

# Stabilizer Mechanisms in Nonstandard Stabilizers

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An improved understanding of the mechanism of nonstandard chemical stabilizers is sought in the mineralogy and chemistry of clays and stabilizers. The mineralogy of clays and the chemistry of stabilizers are described. The complete hydrolysis of the rock mineral feldspar produces the rock minerals opaline and gibbsite. This pathway provides a most probable route for the chemical stabilization process. In the natural weathering process, the presence of alkali metal cations prevents completion of hydrolysis and results in an end product of clay minerals except where lateralization occurs. The process of lateralization is paralleled by the effects of chemical stabilizers. Certain organic ring compounds provide a strong attraction for metal cations. Chemical stabilizers contain these compounds in ionized form so that they can remove cations from the clay environment and permit the hydrolysis to proceed to a stage of lateralization. In a certain construction procedure involving injection, development of a high electrochemical potential results in rapid infiltration through normally impervious clays. In another construction procedure limited to scarification, the developed potential is low, and mixing is required. For either procedure, the behavior of resulting stabilized materials resembles that of natural concretions in various stages of lateralization, and the materials are resistant to moisture penetration and frost action. Strength increases with density, which results in higher intermolecular attractions. The physical manifestation of the proposed mechanisms at work has frequently been observed in the case studies, which are referenced in detail for illus-

tration. A review of recent case studies and some supporting laboratory data are provided.

**S**tudy F-5, Non-standard Stabilizers, was initiated in 1988 under the FWHA Coordinated Technology Implementation Program (CTIP) to provide information on soil and aggregate stabilizers available on the market but not in general use in the United States. The stabilizers tested are given in Table 1. Previously published case studies show a remarkable project performance for the stabilized aggregates (1), and yet laboratory testing indicates only minor changes in engineering properties such as grain size, Atterberg limits, and bearing or shear strength testing. The reason for this apparent contradiction is that chemical stabilization alters the mineralogy of the clay fines to a material with properties that cannot be tested by the standard methods used in highway materials laboratories.

The alteration of clay minerals is but a modification of the weathering processes taking place in nature. Briefly stated, the breakdown of rock minerals by the weathering process, if carried to its ultimate phase, results in the formation of a stable crystalline residue. The presence of alkali metal cations and ionized water in the natural environment stalls this breakdown at an intermediate phase, resulting in formation of clays. In the natural lateralization of clays that results in the formation of pan, iron ore gravels, and bauxite, the cations

TABLE 1 Chemical Stabilizers Tested

NAME	TYPE	USE	200
Condor.SS	Sf nphthin	Subgrade	40%
ISS	Sf nphthin	Subgrade	40%
Road.Bond	Sf limonene	Agg.Surf.	20%
Perma.Zyme	Enzyme	Agg.Surf.	20%
EMC <sup>^</sup> 2	Bioenzyme	Agg.Surf.	15%
BioCat	Bioenzyme	Agg.Surf.	15%

are removed by chelation (2) and leaching, allowing hydrolysis to proceed under certain conditions (3). The application of appropriate chemicals to chelate and remove the cations and ionized water will also permit the breakdown to continue to the stable rock and clay mineral phase (2). Appropriate chemicals must be ionized or in enzyme form and contain aromatic rings with a strong negative charge to attract the cations and ionized water (4,2). These chemicals do not become a part of the rock mineral phase but act solely as catalysts to the breakdown process.

The nature of the structure of the six-carbon benzene ring results in the required negative charge but in the form of an oil (5-7). Treating this oil with sulfur trioxide and sulfuric acid causes the ring structure to ionize, producing a potential stabilizer (7, p. 153). Alternatively, a five- or six-carbon ring may be synthesized into an enzyme system that can accomplish the required result (5, p. 755). Thus the carbon ring is the basic building block of the chemical stabilizer.

## OCCURRENCE OF CLAY MINERALS

These stabilizers react only with the clay mineral fraction of the soil or aggregate. Understanding the formation and occurrence of clay minerals is essential to understanding the observed performance or lack thereof in the case studies (1, p. 11).

Feldspar is the most abundant rock-forming mineral, constitutes 60 percent of the earth's crust, and is the primary source of clay. Clays will not form in arid climates. Clays found in these areas developed during prior climatic periods or were transported. The weathering horizons in a moist climate have ample organic humus to provide the necessary low pH and CO<sub>2</sub> in the soil. The weathering of feldspar results in hydrolysis of the feldspar rock mineral to kaolinite and amorphous silica (2,8).

