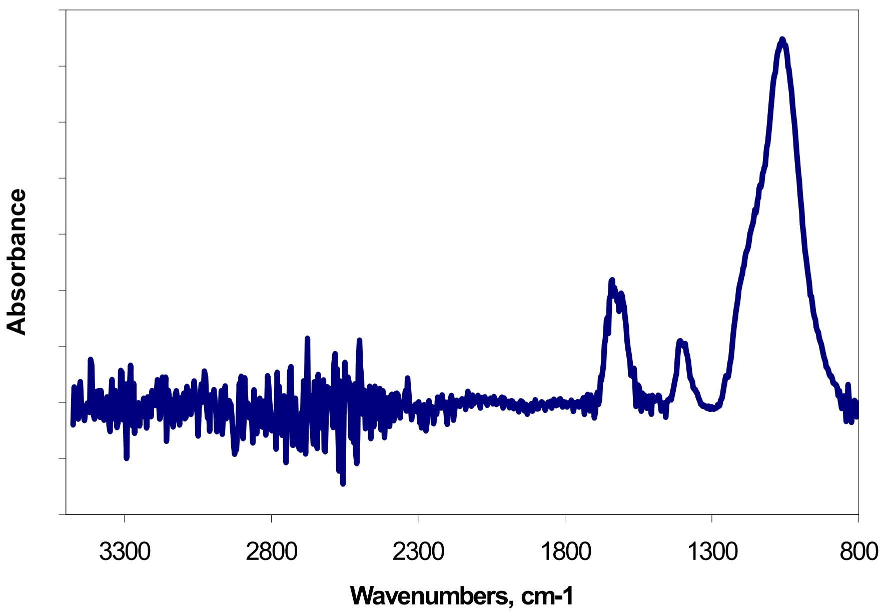


Figure 29. FTIR/ATR spectrum of Ven-Set 950 soil stabilization agent

Based on the information provided in the MSDS and the FTIR analysis above, Ven-Set 950 is hypothesized to be an ionic stabilizer sensitive to certain chemical components in the soil such as clays or humus. Thus, Ven-Set 950 may not provide stabilization to all soil types. The high water solubility of Ven-Set 950 suggests that it is in micellar form in the concentrate and, once adsorbed, will be difficult to resolublize without mechanical action and excess water. Ven-Set 950 would be expected to behave as a surfactant, adsorb onto soil particles, and has the potential to develop strong ionic bonds with cations present in clays such as calcium and magnesium. The presence of higher molecular weight oligomers and polymers will provide some binding of soil particles; however, it is expected to be sensitive to various soil types as an ionic stabilizer.

Enviroseal 2001. Enviroseal 2001 (Figure 30) is a black, opaque, viscous emulsion. The MSDS states that it is composed of an acrylic polymer (52 percent) with zinc oxide (2 percent), activated carbon (8 to 9 percent), and water. The polymer as yet is unidentified. However, it appears to be an acrylate/methacrylate with some aromaticity (peak about 1,635 cm^{-1}). The mechanism of stabilization for Enviroseal 2001 would be that of a cementing action between particles. As such, it should be applicable to a wide variety of soil types. It would be expected that the amount necessary for stabilization would be dependent on the soil physical characteristics such as gradation and surface area. At the proper dosage and after drying, Enviroseal 2001 should form a polymer matrix throughout the soil that improves the soil strength and the resistance to moisture.

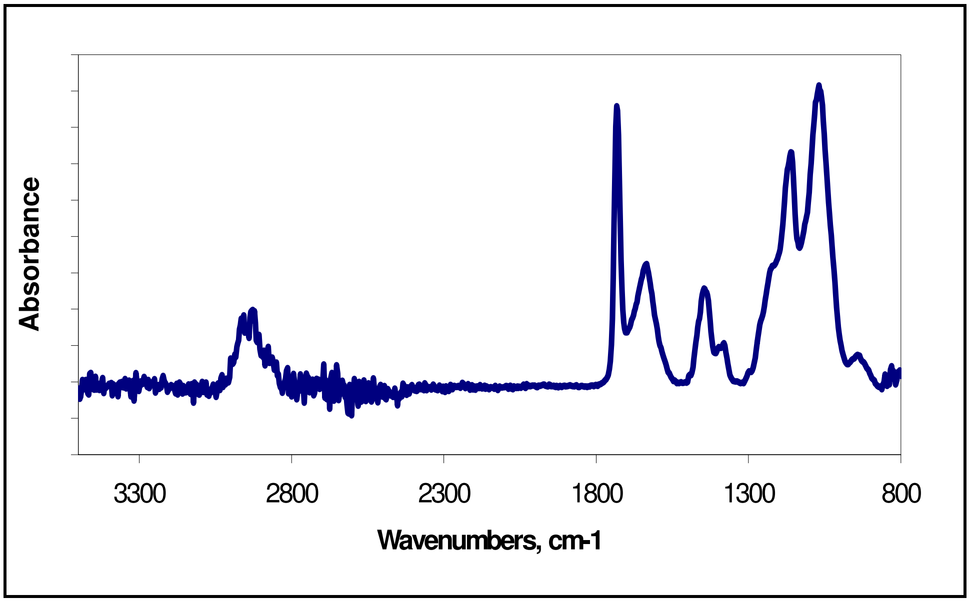


Figure 30. FTIR/ATR spectrum of Enviroseal 2001 soil stabilization agent

Soil-Sement. Soil-Sement is a white, opaque, viscous liquid. The MSDS states that it is an “aqueous acrylic vinyl acetate emulsion.” The FTIR spectrum in Figure 31 shows a very close match to a 1:4 poly (vinyl acetate/ethylene) copolymer. The molecular weight of the polymer is currently unknown. The mechanism of stabilization for Soil-Sement would be that of a binding agent between soil particles, similar to PolyPavement or Enviroseal 2001.

PolyPavement. PolyPavement is a yellow, opaque viscous liquid. The MSDS states that it is a water-based copolymer emulsion. The FTIR spectrum in Figure 32 shows a close match to a 1:4 poly (vinyl acetate/ethylene) copolymer.

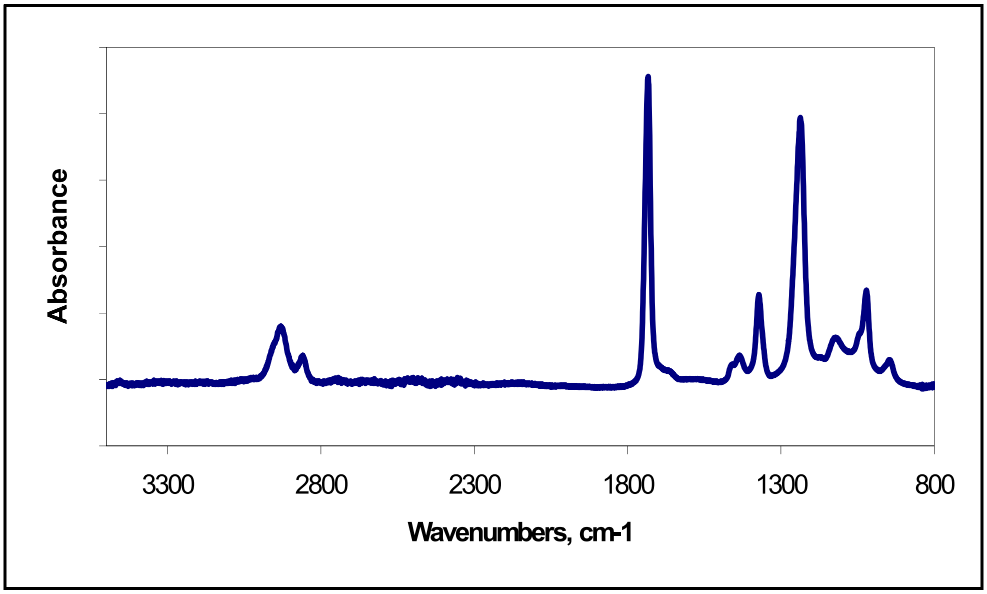


Figure 31. FTIR/ATR spectrum of Soil-Sement soil stabilization agent

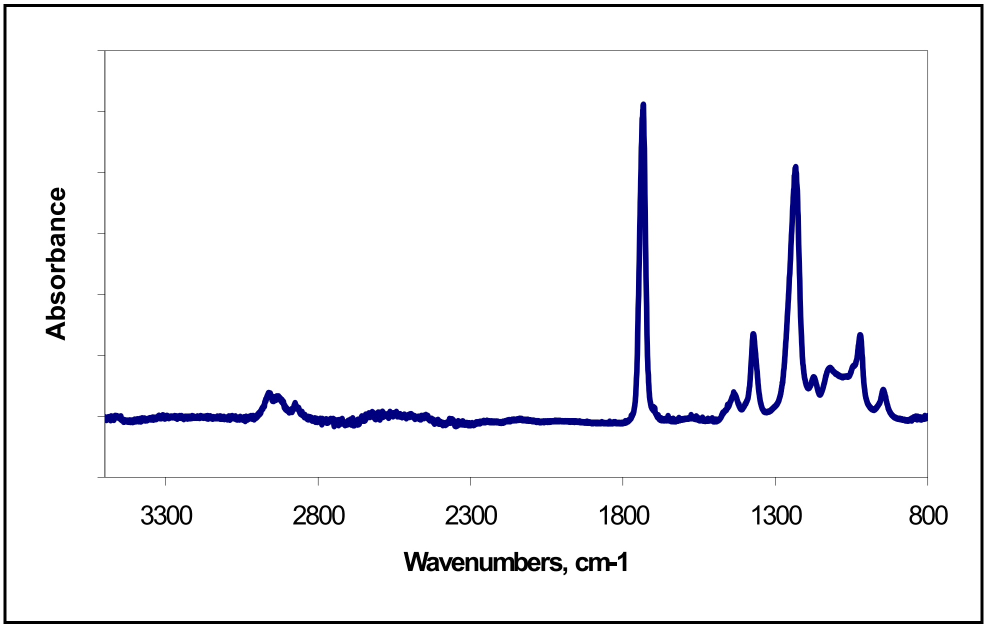


Figure 32. FTIR/ATR spectrum of PolyPavement soil stabilization agent

Although this is similar to Soil-Sement, the molecular weight of the polymer is unknown and may not be similar to Soil-Sement. A yellow color emulsion and additional peaks in the FTIR, compared with Soil-Sement, suggest a different formulation or an added component. The mechanism of stabilization for PolyPavement would be that of a binding agent between soil particles, similar to Soil-Sement or Enviroseal 2001.

Dustac 100. Dustac 100 is an amber powder. The MSDS states that it is calcium lignosulfonate so it falls into the category of an ionic stabilizer. The FTIR spectrum is presented in Figure 33. Dustac 100 may not provide stabilization to all soil types. The high water solubility of Dustac 100 suggests that it is in micellar form in the liquid concentrate and once adsorbed, should be difficult to resolublize without mechanical action and excess water. Dustac 100 would be expected to behave as a surfactant, adsorb onto soil particles, and has the potential to develop strong ionic bonds with cations present in clays. As Dustac 100 contains calcium, it is available for cation exchange with the clay.

