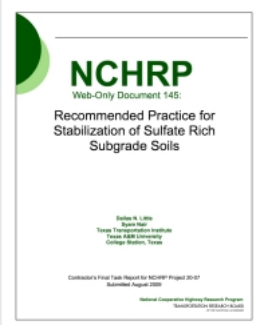

Recommended Practice for Stabilization of Sulfate-Rich Subgrade Soils

DETAILS

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ABSTRACT

Calcium-based stabilizers (CaO-based stabilizers) develop a high pH environment when mixed with water during construction. This high pH condition and the presence of lime (CaO) introduce an environment favorable to the formation of two expansive minerals, ettringite and possibly thaumasite, when sulfate-bearing salts are present in soil. The success of a lime stabilization project depends heavily on the accuracy of predictions regarding the potential of the native soils to form these disruptive minerals. This report describes the nature of these minerals and the mechanism of their formation in soils stabilized with lime, cement, or fly ash. The key issue for the engineer in deciding how to properly stabilize sulfate-bearing soils is to quickly and efficiently determine: (1) the sulfate content of the soils and (2) the threshold quantity of sulfates likely to cause damage. This report addresses both issues but focuses on the methods used to quantify sulfate content. Quick and effective field techniques and more precise laboratory tests are compared and evaluated. Recommendations are presented regarding the appropriate testing protocol to use. Specific recommendations for changes to the American Association of State Highway and Transportation Officials (AASHTO) test method T-290-95 (methods A and B) are made. The report also outlines techniques for effective risk assessment including reconnaissance, topographical assessment, pedological and geological assessment, climatic assessment, and soil sampling plans. The report also outlines construction tests that can reduce risks for various levels of sulfate determined using a method such as AASHTO T-290-95 (revised) or equivalent.

EXECUTIVE SUMMARY

In place soil treatment using calcium-based stabilizers is an economically feasible solution alternative to address strength deficiencies and problematic shrink/swell behavior of unstable subgrade soils. Soil instability may originate from the presence of clay or silt whose instability is normally triggered by a change in moisture content. Even though stabilization improves engineering properties, problems can arise when calcium-based stabilizers are used in soils rich in sulfate-bearing minerals. Stabilization of sulfate rich soils in the presence of excess moisture may lead to the formation of minerals such as ettringite and/or thaumasite and can cause distress in or even destruction of pavement structures due to heaving.

For 1 mole of ettringite to form 6 moles of CaO, 1 mole of Al_2O_3, 3 moles of SO_4, and 32 moles of water are required. Calcium ions are provided by lime, Portland cement, or fly ash; alumina is supplied by dissolution of oxyhydroxides and phyllosilicates; and sulfates are supplied by dissolution of gypsum, oxidation of sulfide, or ion migration of sulfate ions as water diffuses through the matrix. Two theories exist regarding the cause of expansion during ettringite formation. The first theory explains that expansion is due to topochemical formation of ettringite and the anisotropic growth of the crystals. The second theory suggests that expansion is due to absorption of water by ettringite crystals where water molecules can cause interparticle repulsion resulting in overall expansion of the matrix. It is reasonable to believe that either one of the above theories or a combination of both may result in expansive behavior when ettringite is present.

The current methodology to identify risk of sulfate-induced damage is based on the concentration of available (usually water soluble) sulfates in the soil. Sulfate contents are generally expressed either in ppm (parts per million) or mg/kg (which is equal to ppm) or in a percent dry weight of soil (10,000 ppm or 10,000 mg/kg is equal to 1 percent by mass). Many cases are documented in the literature where soils with varying levels of sulfates, from above 1,000 ppm to 10,000 ppm, precipitate ettringite when treated with calcium-based stabilizers. Based on these observations, identifying the threshold level of sulfates required to form a deleterious amount of ettringite in a specific soil is complex. These observed variations are primarily due to the difference in the mineralogy of the soils as the type and percentage of minerals, primarily clay minerals, in the soil determines the release of aluminates required to form ettringite. The Texas Department of Transportation (TxDOT) recommends a safety limit of 0.2 percent by mass for soluble sulfate as a threshold separating a safe acceptable risk from low to moderate risk. This limiting value agrees with studies by other researchers.

Risk assessment along the alignment of the proposed roadway is a key factor in deciding the fate of a project. Risk identification prior to soil exploration can help develop effective soil exploration and sampling techniques, define the scale of testing needed, and help decide the controls required during construction. Sulfate concentrations in soil exhibit high spatial heterogeneity and hence selecting locations to perform sulfate testing is critical. Identification of problem areas depends on the availability of techniques that can characterize important soil properties in a time effective manner. Although the sulfate concentrations in soil can vary for many reasons, identification of problematic locations can be achieved by careful consideration of certain selected features along the alignment. Several factors are key to determining risk as well as identifying where samples should be taken as well as how many should be taken.

Many factors related to soil properties can influence ettringite formation in stabilized soils. This includes ion availability, source for water supply, and system pH history. Therefore,

one way to restrict the formation of ettringite is by limiting one of the above components in stabilized soils. During mixing of lime, soil, and water, lime provides the required calcium needed for cation exchange and flocculation/agglomeration of clay particles. Excess lime in soil, above the amount required for cation exchange and to maintain satisfactory pozzolanic reactions with the soil, maintains the pH level above 10.5, a condition favorable for ettringite precipitation in soils. But, limiting lime concentration in soil can affect long-term strength gain in stabilized soils and hence is not generally advocated. Clay and silt fractions in soil, which provide the source for alumina and silica needed for pozzolanic reactions, also cannot be controlled during stabilization. Water is supplied to support the treatment process as part of water of construction. Water may also enter the system as ground water through processes of infiltration, through capillary rise, or through diffusion. Sulfate movement can also occur under various potentials: dissolved in water moving through gravity potential, water moving via capillary rise, water moving in vapor form due to temperature, humidity, or salt concentration differentials. Attention to drainage design can substantially limit the post-stabilization migration of water, and this may have as great an impact on reduction of sulfate-induced damage as any single design action.

Perhaps the most practical construction-based approach in controlling or limiting deleterious reaction effects when treating high sulfate content soils with calcuium-based stabilizes is to create conditions in the soil system that favor the dissolution of available sulfates and force the formation of these expansive minerals before compaction. The effectiveness of this method depends primarily on the possible extent of dissolution of naturally available sulfates in the soil system. A complete dissolution of all sulfates in the soil is not practical, as the solubility of gypsum, the major sulfate source, is limited. Typically, an additional 3 to 5 percent above optimum moisture content is added to soils during mellowing time. Mellowing periods have been specified, which range from as little as 24 hours to as long as 7 days, primarily depending on soluble sulfate content in the soils. However, the amount of water typically applied during the mellowing period does not approach the amount necessary to solubilize the sulfates normally associated with the threshold level for damage (normally between 2,000 and 3,000 ppm). Even though the amount of water applied during the mixing and mellowing process is far too low to solublize sulfates, increased moisture content during mellowing does help optimize the formation of nucleation sites that trigger the development of ettringite crystal growth sites, leading to a well-dispersed or homogeneous formation of ettringite crystals, and does probably speed up the formation of ettringite and the utilization of soluble sulfates during this growth process.

Since the presence of sulfate ions is the key in the formation of these deleterious minerals, sulfate quantification in soils is critical in defining the reactivity of soils. Sulfur is found in natural soils as sulfide minerals like pyrites, marcasite, and greigite and in sulfate forms like gypsum, anhydrite, barite, and jarosite. A complete sulfur characterization requires identification of different sulfur species existing in soils. Sulfur in soils is assessed under four main categories:

1. Water soluble sulfates,
2. Acid soluble sulfates,
3. Total reduced sulfur, and
4. Total sulfur.

Since the sulfate availability in treated soils is dependent on dissolution and movement of sulfate ions in natural water, an extraction process using water as the solvent is acceptable.

Sulfate content in soils should be determined prior to construction, and techniques outlined for specific sulfate levels should be used to reduce the risk of post-compaction ettringite formation. Colorimetric techniques are fast and economical when compared to other available methods for measuring sulfate concentrations in soil. Efficacy of method AASHTO T 290 may be improved by incorporating a few changes in techniques used for sample preparation. These include: (1) reducing the size of soil particles used in testing to facilitate a faster and more complete dissolution of available sulfates in soil; (2) using a high water-to-soil dilution ratio, which will help prevent underestimation of available sulfates in soil, as the solubility is limited by saturation conditions of the solution; (3) allow the soil-water solution to set idle for at least 12 hours prior to filtration to facilitate complete dissolution of sulfates in soil.

INTRODUCTION

In place soil treatment using calcium-based stabilizers is an economically feasible solution alternative to address strength deficiencies and problematic shrink/swell behavior of unstable subgrade soils. Soil instability may originate from the presence of clay or silt whose instability is normally triggered by a change in moisture content. Even though stabilization improves engineering properties, problems can arise when calcium-based stabilizers are used in soils rich in sulfate-bearing minerals. Stabilization of sulfate rich soils in the presence of excess moisture may lead to the formation of minerals such as ettringite and/or thaumasite and can cause distress in or even destruction of pavement structures due to heaving *(1, 2)*. However, the extent of such distress varies among soils and is dependent on factors including the strength of the soil matrix and the spatial distribution and arrangement of ettringite (and/or thaumasite) crystals in the matrix *(3)*. Sulfate-induced distress is often initiated at the bottom of stabilized layers and therefore remediation may require the removal and reconstruction of the entire pavement section. The cost of reconstruction is often much higher than the costs incurred in the original stabilization process; and, therefore, the risk of sulfate-induced distress may be a reason to eliminate calcium-based stabilizers from consideration.

It is critical to the success of the stabilization alternative to be able to predict or evaluate the potential for sulfate-induced structural distress as part of the design procedure. Ettringite precipitation is a complex problem related not only to soil composition but also to construction methods, availability of water, ion migration, and void structure in pavements. In trying to control the damage associated with sulfate-induced distress, engineers have attempted to determine a threshold value of soluble sulfates, a quantity that is relatively easy and quick to measure, at which significant ettringite and/or thaumasite growth and, therefore, significant structural distress occurs. Unfortunately, experience alone and “rules-of-thumb” based on experience are not sufficient to deal with this complex issue. This report provides guidance for successful stabilization of these sulfate-bearing soils. The guideline provides a brief background on and explanation of:

1. Mechanisms of mineral development responsible for distress,
2. Assessment of the risk potential in the design process,
3. Outline of test methods to support the design process, and
4. Assessment of the practicality of processes to reduce the risk involved in construction operations.