During transport in streams and deposition, kaolinite is converted to illite. Kaolinite is an alumina-rich clay, and illite and smectite each have increasing percentages of silica (2, p. 25), resulting from changing environment. Illite is rich in potassium (K), whereas smectite is

rich in sodium or calcium. Montmorillonite is the predominant type of smectite.

One engineering characteristic that provides an indicator of the mineral content in clays is the activity ratio (AR) (2, p. 185; 9). The AR is the product of the plasticity index (PI) divided by the percent finer than 0.002 mm (2  $\mu$ m). Anything finer than 2  $\mu$ m is considered to be clay. Clays with low activity ratios, less than 0.5, are generally kaolinite. Illites have an AR of less than 1.0, and smectites have an AR greater than 1.0. Mixed layer clays will be above or below 1.0 depending on the percentage of each clay mineral present; thus, the history of the deposit is useful in determining whether a clay is illite or mixed layer. Case studies involved a broad range of clays (Table 2).

## CLAY CHEMISTRY

The basic molecular building blocks of clay (2, p. 25) are silica oxide tetrahedra, SiO<sub>4</sub>, and alumina hydroxide octahedra, Al(OH)<sub>6</sub>.

The positive charge of the silica sheet balances the negative charge of the hydrated alumina sheet, and the two sheets form a stable layer except along the periphery of the layer where bonds are broken. This arrangement forms the kaolin clays. Illite and smectite have a silica sheet on either side of the alumina sheet, totaling three sheets per layer. The layers are loosely bonded by the attraction between the H<sup>+</sup> of the alumina's hydroxyl and the O<sup>-</sup> of the silica's oxygen in the adjacent layer (kaolin) or held together by shared cations (illite and smectite). The excess negative charge holds cations and ionized water, H<sub>3</sub>O<sup>+</sup>, to the surface of the layers.

Thus the molecular structure of clays is latticed. The lattice is made up of repeating layers of silica and hydrate of alumina and has charged metal cations, primarily potassium, sodium, and calcium and ionized water attached to the layers. The weaker clays can absorb layers of ionized water among the lattice layers, allowing them to expand and lose density. In an electron micrograph, the clay structure appears like a disorderly pile of club sandwiches in which the layers of bread and meat are the repeating layers of the molecular lattice.

The stability of the lattice is tenuous. The bonding is susceptible to changes in pH; aluminum hydroxide is amphoteric, forming free ions in solution at low and high pH but becoming insoluble and forming the lattice at moderate pH. Silica dioxide forms its lattice when above certain concentrations at low to moderate pH and forms free ions in solution at high pH. The excess negative charge must be balanced by other ions in solution to maintain the stability of the lattice. Because of their differences, the silica can slowly leach out at mod-

TABLE 2 Test Data on Subgrade Soils

LOC.	PRJ	TP	200	2u	1u	LL	PL	PI	AR	CST	ST
MS...	707	UT	82	30	27	50	21	29	1.0	FE	N
TX	204	T	51	38	36	43	15	28	1.3	INJ	Y
		UT				65	23	42			
		T				59	20	39			
PR	EPL	UT	99	74	73	71	41	30	0.4	INJ	Y
		T	99	76	75	72	36	36			
GA	1235	UT	52	26	23	39	23	16	0.6	FE	N
TX	126	UT	42	24	23	65	20	45	1.9	CE	Y
LA	560	UT	96	52	48	66	22	44	0.9	INJ	Y
AL	728	UT	92	56	47	76	31	45	0.8	FE	N
GA	DF	UT	45	16	12	30	23	7	0.4	CE	Y
TN	HW	UT	62	31	23	34	23	11	0.4	CE	Y

Soil sample type TP: treated T, untreated UT.

Equipment used CST: Drawbar farm equipment FE, Construction equipment CE, Injection INJ.

Stable after treatment ST: Yes-Y, No-N

erate pH, but the alumina is held fast by its low solubility.

The key to stabilizing a clay soil lies in removing cations from the lattice and the surrounding environment. The resulting induced cation-free environment causes a spontaneous breakdown into smaller pieces, allowing moisture to drain out and leave the amorphous or crystallized remains of the lattice, which gradually forms a permanently hardened mineral mass.