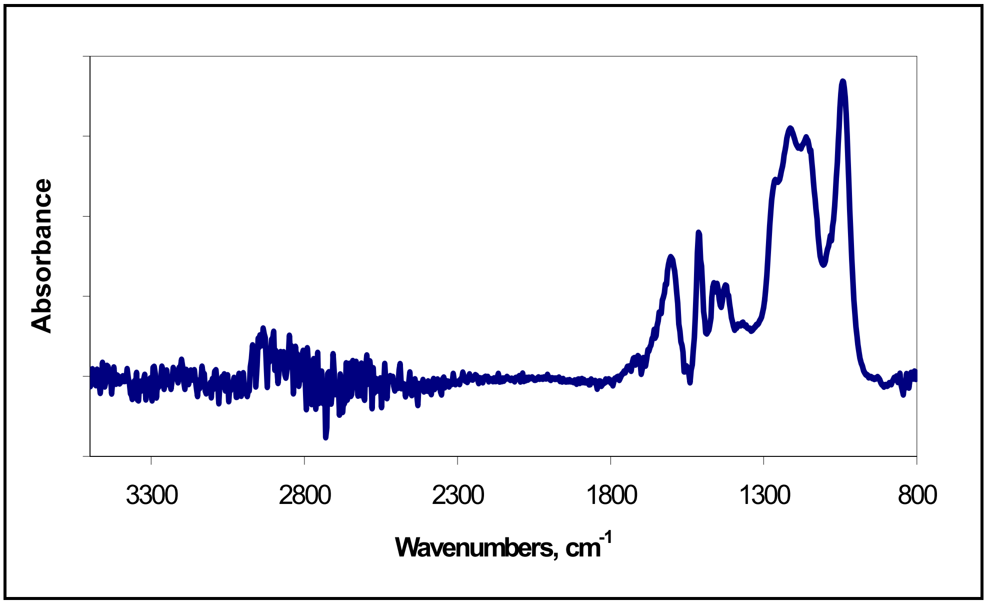


Figure 33. FTIR/ATR spectrum of Dustac 100 soil stabilization agent

Road Oyl. Road Oyl is a tan, creamy emulsion. The MSDS states that it is 50 percent solids with the solids being comprised of a 72:28 blend of pitch/resin tall oil fractions. The FTIR spectrum is presented in Figure 34. The mechanism of stabilization for Road Oyl would be that of a binding agent between soil particles, similar to Soil-Sement or Enviroseal 2001. Although Road Oyl may contain some polymers naturally present in the tall oil, it is not likely to have high molecular weight species. Road Oyl would be expected to show excellent adhesion to most substrates.

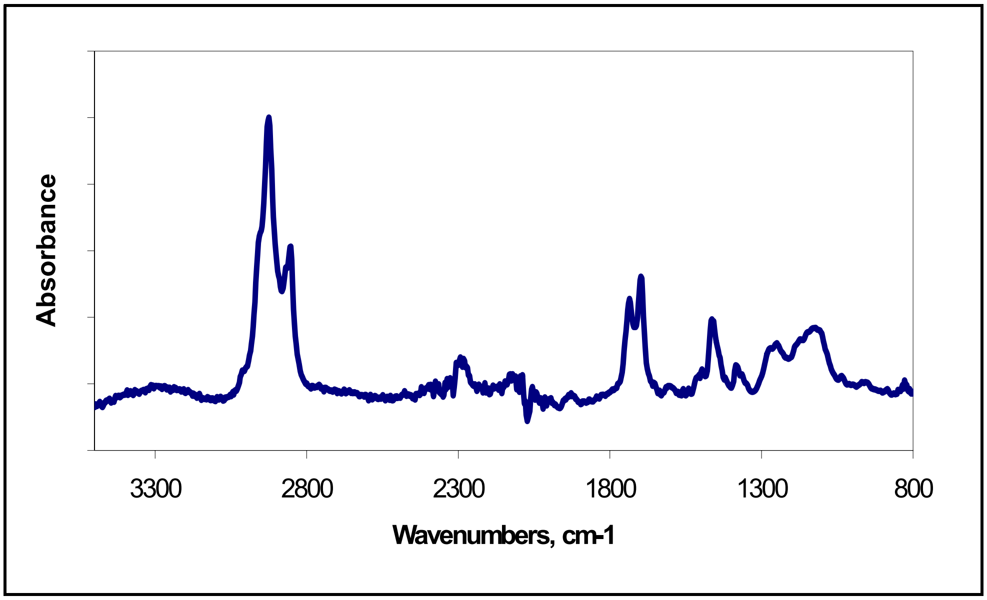


Figure 34. FTIR/ATR spectrum of Road Oyl soil stabilization agent

Comparative solubility results

The comparative solubility results are shown in Table 6 and Figure 35.

Table 6
Comparative Solubility Results

Additive	Dichloromethane	Acetonitrile	Water
Ven-Set 950	--	--	--
Dustac	0.04	0.03	0.73
Enviroseal	0.24	0.31	0.36
Soil-Sement	0.25	0.25	0.26
Road Oyl	0.33	0.26	0.22
PolyPavement	0.35	0.36	0.10
Road Bond EN1	0.20	0.98	0.53

GC/MS results. Six discrete organic compounds were observed in a number of the stabilizer formulations. Table 7 below summarizes which of the compounds were found in the six stabilizer formulations analyzed. Figure 36 displays the molecular structure of each of the six organic compounds observed in the soil stabilizers. All of the compounds are hydrophobic in nature as would be expected in stabilizer extracts obtained using dichloromethane.

ICP/MS. A number of inorganic constituents were observed in the water extracts of the six stabilizer formulations. Table 8 below summarizes which of the compounds were found in the six stabilizer formulations analyzed. Figure 37 displays the inorganic constituents found in each of the stabilizer formulations along with a qualitative estimation of the relative concentrations of each of the inorganic constituents observed.

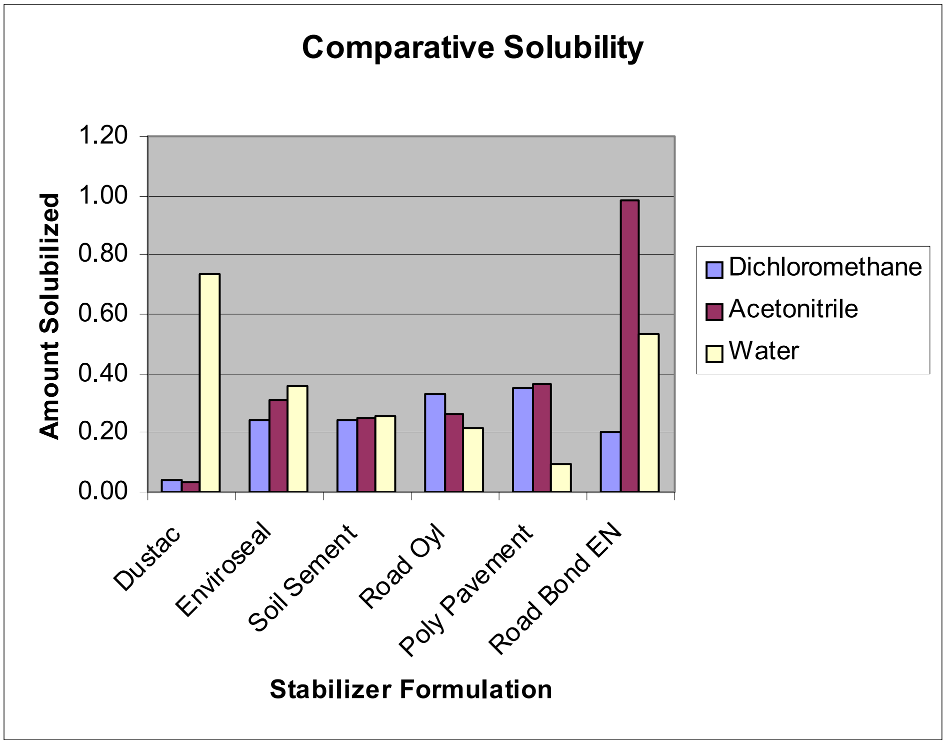


Figure 35. Comparative solubility of stabilization agents

Table 7
GC/MS Results Summary

Stabilizer	Cyclodo-decane $C_{12}H_{24}$	Nonylcyclo-propane $C_{12}H_{23}$	4-hydroxy-3-methyl-benzene acetic acid	1-Dodecanol $C_{12}H_{26}O$	2-Chlorocy-clohexanol	1,2-dichloro-cyclohexane
Ven-Set 950	No Data	No Data	No Data	No Data	No Data	No Data
Dustac 100	X	--	X	--	--	--
Enviroseal 2001	X	X	--	--	--	--
Soil-Sement	--	--	--	--	--	--
Road Oyl	X	--	--	X	--	--
PolyPavement	X	--	--	--	--	--
Road Bond EN1	X	X	--	--	X	X