BACKGROUND

Sulfate-induced damage may occur with any calcium-based stabilizer capable of providing a source of calcium and capable of increasing the pH of the soil-stabilizer-water mixture. However, most of the experience chronicled in the literature is based on interaction of soils with lime. Lime is a broad term which includes a variety of calcium-bearing compounds. Different forms of lime and products with varying concentrations and purity of lime have been used successfully for stabilization purposes. However, the most commonly used products are CaO or quicklime and $Ca(OH)_2$ or hydrated lime. These forms of quicklime and hydrated lime are referred to as high calcium lime. These lime-containing compounds, when added to soils in the presence of water, can bring about significant changes in engineering properties of soil

including strength improvement, increased workability, establishment of a working platform during construction, and reduction in volume change characteristics. But, other calcium-based stabilizers used in soil stabilization also contain certain amounts of lime. For example Portland cement typically contains over 60 percent CaO based on an oxide analysis. Although the vast majority of the CaO is combined with silica or alumina during the production of Portland cement, free CaO is produced during cement hydration. Typically about 25 percent of cement paste by volume is comprised of $Ca(OH)_2$. Lime is also present in Class C fly ash and is added to Class F fly ash to initiate pozzolanic reaction during stabilization. Since it is the presence of lime (CaO or $Ca(OH)_2$) in the stabilizers that provides calcium and raises the pH in the presence of water, the reactions between soil and other calcium-based stabilizers may be considered to be similar to that between lime and soil.

As previously addressed, even though the use of calcium-based stabilizers is beneficial in most cases, the literature as well as practical experience has established that sulfate-bearing soils can develop deleterious reactions when treated with calcium-based stabilizers such as lime or cement *(2, 4, 5, 6)*. Sulfate-induced heave in soils stabilized with lime or cement was first documented as a problem when reported by Sherwood in 1962 *(7)*. But the problem received national attention only in the mid-1980s when Mitchell reported a case study based on his experience at an arterial street in Las Vegas, Nevada *(8)*. The distresses observed along the pavement section were attributed to the formation of hydrous calcium aluminum sulfate minerals, ettringite and thaumasite, causing volumetric expansion in stabilized layers. Ettringite precipitates in environments where the pH remains high with high activities of Ca^{2+}, $Al_{(aq)}$, and SO_4^{2-} *(9)*. Although researchers have reported ettringite to be stable at pH levels close to 9.0, it is generally agreed that ettringite precipitates at pH conditions above 10.7 *(10)*. In many reported cases, stabilized soils were found to expand and heave over extended periods of time, and water was documented to be a part of the process *(2, 11, 12)*. Areas of observed distress in many cases were found to be located near water sources and the disturbed sections showed higher, often considerably higher, water content than the water used in the stabilization process.

Another mineral that is often found to occur in the presence of ettringite is a mineral of a similar structure, thaumasite. Thaumasite may form in lime and cement treated sulfate-bearing soils and in Portland cement concrete structures as a result of low temperature sulfate reaction and intensive carbonation *(13)*. The formation of ettringite is accompanied by expansive reactions, whereas thaumasite formation may result in a softening of the previously stabilized matrix *(14)*. It is believed that under favorable conditions ettringite forms first and thaumasite uses ettringite as the template for initial formation and then forms directly from solution *(15)*. The expansive capability of thaumasite is considered to be less when compared to ettringite. Thaumasite is believed to occupy only 45 percent of the volume of ettringite from which it is derived *(13)*. Hence formation of thaumasite from ettringite would be expected to reduce the net volume of the matrix and result in the deterioration or “crumbling” of the matrix as thaumasite is formed. This agrees well with field observations of a deteriorating, powdery, and often wet matrix when thaumasite is present. Some controversy does exist regarding thaumasite formation, and some literature suggests that thaumasite may form at the same time as ettringite or even in lieu of ettringite *(15, 16)*.

It is possible to create conditions where the detrimental effects of ettringite formation can be reduced in stabilized soils. Specific techniques to be followed and the reasoning behind each approach are detailed later in the report. The role of additives in limiting ettringite formation is

also detailed in the report. As will be discussed later, it is possible that providing high concentrations of soluble silica from fly ash or, for example, ground granulated blast furnace slag (GGBFS) can provide a ready source of soluble silica which will alter the thermodynamic mechanisms to favor the formation of cementitious products rather than ettringite and/or rapidly lower the pH of the system so that additional ettringite will not form *(17)*. The chemical composition among fly ashes varies considerably, and therefore whether or not a specific ash will impact ettringite formation is a complex issue.

CHEMISTRY OF ETTRINGITE AND THAUMASITE

Ettringite is a hydrous calcium alumino-sulfate mineral that precipitates under alkaline (high pH) conditions in soil and concrete systems with high sulfate activity *(4, 11, 14)*. A categorical explanation of the mechanism of formation of these minerals was first provided by Hunter *(2)* and was based on the geological, geochemical, and mineralogical reasons for their precipitation. Chemistry of ettringite formation is given in equation [1].

$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2.(SO_4)_3.2(\quad ...(1)$$

Resources needed to form ettringite are made available partly by the additive and partly by minerals present in soil. For 1 mole of ettringite to form 6 moles of CaO, 1 mole of Al_2O_3, 3 moles of SO_4, and 32 moles of water are required. Calcium ions are provided by lime, Portland cement, or fly ash; alumina is supplied by dissolution of oxyhydroxides and phyllosilicates; and sulfates are supplied by dissolution of gypsum, oxidation of sulfide, or ion migration of sulfate ions as water diffuses through the matrix *(2-5)*. Even though these components may be available, thermodynamic favorability and concentration of limiting reagents control the precipitation of ettringite and thaumasite *(3)*. Although several calcium-aluminum-sulfate hydrates can form during stabilization, only mono-sulfate hydrate and tri-sulfate hydrate forms are stable in solution *(18)*. Formation or hydration of the mono-sulfate phase does not result in expansion, whereas the formation and/or hydration of the tri-sulfate phase can cause significant volume changes in stabilized layers.

The silica-bearing analog of ettringite, thaumasite, is a complex calcium carbonate silicate sulfate hydrate mineral represented by the structural formula $[Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \bullet 24H_2O]$ which, as previously stated, probably proceeds from an isostructural alteration of ettringite in the presence of carbonates and soluble silica as described in equation [2].

$$\begin{aligned} &Ca_6[Al(OH)_6]_2 \bullet (SO_4)_3 \bullet 26H_2O + 2(H_2SiO_4)^{2-} + 2CO_3{}^{2-} + O_2 \rightarrow \\ &Ca_6[Si(OH)_6]_2 \bullet (SO_4)_2 \bullet (CO_3)_2 \bullet 24H_2O + 2Al(OH)_4^- + SO_4{}^{2-} + 4OH^- + 2H_2O \end{aligned} \quad \ldots(2)$$

A low temperature, generally considered to be 15°C, and intensive carbonation are required to form and maintain thaumasite as a stable phase in the matrix *(2, 13)*. Along with carbonates and sulfate ions, thaumasite consists of silicon, which is generally considered to be primarily derived from the decomposition of C-S-H formed during cementing reactions or possibly pozzolanic reactions in treated soils. A lesser concentration of reactive alumina combined with a higher calcium and sulfate content favor the decomposition of cementitious materials. Remnants of

unreacted calcium silicates in cement or soluble silica from clays or microcrystalline silts can also provide silicon needed for thaumasite formation in treated soils *(15, 16)*.

MECHANISMS OF REACTION

Our current knowledge of the problem revolves around our understanding of the mechanisms of ettringite formation in cement chemistry, which is rapid during initial cement hydration *(19)*. Of course, ettringite formation is expected early in the cement hydration process during hydration of tri-calcium aluminate and is not considered to be deleterious. This should not be confused with secondary ettringite formation that forms after the cement matrix has developed and is deleterious. The kinetics of ettringite formation during initial cement hydration is rapid because in cement the components in dry form are amorphous and uniformly blended. Also, due to the nature of their particle size distribution, they have a very large surface area. When mixed with water to form cement paste, this high surface area translates to a higher rate of reactivity and the reactants immediately become available in solution as soluble ions. Hence ettringite formation in Portland cement concrete is fast and is dependent solely on available sulfate content in the matrix. On the contrary, when soil systems are treated with calcium-based stabilizers, ion availability in solution is defined by mineralogy and dissolution properties of soil minerals. The flocculation/agglomeration during initial reaction periods contributes to reduction in surface area of soil particles. Hence the particles, or what may be better classified as agglomerates of particles, normally have a substantially smaller surface area when compared to Portland cement. Moreover, the soil minerals have a well-defined crystal structure and the effects of weathering and varying environmental conditions make the distribution of soil minerals more heterogeneous when compared to Portland cement. Hence the extent of ions available in solution to form ettringite is limited in stabilized soils when compared to cement pastes. Therefore, there is no reason to assume that because ettringite occurs rapidly in cement, say within the first day or so of cement hydration, it should occur as rapidly in stabilized soils. Furthermore, the behavior of treated soils and the extent of damage have to be considered to be soil specific and dependent on factors other than sulfate content alone *(3, 5, 20)*. Research has proven that ettringite precipitation and the resulting volume changes in stabilized soils are higher in clays when compared to sandy soils under similar environmental conditions *(5, 20)*.

Mechanism of Formation

There are two proposed mechanisms for ettringite formation in cement chemistry: by topochemical reaction and through solution reaction *(21)*. In a topochemical reaction, ettringite crystal growth occurs at the solid solution interface *(22, 23)*. In sulfate rich environments with a high concentration of lime, aluminum ions which dissolve cannot migrate far from the source due to the supersaturation of the liquid phase with respect to ettringite. Ettringite crystals therefore precipitate preferentially on the surface of the alumina-bearing phase in a topochemical reaction *(24)*. Microscopy images of needle shaped crystals growing perpendicular to the surface of aluminum-bearing phases during cement hydration support the topochemical reaction mechanism *(23)*. Other than a topochemical reaction, ettringite can form through a solution mechanism where the products precipitate randomly from the liquid phase after attaining a state of supersaturation. When the concentration of lime is low, the aluminum ions can migrate more freely in solution and ettringite can precipitate from solution under favorable conditions *(24)*.

There are no published data suggesting that either of the mechanisms described above is the exact reason for ettringite formation in stabilized soils. Due to limited ion availability in solution, it is probable that the small amount of ettringite formed during the initial stabilization period or mellowing time may act as nucleation sites for future growth. Distribution of these nucleation sites may influence the extent of damage in stabilized soils. If a small number of random nucleation sites are created, then the limiting reagent, normally sulfate, may continue to migrate to these sites over time and form larger, concentrated crystals that ultimately cannot be accommodated by the soil matrix. The result would be a disruption of the matrix or heaving. On the other hand, if a larger number of well-dispersed nucleation sites are formed, the limiting reagent gets distributed over these sites and hence produces crystal growth that can be accommodated by the soil matrix (within the voids). This reaction can be promoted by using as much water as possible during construction and mellowing in order to place into solution as much sulfate as possible to form ettringite followed by thorough mixing to homogenize the system. Water moving through the system can solubilize unreacted lime and also act as a medium for ion migration. Water influx to the pavement layers and diffusion through the layers can therefore become a continuous source of reagents needed for future ettringite growth at these nucleation sites *(1, 25)*.