To accomplish this, a chemical base that has a strong attraction for the positively charged cations and ionized water to be removed, an attraction stronger than that of the clay lattice holding them, is used. Once removed, the cations are permanently disposed of by precipitating as salts or combining with organic molecules so that they cannot return to the solution.

## CHEMISTRY OF SULFONATED OIL STABILIZERS

Sulfonated oils have reacted with sulfuric acid to produce a milder acid, sulfonic acid, one in which the sulfite anion ( $\text{SO}_2\text{OH}^-$ ) will perform as a base with the hydrogen cation as its conjugate acid. Because some residual sulfuric acid is also present, the stabilizer may be labeled sulfuric acid to comply with shipping regulations.

The oils selected for this purpose are called aromatic oils because their hydrocarbon molecular structure contains one or more rings of six carbon atoms, similar to benzene, that gives them a characteristic aroma. The carbon atom can attach to four other atoms in a molecular structure. The benzene ring has only one hydrogen atom attached to each carbon in addition to the other carbon atoms on either side, leaving an extra electron free at each carbon to form a double bond. This high net (negative) electron density of the ring provides

a strong attraction for the (positive) cations on the clay lattice.

Oils do not ionize in solution and therefore cannot react with cations. To produce an ionized solution, the oil must be treated with an oxidizing agent such as sulfuric acid.

The sulfonation process attaches a sulfite ion to the ring, forming a sulfite anion base in conjugate with a hydrogen cation acid (7, p. 153; 6, pp. 508,514). When this solution is diluted to application strength, ion activity is greatly increased and the resulting complex is only mildly acidic. The anions will actively attract cations in their vicinity, moving them away from the clay lattice by chelation (2,5). The ring surrounds the cation and holds it by electron sharing between the carbon atoms and the metal atom.

## BREAKDOWN OF CLAY LATTICE

Through application of the basic principles of chemistry to the reactants present during the stabilization procedures for a clay soil, chemical reactions between the clays and the stabilizer solution can be inferred and appropriate equations developed to illustrate the process and the observed results. In the case studies, the reactions between the stabilizer solution and the clay fraction were apparent within 48 hr and had achieved major effects within 5 days (1, pp. 55,61,62,80).

When applied to the clay, the negatively charged oil/sulfite anions attract the positive cations and ionized water away from the lattice, resulting in a net negative potential toward the outside of the layer and destabilizing the clay lattice consisting of the sandwiched silica and alumina sheets. The substituted aluminum atoms in the silica sheets lose their bonds to the oxygen atoms



and are drawn out by the stabilizer anion and hydrolyzed in solution.

The hydrogen cations associated with the stabilizer penetrate the lattice structure to the alumina sheet. As the substituted Al atoms are drawn from the silica lattice, amorphous silica  $\text{SiO}_2$  is formed from the silica sheet. The alumina in the alumina sheet is hydrolyzed, forming gibbsite,  $\text{Al}(\text{OH})_3$ . The remaining clay minerals are precipitated as amorphous allophane, which is encrusted with the precipitating gibbsite and amorphous silica.

The injected solution is highly diluted because ionization increases with dilution. Unlike standard stabilizers that actually enter into the final product of the process, these stabilizers act as catalysts to rearrange the molecular structure to a more stable configuration and release bonded moisture. The injected chemical does not become a part of the stabilized clay structure.

## ANION RENEWAL

High ionization is required to promote maximum activity with exchangeable cations. The ratio of exchangeable cations in the clay to active stabilizer anions in the solution may vary from  $10^3$  to  $10^4$  depending upon the type of clay. Smectite clays have 10 times the cation exchange capacity (cec) of kaolinite and 5 times the cec of illite (4, p. 189). Therefore, the stabilizer anions must act repeatedly, 10,000 times each, and must dispose of the exchangeable cations as soon as they have been removed from the lattice. This is possible because other anions are available in the solution to hold the cations and are not involved in reacting with the clay lattice.

These available anions may be provided by colloidal organic humus present in the soil. Less than 0.4 percent by weight of soil, comparable to an average gray clay shale (10), would be required for an average clay content (45 percent). This reaction may be catalyzed by resin catalysts added to the solution. The nature of these resins is proprietary and is not revealed in product literature.

## ELECTROCHEMISTRY

Clays have extremely low permeability, and yet the reactions between the stabilizer solutions and the clays were observed to proceed at a rapid rate in all the case studies, indicating an electrokinetic phenomenon at work (1, pp. 61,62,65,78,80,85).