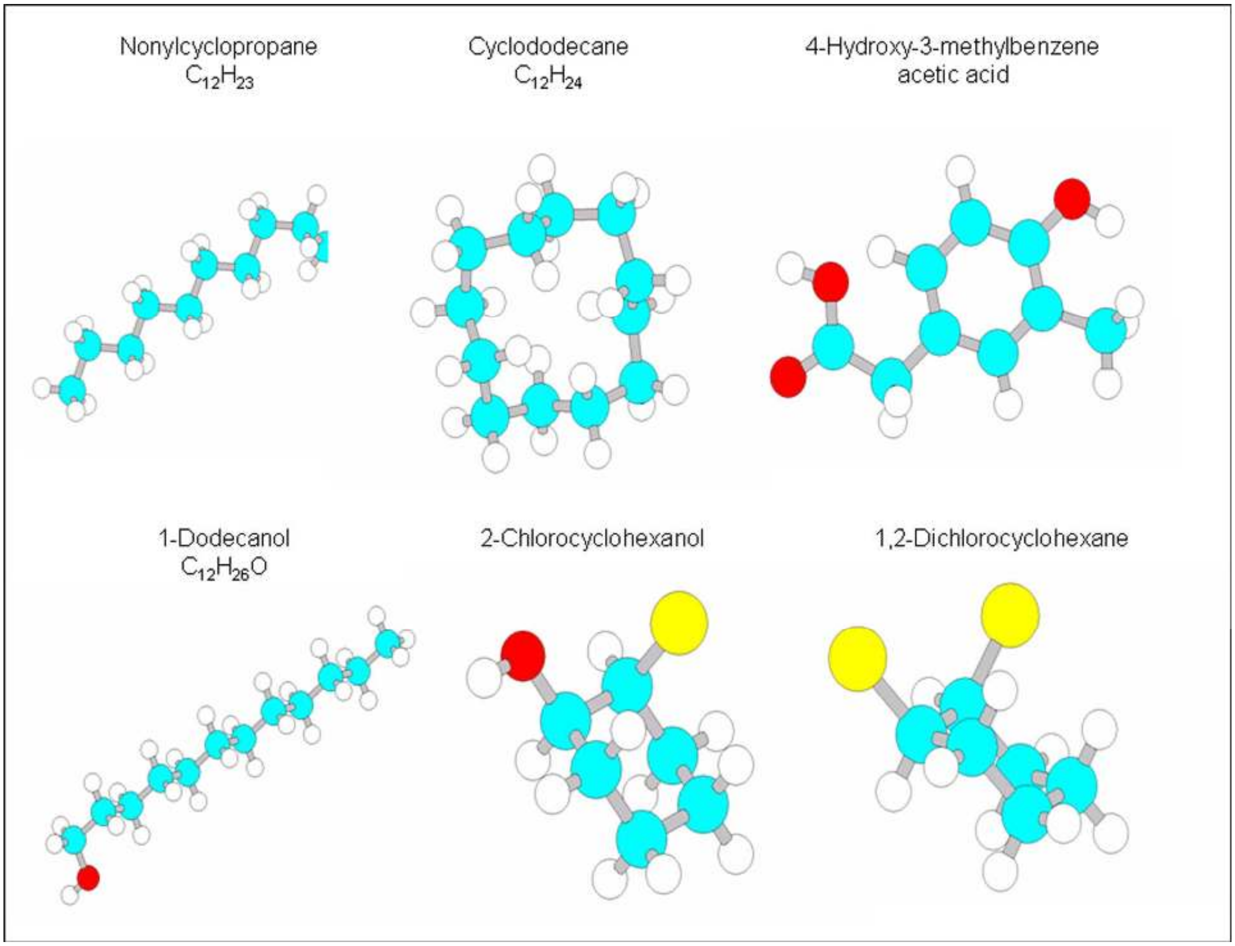


Figure 36. Graphical representations of organic compounds observed in GS/MS analysis

Table 8
ICP Results Summary

	Element Composition															
Stabilizer	**Mg**	**P**	**K****	**Ca***	**V**	**Mn**	**Fe**	**Ni**	**Zn**	**Se**	**Sr**	**Mo**	**Ag**	**Sn**	**Na***	**Ba**
Dustac 100	548	81	165	502	1	289	232	2	10	2	223	--	2	26	115	7
Enviroseal 2001	--	--	53.5	--	0.909	--	176	--	141	1.82	--	1.67	2.73	23	33	--
Soil-Sement	--	89.6	--	--	0.769	--	208	--	10	1.54	--	--	1.54	203	54.9	--
Road Oyl	--	--	--	--	1.67	--	259	--	10	1.67	--	--	1.67	24	47.9	--
PolyPavement	--	--	--	--	1	--	279	--	10	--	--	--	1	26	--	--
Road Bond EN1	--	--	--	--	1	--	312	--	16	--	--	--	2	27	--	--

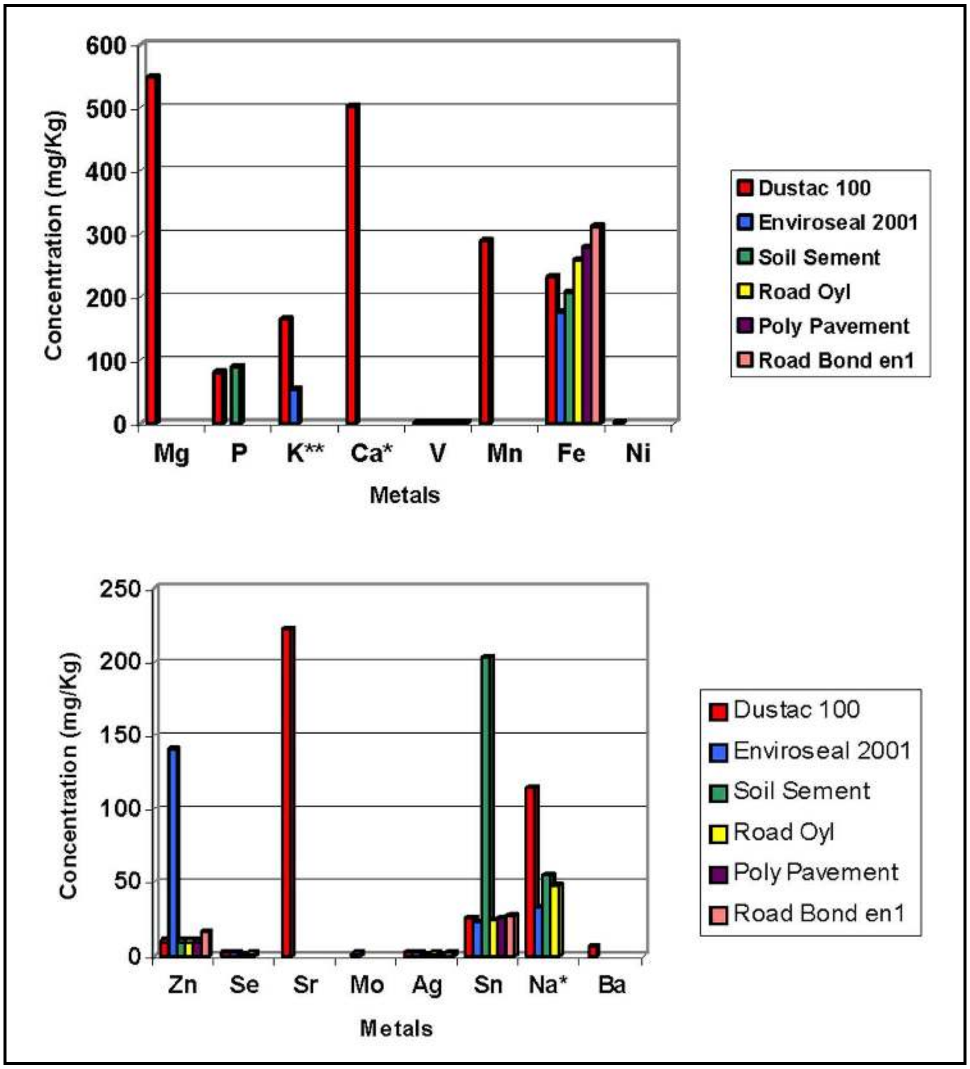


Figure 37. Representation of water-soluble inorganic components found in six stabilizer formulations

GPC results. PEG molecular weight standards were used to calibrate the polystyrene molecular weight ranges for the organic phase samples. A typical chromatogram of a polystyrene molecular standard is shown in Figure 27. Retention times of the polystyrene molecular weight standards were used to determine the collection times of the polystyrene equivalent molecular weight fractions of the samples (Table 9). Figure 28 illustrates the standard curve for the polystyrene molecular weight standards. The r^2 value of the regression was 0.9986 with slope of 5.098 and y-intercept of 17.9678. For each of the stabilizers, the GPC elution profile is presented in Figures 38 through 42. Table 10 summarizes the peak retention time, the PEG equivalent molecular

Table 9
Retention Times for the Polyethylene Glycol Molecular Weight (PEGMW) Standards

Start Times (min)	End Time (min)	PEGMW Fraction (Da)
12.5	18.1	>6000
18.1	18.7	6,000 to 3,000
18.7	19.8	3,000 to 1,500
19.8	20.7	1,500 to 1,000
20.7	21.2	1,000 to 750
21.2	21.7	750 to 500
21.7	22.3	500 to 250
22.3	22.7	250 to 100
22.7	25	<100