Mechanism of Expansion

As one would expect, the discussion here is similar to that in the preceding section, "Mechanism of Formation," as formation and expansion are allied. Although the formation of ettringite is known to induce volume changes in stabilized soils, as with formation, the mechanism of expansion is not completely understood. Once again, two theories exist regarding the cause of expansion during ettringite formation. The first theory explains that expansion is due to topochemical formation of ettringite and the anisotropic growth of the crystals *(22, 23)*. The second theory suggests that expansion is due to absorption of water by ettringite crystals *(26)*. There is no intercrystalline chemical bonding among ettringite crystals, and hence water molecules can cause interparticle repulsion resulting in overall expansion of the matrix. Based on our current understanding it is difficult to select one of the above theories as the sole reason behind the observed expansion in soil systems. Hence it is reasonable to believe that either one of the above theories or a combination of both may result in expansive behavior when ettringite is present.

Again, there is no simple proportionality between amount of ettringite and extent of expansion. Both theories described here suggest that water is the decisive factor in causing deleterious reactions. But the source of water that forms ettringite is critical in determining the extent of expansion in the matrix. Molar volume calculations based on ettringite stoichiometry show that the volume increases by 1.37 times the initial volume of reactants consumed from the matrix $(CaO, Al_2O_3 \text{ and } SO_4)$ when the influx of external water triggers ettringite formation. In other words, the increase in molar volume of ettringite when fully hydrated by external water is 1.37 times that of the un-hydrated original reactants. On the other hand, ettringite formed from water available from within the matrix actually causes shrinkage, as the molar volume of ettringite is less than the components $(CaO, Al_2O_3, SO_4 \text{ and } H_2O)$ when water is considered to be contained within the matrix and no external water is accounted. Moreover, it is noteworthy that a combination of negative charge and high surface area of ettringite crystals can attract water into the matrix *(27)*. In fact, a recent study at Texas A&M University on controlled low

strength mixtures (CLSMs) has demonstrated that sorption of water by the ettringite matrix is responsible for moderate expansion (*28*). The study compared the ettringite content and the measurable expansion in CLSM samples under different curing regimes to identify the role of water in expansion of ettringite crystals. The observations suggest that the presence of ettringite crystals in the stabilized matrix can induce increased potential for moisture movement, causing deleterious expansion in the system *(22, 28).* Again, the extent of measurable expansion further depends on the time and location of mineral formation and also on how well they are accommodated in the voids in stabilized layers.

ETTRINGITE FORMATION IN STABILIZED SOILS

Soil particles range in size from small cobbles and gravel to clay-size particles. In general, sand and silt are composed of primary minerals that form under geologic conditions and on a geological time scale. These larger size fractions in soil generally remain unreactive during stabilization. The clay-size particles are generally the most reactive minerals in soils, due partially to their very high surface area. Most of the clay minerals are susceptible to at least partial dissolution at high pH levels due not only to their high surface area, but also to their less stable crystalline structure. Dissolution of clay minerals and aluminum-bearing phases in soil normally provides the aluminum needed for ettringite formation. Feldspars, oxyhydroxides, and amorphous forms of alumina are some of the additional sources for alumina in soils that can undergo congruent or incongruent dissolution, releasing aluminum into solution. Surface defects or impurities in the structure can also enhance dissolution of these minerals. The amount of and type of clay particles and other reactive alumina-bearing phases, therefore, determine the rate and degree of release of aluminum in soils at high pH conditions *(4, 5).* The difference in behavior among soils when treated with calcium-based stabilizers and their sensitivity to form ettringite/thaumasite during calcium-based stabilization is certainly impacted by the type of soil minerals and the percentage of clay and microcrystalline silt particles present in the soil.

Of course, sulfate ions are required to form ettringite and are generally provided from the dissolution of gypsum or oxidation of sulfide-bearing minerals in the soil. The predominant sulfate-bearing mineral, gypsum, has a solubility of 2.58 grams per liter of water *(25)*. Due to the low solubility, the availability of water is critical in deciding the extent of dissolution of gypsum in soils. But the amount of water used to mix and compact stabilized soils is too low to solubilize all available sulfates. One mole of gypsum has a mass of 172 grams and contains 96 grams of SO_4. Therefore, if we consider that 100 grams of dry soil contains only 0.3 percent or 0.3 grams of gypsum (0.167 percent sulfate) and if we add 25 grams of H_2O (25 percent water) to accommodate mixing of the calcium-based stabilizer with the soil, only about $1/5^{th}$ of the available water-soluble sulfates can be solubilized by the mixing and/or compaction water. This is given in equation [3].

$$25\ g\ H_2O \times \frac{2.58\ g\ Gypsum}{1000\ g\ H_2O} \times \frac{96\ g\ SO_4}{1\ mole\ Gypsum} \times \frac{1\ mole\ Gypsum}{172\ g\ Gypsum} = 0.036\ g\ SO_4 = 0.036\ \%\ SO_4 \quad \ldots(3)$$

This example can be translated into practice in an attempt to create conditions suitable for ettringite precipitation prior to compaction. This is done by providing an extended mellowing period for high sulfate soils where the soil is allowed to react with lime and water before compaction. But, based on the stoichiometric example just presented, if even a moderate level of

soluble sulfate is present in the form of gypsum, it is impossible to solubilze all of the gypsum in the mixing and mellowing process. Instead, by using as much water as is practical during mixing and extended mellowing, it is more likely that a greater number and well-dispersed nucleation sites will develop in the stabilized matrix. Under these conditions, crystal growth will more likely be uniform and more likely to be accommodated within the compacted soil matrix, as explained in the section entitled "Mechanisms of Formation."

MISCONCEPTIONS REGARDING ETTRINGITE FORMATION IN SOILS

The most common misconception in dealing with stabilization of sulfate rich soils is that lime is the only stabilizer that causes sulfate heave. This is not true, as any of the calcium-based stabilizers can cause sulfate heave in soils. In fact, free lime formed during hydration of calcium silicate can induce the formation of these expansive minerals. Cases have been reported where soils stabilized with Portland cement and/or fly ash has heaved *(29).* The effect of different cement types and the influence of various compositions of fly ash on ettringite/thaumasite formation are not completely understood and further investigation in this area is needed. The literature does demonstrate rather convincingly that an abundance of readily soluble silica, such as that that might be present in some fly ash, ground granulated blast furnace slag, or in cement, can favor the formation of a type of calcium-silicate-hydrate mineral that is thermodynamically favored over the formation of ettringite. To this end sources of soluble silica have been used to avert the formation of ettringite (*17*).

Another common belief is that sulfate-resistant cement can be effective in reducing ettringite formation in soils. Sulfate-resistant cement has a limited concentration of alumina in the form of tri-calcium aluminate and can therefore resist the formation of delayed ettringite in cement concrete structures where the source of alumina is solely from the cement. However, the use of a low aluminum cement to treat or stabilize a clayey soil, where the sources for aluminum are essentially unlimited, may not be effective in preventing ettringite formation over time. Although the kinetics of the dissolution of alumina from the clay may be very slow, it may occur over time if the pH remains high enough to solubilize the clay minerals.

Based on the principles elucidated here, it should be possible to engineer a blend of soil and stabilizers that will either drive the reaction to the formation of a mineral other than ettringite due to an abundance of soluble silica and/or to induce a rapid drop in pH, which does not favor the formation of ettringite.

SOURCE OF SULFATES IN SOIL

It is not uncommon to observe sulfate heaves in small, localized areas and along isolated locations within the stabilized section. One plausible reason for this is the irregular occurrence of sulfate sources in soil. Sulfate occurrence is not normally uniform but rather exists in seams and stratified pockets. Sulfate ions are made available from dissolution of these sulfate salts and from oxidation of sulfur-bearing minerals in soil bedrock. Available sulfate concentrations also depend on the amount and type of sulfate salts present and their solubility properties. Among the different analogues of calcium sulfates present in environment, gypsum is the most commonly observed mineral in natural soils *(30).* Considering the solubility of gypsum in natural water, 2.58 g/L, gypsum saturated soils can provide up to 1,440 ppm of sulfate ions per liter of water by

dissolution at a 1:1 dilution ratio *(25)*. But in natural soils, replenishment of water due to precipitation and ground water flow can result in continuous dissolution of gypsum, providing a source of sulfate for ettringite formation.

Surface bedrocks are also a major source of sulfur for soils all around the world. Among the sulfur-bearing minerals identified in sedimentary rocks, iron sulfide polymorphs, pyrite and marcasite, are the more common forms, of which pyrite is the most common *(31)*. Oxidation of these sulfide groups in an acidic environment releases sulfate phases into soils. Soluble ions migrate with water and, therefore, sulfate availability changes with the spatial variability of surrounding soils depending on their geologic origin *(30)*. Since sulfate ions in soils form the critical reactant in the formation of ettringite, an accurate assessment of the amount of soluble sulfates is probably the most important parameter in identifying the risk of deleterious sulfate reactions during the stabilization process.

THRESHOLD SULFATE LEVELS IN SOILS

The current methodology to identify risk of sulfate-induced damage is based on the concentration of available (usually water soluble) sulfates in the soil. Sulfate contents are generally expressed either in ppm (parts per million) or mg/kg (which is equal to ppm) or in a percent dry weight of soil (10,000 ppm or 10,000 mg/kg is equal to 1 percent by mass). Many cases are documented in the literature where soils with varying levels of sulfates, from above 1,000 ppm to 10,000 ppm, precipitate ettringite when treated with calcium-based stabilizers *(2, 3, 5, 32)*. Based on these observations, identifying the threshold level of sulfates required to form a deleterious amount of ettringite in a specific soil is complex. These observed variations are primarily due to the difference in the mineralogy of the soils as the type and percentage of minerals, primarily clay minerals, in the soil determines the release of aluminates required to form ettringite *(4, 5)*. The Texas Department of Transportation (TxDOT) recommends a safety limit of 0.2 percent by mass for soluble sulfate as a threshold separating a safe acceptable risk from low to moderate risk. This limiting value agrees with studies of Petry and Little *(4)*. But Mitchell and Dermatas *(5)* defined 0.3 percent soluble sulfates by mass as the safe limit for sulfates in soils, whereas Pappula et al. *(32)* observed sulfate concentrations from as low as 0.1 to 0.2 percent to be capable of causing expansive reactions.

Identifying sulfate levels in soil is important and the use of laboratory based physical tests, like the swell test, alone to determine expansion potential of treated soil may sometimes be misleading or at least incomplete. Tests to determine volumetric expansion are most certainly valuable and effective methods of volumetric expansion testing have been used in Europe (NF P 94-100). However, laboratory swell testing suffers from three limitations. First, distress in the field does not necessarily manifest quickly, but can take several months or even years to occur. Hence, levels of volume change that are measured in the laboratory in a time frame defined for the laboratory test and that fall below acceptable thresholds do not necessarily translate to acceptable performance under field conditions. Second, whether or not expansion is likely depends on where the expansive minerals form within the soil matrix (within voids or in dense matrix) as previously discussed in the section entitled “Mechanisms of Expansion.” Where and how the expansive mineral forms can depend on the procedures followed in mixing and mellowing, which may help define the timing and nature of crystal nucleation and growth. If the laboratory conditions fail to mimic field conditions, the results may be misleading. Thirdly, and finally, other laboratory curing conditions may fail to mimic field conditions in terms of whether

the water for ettringite formation comes solely from the soil matrix or if it is transported from an external source.