In the saturated capillary spaces between parallel flat clay flakes, a concentration of cations develops because of the negative charge on the surfaces of the clay. The

negatively charged surfaces and the positively charged cation concentration are called the diffuse double layer. This charged double layer responds to electrokinetic phenomena.

The injection of the stabilizer solution into the clays results in a highly concentrated "ion cloud" at the point of injection. In the ionized solution, positive cations are attracted to the injected negative anions. An electrical potential develops between the injected "ion cloud" and the solution cations. The magnitude of this potential should be a function of conditions developing in the clay layers as a result of the removal of the cations. As the cations are withdrawn from the clay lattice, the lattice develops a net negative charge in the silica sheets, destabilizing the layers. Molecular bonds collapse. The alumina breaks away and is hydrolyzed to gibbsite, and the silica sheet hydrolyzes and decomposes to amorphous silica.

At the time of injection, the voltage gradient is substantial because of the short distance between the ion cloud and unaffected clay and could reach 10 V/cm or more (2 V over 5 mm). This sharp gradient at the ion cloud front results in rapid initial movement of ions into the clay mass surrounding the point of injection.

As the ion cloud moves outward from the point of injection in an expanding cylinder, the concentration of ions is reduced, resulting in a reduction of the voltage gradient and the rate of movement of the ion cloud. Thus, there is a limit to the field of movement. In practical application, this limit has been found to be about a meter from the point of injection for sulfonated naphthalene.

Allowing for a reduction in voltage as the ion cloud travels outward from the point of injection, about a week is required for the ion cloud to traverse a meter of clay. The success of this process has been observed in case studies in Texas, Louisiana, Mississippi (1, pp. 59,60), and Puerto Rico (see case study for Caribbean National Forest). No failures have been observed or reported.

The limiting distance of ion travel is much less in the scarification method of application in which the solution is applied over a wide area with greatly reduced initial concentration. Instead of full application at a point, as in the injection method, half the same quantity of solution is applied over nearly 4 m<sup>2</sup> in two applications. In this case the voltage gradient developed is small and is lost after a few inches of penetration. Osmotic diffusion plays a greater role in this type of application (2, p. 254). Failures were observed in case studies in Mississippi, Alabama (1, pp. 13,62), and Georgia when inadequate penetration resulted from using draw bar farm plows instead of hydraulically pressured rippers. Sulfonated naphthalene has been applied by scarification as well as by injection. Sulfonated lim-

onene has been applied only by scarification, as are the enzyme and bioenzyme stabilizers.

## ENZYMES

Enzymes are the catalysts of biological systems. They not only control the rate of reactions but, by favoring certain geometries in the transition state, can lower the activation energy for the formation of one product from another. The basic structure of enzymes is built of proteins (5, p. 753). A typical enzyme consists of a protein chain of over 300 amino acid residues plus a metal cation and has a molecular weight approaching 35,000. The metal cation is located in a cleft of a size and shape that excludes all but certain specific organic molecules whose reactions are to be catalyzed. Various groups and linkages, which include aromatic rings within the enzyme, all work with the metal cation to cleave bonds and form new linkages in intermediate products. These products then react to form the end product and regenerate the original enzyme.

Unlike the inorganic catalysts, enzymes are very specific in the breakdown process. They synthesize certain groups of chemical compounds and limit their action to specific bonds in the compounds with which they react. When the enzymes of a soil stabilizer are mixed with water and applied to the soil, they can act in several ways depending upon their design. These actions may include breaking down the clay lattice and combining cations and other components with organic molecules present. Because of the diversity of action available from enzymes, a combination of several activities from an enzyme stabilizer is possible.

Initial reactions with enzymes are similar to those with sulfonated oils. In some case studies a breakdown of clods was observed in the field during mixing operations (1, pp. 61,62,65,78,80,85). The lattice breakdown reduces the size of the clay particles and helps them combine with the organics.

The origin of the stabilizing organic molecules may vary with the type of stabilizer. In the enzyme stabilizer, a higher fraction of silt and clay is required, and the humus present in these fines provides the organic source. In the bioenzyme stabilizer, a bacteria culture that may produce additional organics from the carbon dioxide, nitrogen, and oxygen present in the air is included. Thus, the bioenzyme may be effective with a smaller fraction of clay fines. In either case, the enzyme in the aggregate remains permanently active to deal with additional clays mixed in at a later date (see case study for Lewis and Clark National Forest).