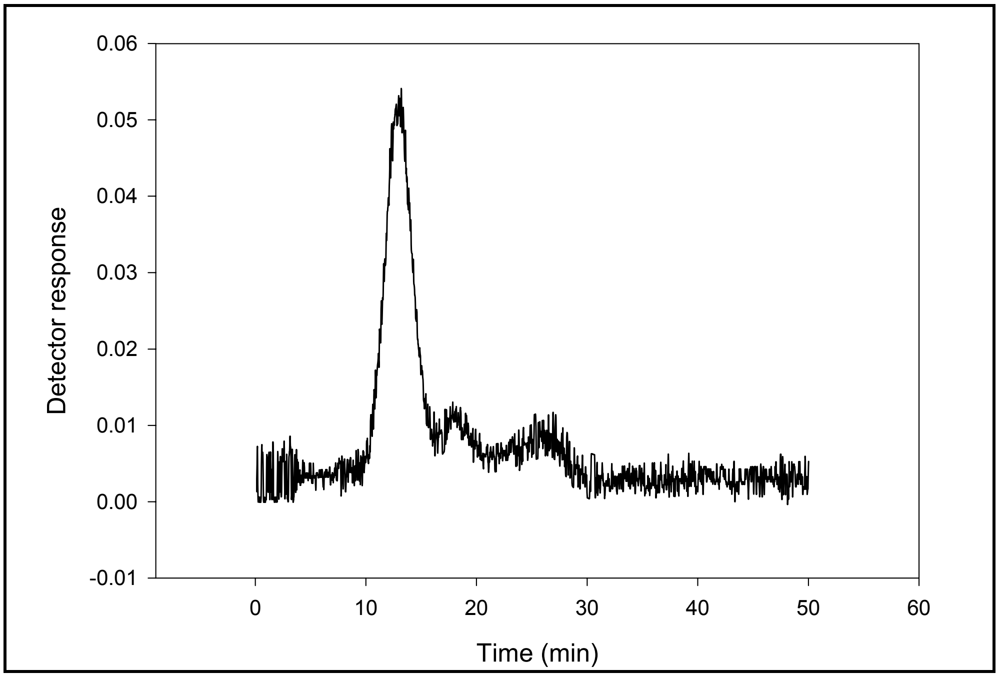


Figure 38. GPC results for Dustac 100

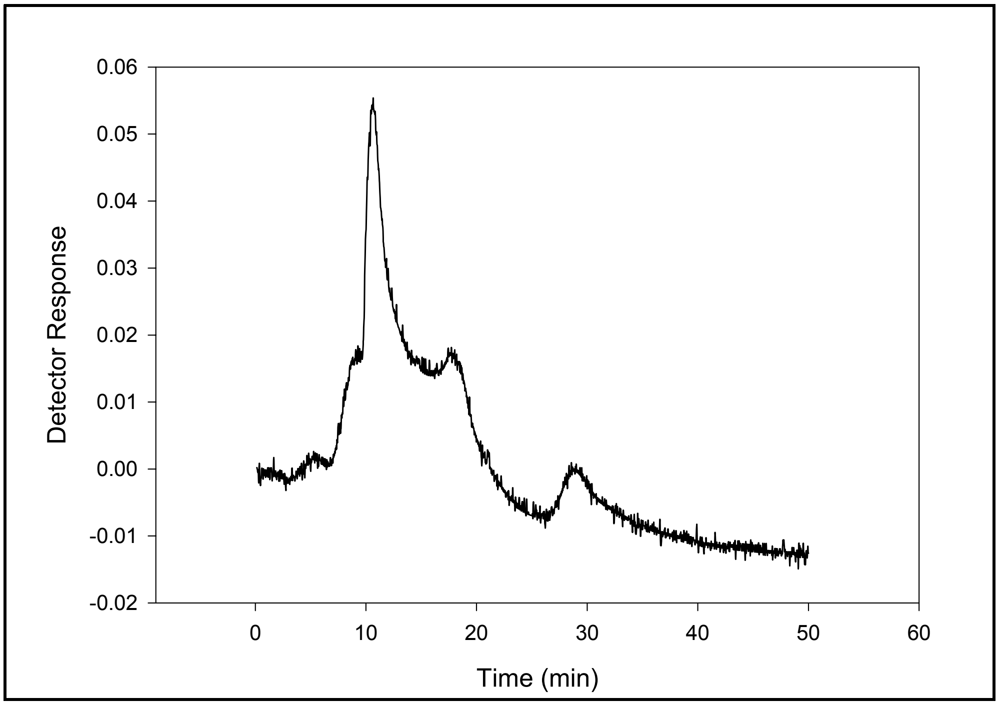


Figure 39. GPC results for PolyPavement

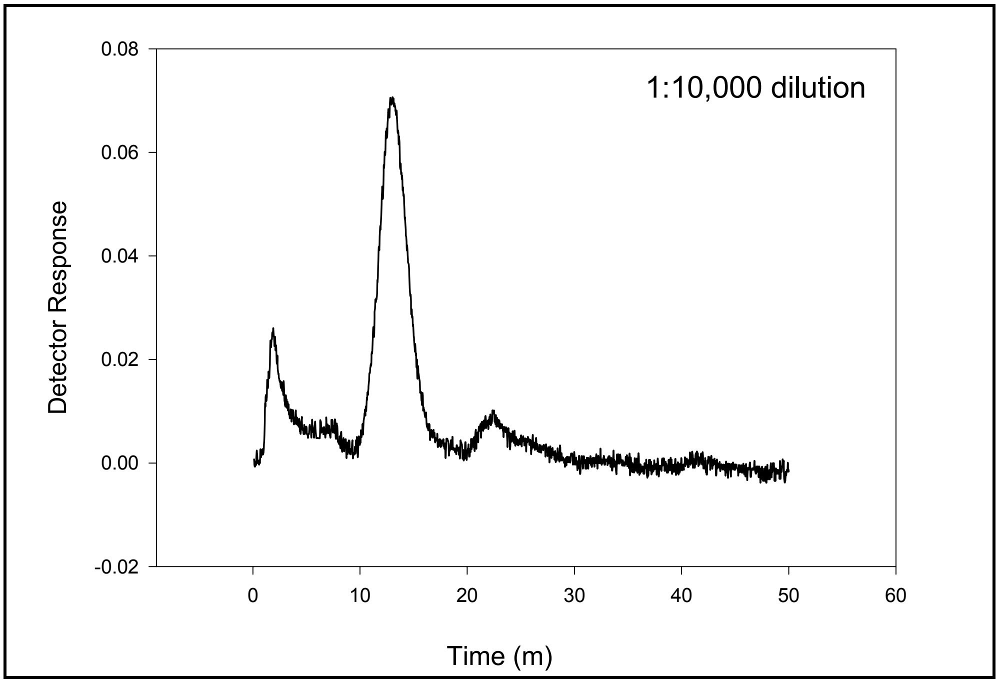


Figure 40. GPC resluts for Road Bond EN1

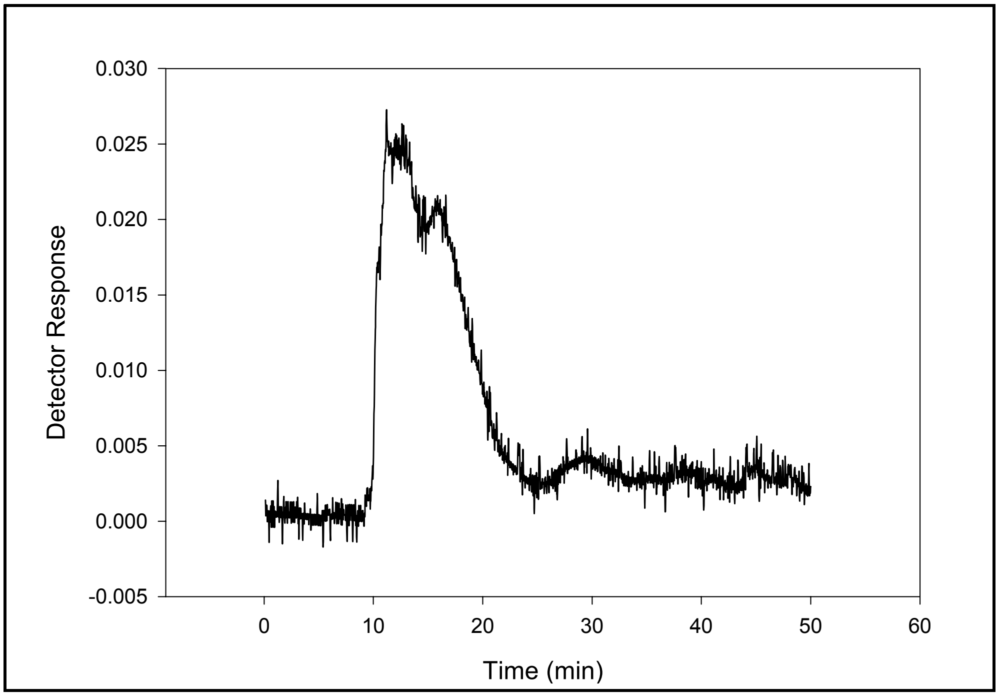


Figure 41. GPC results for Soil-Sediment

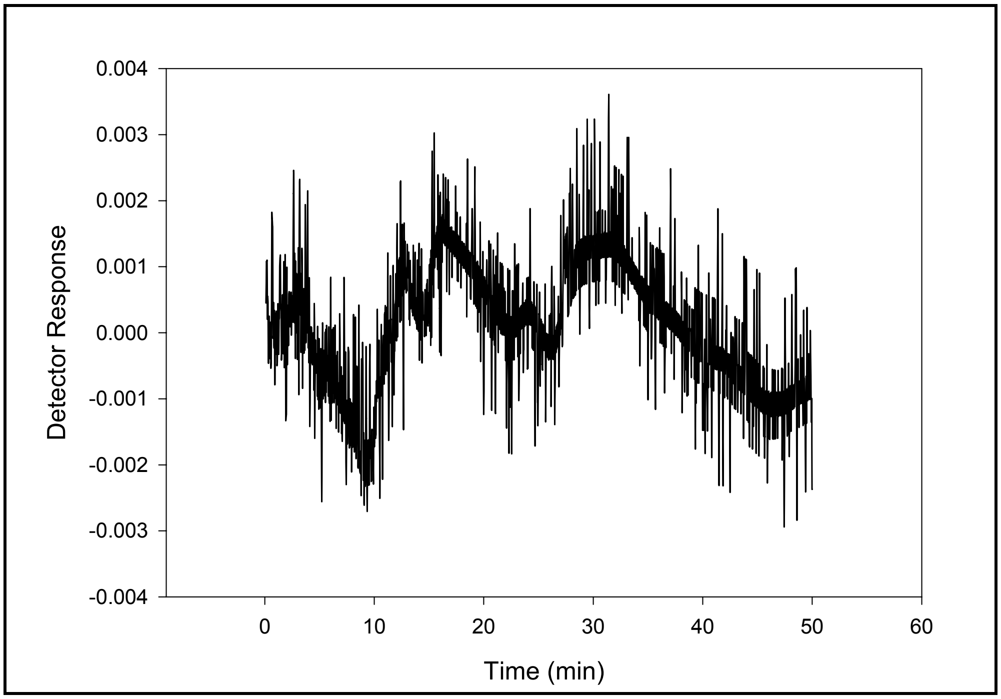


Figure 42. GPC results for Road Oyl

Table 10
Summary of Peak Retention Time, PEG Equivalent Molecular Weight, and the Relative Intensity of Absorbance

Peak Number	Retention Time	PEGMW Equivalent (Da)	Intensity Rank
Dustac 100			
1	13.2	>6000	1
2	18.4	3000 - 6000	2
3	26.2	<100	3
PolyPavement			
1	11.9	>6000	3
2	12.1	>6000	1
3	19.0	3000-1500	2
4	28.7	<100	4
Road Bond EN1			
1	14.2	>6000	1
2	21.6	750 - 500	2
Soil-Sement			
1	11 to 19	>6000 to 1500	1
2	30	<100	2
Road Oyl			
None	--	--	--

weight, and the relative intensity of the absorbance of each significant peak for each stabilizer. Because the Enviroseal 2001 sample could not be filtered effectively to a <0.45 μm soluble aqueous sample, the GPC evaluation on this stabilizer was not performed.

In the case of the Road Bond EN1 soil stabilizer, the solubility of the stabilizer in water was high, 53 percent of the solid mass dissolved in water under the solubility testing procedure. The dominant peak observed during GPC analysis was observed to be a large molecular weight peak (>600 PEGMW Equivalent). Two possible factors could influence the retention time of this peak based on the initial concentration of the water soluble compounds in the extraction solution analyzed: (1) the high concentration of smaller molecular weight surfactants resulted in the formation of large molecular weight micelles in the analyzed solution resulting in shortened retention times and an under estimation of the individual component's molecular weight and (2) the high concentration of surfactant molecules overloaded the column resulting in lengthened retention times and an over estimation of the individual component's molecular weight.

Figure 43 shows elution profiles for three serial dilutions of the Road Bond EN1 stabilizer. As can be seen the retention time of the largest peak decreases slightly as the concentration of the solution decreases. This result suggests that the second possibility discussed above is governing the molecular weight prediction for this stabilizer. At high concentrations the large (>600 PEGMW Equivalent) component is overloading the sorptive sites on the GPC column and lengthening the retention time. This suggests that the large molecular weight component is a discrete molecular component and not an agglomeration of multiple smaller surfactant molecules.