Although volumetric swell tests are valuable, it is also necessary to have a reliable measure of the sulfate content and to link that level to a threshold risk. The sulfate concentration should be determined based on an accepted specification such as AASHTO T 290 (modified), which is discussed later in this report. Table 1 outlines the level of risk associated with stabilizing soils with varying sulfate concentrations *(33)*.

Table 1. Level of risk associated with lime stabilization in sulfate-bearing clays.

Risk Involved	**Soluble Sulfate Concentrations**	
	Parts Per Million	**Percent dry weight**
Low Risk	Below 3,000 ppm.	Below 0.3%
Moderate Risk	Between 3,000 and 5,000 ppm	Between 0.3% and 0.5%
Moderate to High Risk	Between 5,000 and 8,000 ppm	Between 0.5% and 0.8%
High to Unacceptable Risk	Greater than 8,000 ppm	Greater than 0.8%
Unacceptable Risk	Greater than 10,000 ppm	Greater than 1.0%

Little and Nair *(34)* investigated the threshold levels of soluble sulfates that caused significant ettringite formation in a study on five different soils selected from the state of Colorado. The soils were selected on the basis of their mineralogical diversity and the fact that they represented distinct regions of the state of Colorado as selected by the Colorado Department of Transportation (CDOT). Little and Syam used two protocols to assess the threshold levels required to induce substantial ettringite growth: thermodynamic phase diagrams and differential scanning calorimetry (DSC). In the phase diagram approach, predictions were made based on the Gibbs free energy associated with the formation of the minerals for each soil at varying soluble sulfate concentrations (Figure 1a). The protocol used is discussed by Little et al. *(3)*. Then mass-balance calculations were used to determine the amount of ettringite that would form as the sulfate level was increased. An example for stoichiometric calculation to determine the mass of ettringite formed in soils with 3,000 ppm (0.3 percent) sulfates is given below in equation [4].

$$\frac{0.3\,g\,SO_4}{100\,g\,Soil}\times\frac{1\,mol\,SO_4}{96\,g\,SO_4}\times\frac{1\,mol\,E}{3\,mol\,SO_4}\times\frac{1254\,g\,E}{1\,mol\,E}=\frac{4.36\,g\,E}{100\,g\,Soil}=1.31\%\,E \qquad \ldots(4)$$

Similar stoichiometric calculations were used to determine the concentration of ettringite that can form for a given sulfate content, and these values are presented in Figure 1 as the line labeled “stoichiometry.” Ettringite concentrations predicted to form in these soils based on the thermodynamic phase diagram approach are compared with the actual quantities of ettringite formed in these soils when treated with 5 percent CaO and with varying concentrations of soluble sulfates in Figure 1. Figure (1b) shows the result of laboratory measurements of the quantities of ettringite formed after 56 days of cure measured using a differential scanning calorimeter.

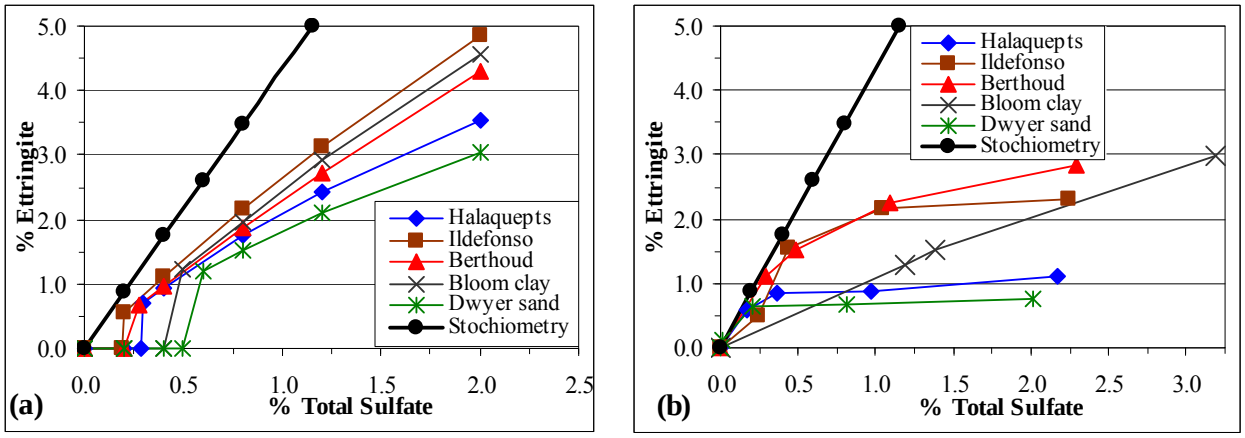

Figure 1. Comparison of ettringite concentrations in soil (a) Predicted using phase diagram approach and (b) Measured using a Differential Scanning Calorimeter.

Figure 1 shows three important results: (1) the threshold sulfate content for the five soils is different and, since all other factors are constant, threshold levels must depend on mineralogical differences of the soils; (2) the threshold levels determined based on phase diagram/mass-balance calculations and the DSC measurements are in reasonable agreement with each other and are less than the stoichiometrically determined maximum possible values; and (3) the threshold levels are in reasonable agreement with the levels defined in the literature as problematic levels (*33*).

RISK IDENTIFICATION

Risk assessment along the alignment of the proposed roadway is a key factor in deciding the fate of a project. Risk identification prior to soil exploration can help develop effective soil exploration and sampling techniques, define the scale of testing needed, and help decide the controls required during construction. Sulfate concentrations in soil exhibit high spatial heterogeneity and hence selecting locations to perform sulfate testing is critical. Identification of problem areas depends on the availability of techniques that can characterize important soil properties in a time effective manner. Although the sulfate concentrations in soil can vary for many reasons, identification of problematic locations can be achieved by careful consideration of certain selected features along the alignment. These are discussed in the following paragraphs.

Geology and Mineralogy

Soil characteristics can influence the potential of a selected soil to precipitate ettringite or thaumasite. Clay-rich soils generally have higher salinities, carbonate, sulfate (as measured in gypsum), and water-holding capacities than other soils, all of which are important components for the formation of ettringite/thaumasite. The probability of finding sulfate sources, like gypsum, in soil varies among soil formations and can be identified using geologic maps of the location. Soil formations that overlap the alignment can be identified by overlaying the alignment of the project on appropriate geological atlas maps. These maps also contain information regarding mineralogical composition of the soil formations. Details of parent rock formation provide insight into the mineralogy of the bedrock and soils in a given location. Potential sulfate-bearing minerals can be identified from these maps and incorporated into design considerations for the location. This information is to a degree compiled in County Soil Survey

Reports, published and updated by United States Department of Agriculture and the National Resources Conservation Service (NRCS), and can be used as a source by which to assess the potential of a selected soil to develop sulfate-induced distress *(35)*.

Initial identification of areas with potentially high concentrations of the chemical constituents of ettringite can be made using existing soil geospatial databases and using geologic and topographic maps of the location. The geospatial data can be used to identify important soil characteristics including mineralogy, clay content, and carbonate and sulfate levels which can be used to identify potential "hot spots" along the alignment. These hot spots can vary in shape and size from as little as 10-25 m in diameter to extended sulfate seams. GIS maps are an effective source of information by which to identify the locations with high sulfate concentrations. Like soil survey reports, decisions should not be based solely on the information acquired from these maps, but rather such information should be used as a preliminary identification of potential problematic areas. Laboratory-based sulfate testing must be performed to confirm any level of reconnaissance before soil treatment.

Climatic Characteristics and Drainage Features

Climatic conditions can also influence movement of ions in soils. In dry arid areas, sulfate deposits are likely to be found in near-surface environments due to evaporation processes, which leave previously dissolved sulfate ions in the soil. In wet and humid areas, water infiltration can carry sulfate ions into deeper strata which can be transferred back to the surface due to capillary action. In rolling terrains, significant sulfate concentrations may accumulate in low-lying areas due to surface runoff creating sulfate hot spots in the soil. Moving water also acts as a medium for ion migration into the stabilized layers to form a continuous source for limiting reagents in the system *(2, 25)*.

Copious amounts of water are needed to form these hydrous minerals. Water may be provided by fluctuation of the water table in the location, by surface infiltration, or by capillary suction *(4, 28)*. Surface runoff and rainfall can also be the source of water needed for ettringite formation. Water can gain access to sulfate minerals in soil through seepage, through surface cracks and openings, or through permeable layers in the pavement section. Low-lying areas can accumulate water which increases the risk for sulfate heave in the location. Rolling terrain or slopes along the corridor can promote water accumulation along the pavement section. Sulfate crystals precipitating in soils during dry seasons can be washed along the slopes or through desiccation cracks in clays into stabilized layers along with rain water. A rise in the water table during wet periods can dissolve sulfates in the soil or transport sulfate ions from underlying parent rocks.

Soil Classification

Soil type has a strong impact on soil conductivity, and by implication, on sulfate concentration. Hence, soil classification can also be used in accessing the potential for ettringite formation in soils. Soil matrix suction can provide a potential to draw water from the underlying water table. This uplift of water can transfer the dissolved sulfate ions in to the pavement layers. Swift movement of water in the pavement section carries these dissolved sulfates to streams or other areas of low hydraulic potential. But, when the soil has high capillarity and low hydraulic conductivity, water cannot flow readily through these soils and the dissolved sulfate ions are not easily transported through the pavement sections. Therefore, soils with low hydraulic

conductivity, high capillarity, and high suction properties can create sulfate reservoirs in subgrade sections. Evaporation/transpiration can also remove water from these soils, leaving behind residual crystalline sulfate formations in the soil. These properties are typically associated with clays and shales. Once these problematic soil types along the project alignment are identified, conductivity measurements, detailed later in the report, can effectively be used to target these sulfate reservoirs. It is also important to note that soil texture is not the controlling factor in determining soil conductivities. High sulfate pockets can also exist in gravely, sandy, and silty soils.

Topography and Spatial Variability

Topographic slope influences hydrologic processes, including overland flow and subsurface flow and therefore has a strong influence on residual sulfate concentrations in soils. The major sources of sulfur in soil are evaporates like gypsum ($CaSO_4$) or sodium or potassium sulfates or from SO_4^{2-} that is the product of the oxidation process of pyrite (*30*). Topography influences the transport of these relatively nonreactive solute sulfates along a gravity gradient (downhill). Slopes shaped by erosion can transport sulfate ions to locations far from parent source and into pavement sections that might intercept these flow channels. A rolling topography favors the process and the risk due to sulfate heave is increased when these soils occur in areas that are dissected by stream erosion. Sulfate accumulation typically occurs in low-lying areas and near dry stream channels since evaporation/transpiration processes are likely to favor the accumulation of sulfates near the stream channel in the drier months due to the proximity of the groundwater table to the land surface in these areas. Therefore, topography, through its influence on hydrology, is likely to have a strong influence on the redistribution of sulfates along the landscape. The influence of topography on sulfate accumulation should be identified and considered during soil investigations.