The residual  $\text{SiO}_2$  gel and gibbsite serve as a cementing compound that adds strength to the stabilized layer. Other potential cements include insoluble alumi-

num and iron hydroxides that may develop out of side reactions. Compaction is the key to realizing the effect of these stabilizers. Close contact between soil grains is essential to the cementing process. The greater the compacted density achieved, the more effective the cementing will be.

## MINERAL ANALYSIS OF SAMPLES

A preliminary mineral analysis was arranged through a contract. The analysis included transmission and scanning electron microscopy and x-ray diffraction. Samples of two subgrade soils from the Puerto Rico El Portal site and Texas Road 126, both previously treated with a sulfonated naphthalene stabilizer, were obtained together with samples of the untreated soils taken from adjacent areas. The four samples are currently under analysis, and the results of the treated soils will be compared with the results of the untreated soils in the attempt to detect changes in molecular structure. An extensive program of testing beyond the scope of this study may be required to determine the exact nature of these changes.

## MECHANICAL EFFECTS OF STABILIZERS

Laboratory testing performed on samples of stabilized aggregates has shown little or no change in grain size distribution and only minor changes in Atterberg limits (Table 2). In normal clays placed in water, the cations diffuse along the exterior but are held close by the negative charge of the clay. Ionized water is attracted and a diffuse double layer of surface charge and adjacent charge develops that attracts and holds moisture (2, p. 111). The moisture results in the increase in plasticity noted in clays.

In a number of case studies on treated subgrade soils (1, pp. 55,62), the clay fraction hardened irreversibly, leaving the mixture unaffected by moisture and highly resistant to erosion; formerly the mass would have dissolved in a heavy rainfall. This change can result from hydrolysis to gibbsite and opaline.

Gibbsite forms monoclinic (micalike) crystals or spheroidal concretions with a specific gravity of 2.3 to 2.4. Gibbsite is harder than kaolinite and half as hard as quartz. Opaline forms amorphous masses containing 6 to 10 percent water and a specific gravity of 1.8 to 2.3. Opaline is nearly twice as hard as gibbsite and slightly softer than quartz. These encrustations cement the aggregate mass, isolate the clay remnants, and eliminate the attraction of moisture. Both minerals have poor resistance to abrasion and fracture, severely limiting the ultimate strength achievable by this means of

stabilization. The major benefit is the increased resistance to moisture assisted by a tensile strength developed from the gel cements.

Rock may be differentiated from soil by its inability to slake (11). Pure colloidal rock dust will not develop plasticity with water (2, p. 183). In nature, low-grade metamorphic rocks can contain mixed layers of the micas muscovite and illite (a hydrous mica), which may persist with increasing metamorphic grade (12,13). The presence of residual clay mineral does not detract from the rock nature of the material. The clay minerals are bound up and isolated from the effects of any moisture present. When crushed, colloid-sized gibbsite particles (less than 1  $\mu\text{m}$ ) with a platy shape resemble and contain similar mixed layer remnants of the chemically active clay minerals. These impart cohesive strength and plasticity when granularized and manipulated with moisture, but to a lesser extent than the pure active clay colloids. The PL of higher AR clays shows some reduction when treated, whereas the PL of a low AR clay shows little change (Table 2). The LL of an active clay is high because the expanding lattice absorbs moisture. The treated colloid has no lattice, reducing the LL. The net PI may remain the same or go either way.

In retrospect it can be seen that altering the clay minerals to silica gel and platy gibbsite that contains remnants of clay structure probably would have little effect on grain size and Atterberg limits in a laboratory sample. The destructive processes of sampling, drying, quartering, and wet and dry sieving all tend to remove any interparticle bonding that has been developed by the gibbsite and silica gel in the compacted layer. Remolding of lateritic soils results in substantial increases in plasticity (2, p. 57). The significant difference between these two rock minerals and the clay minerals is their neutral charge as compared with the negative charge of the clays and their lack of attraction for moisture as compared with the hydrophylic nature of clays. This indifference to moisture, together with the developed tensile strength, is the key to improvements in performance as road surfacing materials.