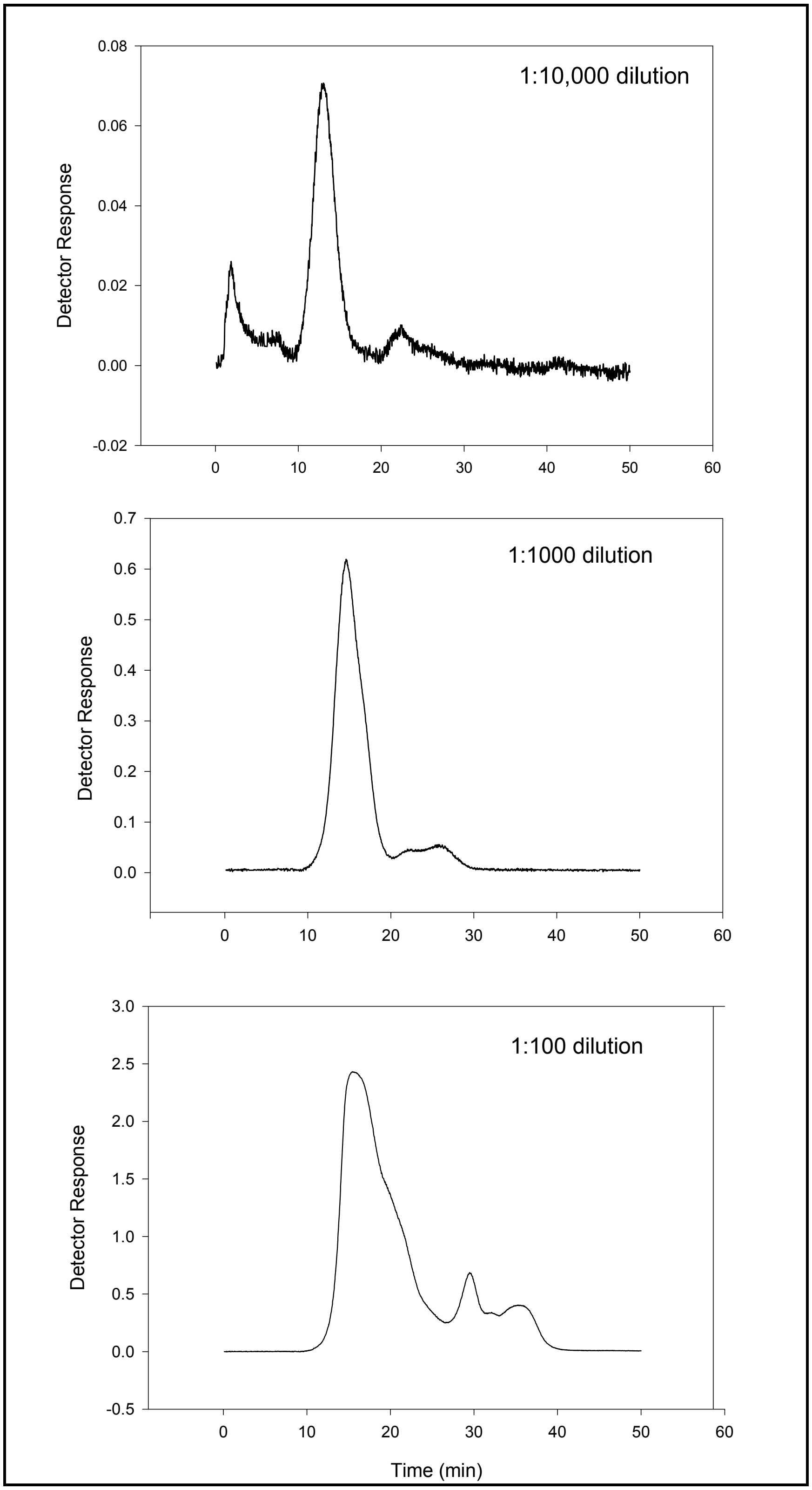


Figure 43. Elution profiles for three serial dilutions of Road Bond EN1

5 Modeling Approach

A pavement is a composite of materials that operate as a system to resist loads. The design of a pavement is a matter of optimizing the properties of materials to gain the greatest benefit by the least cost. The cost is due to the amount of material and the cost to suitably place it. Additives can be used improve the mechanical performance, thereby reducing quantities, or reducing cost of placement. To achieve either improvement, it is necessary to predict how the additive affects the mechanical performance of the material.

Analysis of the pavement system is based on non-linear finite element analysis as described by Smith et al. (2000). The particular model used was developed by Smith (2000) who incorporated a constitutive model for the granular materials into commercial finite element codes. The premise of the work was that any suitable finite element analysis code could be customized by addition of the module for computing constitutive response thus separating the issue of material response from the details of the analysis code. The focus of the work by Smith (2000) was simulating the permanent deformation caused by repetitive loading, which required the constitutive model account for hysteresis as well as the usual non-linearity accounted for in simple models based on the theory of plasticity. The model selection was also influenced by a desire for simplicity in computer implementation and calibration. The constitutive model developed for this purpose had its roots in endochronic plasticity first proposed for metals by Valanis (1971, 1980), for concrete by Valanis and Reed (1986), and soils by Valanis and Peters (1991). The work on soils was founded on critical state concepts of Roscoe and his coworkers (Roscoe et al. 1958, Schofield and Wroth 1968), which created strong ties between classical soil mechanics concepts and the irreversible thermodynamics. Unfortunately, the endochronic model was both difficult to calibrate and implement efficiently in a modular computer model. Through a subtle change in definition of the endochronic time scale, the model was converted to a form reminiscent of a rheological model comprised of elastic springs and plastic sliders; it was thus coined the multi-mechanical model (Smith et al. 2001). Despite its apparent simplicity, the multi-mechanical model retained the tie to critical state soil mechanics, which gave it predictive capabilities for shear-induced volume change and Mohr-Coulomb yield behavior. The ability to predict the response to repeated loading, the hallmark of the endochronic theory, was likewise retained.

The effect of treatment on pavement performance is addressed from the standpoint of the effect of additives the calibration parameters for the constitutive model. The multi-mechanical constitutive model is phenomenological and does not explicitly consider the micromechanics as viewed from the scale of individual soil particles. The effect of the various model parameters can be given engineering significance based on their effect on mechanical performance. To some extent, that performance can be qualitatively related to micromechanical processes. Therefore, the action of each additive is assessed by the extent that each model parameter is altered.

Components of a Soils Model

The multi-mechanical model can be roughly viewed as consisting of four parts:

a. Multiple elastic components for shear and hydrostatic response,

b. Functions that depend on prevailing void ratio and hydrostatic stress that define the limiting state,

c. Rate relationships that define the coupling between shear strain rate and hydrostatic strain rate (stress-dilatancy relationship), and

d. Parameters that control the change in free energy due to change in water content.

The first part captures the hysteretic response and is critically important for modeling system response. The second part controls the limits of the elastic-plastic response. The third part controls the volume change that occurs as a result of shear strain. These three parts are not independent. However, it is expected that the parameters most affected by additives will be those associated with part b, the functions that control the limiting state. The fourth part is a relative new addition to the model that accounts for effects of soil suction potential derived from capillary stresses that influences collapse, swell, and moisture-density relationships for compaction. Additives directly influence the parameters related to the fourth part (part *d*).

The limiting state depends on resistance derived from a combination of cohesive and frictional forces. From an engineering standpoint friction is that part of resistance that is proportional to the applied load whereas cohesion is that part of resistance that is independent of the applied loads. The distinction between the two types of resistance is important in a pavement system because the magnitude of normal stress is generally low except immediately below the load. Cohesive resistance tends to be a primary mechanism to spread the load by shear transfer, whereas frictional resistance is effective only in the presence of confinement. The comparison of cohesion versus friction is complicated by the relationship between stiffness and cohesion whereby cohesionless soils tend to be stiffer and perform better. This fact overrides the benefits of shear-transfer.

Another subtlety is the effect of friction on accumulated strain under cyclic loading. The fact that the stress-strain response (of part *a*) depends on the limit state creates a dependency between the hydrostatic stress and the shear response. As a result, hysteresis loops created by cyclic loading in shear do not close. Accumulated shear results from this lack of closure. If resistance is the result of cohesion, the model predicts less accumulated shear. This is an experimentally verifiable aspect of the model that needs to be investigated as a potential secondary effect of additives.

Effect of Additives on Model Behavior

Additives create resistance by increasing non-frictional forces. A mechanical interpretation of how additives enhance soil behavior requires consideration of particle interactions at the particle level. The concepts used for engineering analysis are effective but often misleading from the standpoint of defining the interparticle behavior. A notable example is the concept of internal friction. The traditional interpretation of shear resistance is based on the Mohr-Coulomb failure concept by which failure depends on the shear and normal traction on a critical sliding plane. The implication is that the principal mechanism of failure at the particle level is sliding. It has long been known that the internal friction can be separated into a dilative component and a dissipative component (Schofield and Wroth 1968) implying that the friction angle measured in a laboratory specimen is not strictly a sliding phenomenon. By the traditional interpretation the dissipative friction (or true friction) is a property of the mineral-mineral sliding resistance and the dilative friction comes about by particle rearrangement. More recent investigations into the micromechanics of granular media (Thorton 2000) reveal a more complicated picture that is important to understand if additives are to be understood from a mechanical viewpoint.

The concept of resistance along sliding planes has utility for engineering computations but does not describe the particle-scale behavior and is misleading for predicting the effect of additives. Forces are carried through a granular media as compressive forces. The resistance of particle contacts to sliding and the stability of particle groups that form force chains to resist rotation determine the load carrying capacity (Oda 1999). Micromechanical studies by Thornton (2000) indicate that the interparticle friction is not directly related to the measured internal friction of the media. Rather, an increase in interparticle friction stabilizes particle chains, which increases the ability of the soil to dilate.

The ability of an additive to increase soil strength comes about by enhancing the stability of the interparticle contacts. At the scale of the particle contacts, resistance is primarily frictional. However, the normal contact force that enhances friction can be derived from either applied boundary loads, carried through force chains, or from micro-scale forces that act independently from boundary forces. In the first instance, the soil appears to be frictional, while in the second the soil appears to have cohesion. The premier example of an internal force is water menisci in a partially saturated soil that creates so-called apparent cohesion, illustrated in Figure 44. The resistance to sliding at the contacts is frictional but the normal force is supplied by capillary tension in the water phase rather than the boundary load. From a micromechanical viewpoint, the contact strength is derived from friction. From the standpoint of engineering behavior, the resistance is cohesive because it can be derived in the absence of a boundary load.

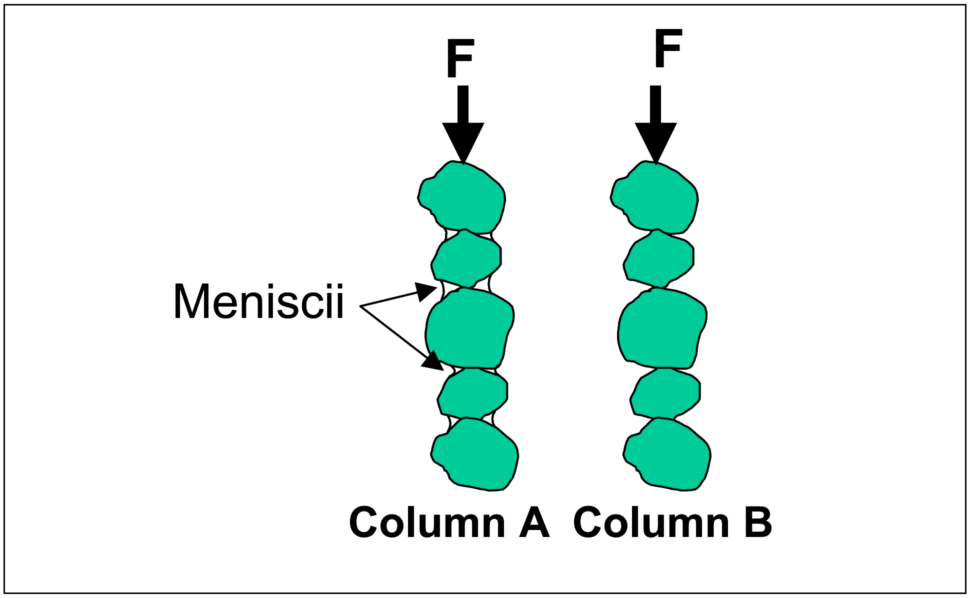


Figure 44. Effect of menisci on the stability of a soil column

Influence of Water Phase

Additives can also alter the affinity of the solid phase for water. Thus far the discussion has centered on granular soils in which the interaction between soil grains and additive is through surface tension. If the soil contains a significant clay fraction, the interaction includes the effects of ion exchange. In untreated soils, the clay minerals interact with the water phase to cause shrinking or swelling. One role of the additive is to replace the water in the ion exchange process such that the material is less susceptible to changes in water content. The effectiveness of the additive depends critically on the interaction of the additive with the particular clay minerals present.

