Environmental Soil Stabilization, L.L.C.

March 25, 1999

Ing. José A. Esquivel, President
EXPER S.A.
Apartado 97-3006
Heredia, Costa Rica

Re: Treatment Theory and Results of Initial Research at Texas A&M University
Treatment of Expansive Clay Soils Using EcSS 3000
Environmental Soil Stabilization, L.L.C.

Dear Sr. Esquivel:

This letter summarizes how the Environmental Soil Stabilization, LLC (ESSL) application process, using EcSS 3000, treats clay soils to reduce shrink/swell characteristics and increase strength. The theory of treatment is presented and then a summary of research conducted to date at Texas A&M University is provided with the results compared to the theory. The chemical concentrate is normally diluted at a rate of 1 gallon of chemical to 300 gallons of water and injected into the in situ clay soils or compacted clay fill under pressure through injection rods. In Costa Rica, the chemical mixture is injected with hand-held rods by EXPER S.A. but could also be mechanically mixed with the expansive soil, and then placed and compacted in thin lifts.

EcSS 3000 does not become part of the treated soil, but acts solely as a catalyst to the clay lattice breakdown. EcSS 3000 is a mixture of naphthalene oil, mixed with sulfur trioxide and sulfuric acid and other additives. A proprietary resin catalyst is also added to enhance reaction times. This was the first product of its kind to be developed for clay roadway subgrade and building pad stabilization. EcSS 3000 has been applied to clay soils since the mid-1960's (it was previously called Reynolds Road Pack, ISS and ISS-2500, but all are the same product manufactured by the same manufacturer).

THEORY OF TREATMENT

The treatment results in both a physical change and a chemical change and, therefore is termed a physico-chemical treatment. It is often called electrochemical treatment as well.

Each clay particle has a net negative surface charge that repels other clay particles of like charge near it. This negative charge is caused by broken bonds at the edges of the clay particles and isomorphic substitution of higher valence cations by lower valence cations within the silica sheet (silicon, Si^{+4}, is replaced by aluminum, Al^{+3}) and alumina sheet (aluminum, Al^{+3}, is replaced by magnesium, Mg^{+2}) of the clay lattice. This excess negative charge must be balanced by other positive ions in solution to maintain stability of the clay lattice. Therefore, the negative surface charge attracts and adsorbs positive cations and water from the surrounding soil-water system. The adsorbed water and cations attracted by the clay surface are called the electric double layer or adsorbed water layer. The double layer of each clay particle repels the double layer of nearby clay particles. Water outside the double layers is not bound and moves freely throughout the soil-water system. It is the double layer water that shrinks and swells with changes in moisture content of the soil system. Interlayer water and cations within the clay lattice will also shrink and swell with changes in moisture content for the more expansive clay minerals.

The injection of the EcSS 3000/water solution into the clays results in a highly concentrated "ion cloud" at the point of injection. This high concentration of ions results in rapid movement of the injected ions by osmosis into adjacent areas as the ion density of the entire soil-water system tries to equalize in charge. The ion cloud will continue to move through the soil-water system until the ion charge is equalized throughout the system. The ions move much faster than the actual injected liquid penetration. The ion cloud will typically travel as an expanding cylinder about a maximum 3 feet from the point of injection over a period of approximately one week, when injected by ESSL. Therefore, injection is normally performed on 3-foot centers to provide a "factor of safety" of about 2 for ion penetration and soil treatment. Sufficient soil treatment to reduce shrink/swell characteristics to a level that satisfies the project requirements has been found to occur within about 72 hours after injection.

The naphthalene in EcSS 3000 provides a six-carbon ring structure that is ionized by the sulfur trioxide and sulfuric acid to produce mild sulfonic acid. This sulfonation process attaches a sulfite anion, $(SO_2)OH^-$, to the carbon ring, forming a sulfite anion base in conjugate with a hydrogen cation, H^+, acid. When the solution is diluted with water, the sulfite anions will actively attract substituted aluminum cations from the silica sheets of the clay lattice. The carbon ring surrounds the aluminum cation and holds it by electron sharing between the carbon atoms and the cation's metal atom. At the same time hydrogen cations, H^+, penetrate to the clay lattice, resulting in an ion exchange with the aluminum cations. The hydrogen cations also exchange with the potassium, calcium and sodium cations "attached" to the surface of the clay particle, within the electric double layer, reducing the thickness of the double layer.

The key to stabilizing the clay lies in removing the cations from the clay lattice and surrounding environment. As the sulfite anions remove the aluminum cations from the clay lattice, the lattice develops a net negative potential in the silica sheets, resulting in destabilization of the lattice. Molecular bonds collapse and the lattice structure is destroyed. The remaining structure is a more stable amorphous (noncrystalline) structure. This new structure results in a reduced or neutral charge and, therefore, less or no attraction to water. Also, the resulting clay particles can come closer together, or agglomerate, since the repulsive forces between particles have been reduced or eliminated, thus increasing the strength as previously adsorbed water is released from the former double layer.

The stabilizer sulfite anions act repeatedly, which is especially important since the number of available cations greatly outnumber the sulfite anions. The captured cations are "disposed of" after removal from the clay lattice and clay surface by precipitation as salts or by combining with organic molecules so that they cannot return to solution.