Among all the chemical constituents that comprise ettringite, SO_4^{2-} ions are likely to have the highest spatial variation due to variation in source rocks and as a result of their hydrologic mobility. The relative amount of sulfate in a soil's parent material can vary considerably among soil formations. Sulfate is also fairly mobile in the environment because of its relatively weak adsorption to soil minerals and due to solubility of gypsum and other evaporates in near-surface environments. Two hydrologic processes account for the mobility of sulfates and their accumulation in low-lying areas: surface/subsurface runoff and the upward migration of water from a shallow water-table aquifer through capillary action. In both cases, sulfate accumulates as the water evaporates and dissolved salts precipitate. Sulfate concentrations are generally higher in subsurface layers where the processes of moisture infiltration and evaporation and transpiration reach a state of general equilibrium and deposit a higher concentration of sulfates at a specific depth within the pedological profile of the soil. Because the NRCS soil survey reports provide in-depth pedological profile descriptions, these documents are an excellent source by which to identify where sulfates accumulate in the pedological profile and the spatial distribution of sulfates along the alignment. Since the pedological profile descriptions extend to a depth of several feet, they generally also provide an excellent source of data to determine whether or not cut and fill operations or whether fill sources may run the risk of containing high sulfate levels.

Visual Inspection

Field evaluation for sulfates is critical and should be performed if any project location carries the risk for sulfate heave based on the criteria discussed above. Visual inspection should be performed along these selected locations of the highway and for all potential borrow sources. Size distribution of gypsum crystals can vary from visible crystals to microscopic crystalline phases in soil (Figure 2).

Figure 2. Variability in size of gypsum crystals found in soil.

Solubility of gypsum is dependent on particle size and surface area of crystals *(36)*. Smaller particle size provides higher surface area which translates to faster dissolution of minerals when in contact with water. Therefore, fine-grained gypsum, if present, can dissolve faster and release ions faster when compared to coarse-grained fractions in soil. Well-formed gypsum crystals can be easily identified during visual inspections, whereas fine gypsum crystals can be detected as white powdery efflorescence on the surface, especially during dry seasons. The efflorescence is due to precipitates left behind after evaporation of ground water.

Soil Investigation

Identifying sulfate levels in soil is a critically important step. Soil investigations, prior to mix design, can assist engineers in selecting the effective type and levels of additives to be used and to choose appropriate techniques to be followed during stabilization. Sulfate level quantification can also be used to make a rough estimate of the quantity of ettringite that can form in soils based on stoichiometric calculations. Although this is a good technique for risk assessment, the extent of expansion of stabilized layers depends on whether or not the ettringite formed can be accommodated within the soil matrix. Moreover, ettringite precipitation and stability depends on geochemical controls including pH, activities of participating ions in solution, temperature, and activities of dissolved CO_2 and H_2O *(3, 10, 37)*. Hence, based on these factors, it must be remembered that the estimated ettringite concentrations based on stoichiometric calculations are only approximate. In some cases this estimate must be validated by actual testing of the volumetric expansion potential of the treated soil. But, even when swell testing is done, such as “one dimensional” swell testing (ASTM D 4546) or the “three dimensional” swell testing advocated by Petry *(38)*, one must remember that the field

environment is seldom simulated in the laboratory. For example, almost all swell testing is based on swell that occurs within a "closed system" where either distilled water or water from the local site with no additional sulfate content is used in the test. In fact, an "open system" is normally the case where water feeding the swell may well be laden with additional sulfates. The best way to test for sulfate expansion potential is to try to simulate the actual system and environment for the location being evaluated. This is often prohibitive because of the time and expense involved. Swell tests normally require over 30 days to complete and requires several closely monitored replicates. The alternative is to select a threshold level of soluble sulfate content below which the stabilized soil system either does not have the thermodynamic potential to form ettringite or thaumasite or if these minerals do form, an insufficient amount of product will form and expansion will not be significant, and the risk involved will be acceptable.

Sulfate salts can concentrate in surface soils or at depths depending on climatic conditions and geologic profile of the location. Hence geologic, climatic, and topographic profiles of the location need to be considered while selecting location and samples for sulfate testing in soils. In soils, sulfate seams or pockets are not uniformly distributed along the alignment and hence chances of missing these locations while sampling is highly probable. Geospatial mapping tools, county soil survey reports, recent experiences in adjoining locations, and expert opinions of these locations all need to be used effectively to decide sampling locations. Sampling has to be done at all pertinent locations and to appropriate depths to reasonably assess the level and extent of sulfates in soil. Research conducted by Bredenkemp and Lytton *(39)* demonstrated that electrical conductivity can be used to screen for salt contents and to rapidly screen for the presence of sulfates. Conductivity measurements can therefore be used as a good approximation of dissolved salt contents in soil and to identify sulfate seams or pockets during soil investigations (*40*).

For soil investigations in sulfate-laden soils, the minimum recommended frequency for drilling and logging test holes is every 500 feet on alternating sides of the width of the road bed *(41).* For cut sections, test holes should be drilled to a depth corresponding to the final grade elevation of the subgrade in order to capture samples for sulfate testing. The test method AASHTO T-290 (modified test method), or equivalent, should be followed in testing sulfate levels in soil. This method is discussed later in this report. After sulfate testing, the level and distribution of sulfate concentration should be plotted and used to make decisions regarding the technique to be used in stabilization. These sulfate distribution plots will help identify the locations and depths that may require alternative material and pavement designs. Since sulfate distribution can be highly variable, it is not uncommon to select more than one construction technique or to use different stabilizers along the alignment of the pavement. These plots are also useful in providing more efficient and effective use of resources. TxDOT *(41)* recommends that material design and construction techniques consistent with the highest concentrations measured along the selected section of the alignment should be used.

CONTROLLING ETTRINGITE FORMATION

Regulating Reactant Concentrations

Many factors related to soil properties can influence ettringite formation in stabilized soils. This includes ion availability, source for water supply, and system pH history. Therefore, one way to restrict the formation of ettringite is by limiting one of the above components in

stabilized soils. During mixing of lime, soil, and water, lime provides the required calcium needed for cation exchange and flocculation/agglomeration of clay particles. Excess lime in soil, above the amount required for cation exchange and to maintain satisfactory pozzolanic reactions with the soil, maintains the pH level above 10.5, a condition favorable for ettringite precipitation in soils. But, limiting lime concentration in soil can affect long-term strength gain in stabilized soils and hence is not generally advocated. Clay and silt fractions in soil, which provide the source for alumina and silica needed for pozzolanic reactions, also cannot be controlled during stabilization *(35, 42).* Water is supplied to support the treatment process as part of water of construction. Water may also enter the system as ground water through processes of infiltration, through capillary rise, or through diffusion. Sulfate movement can also occur under various potentials: dissolved in water moving through gravity potential, water moving via capillary rise, water moving in vapor form due to temperature, humidity, or salt concentration differentials *(2, 3, 25).* Attention to drainage design can substantially limit the post-stabilization migration of water, and this may have as great an impact on reduction of sulfate-induced damage as any single design action.

An alternative approach to this problem is to create conditions in the soil system that favor the dissolution of available sulfates and force the formation of these expansive minerals before compaction. The effectiveness of this method depends primarily on the possible extent of dissolution of naturally available sulfates in the soil system. A complete dissolution of all sulfates in the soil is not practical, as the solubility of gypsum, the major sulfate source, is limited *(25).* Typically, an additional 3 to 5 percent above optimum moisture content is added to soils during mellowing time. Mellowing periods ranging from as little as 24 hours to as long as 7 days have been specified, primarily depending on soluble sulfate content in the soils. However, as previously illustrated, the amount of water typically applied during the mellowing period does not approach the amount necessary to solubilize the sulfates normally associated with the threshold level for damage (normally between 2,000 and 3,000 ppm). However, as previously discussed, even though the amount of water applied during the mixing and mellowing process is far too low to solublize sulfates, increased moisture content during mellowing does help optimize the formation of nucleation sites that trigger the development of ettringite crystal growth sites, leading to a well-dispersed or homogeneous formation of ettringite crystals, and does probably speed up the formation of ettringite and the utilization of soluble sulfates during this growth process. In fact, empirical data to support this are presented by Harris et al. *(43),* and this is reproduced in Figure 3.

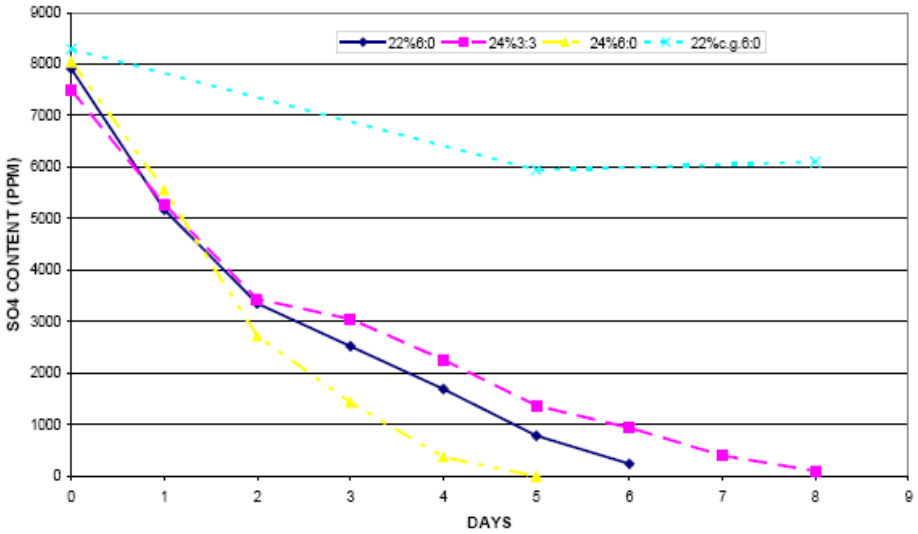

Figure 3. Effect of mellowing on sulfate content in soil *(43)*.

A decrease in sulfate contents with mellowing time as observed by Harris et al. *(43)* supports the above hypothesis. A longer mellowing time may be needed if sulfates are present in coarse size fractions due to the smaller surface area of the larger particles (*36*). The water content used in compaction is also critical in dissolution of sulfates present in soil. But above all, if less water is added during compaction and mixing, then water migrating into these stabilized sections after construction may activate a high pH (e.g., by hydrating previously unhydrated quicklime), resulting in post-compaction ettringite formation. For this reason use of lime slurry is sometimes specified in order to try to ensure complete hydration of all CaO. Lime slurry provides uniformity of mixing and abundance of water, thereby reducing the risk of unhydrated lime causing expansion in soils.

Techniques for Treating Sulfate Rich Soils

Most research on sulfate-induced heave in stabilized soils has been directed toward lime stabilization. Figure 4 is taken from the TxDOT guidelines for stabilization *(41)*. These guidelines are very similar to those developed by Little (*35*).