Soil Compaction

Additives can alter the soil's performance both by altering its in-place properties and by improving the effectiveness of compaction. The compaction curve is a result of the relationship between water content and the resistance to compaction (Holtz and Kovacs 1981). On the dry side, compaction is resisted by the increase in grain-to-grain forces created by tension of water menisci that form between grains. These forces enhance the frictional resistance across the inter-particle contact creating an apparent cohesion. At very low water contents, menisci play a small role because most of the moisture adheres to the grain surfaces. As water content is increased, more water is available for meniscus formation and inter-granular forces are increased. Reduced density or bulking is the result of the increased inter-granular resistance. As the water content is increased even more, the menisci become more numerous but are also larger, thus reducing the effect of the surface tension in creating inter-granular stress, thereby reducing the resistance to compaction. As more water is added, significant pore space becomes filled with water, virtually eliminating the effect of surface tension leading to an optimum state in which to induce compaction known as the maximum dry density. At higher water contents, nothing more can be gained from reduced capillary tension as the bulk pore water itself creates compaction resistance through excess pore pressure leading to a reduction in dry density on the wet-side of the optimum moisture content. Therefore, the mechanism that imparts greater in-place strength also resists efforts to obtain target compaction densities. The ideal additive would reduce resistance to compaction then increase resistance in-place.

Example of Surfactant Additive

The effect of surfactant on pore water is a simple example of the mechanical effects of a soil additive. The account described here is summarized from Berney et al. (2003), which investigated a silty-sand. Lambe (1954) reported a similar study for clays.

The principal effect of the added surfactant is to reduce the surface tension in the capillary water thereby altering the manner forces are transmitted in grain-to-grain contact. In granular soils, inter-granular stresses arise from compressive forces at inter-particle contacts. The strength of these contacts is derived from the frictional forces, which are proportional to the contact force. For partially saturated soil the inter-granular force is the sum of applied stresses carried through chains of particles and by forces imparted by tensile forces in the capillary water as in Figure 44, column A. The allowable applied stress is limited by the stability of inter-particle contacts. The forces carried through particle chains increases the frictional resistance, but any applied stress also acts as a de-stabilizing force shown in Figure 44, Column B. The presence of capillarity due to menisci in Column A will allow it to sustain a greater applied force before buckling over the unsupported Column B. The capillary forces act independently at each contact, not through force chains and are primarily a stabilizing presence, commonly referred to as apparent cohesion.

The capillary component of inter-granular stress is derived from the surface tension, which is a property of the water-mineral interaction and the size of the meniscus, a function of pore geometry and saturation (Croney and Coleman 1961). It is proposed that the addition of a water surfactant will reduce this surface tension component. Therefore, bulking and its reduction by adding water is still observed, but with reduced effect. As a result, it is possible to achieve higher dry-side densities while reducing the sensitivity of compaction efficiency to water content. Also, inter-granular stress in the as-compacted state is reduced.

Moisture-density relationship

Figure 45 illustrates the role of a surfactant (4 percent AOT) on the moisture-density behavior, by providing a comparison between soil compacted with and without surfactant. From this figure, there exists a range of moisture contents for which the surfactant has an effect on the final dry density, ranging from about 2 to 5.5 percent shown in Figure 46. The densities lying outside of this range all exhibit similar response properties independent of treatment. Within this range the treated soil exhibits a higher dry density than the untreated soil, yet the upper end of the range coincides with the wet-side curve of the untreated soil. Therefore, a treated soil provides a wider range of moisture contents at which a certain minimum density may be achieved.

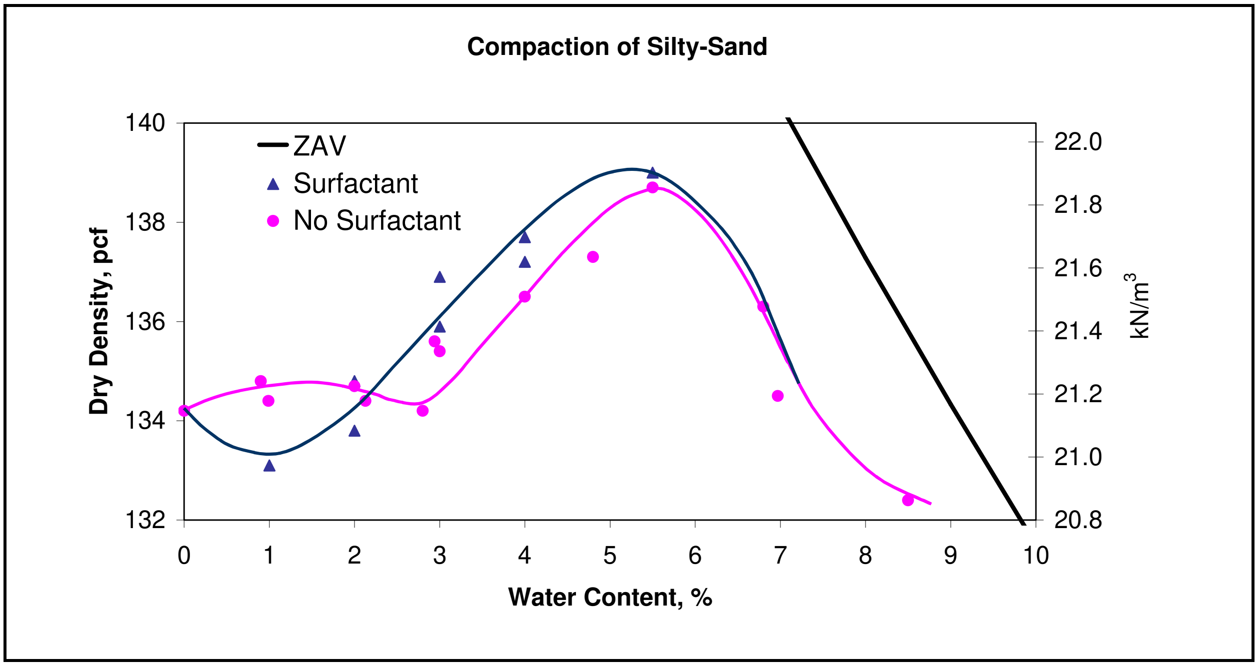


Figure 45. Moisture-density relationship for silty-sand

The shapes of these curves support the supposition that the surfactant does indeed reduce the surface tension of the menisci. When the soil is very dry (below 2 percent moisture content), there is little to no influence due to the surfactant because there is not enough moisture present to generate menisci that will affect the compaction behavior of the material. Once enough menisci are present to inhibit compaction for moisture contents above 2 percent, the surfactant treated soil exhibits a higher dry density until the optimum moisture content is reached. The observed trend supports the idea that by reducing the grain-to-grain forces created by the tension in the water, the particles are allowed to compact more easily. Once the moisture exceeds optimum, the densities become similar since the surfactant does not change the stiffness of the now interconnected pore water.

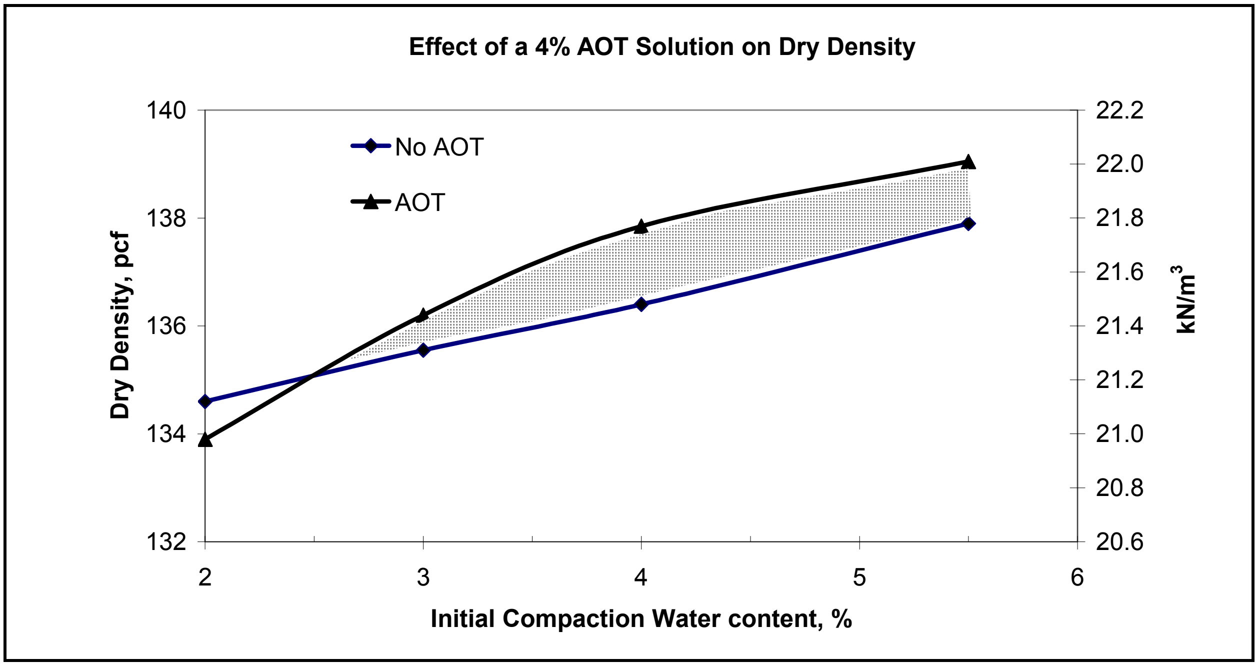


Figure 46. Summary of surfactant effects on dry density

Most often, construction specifications for earthwork contain criteria for a certain percentage of a maximum dry density and a range of moisture contents in which those densities can be achieved. The compaction curve in Figure 45 shows that a soil treated with surfactant can extend the range of moisture contents in which a certain minimum dry density can be achieved. Therefore, this allows the contractor more flexibility in deciding the compaction effort and construction water content that are required to provide an earthwork of suitable density. As well, for a given compaction energy the contractor could wet the soil to an optimum moisture content level and not be penalized in density if the soil were to dry back during a delay in operations.