RESULTS OF RESEARCH TO DATE

A shelby tube sample of Eagle Ford Shale residual soil and one gallon of EcSS 3000/water solution diluted at 1:300 were submitted to Texas A&M's Texas Transportation Institute for evaluation. The delivered soil had a liquid limit of 96, a plasticity index of 63, a moisture content of about 30% and a percent passing the no. 200 sieve of 95.6%. One undisturbed sample of soil was soaked in water only and one undisturbed sample of soil was soaked in the EcSS 3000 diluted chemical mixture. The samples were soaked in a consolidometer for a period of about five days, allowing both soil samples to come to a new moisture equilibrium and volume. Both soaked samples had a moisture content of about 42% after soaking.

Testing of the delivered, water soaked and chemical soaked samples consisted of microstructure photographs (Environmental Scanning Electron Microscope(ESEM), Transmission Electron Microscope(TEM)), mineral identification (X-Ray Diffraction (XRD)) and electrokinetic potential (Zeta Potential).

The ESEM tests show soil structure and were conducted on "wet" samples to investigate the moisture effects better then "dry" samples could. The structure of the delivered sample showed rows of narrow clay layers with distinct, clear edges. The water soaked sample structure showed a swollen mass with the clay layers spread far apart and bulging clay layers with indistinct edges. The chemical soaked sample structure was nearly identical to the delivered sample structure, with narrow clay layers and distinct, clear edges, even though the moisture content of the sample was the same as for the water soaked sample.

The TEM tests show clay particle structure and were conducted on the water soaked sample and chemical soaked sample. The electron diffraction results showed a crystalline lattice structure for the water soaked sample, as expected. The chemical soaked sample, however, showed an amorphous (noncrystalline) structure indicating that the crystal lattice was destroyed, consistent with the theory.

The TEM analysis also identified the elemental composition (magnesium, aluminum, silicon, potassium and iron ions), in percent, of the water soaked and chemical soaked samples. Five samples of water soaked soil and four samples of chemical soaked soil were analyzed. The magnesium, silicon and iron ions did not show appreciable differences between the water soaked and chemical soaked samples. However, the aluminum ion concentration was reduced from a water soaked average value of 16.65% to a chemical soaked average value of 11.35%, which is consistent with the theory. The potassium ion reduction was even more dramatic, with a water soaked average value of 1.80% and a chemical soaked average value of 0.19%. The chemical treatment appears to have an affinity for removal of the single valence potassium ion.

A separate check was made for the soluble concentrations of selected ions to determine if the ions went into solution when removed from the clay lattice and surface. The soluble aluminum ion concentration was non-detected for both samples, indicating that the removal of the aluminum ion from the clay lattice did not result in aluminum ions being placed in solution. The soluble potassium ion concentration of the water soaked sample was 1.21 mg/l and of the chemical soaked sample was 0.66 mg/l, indicating that the elemental reduction of the potassium ion did not result in an increase in the soluble ion concentration and, in fact, showed a decrease in concentration. These results are consistent with the theory that the cations removed are disposed of.

The XRD testing was performed on the water soaked and chemical soaked samples to identify mineralogy. No major discernible difference in clay mineralogy was noted between the two samples. The samples contained 21 to 28% clay minerals, with smectite (montmorillonite) identified as about 60% of the clay fraction.

The Zeta Potential testing provides a measurement of the electrokinetic potential, or water adsorbing capability, of the clay particles. Each clay particle is surrounded by the double layer neutralizing ions. This causes an electric potential on the order of millivolts to develop across the double layer between the clay particle/double layer (slip plane) and the bulk of the liquid outside the influence of the clay's negative charge. The magnitude of this potential is approximately proportional to the surface charge of the clay particle and it is called the Zeta Potential. It is also indicative of the potential attraction of water to the clay particle.

Testing was conducted on a low-expansive kaolinite soil standard, the water soaked sample and the chemical soaked sample. The results indicated that the kaolinite standard had a Zeta Potential of 10.3 millivolts, the water soaked sample had a Zeta Potential of 19.2 millivolts and the chemical soaked sample had a Zeta Potential of 13.0 millivolts. This indicates that the chemical soaked sample "wants" to act more like a low-expansive kaolinite clay mineral than a highly expansive smectite (montmorillonite) clay mineral. This is consistent with the theory as well as the large amount of swell test data for treated soils.

SUMMARY

The preliminary research testing to date at Texas A&M University indicates the following:

- The EcSS 3000/water solution does not cause expansion of the clay lattice and adsorbed water (double layer) as water, alone, does. In fact, the soil layering remains similar to the soil structure of the as-delivered soil.
- Aluminum ions are removed from the clay lattice and positive cations are removed from the double layer surrounding the clay particle and replaced with the smaller hydrogen ion. These removed ions are not placed in solution only to be adsorbed again in the future, but are actually removed from the soil-ionic water system.
- The EcSS 3000 solution changes the molecular structure of the clay particle from an expansive crystalline lattice to a relatively stable amorphous (noncrystalline) structure.
- The clay mineralogy of the EcSS 3000-treated and untreated soil does not seem to change appreciably.
- The EcSS 3000-treated clay particles appear to have a water-adsorption potential similar to a low-expansive kaolinite mineral rather than a highly expansive smectite (montmorillonite) mineral.

We will be injecting a site on Texas A&M property in the near future to allow for testing and longer term monitoring of injected soils.

Very truly yours,

Russell J. Scharlin, P.E.
Vice President

Johnny Sherwood
President