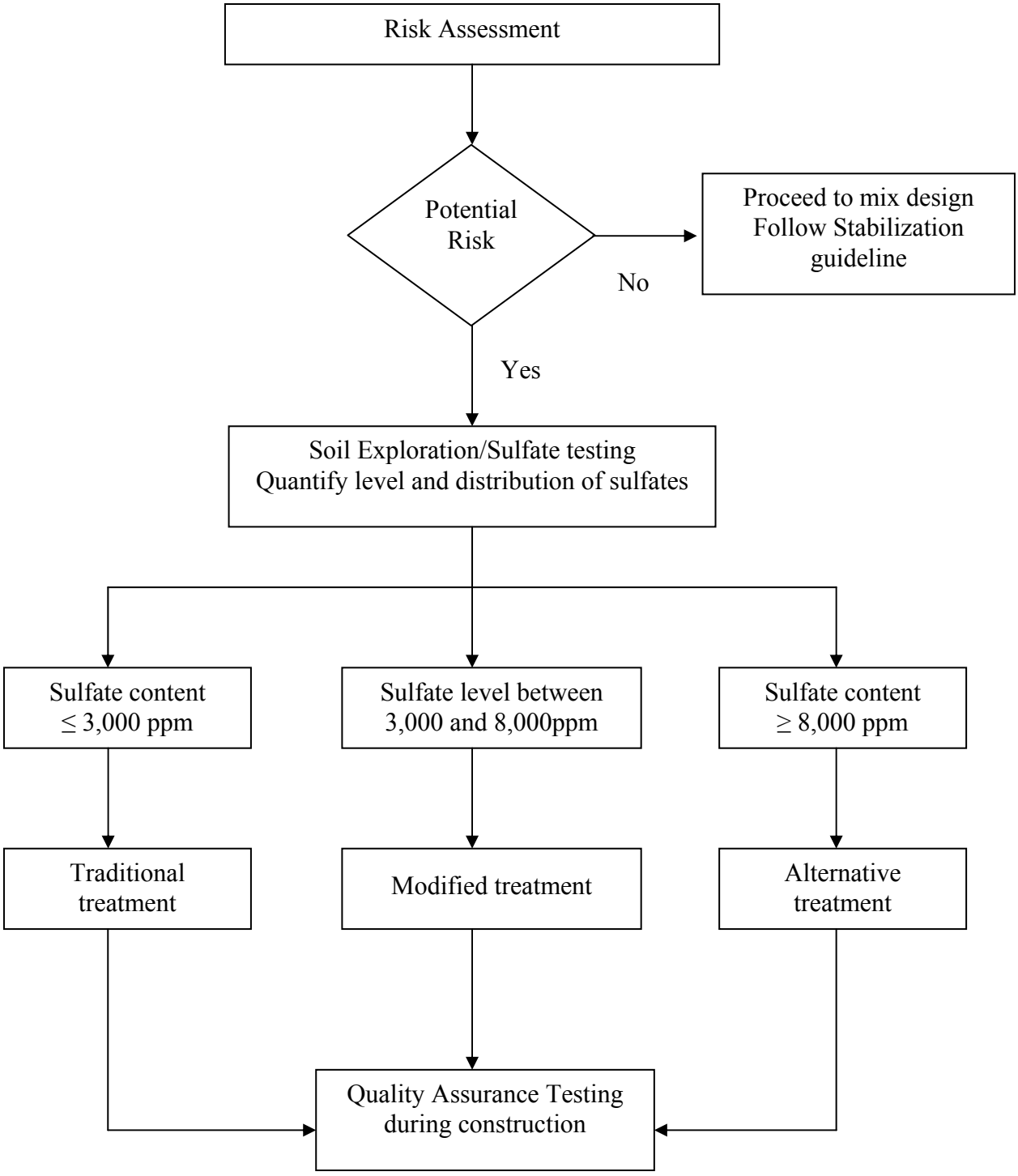

Figure 4. Guideline for stabilizing sulfate rich soils with lime *(41)*.

Traditional Lime Treatment

According to these guidelines, if the total soluble sulfate levels in soil are below 3,000 ppm or 0.3 percent by dry weight of soil, then lime stabilization should not be of significant concern. This does not mean that the potential for sulfate-induced expansion does not exist, but that, if external sulfate migration can be prevented, then the level of expansion due to ettringite/thaumasite formation should be manageable and detrimental expansions can be limited by adequate mixing and moisture treatment. If soluble sulfates are detected, then the use of lime slurry is recommended in lieu of the use of calcium oxide in order to eliminate the risk of inadequate hydration during construction and the possibility of post-construction hydration.

Modified Treatment

Soils with soluble sulfate levels between 3,000 ppm (0.3 percent) and 8,000 ppm (0.8 percent) are deemed to be of moderate to high concern in terms of ettringite formation. These sulfate levels can induce localized distress zones if sulfates are heterogeneously distributed. Although lime stabilization is a possible alternative for stabilizing these soils, special care must be taken during mix design and in selection of construction techniques.

Both TxDOT guidelines for stabilization *(41)* and National Lime Association *(44)* guidelines recommend the use of an extended mellowing period and the application of at least 3 percent above optimum moisture content during mixing. This moisture level must be sustained during the mellowing period. The length of the mellowing period as well as the moisture content required during mixing and mellowing should be determined from the mix design process. The procedure detailed below is adapted from TxDOT stabilization guidelines for treatment of sulfate rich soils *(41)*. Design lime content and optimum moisture content of the soil are determined as recommended for lime stabilization in Task 1 using a representative soil sample. The sample should have a representative concentration of sulfates as measured during sulfate tests. Once the optimum moisture content is determined, multiple soil samples with varying moisture contents above optimum are prepared using the design lime content. Sulfate contents in these mixes are monitored over time following recommended sulfate test methods. Mellowing time may vary among soils depending on available sulfate levels from 24 hours to as long as 7 days. The time of mellowing and the amount of water used during mellowing are determined by monitoring the residual sulfate concentration until it drops below 3,000 ppm. The combination of mellowing time and moisture content that achieves this goal is selected.

Water is a critical element in the formation of ettringite. The purpose of extending mellowing time before compaction in soils is to force ettringite formation prior to compaction of pavement layers. To achieve this, additional water is normally required during mellowing and must be added to the surface during curing. Engineering judgment must be exercised during field operations, as laboratory conditions vary significantly from field conditions. During compaction, it may be necessary to dry the soil back from the level of moisture required for mellowing, but good practice is to compact at as high moisture content as possible and still achieve the target density.

TxDOT recommends the use of lime in a single application. Lime, soil, and water should be thoroughly mixed to facilitate the consumption of sulfates in the soil. Lime should be applied preferably as slurry to facilitate mixing and avoid formation of unreacted lime pockets. Light

compaction will help seal the mixture and reduce oxidation of lime. The soil should be remixed after mellowing and before final compaction.

Alternative Treatments

Soils with soluble sulfate levels above 8,000 ppm are deemed potentially problematic in terms of ettringite formation. The extent of expansion or other deleterious reactions depends on several factors discussed earlier in this report. Successful stabilization of these soils is challenging and treatment should be performed with utmost caution combined with proper engineering judgment. Strategies given below are adapted from recommendations by TxDOT *(41)* in treating soils with high potential for ettringite formation.

Replace High Sulfate Soils

High sulfate soils along the alignment can be removed and replaced with borrow soils containing acceptable sulfate contents. This strategy may be ineffective if there are chances for sulfate ion migration from outside areas, and this potential must be evaluated before selecting the replacement option. As discussed in the section "Risk Identification," sulfate ion migration may occur due to a fluctuation in the ground water table, flow or lateral migration from a sulfate-bearing seam due to gravity potential, or migration from subsurface layers due to capillary suction gradients.

Blending Low Sulfate Materials

Another alternative for stabilizing high sulfate soils is to dilute the sulfate concentration in soil by blending it with soil containing no sulfates or acceptably low levels of sulfate. This process may help reduce/neutralize the sulfate concentrations to acceptable levels. Blending non-plastic and granular materials like sand and gravel with plastic clays can reduce the plasticity index (PI) and swell properties of the blend and improves their strength properties. Reduction of soil Plasticity Index (PI) may also help eliminate the need for stabilization of these sulfate bearing soils. TxDOT *(41)* recommends the use of potential vertical rise (PVR) measurements of the mixture in accordance with Tex-124 E to select the amount of granular materials to be added to the soil. This is done by varying the amount of granular material blended into sulfate rich soil so that the PVR value reduces to 1 inch or less. If the blend satisfies the strength requirements or can be adjusted by varying design parameters and if the blend has PVR value of less than 1 inch, it may be used directly in pavement sections without further treatment *(41)*. Maintaining proper mixing and moisture density requirements and increased density control testing should be followed in construction to ensure uniformity of these mixtures. The Texas approach of establishing an acceptable blend of soils using PVR was developed based on blending soils whose swell potential is based on moisture adsorption of clay minerals and not on expansive mineral growth.

In soil blends where stabilization is needed, the goal of blending is to neutralize the effective sulfate concentration in high sulfate soils. A three dimensional expansion of below 2 percent after lime treatment, which is considered acceptable for expansive soils after lime treatment by National Lime Association, can be considered as the permissible volume expansion for the lime treated sulfate bearing soil-blends (*44*). Once again, it should be noted that the method does not attempt to mimic outside migration of sulfate-bearing water. This must be considered separately as discussed in the previous section.

The issues related to expansion of matrix are complex and deal with the pressure of the expanding matrix and the level of anisotropy of the expansion process. Whereas a certain percentage of vertical expansion may be tolerable, if that expansion is translated laterally over the expanses we deal with in pavements, then the accumulation of lateral movement due to only a small strain can be problematic. Consider for example the projection of only 1 percent strain accumulated over 100 feet of pavement. This is 1 foot of movement. Such accumulation of lateral strain is probably the reason for the serpentine-type meandering ridges we see in stabilized layers of sulfate-bearing soils such as shown in Figure 5a. Figure 5a shows transverse and longitudinal ridges due to accumulation of lateral strain in a lime treated, high sulfate soil. In this case distress is noted during the curing process. Note the bituminous seal over the curing subbase. In Figure 5b, the accumulation of lateral strain has caused a passive earth pressure failure as one part of the stabilized, sulfate-bearing soil is thrust over the other part.

Figure 5. (a) Evidence of failures due to the accumulation of lateral strain due to sulfate-induced expansion *(43)* and (b) accumulation of considerable lateral strain resulting in shear failure in lime-treated high sulfate soil layer (Photograph courtesy of Dr. Thomas Petry).

Use of Additives

Research is in progress to identify the efficacy of the use of certain additives such as soluble silica (normally in the form of fly ash/lime blends or ground granulated blast furnace slag) in reducing the risk associated with ettringite formation in stabilized soils *(17, 41).* The possible mechanisms responsible for the efficacy of using additives with high soluble silica content are discussed in the section entitled "Misconception Regarding Ettringite Formation." Since these are additives external to the soil system, their effectiveness should be evaluated for the specific soil prior to field application. Alternatives like extended mellowing and blending of soils can be used in combination with additives to arrive at an effective strategy for use in these soils. Again, these modified mixes should satisfy all required engineering properties including strength, shrink/swell, sulfate levels, and durability properties for acceptability in field application.