CBR strength

Analysis. The CBR strength over the range of moisture contents influenced by the presence of a surfactant (4 percent AOT) is shown in Figure 47. The top two curves represent the unsoaked CBR strength, and the bottom two curves, the soaked CBR strength with each pair of curves providing a comparison between the treated versus the untreated silty-sand. For the unsoaked CBR tests, the strength is greater for the untreated soil over the entire range of moisture contents. This suggests that the additional strength provided by capillary forces present in the untreated sample is larger than the strength gained from the increased number of grain-to-grain contacts of the denser, treated sample.

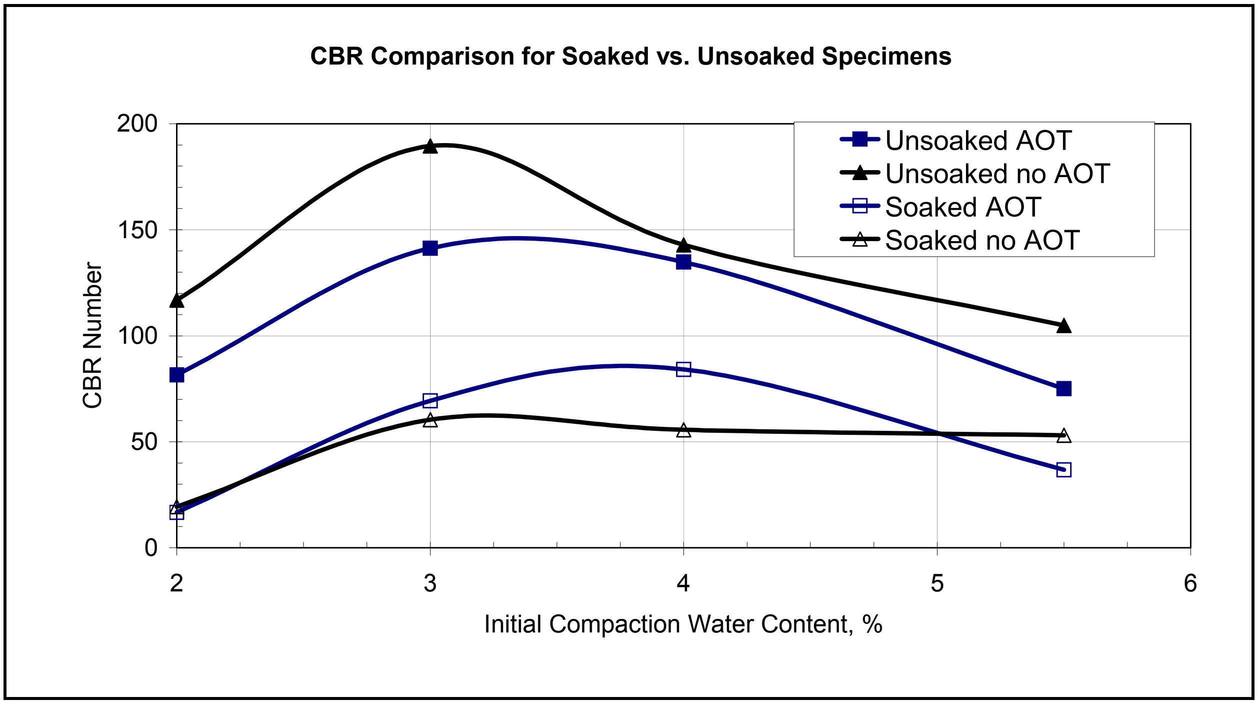


Figure 47. CBR strength comparison for silty-sand

Analysis of the soaked CBR tests shows a reversal to the trend in strength found in the unsoaked condition, as the soil treated with surfactant now exhibits the same or greater CBR strength over the range of affected moisture contents. Using the premise above, mechanically this follows, since when the soil becomes inundated with water, any strength gained from effective cohesion is lost as the menisci disappear at high water contents. This leaves only the friction effects occurring from grain-to-grain contact forces to resist the applied loads. The treated soil has the advantage of a greater number of those contacts due to its higher dry density. This results in a higher soaked CBR strength. The value obtained from a soaked CBR test often dictates the criteria used for determining the suitable design strength of a chosen soil. Since treating a soil with surfactant has the potential to increase its soaked CBR value this becomes a beneficial soil treatment for increasing the allowable loading imposed on pavement layers.

In comparing the relative change in CBR strength due to inundation, the treated soil retains a greater percentage of its as-compacted strength than for the untreated soil. Thus, the surfactant provides a stabilizing effect on the strength. So while the untreated soil is stronger in the as-compacted moisture condition, the use of surfactant allows for a more consistent long-term strength over the life of a pavement system with the expectation that environmental effects might induce changes in the moisture condition over time.

Swelling characteristics. While silty-sand is not a swelling soil, measurable volume changes occurred during soaking. These volume changes illustrate the interaction between applied stresses and capillary stresses already noted in the CBR strength test. Figure 48 shows that the treated silty-sand over the range of affected water contents exhibited less swelling on the order of 25 to 50 percent from the untreated soil. For a granular media like the silty-sand, the mechanics that drive this response rely solely in the energy stored in the menisci between grains. The surfactant reduces the tensile forces present in the inter-granular menisci, which in turn reduces the potential energy in the compacted soil. When the sample is inundated, there is less relaxation of the soil, which manifests itself as a lessening of the soil's swell potential. As well, by breaking down the presence of the menisci, the surfactant allows for a greater initial density at compaction and reducing the possibility of collapse when wetted.

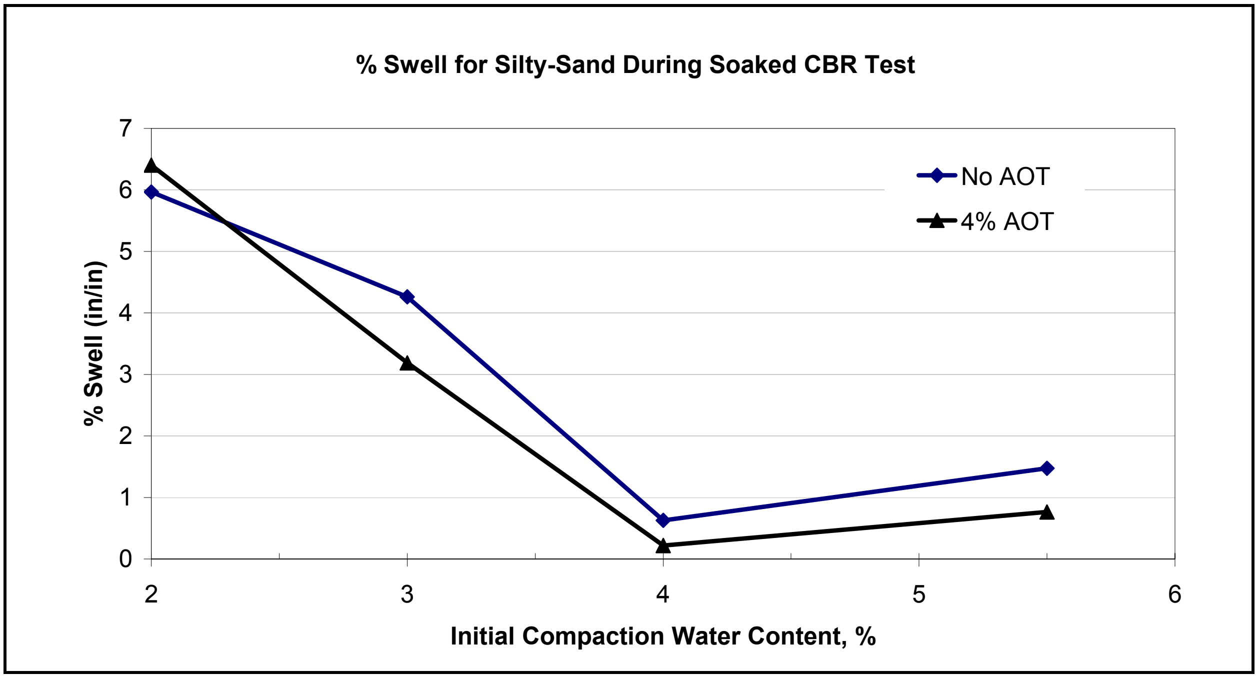


Figure 49. Swelling response on silty-sand during soaked CBR test

Therefore, the higher the surface tension, the more resistance to compaction, and the greater unsoaked strength the soil has. When the inter-granular stress is relaxed upon soaking, the strength derived from capillary stress is lost. The magnitude of stress relaxation is proportional to the swell upon soaking, which is greater for the untreated soil.

Summary

Each treated soil will be calibrated to determine which parameters are affected by treatment. The parametric effect gives direct indication on how the engineering behavior is influenced behavior and indirect evidence on the particle-scale mechanisms that are affected by treatment. The tests to be performed are as follows:

a. *Consolidated undrained triaxial test with hydrostatic consolidation:* This test is run on the untreated soil with backpressure saturation. This test provides the complete stress-strain response for hydrostatic and shear conditions, the failure envelope, and the shear-volume coupling behavior.

b. *Complete compaction test:* A complete compaction test should be performed for each additive-soil combination.

c. *Constant volume swell-pressure test:* The relationship between suction potential and water content can be established from the relationship between swell pressure and water content.

d. *Unconsolidated undrained* strength *test:* This test is run on the treated soil in the as-compacted state.

6 Conclusions

Personnel of the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, conducted a series of laboratory experiments designed to characterize the constitutive properties of selected soil minerals and nontraditional stabilization additives. The results of these experiments were analyzed and are included in this report to document the baseline characteristics prior to mixing the stabilizers and individual soil minerals. Analyses of the potential of individual stabilization products to reinforce specific soil types were conducted and reported. Additionally, an experimental modeling approach for describing the reinforcement mechanisms of individual stabilization agents was developed.