## PROJECT TEST DATA

Laboratory tests were run on several clay subgrade stabilization projects in which sulfonated naphthalene was used as the stabilizer. (One exception is GA 1235 on which the enzyme stabilizer Permazyme was used; this stabilizer has been successful on many other projects.) Test data are given in Table 2. A broad variety of clay minerals was involved, and initially it was thought that the presence of smectite reduced the effectiveness of the stabilizers. However, contrary to the discussion in the CTIP Final Report (1, p. 13), the results of the testing

indicated that the only significant variable was the type of construction method used. All projects using draw bar farm equipment (FE-disk plows or chisel plows) or front-mounted grader scarifiers failed to stabilize. Projects using CE-rear mounted, hydraulically operated rippers or scarifiers or injection (INJ) were successfully stabilized. The AR indicates that the clay minerals ranged from kaolinite ( $\text{AR} > 0.5$ ) to illite ( $0.5 > \text{AR} < 1.0$ ) to smectite ( $\text{AR} > 1.0$ ). Uniform, full-depth mixing to a depth of 20 to 30 cm is essential to successful stabilization. In the injection method, subgrade injection on 2-m centers to a depth of 1 m was successful in every case.

## CLAY AGGREGATE MIXES

For well-graded aggregates, the minimum PI should be 17 or more or the minimum clay content between 5 and 10 percent. For pitrun aggregates, a potential guideline could require the clay content, determined as the percent finer than 0.002 mm in the hydrometer analysis, to be about one-third to one-tenth of the percentage passing the No. 40 sieve (0.4 mm). The clay flakes form a coating on the grains of silt and fine sand that binds them together permanently with compaction. The thickness of the coating must be adequate to provide strength but not so great as to interfere with a high density. A thickness between 1 and 10 percent of the grain diameter appears to meet these requirements and will result in a clay content of between one-tenth and one-third of the No. 40 material in graded aggregates. The finer quartz silt grains are about 10  $\mu\text{m}$  in dimension, requiring a clay coating 0.1 to 1.0  $\mu\text{m}$  thick. Although this seems thin, 0.1  $\mu\text{m}$  is equivalent to 1000 Angstrom units (A), whereas the stacks of clay platelets may vary in thickness from 30 to 1000 A (2, p. 6).

The lower end of this guideline range, from one-fourth to one-tenth of the No. 40 sieve, should be used with caution in poorly graded mixtures on steeper grades over 6 percent. Poorly graded aggregates fail to develop the uniform surface armor of well-cemented coarse aggregate particles required to resist severe surface erosion. Frequent blading will be required to smooth surface rilling, resulting in loss of stability in the upper aggregate layer.

## EFFECT OF STABILIZERS ON FROST HEAVE

The soil grain size is critical to the growth of ice lenses (14). Clays attract and hold moisture, but their low permeability limits suction. Pure silts have less attraction for holding moisture above the zone of capillary rise but can develop very high capillary suction. A combination



of silt with a small percentage of clay should have the greatest potential for frost heave under the conditions of good surface drainage usually encountered in road construction. Enough moisture can be maintained in the surface layers to promote initial formation of ice crystals, and high suction can develop to draw moisture up from a suppressed water table.

Hydrolysis of the clay minerals to hydroneutral, free-draining clay and rock minerals greatly reduces moisture holding and ice lens formation. The treated layer then becomes an overburden layer, which tends to reduce the suction and further reduce the potential for development of ice lenses.

Subgrade stabilization with sulfonated naphthalene was used in Pocatello, Idaho, to stop severe frost heaving (reported over 18 cm) under city streets. There has been no recurrence (1, p. 55).

In the mountains of north central Arkansas, on the Ozark National Forest, a number of kilometers were stabilized with pozzolans or enzymes to a depth of 10 cm. This protection was adequate for a mild 10-day freeze common to that area. Freezing has not affected the quality of the stabilized aggregate surfacing (1, pp. 71,72).

## LABORATORY AND FIELD RESULTS

### Improving Test Results

Field testing provides the most reliable data. Problems arise in the laboratory. Unless unusual care is exercised, the destructive processes of sampling, drying, quartering, wet and dry sieving, and mixing all tend to remove any interparticle bonding that has been developed by the gibbsite and silica gel in the compacted layer. The significant difference between the alteration products and the original clay minerals is their neutral charge as compared with the negative charge of the latticed clays and their free-draining lack of attraction for moisture compared with the hydrophylic nature of latticed clays. Significant interparticle tensile strength may also be developed. When subjected to established testing procedures, chemically treated clay aggregates are broken apart and have water forced into their interstices in a way that cannot occur naturally because of their acquired cemented hydroneutral nature. Atterberg limits and shrinkage are no longer valid measures of field performance without adjustments in handling procedures. An analogy might be to pulverize a hardened concrete specimen and then compact the remains into a mold to determine the concrete strength.