SULFUR CHARACTERIZATION IN SOILS

Sulfur is found in natural soils as sulfide minerals like pyrites, marcasite, and greigite and in sulfate forms like gypsum, anhydrite, barite, and jarosite (*25, 30*). The presence of these minerals alone does not make the soil problematic, as their dissolution properties and the existing environmental conditions contribute to the release of sulfur into solution (*25*). Sulfate minerals like barite and celestite, for example, are resistant to normal weathering conditions and do not contribute soluble sulfates to ground water. Organic sulfur is also relatively stable due to its hydrophobic nature and does not provide sulfur in ground water unless the organic matter is completely decomposed *(30).* Identifying sulfur species that can provide soluble sulfates is therefore important in selecting an effective test method to identify problematic soils. Although some sulfur-bearing minerals, like gypsum and pyrite, can easily be identified by visual observation, a quantitative estimation using this technique is not easy. Quantification of sulfur species in soils requires mineralogical and chemical analyses. Mineralogical techniques, such as X-ray diffraction (XRD), are good tools for use in mineral identification; but quantification based on XRD, for example, may not be accurate and may be impossible at low levels (e.g., less than about 5 percent). Therefore, either chemical identification techniques or more precise methods of quantification of compounds are required. A complete sulfur characterization requires identification of different sulfur species existing in soils. Sulfur in soils is assessed under four main categories:

1. Water soluble sulfates,
2. Acid soluble sulfates,
3. Total reduced sulfur, and
4. Total sulfur.

Water Soluble Sulfates

To identify water soluble sulfates in soil a representative air dried soil sample is typically used. This sample is sieved, typically using a No. 40 sieve, and sulfate ions in soil are extracted using deionized water. Dilution ratios, soil to water ratios, ranging from 1:10 to 1:20 are typically used in sulfate extraction (*4, 25, 45*). The soil and water is then agitated by one of several means such as by shaking in a mechanical shaker or by shaking by hand for about 1 minute every 15 minutes for 1 hour (*45*). The solution is then left idle to allow sulfate salts to dissolve from the soil. The aliquot is then typically centrifuged or filtered using filter paper to remove suspended solid particles. The solution is analyzed to identify the concentration of water soluble sulfates in the soil. The concentration of sulfate ions can be determined by one of three methods, inductively coupled plasma (ICP) atomic emission spectroscopy or by gravimetric or colorimetric methods (*36*). Using water soluble sulfate tests is reasonable, as gypsum is the major sulfur-bearing species in surface soil and its dissolution in the natural water is dependent on soil to water dilution ratio.

Acid Soluble Sulfates

Determining total sulfates in soil involves acid extraction of sulfates. To do this the sulfates are typically partitioned with dilute hydrochloric acid. This method effectively releases sulfates by dissolving gypsum, anhydrite, epsomite, mirabilite, and jarosite but results in partial loss of mono-sulfides. Nondissolution of barite and celestite does not affect the test results, as they are not reactive under most environmental conditions. Acidification of the sample releases

sulfate ions into solution, which is precipitated as barium sulfate when heated to near boiling and after addition of barium chloride *(30)*. The precipitate is filtered, weighed, and dried to quantify sulfates in solution. Sulfides present in soils are not determined by the test, as HCl digestion releases sulfur as H_2S gas. Acid dissolution solublizes most sulfate components in soil and therefore yields the maximum possible sulfate level in soil. This method is an overestimation of the sulfate problem as the pH in lime-treated soils is high (alkaline) and some of the sulfate species mentioned above may not be soluble under those conditions. Again, the test for acid soluble sulfates may be considered a conservative approach for screening purposes. But this method does not differentiate among different sulfur species, which is important in deciding minerals that can provide sulfate ions for ettringite formation.

Total Reduced Sulfur

Reduced sulfur is formed when sulfate-reducing bacteria converts SO_4^{2-} to S^{2-} in anoxic and reducing environments. Aerobic bacterial reduction of organic components in soil creates this reducing environment resulting in formation of reduced sulfur. Reduced sulfur is mostly finely crystalline and impure in nature. H_2S evolved reacts with Fe^{2+} in solution forming a metastable iron sulfide, which is transformed into pyrite during diagenesis. Currently, no standard procedure is available for quantification of total reduced sulfur in soils *(30)*. As reduced sulfur is closely associated with pyrites in soil, indirect methods can be used to determine its concentration. The difference between total iron determined by nitric acid digestion and nonpyritic iron from hydrochloric acid digestion gives the concentration of reduced sulfur in soils. Indirect methods may not be a very accurate all the time, as nitric acid digestion may not completely dissolve all the pyrites, leading to underestimation of reduced sulfur, whereas the oxidation of organic matter can release iron resulting in overestimation of pyrites. If mono-sulfides are present in soils, acid soluble sulfate content may be overestimated as the H_2S gas released is oxidized by atmospheric oxygen present in dilute hydrochloric acid solution. Pyrite concentration will also be overestimated in presence of organic sulfur, elemental sulfur, acid insoluble sulfur, and iron mono-sulfides.

Total Sulfur

Total sulfur in soils is determined by digestion of samples using an oxidizing acid system. A mixture of nitric acid and hydrochloric acid is used as the digestive system *(30)*. Quantification of total sulfur can be done based on gravimetric analysis of precipitated barium sulfate in solution.

METHODS FOR SULFATE QUANTIFICATION IN SOILS

A wide range of test methods are currently used to extract and quantify the amount of sulfates in soils. These methodologies use different sulfate measurement techniques, e.g., chromatography, ICP, gravimetry, colorimetry, etc., and different sample preparation techniques. However, most of the test methods are based on determining water soluble sulfates in the soil. The extraction techniques are often derived from water chemistry analysis and are modified for application in soils. Since the sulfate availability in treated soils is dependent on dissolution and movement of sulfate ions in natural water, an extraction process using water as the solvent is acceptable. Again, the accuracy of sulfate extraction depends on the type and the solubility properties of sulfate minerals present in soils. Therefore, use of as high an extraction ratio of soil

to water as possible in an attempt to solubilize all available sulfate ions is recommended. Although the different test methods follow accepted principles, the procedures and sequences of testing are different, which can significantly influence the end result of the tests (*32*, *36*). A comparison of AASHTO sulfate testing methods to other available test methods is given in Table 2. The following sections outline some of the key steps in different sulfate quantification techniques that are currently in practice: Texas Department of Transportation, Colorado Department of Transportation, and AASHTO T 290.

TxDOT Method—Tex-620-J

Tex-620-J is a gravimetric method based on precipitation of $BaSO_4$ by adding a barium chloride solution as a reagent to the soil-water mixture. Thirty (30) grams of soil passing the 425 μm sieve are mixed with 300 mL of deionized water, giving a dissolution ratio of 1 part soil to 10 parts water for analysis. The mix is then brought to near the boiling point and kept there for 24 hours. The sample is stirred intermittently to disintegrate the sulfate minerals within the soil matrix. At the end of the heating period the sample is filtered through a No. 42 Whatman filter paper and the filtrate collected for further analysis. Ten (10) mL of concentrated HCl is added to 80 mL of the filtered solution *(46)*. This prevents the precipitation of barium carbonate and barium phosphate in solution. Barium chloride is then added and the solution is heated to near 100°C for 10 minutes. The precipitate is then filtered using a 2.5 μm filter paper to collect the precipitated barium sulfate, which is washed and weighed. The results are compared with the weight of natural soil to determine the percent of sulfates in solution.

U.S. Army and Air Force Method

Gravimetric Method

The U.S. Army and Air Force method-TM 5-822-14/AFJMAN 32-1019 *(47)* uses a gravimetric technique to determine the concentration of sulfates in solution. Ten (10) grams of soil is mixed with 300 mL of demineralized water, giving a dilution ratio of 1:30. Fifteen (15) mL of HCL is then added to the mix, which is heated for 1.5 hours. The solution is filtered using Whatman No. 40 filter paper using hot water to facilitate filtration of the solute. $MgCl_2$ is added to 100 mL of the above filtrate until precipitation ends, at which time the solution is filtered with Whatman No. 42 filter paper, again using hot water. One hundred (100) mL of the resulting solution is collected and heated to near the boiling point, and barium chloride is added slowly until there is no further precipitation. Boiling of the solution is continued for 5 minutes, and the solution is left to stand overnight in a warm place. The solution is then filtered using Whatman No. 42 filter paper, and the filtrate is washed with hot water until chlorides are removed. The filter paper is dried and ignited and the residue is weighed to determine the sulfate content.

Turbidimetric Method

Point five (0.5) N ammonium acetate solution with pH 4.2 (from adding dilute HCl) is added to a 10 gram representative sample of air dried soil to form a solution ratio of 1:5 by weight *(47)*. The mixture is boiled for 5 minutes and filtered through Whatman No. 40 filter paper until a clear filtrate is obtained. Ten (10) mL of extracted solution is diluted to 40 mL with distilled water. Two tenths (0.2) of a gram of barium chloride is added, and the mixture is diluted to 50 mL. The solution is stirred for 1 minute and the turbidity measured using a

spectrophotometer at 30 second intervals for 4 minutes. The maximum reading is considered as the turbidity and the value is compared with a standard curve to determine the sulfate ion concentration.

University of Texas Arlington (UTA) Method

The University of Texas Arlington method formulated by Petry *(38)* is also based on gravimetric analysis and uses a dilution ratio of 1:10. Ten (10) grams of soil is dissolved in 100 mL of distilled water, and the solution is shaken for 30 minutes to disintegrate sulfate salts in soil matrix. The mix is then centrifuged at 4,500 rpm for 15 minutes to obtain a clear extract. If the filtrate is not clear, centrifuging is repeated at a higher speed for longer durations until a clear extract is obtained. After centrifugation the solution is filtered through Whatman No. 541 filter paper and diluted to 200 mL with distilled water. The pH of the solution is then adjusted to between 5 and 7 using concentrated HCl, and the filtrate is heated to near the boiling point. Warm $BaCl_2$ is added to the solution until no precipitate is obtained. The precipitate is then digested at 80°-90°C for 12 hours and filtered through a 0.45 μm filter membrane. The precipitate is dried and weighed to determine the sulfate content in soil.

The modified University of Texas Arlington method is similar to the regular UTA method, but with minor changes to improve the efficiency of the test procedure for use in fine-grained soils. The pore size of the filter membrane is reduced to 0.1 μm to improve the efficiency of removal of suspended fine clay particles, as they tend to interfere with precipitated sulfate compounds. This can give a higher sulfate reading during gravimetric analysis *(32)*. Since the average grain size, for fine clays like montmorillonite, is smaller than normal clay particles a longer settling time will be needed for these clays. Hence a centrifugation speed of 14,000 rpm for duration of 30 minutes is used to remove the suspended particles from soil samples.