The following conclusions were derived from the constitutive analyses of material characteristics and subsequent analyses of the potential effectiveness of each additive in different soil types:

a. Literature hypothesizes that the mechanism for soil stabilization using electrolytes or ionic stabilization additives consists of the additive serving as a catalyst to accelerate the weathering of the clay mineral structure. The ionic stabilizers alter the concentration of the electrolyte pore fluid resulting in cation exchange and flocculation of the clay minerals. As the clay minerals attract stronger cations from the pore fluid, the higher valence cations collapse the clay mineral structure into a more stable configuration exuding excess double-layer water in the process. Thus, based upon this mechanism, ionic additives would be suitable for soils that have a significant amount of clay material in order for the change in the clay structure to have a pronounced effect on the soil. In addition, the process of altering the properties of the electrolyte pore fluid, inducing the flocculation of clay minerals, and the collapse of the clay mineral structure would be expected to require a significant amount of time.

b. Research also speculates that the mechanism by which enzymes stabilize soils consists of bonding between the enzyme and large organic particles. The large organic particles are then attracted to the net negative surface charge of the clay minerals, and the organic molecule attraction eventually balances the net negative charge of the clay minerals. This reduces the clay's affinity for water. This mechanism suggests that the use of enzymes to stabilize soil requires that the soil composition include a significant amount of organic molecules and clay minerals. This process is also expected to require significant time.

c. Historical experiments indicate that the stabilization mechanism of most polymer products is based upon physical bonding between individual soil particles. Thus, polymer-based additives are more suitable for the stabilization of granular soils. The actual chemistry of the particular additive may include other chemicals that could provide some secondary stabilization benefits.

d. Minerals such as quartz or calcite, which have no double-layer water, are more likely to perform better with stabilization additives whose primary reinforcement mechanism is physical bonding. Materials such as smectitic clays would probably work better with hydrophilic materials than hydrophobic materials because of the high water content of clays. Stabilizers that can produce a chemical bond between the stabilizer and the substrate should produce the best bonding characteristics. The high specific surface area of clay minerals also suggests that additives that rely on physical bonding may be difficult to adequately disperse in fine-grained clay materials.

e. The soil analyses conducted on the clayey silty-sand (SM-SC) indicate that it is a granular material with some plasticity characteristics due to significant fines content. Thus, additives that rely upon a physical bonding mechanism will be more effective with this soil than those with a chemical reaction mechanism due to the lack of a significant amount of clay minerals, exchangeable cations, or bound water.

f. The analyses conducted on the low plasticity clay (CL) suggest that both physical bonding and chemical reaction mechanisms may be beneficial in improving the strength properties of the material. The magnitude of the strength improvement due to physical bonding additives will be less than a similar quantity used in a granular material. This is due to the high specific surface area of the clay minerals, reduce individual grain size, and the inability to adequately mix the additive into fine-grained soils. Chemical additives may be successful in altering the properties of the CL soil due to the soil possessing a significant amount of clay minerals and bound double-layer water.

g. The soil tests conducted on the high plasticity clay (CH) demonstrated only minor changes in the soil when combined with additives that rely upon physical bonding mechanisms due to high specific surface area minerals, reduced grain size, and the inability to adequately coat individual particles. Stabilization additives that rely upon chemical reactions with the clay minerals should be successful in altering the properties of the CH soil through cation exchange, flocculation, and reduction of the double-layer water within the mineral structure.

h. Ven-Set 950 appears to be an ionic stabilization additive and, as such, its ability to effectively alter the properties of a soil is dependent upon the soil's mineralogy. Ven-Set 950 would be expected to behave as a surfactant, adsorb onto particles, and has the potential to develop ionic bonds with cations present in clay soils.

i. The reinforcement mechanism of Enviroseal 2001, a polymer emulsion, is a physical bond generated by a cementation between particles. The amount of product required to effectively stabilize a soil will be dependent upon the soil's grain size distribution and ability to adequately mix the material into the soil.

j. Soil-Sement is a polymer emulsion that will provide a physical bond between soil particles. Soil-Sement's effectiveness will also be dependent upon the soil's gradation and will be more effective in granular materials.

k. PolyPavement is also a polymer emulsion that will physically bind soil particles together similar to Soil-Sement and Enviroseal 2001. Thus, PolyPavement would be expected to be more effective in granular materials than fine-grained soil.

l. Dustac 100 is a lignosulfonate that may act as an ionic surfactant capable of forming ionic bonds with cations present in clay soils with minor physical bonding attributes. As a lignin, this product may be susceptible to leaching from the soil with moderate precipitation.

m. Road Bond EN1 is an acid that is expected to act as an ionic stabilizer by altering the properties of the electrolyte fluid in the clay mineral structure. Thus, its stabilization mechanism is a chemical reaction and may require time to produce significant changes in the soil's engineering properties.

n. Road Oyl is a natural resin that would produce a physical bond between soil particles similar to Soil-Sement, Enviroseal 2001, and PolyPavement. However, since Road Oyl is a by-product, it may not be as efficient in generating the physical bonds as engineered bonding agents for the same percent solids.

o. Soil stabilization additives directly influence the void ratio, hydrostatic stress state, and the free energy resulting from changes in water content. These factors affect the limiting state of the soil and influence the ability to model the behavior of stabilized soil within a pavement system.

p. The ability of an additive to increase soil strength is derived from its enhancement of the stability of the interparticle contacts. This increase in soil strength is often attributed to increased internal friction or cohesion, but may be more generally described as the change in surface tension between particles and/or the additive.

References

Ajayi-Majebi, A., Grissom, W. A., Smith, L. S., and Jones, E. E. (1991). Epoxy-resin-based chemical stabilization of a fine, poorly graded soil system. *Transportation Research Record* 1295, Transportation Research Board, National Research Council, Washington, DC.

American Coal Ash Association. (1995). "Fly ash facts for highway engineers," Report FHWA-SA-94-081, Federal Highway Administration, U.S. Department of Transportation, Washington, DC.

American Concrete Institute. (1990). "State-of-the-art report on soil cement," *ACI Materials Journal* 87(4), 395-417. Farmington Hills, MI.

Berney, E. S., IV, Peters, J. F., Newman, J. K., and Smith, D.M. (2003). "Effect of surfactant on the dry-side compaction of silty sand," *Journal of the Transportation Research Board* 1819, 57-62.

Croney, D., and Coleman, J. D. (1961). "Pore pressure and suction in soils," *Proceedings, conference on pore pressure and suction in soils*. Butterworth Publishers, London.

Gopal, R., Singh, J., and Das, G. (1983). "Chemical stabilisation of sand; Comparative studies on urea-formaldehyde resins as dune sand stabiliser and effect of compaction on strength, Part IV," *Transactions of Indian Society of Desert Technology and University Centre of Desert Studies* 8(2). Indian Society of Desert Technology, Jodhpur, India, 13-19.

Holtz, R. D., and Kovacs, W. D. (1981). *An introduction to geotechnical engineering*. Prentice-Hall, Englewood Cliffs, NJ.

Katz, L. E., Rauch, A. F., Liljestrand, H. M., Harmon, J. S., Shaw, K. S., and Albers, H. (2001). "Mechanisms of soil stabilization with a liquid ionic stabilizer." *Transportation Research Record* 1757. Transportation Research Board, National Research Council, Washington, DC, 50-57.

Lambe, T. W. (1954). "Improvements of soil properties with dispersants," *Journal of the Boston Society of Civil Engineers* 41(2), 186-207.

Oda, M. (1999). "Particle rotation and couple stress." *Mechanics of granular materials: An introduction*. M. Oda, K. Iwashita, ed., A. A. Balkema, Rotterdam, 14-19.

Oldham, J. C., Eaves, R. C., and White, D. W. (1977). "Materials evaluated as potential soil stabilizers," Miscellaneous Paper S-77-15, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Palmer, J. T., Edgar, T. V., and Boresi, A. P. (1995). "Strength and density modification of unpaved road soils due to chemical additives," Master's thesis, University of Wyoming, Department of Civil and Architectural Engineering, Laramie, WY.

Rauch, A. F., Harmon, J. S., Katz, L. E., and Liljestrand, H. M. (2002). "Measured effects of liquid soil stabilizers on engineering properties of clay," *Journal of the Transportation Research Board* 1787, Transportation Research Board, National Research Council, Washington, DC, 33-41.

Robinson, J. H., and Rabalais, C. P. (1993). "Performance of the combat engineer vehicle with mineplow operating worldwide and in theaters of operations," Technical Report GL-93-23, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Roscoe, K. H., Schofield, A. N., and Wroth, C. P. (1958). "On the yielding of soils," *Geotechnique* 8(1), 25-53.

Schofield, A. N., and Wroth, C. P. (1968), *Critical state soil mechanics*. McGraw-Hill, London.

Scholen, D. E. (1992). "Nonstandard stabilizers," Report FHWA-FLP-92-011, Federal Highway Administration, Washington, DC.

__________. (1995). "Stabilizer mechanisms in nonstandard stabilizers." *Proceedings, 6th international conference on low-volume roads*. Transportation Research Board, Washington, DC. 2, 252-60.

Smith, D. M. (2000). "Response of granular layers in flexible pavements subjected to aircraft loads," ERDC/GL TR-00-3, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Smith, D. M., Rollings, R. S., Peters, J. F. and Metcalf, J. B. (2000). "Mechanical response of unbound granular base course for a flexible pavement," *Unbound aggregates in round construction*. Balkema Press, Rotterdam, 325-34.

Smith, D. M., Peters, J. F., and Rollings, R. S. (2001). "Development of a granular media model for finite element analysis," Technical Report ERDC/GL TR-01-03, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Thornton, C. (2000). “Numerical simulations of deviatoric shear deformation of granular media," *Geotechnique* 50(1), 43-53.

Transportation Research Board. (1987). “State of the Art Report 5; Lime stabilization, reactions, properties, design, and construction,” Transportation Research Circular No. 180, Washington, DC.

Valanis, K. C. (1971). “A theory of viscoplasticity without a yield surface; Part I, General theory,” *Archives of Mechanics* 23, 517-33.

__________. (1980). “Fundamental consequences of a new intrinsic time measure; Plasticity as a limit of the endochronic theory,” *Archives of Mechanics* 32, 171-91.

Valanis, K. C., and Peters, J. F. (1991). "An endochronic plasticity theory with shear-volumetric coupling," *International Journal for Numerical and Analytical Methods in Geomechanics* 13, 77-102.

Valanis, K. C., and Reed, H. E. (1986). “An endochronic plasticity theory for concrete,” *Mechanics of Materials* 5, 227-95.

Vvedenskaya, V. A., Ogneva, N. E., Korshak, V. V., Mekhant’eva, L. I., and Goguadze, Ts. A. (1971). “Consolidation of over-moist soils by copolymers of guanidine acrylate and methacryloguanidine-urea hydrochloride with certain alkylidene bisacrylamides” (translated by E. A. Inglis), *Soviet Plastics* 7. Rubber and Technical Press, London, England. 55-58.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* November 2004	**2. REPORT TYPE** Final report	**3. DATES COVERED** *(From - To)*

4. TITLE AND SUBTITLE Constitutive Analyses of Nontraditional Stabilization Additives	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Jeb S. Tingle, Steve L. Larson, Charles A. Weiss, J. Kent Newman, John F. Peters, Barbara Tardy, and Ernest S. Berney IV	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center Geotechnical and Structures Laboratory and Environmental Laboratory 3909 Halls Ferry Road Vicksburg, MS 39180-6199	**8. PERFORMING ORGANIZATION REPORT NUMBER** ERDC TR-04-5
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Headquarters, U.S. Army Corps of Engineers CECW-EW Washington, DC 20314-1000	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Personnel of the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, conducted a series of laboratory experiments designed to characterize the constitutive properties of selected soil minerals and nontraditional stabilization additives. The results of these experiments were analyzed and included in this report to document the baseline characteristics prior to mixing the stabilizers and individual soil minerals. Analyses of the potential of individual stabilization products to reinforce specific soil types were conducted and reported. Additionally, an experimental modeling approach for describing the reinforcement mechanisms of individual stabilization agents was developed.

15. SUBJECT TERMS

Nontraditional additives	Soil improvement	Strength improvement
Reinforcement	Soil stabilization	

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT UNCLASSIFIED	**b. ABSTRACT** UNCLASSIFIED	**c. THIS PAGE** UNCLASSIFIED		77	**19b. TELEPHONE NUMBER** *(include area code)*