Agricultural soil tests, such as cation exchange capacity and chemical content and mineral analysis by electron microscopy, may provide useful information on

the effect of chemical treatment on clay aggregates by indicating the mineral changes taking place and the potential engineering properties based upon the end materials that develop.

## Recent Case Histories

### *Homochito National Forest, Mississippi*

The completion of an embankment stabilization project was discussed in the Final Report (1, p. 56). The sidehill embankment was constructed in 1992 on a 3:1 slope in three lifts, injecting the foundation to 4.5 m and each 1.5-m lift with a sulfonated naphthalene solution. In late January 1993, a major subsidence occurred 3 to 6 m downslope from the road shoulder, resulting in a scarp height of 3 m. The scarp slope ratio is approximately 3/4:1. Since then no major changes have occurred. Continued rainfall has had no erosive effect on the scarp or road shoulder. The clay in the scarp has hardened without cracking to firm, smooth material with a mineral consistency and shows no signs of sluffing or other deterioration.

### *Cherokee National Forest, Tennessee*

In September 1991, several areas of subgrade failures on the Hiawassee Camp Ground road were repaired. The pavement was removed, and the clay subgrade was scarified to a 30-cm depth using rear-mounted grader rippers. A sulfonated naphthalene solution was hand sprayed on the subgrade from a 1140-liter tank and mixed in using the grader rippers. The areas were compacted with a steel wheel vibratory roller and chip-sealed. No failures have been observed since treatment.

### *Chattahoochee National Forest, Georgia*

In January 1992, the parking area at the Desoto Falls Camp Ground was completed after one year of delay because of excess subgrade moisture caused by frequent rainfall in the area. The silty clay subgrade was scarified using bulldozer rippers. A water tanker was used to apply the sulfonated naphthalene solution, followed by mixing with the rippers. Portions of the entry ramp were done in three lifts. The treatment induced draining, and compaction was achieved with a steel-wheel roller. The area was then paved with hot mix and has performed satisfactorily since.

### *Apalachicola National Forest, Florida*

In May 1992, 2.7 km of logging access road was surfaced with 10 cm of sandclay, which was rotary mixed

with the clay subgrade to a depth of 20 cm. A sulfonated naphthalene solution was sprayed on from a water truck with a front-mounted spray bar and mixed in using a spike harrow facilitated by the rotary mixing. The surface was compacted with a vibratory steel-wheel roller, and an inch of sand was spread to improve traction. The road supports hunter traffic and during July 1993 was used for log hauling. No rutting has occurred through considerable wet weather since construction.

#### *Sabine National Forest, Texas*

In September 1992, 1.3 km of Road 126 subgrade was treated with sulfonated naphthalene stabilizer applied by scarification and covered with 8 cm of crushed sandstone aggregate. The road carries heavy oil well servicing traffic and had suffered frequent failures during wet periods. No failures have occurred since treatment.

#### *Carson National Forest, New Mexico*

In July 1993, 3 km of the Cerrososo Canyon road was resurfaced. The 10 to 15 cm of existing unbound coarse crushed aggregate was mixed with the silty clay subgrade to a depth of 30 cm using rear-mounted grader rippers. The sulfonated naphthalene solution was sprayed on from a water truck equipped with a side-mounted nozzle. Mixing was performed with the grader rippers. The surface was compacted with a vibratory steel-wheel roller. No raveling has developed on the surface since construction.

#### *Caribbean National Forest, Puerto Rico*

In July 1993, a 1-m<sup>2</sup> area proposed for excavation was injected to a 2-m depth with a sulfonated naphthalene solution to determine whether the treated soil could be used for structural backfill. Laboratory testing (Table 2) showed 50 percent clay colloids with a steep compaction curve beyond optimum moisture. Sampled and retested a week following treatment, the treated soil showed improved stability with a flatter compaction curve above optimum but remained highly resilient and was wasted (Table 1).

#### *Ozark National Forest, Arkansas*

During September 1992, 19 km of crushed aggregate surfacing was mixed with subgrade silty clay fines and treated with sulfonated D-limonene. Application was by water truck, mixing by blade, and compaction by steel-wheel roller. The roads carry heavy traffic and have required no maintenance since construction. An additional 8 km was completed in October 1993 using similar techniques.

#### *Lewis and Clark National Forest, Montana*

Clay shale was added to sandstone aggregate on sections of the Spring Creek Road and stabilized with a bioenzyme stabilizer in 1989 (1, p. 84). Corrugations in some areas indicated that the shale percentage was deficient. In 1992, during mixing of additional shale, clods were observed to breakdown rapidly, indicating that the enzyme was still present and active. These sections have been free from washboarding and raveling since, but raveling can be observed on untreated sections. On the Lick Creek and Logging Creek roads, the 1989 bioenzyme treatment of a low PI clayey limestone had little effect for 2 years (5, p. 753) but recently has shown less washboarding and potholing than untreated sections.

#### *Ouachita National Forest, Oklahoma*

A sandy clay subgrade on the Red Maple road was treated with an enzyme stabilizer in September 1991. Log hauling in 1992 did not rut the surface, although severe rutting occurred on the adjacent collector road.

#### *Oconee National Forest, Georgia*

An expansive clay subgrade on Gully Road 1235 was treated with an enzyme stabilizer in October 1991. Depth of treatment was only about 8 cm. Severe rutting occurred during log haul in heavy rains immediately after construction because the subgrade under the treated layer failed.

#### *Kisatchie National Forest, Louisiana*

In 1990 and 1991, 6.5 km of severely expansive clay subgrade was injected with Condor SS (1, p. 55). Subgrade movement ceased completely, but some local failures in the 40-cm base were attributed to saturation by moisture escaping from the treated subgrade. During an inspection in November 1993, it was discovered that these failures were being caused by fire ant nests under the pavement, which involved continual removal of the oversanded base material because the pavement subsided under traffic.

#### CONCLUSIONS

An extensive literature search on the chemistry of clays and chemical stabilizers indicates that chelation of alkali metal cations occurs following application of certain chemical stabilizer solutions to clays and results in partial lateralization of clay minerals to stable rock minerals. A preliminary mineral analysis of samples of



treated clays found that a change in molecular structure did occur following treatment.

#### REFERENCES

1. Scholen, D. E. *Non-standard Stabilizers*. FHWA-FLP-92-011, Final Report. FHWA, U.S. Department of Transportation, July 1992.
2. Mitchell, J. K. *Fundamentals of Soil Behavior*, 2nd ed. Wiley, New York, 1993.
3. Nahon, D. P. Evolution of Iron Crusts in Tropical Landscapes. In *Rates of Chemical Weathering of Rocks and Minerals*, Academic Press, New York, 1986, p. 173.
4. Grim, R. E. *Clay Mineralogy*. McGraw Hill, New York, 1968, p. 231.
5. Huheey, J. E. *Inorganic Chemistry*, 2nd ed. Harper & Row, New York, 1978, pp. 542, 457.
6. March, J. *Advanced Organic Chemistry*, 4th ed. Wiley, New York, 1992, p. 36.
7. Smith, M. *Organic Chemistry*, HarperCollins College Outline, New York, 1993, p. 149.
8. Aston, S. R., ed. *Silicon Geochemistry and Biogeochemistry*. Academic Press, New York, 1983, p. 43.
9. Attewell, B. P., and I. R. Farmer. *Principles of Engineering Geology*. Wiley, New York, 1976, p. 176.
10. Potter, P. E., J. B. Maynard, and W. A. Pryor. *Sedimentology of Shale*. Springer-Verlag, New York, 1980, p. 55.
11. Morganstern, N. R., and K. D. Eigenbrod. Classification of Argillaceous Soils and Rocks. *Journal of Geotechnical Engineering Division*, ASCE, Vol 11, No. GT 10, pp. 1137, 1156.
12. Mason, R. *Petrology of the Metamorphic Rocks*. Unwin, Boston, 1978, p. 152.
13. Winkler, H. G. F. *Petrogenesis of Metamorphic Rocks*, 5th ed. Springer-Verlag, New York, 1979, pp. 206, 207.
14. Penner, E. The Mechanism of Frost Heaving in Soils. In *Highway Pavement Design in Frost Areas, A Symposium: Part 1, Basic Considerations*, Highway Research Board Bulletin 225, Washington, D.C., 1959 (University Microfilms International, Ann Arbor, Mich., on demand, pp. 1, 6.)