Ion Chromatography

Ion chromatography (IC) is a good technique by which to measure sulfate concentrations at lower concentrations *(36)*. Sulfate measurement using ion chromatography involves dissolving sulfate compounds and then introducing small quantities of the aliquot into the IC system. The sample is passed through ion exchange columns using inert compounds like polyetheretherketone. The different ions are attracted to the resins in the column and released at different times by the conductivity detectors. The conductivity of the solution is compared with conductivities of standard solutions to quantify the concentration of ions. Harris et al. *(36)* in their comparison of various available sulfate test procedures emphasized the capability of ion chromatography in measuring low sulfate concentrations. The retention time of ions decreases with increase in concentration, and hence for higher concentrations, the dissolution ratio must be increased.

TxDOT Colorimetric Method

Tex 145-E *(45)* determines the sulfate content of soils based on colorimetric techniques. The technique measures the cloudiness of a liquid and correlates that to concentration. Ten (10) g of an air dried soil sample passing the 425 μm sieve is added to 200 mL distilled water in a high-density polyethylene bottle. The solution, having an initial dilution ratio of 1:20, is shaken vigorously for 1 minute to disintegrate the sulfate salts and then left idle for 12 hours. After 12 hours the sample is filtered and 10 mL of the filtrate is collected in a glass vial and used to

calibrate the colorimeter for the initial sulfate level in the solution. A barium chloride tablet is then added to the vial and dissolved completely to precipitate barium sulfate, which appears as turbidity in the solution. The colorimeter is used to measure the turbidity of the solution, which, in turn, provides the sulfate ion concentration in the solution. The dilution ratio must be increased if the sulfate content is above the measuring limit of the colorimeter.

CDOT Colorimetric Method

Like the TxDOT method discussed earlier, the Colorado Department of Transportation (CDOT) method (CP-L 2103) is also based on the principle of colorimetry. The procedures are similar with only minimal differences between the two. One of the differences is the dilution ratio for extracting soluble ions. The TxDOT method *(45)* uses a soil to water dilution of 1:20, whereas CDOT *(48)* recommends a 1:10 dilution at a higher temperature. Since the solubility of sulfates is linearly dependent on the dilution ratio, the TxDOT method will identify a larger value for soluble sulfates than the CDOT method if the sulfate content of the soil is greater than the quantity a 1:10 ratio can solubilize. However, 1:10 dilution ratio is capable of extracting sulfates higher than the threshold levels considered problematic in soils and hence use of this lower dilution is justified on this basis *(4)*. Another difference between the two methods is that the CDOT method recommends the soil water mixture to be left idle for 16 hours at a temperature close to 140°F to dissolve the soluble sulfates, whereas the TxDOT recommends only 12 hour dissolution at room temperature. This difference in procedures is insignificant if gypsum is the major sulfate source in soil, as the temperature dependency of gypsum solubility is insignificant when compared to other calcium sulfate forms like anhydrite and hemi-hydrate at water temperature below boiling conditions *(49, 50)*. Solubility of anhydrite generally decreases with increases in temperature but increases with time *(49)*. Hence using a higher temperature for longer duration might favor the dissolution of anhydrites if any are present.

TxDOT Conductivity Method

Measurement of conductivity of a solution extracted from soil reflects the presence of soluble salts including sulfate concentrations in soil. Tex 146-E *(40)* describes a method of conductivity testing where 5 g of air dried soil passing the 425 μm sieve is placed in solution and the conductivity of the solution is measured. In the first step, 100 mL of distilled water is added to a high-density polyethylene bottle, and the initial conductivity of the water is recorded. The soil sample is placed in the bottle, and the sample is shaken vigorously for 1 minute and the conductivity is measured immediately after that. The sample is kept idle for 12 hours, after which it is shaken vigorously for 1 minute and the conductivity measured. The conductivity of distilled water is subtracted from the two readings in order to determine the conductivity of the soil solution. An initial conductivity reading above 238 μS or a difference of 50 μS between the initial and final readings indicates the presence of excessive soluble ions in solution. If this is the case, the soil should be tested using colorimetric techniques to identify the magnitude of soluble sulfates.

Inductively Coupled Plasma Atomic Emission Spectroscopy

Inductive coupled argon plasma (ICP) atomic emission spectroscopy is an effective method by which to determine the level of sulfate ions in solution. Soil samples are digested or solubilized using appropriate sample preparation methods prior to analysis. Soil samples are made to dissociate in an argon plasma stream producing element-specific spectral lines by the

excited atoms. Recorded spectra are compared with calibration lines and their intensities are converted to concentrations. The method is capable of accurate measurements at low detection limits and good precision is achieved at these low levels *(30)*. High dilution ratios used in testing increases the accuracy and measurement range of ions. The presence of different trace ions can influence the concentration of soluble ions entering into solution, and this needs to be taken in to consideration. This method identifies all elements in the system simultaneously, and the effects of the influence of trace elements are automatically taken into consideration in the analysis.

EVALUATING TECHNIQUES USED IN AASHTO SULFATE TESTING

Gravimetric Techniques

Sulfate concentrations determined from gravimetric procedures are highly variable and are dependent on the original sulfate levels in the soils *(32)*. The gravimetric technique is based on a weight comparison of soil and precipitated barium sulfate, and therefore experimental errors may be high when the amount of available sulfates in the soil is low. Due to the high standard deviation at low concentrations, repeatability of the test is low and significant repetitions are required to get an accurate estimate of sulfate content *(36)*. Barium chloride, if added quickly into the solution, can precipitate out, which affects the precipitation of sulfates in solution. In gravimetric testing, barium sulfate must be precipitated under acidic conditions where barium carbonates and phosphates can also precipitate out in the solution. The solubility of barium sulfate is also greater under acidic conditions, which can also affect the test results. Moreover, co-precipitation of barium sulfate with other ions and encapsulation of suspended colloidal clay fractions in the precipitate can exaggerate the sulfate levels in soils during gravimetric testing. Again, barium sulfates precipitated from cold solutions are finely dispersed and cannot be completely retained on a Whatman No. 42 filter paper *(47)*.

Colorimetric Techniques

Sulfate tests of soils conducted based on colorimetric measurements are accurate at lower sulfate ion concentrations (*36*). Colorimetry is a good, repeatable test when performed under exact standards. The colorimetric technique measures the concentration of ions based on the degree of absorption of radiation of a specific wavelength and assumes the concentration to be proportional to the absorption of light. The relation holds true only at low concentrations and hence the method has a low detection limit. For higher sulfate concentrations in soil, higher dilution ratios need to be used. Solubility of sulfates also increases as water content increases and therefore the use of a higher soil to water dilution ratio when compared to field conditions is effective in extracting all available sulfates for quantification purposes. Sulfate extraction using distilled water may not exactly reflect the dissolution of sulfates in natural water. Mineral dissolution will be slightly higher with distilled water, as the former is devoid of suspended charged ions. Colorimetric measurements also cannot compensate for the dark colors in solution. These may interfere with the measurement of precipitated barium sulfate in solution. Accuracy of measurement therefore depends largely on the effective removal of suspended impurities in solution as absorption of soluble salts can induce a small error in the results *(32)*.

RECOMMENDATIONS TO MODIFY AASHTO TEST METHODS

Sulfate measurements in soil based on the colorimetric technique can be made quickly and economically and are therefore favored over other techniques by most people. But measured sulfate concentrations may vary depending on testing equipment, extraction techniques, and procedures and sequences followed in testing. Therefore it is important to devise a standard and acceptable testing method for identifying the sulfate problem in soils. Among all the available test methods, the CDOT sulfate test procedure CP-L 2103 *(48)* and TxDOT method Tex 145-E *(45),* which are based on colorimetry, are effective methods by which to identify high sulfate soils when performed as specified. Colorimetric determination of sulfate in the form of barium salt is sensitive and, therefore, should only be used when interfering substances are either compensated for or removed *(36).*

To identify sulfate concentrations in soil, AASHTO T 290 uses a 1:3 soil to water extraction ratio (Table 2). But the amount of soluble sulfates that can be dissolved using this extraction ratio is limited. Gypsum, the major sulfate source in soil, has a limited solubility of 2.58 g/L, whereas the solubility of $NaSO_4$ and $MgSO_4$ in water are 240 g/L and 180 g/L, respectively. If $NaSO_4$ and $MgSO_4$ are present in significant quantities in soil, then the extraction of all the sulfate ions is possible with a 1:3 extraction ratio *(30).* One mole of gypsum has a mass of 172 g and contains 96 g of SO_4. Therefore based on solubility of gypsum, 2.58 g of gypsum in natural water can release only 1.44 g (1,440 ppm) of sulfate ions per liter of water *(25).* Therefore, if we consider 100 g of dry soil contains gypsum as a sulfate source and if we add 300 g of H_2O to facilitate extraction of sulfates in soil, the amount of water soluble sulfates that can be solubilized with this quantity of water is given in equation [5].

$$300\ g\ H_2O \times \frac{2.58\ g\ Gypsum}{1000\ g\ H_2O} \times \frac{96\ g\ SO_4}{1\ mole\ \ Gypsum} \times \frac{1\ mole\ Gypsum}{172\ g\ Gypsum} = 0.432\ g\ SO_4 \qquad \ldots(5)$$

Therefore, if gypsum is the sole source of sulfates in soil, the maximum amount of sulfates that can be extracted using this dilution ratio is 4,320 ppm. However, in natural soils, replenishment of water due to precipitation and ground water flow can result in progressive dissolution of gypsum, providing a continuous source of sulfate ions. Therefore, when gypsum is the major sulfate species in soil, partitioning sulfates using a 1:3 dilution ratio may substantially underestimate the sulfate concentrations in soil. To address this problem, a dissolution ratio of 1:10, capable of solublizing 14,400 ppm sulfates, or higher should be used. Equation [5] also emphasizes the fact that, in the soil – calcium-based stabilizer system, it is not likely that using a high level of initial mixing water will place the entire quantity of available sulfates into solution to be consumed in ettringite formation.

Initial sample preparation in AASHTO T 290 involves breaking down of aggregations of soil particles using a pulverizing apparatus so that the soil fraction used in testing passes through a 2 mm sieve (No. 10 sieve). The size of particles used in testing is critical in determining the time required to dissolve the available sulfates from the soil. Fine-grained gypsum, if present, can dissolve faster and release ions faster than coarse-grained fractions in soil *(36).* The AASHTO T 290 colorimetric method does not mention dissolution time as a factor in testing. Therefore the larger grain size of particles may reduce the amount of sulfates dissolving into solution in a given time when compared to fine-grained particles. TxDOT recommends *(45)* the use of a soil fraction passing the 4.75 mm (No. 4) sieve, which is further processed to pass

through the 425 μm (No. 40) sieve for testing purposes. The method also recommends that the samples are left idle for 12 hours to facilitate dissolution of most of the available sulfates in soil.

Furthermore, method AASHTO T 290 recommends centrifuging the sample followed by filtration using a 0.45 μm membrane filter to remove suspended impurities. The AASHTO T 290 colorimetric method also uses a significant amount of chemical reagents including nitric acid, hydrochloric acid, and perchloric acid to remove silica and uses glycerin and sodium chloride to stabilize the suspension and minimize interference during testing. The TxDOT 145 E *(45)* method, on the other hand, recommends the use of water alone in extracting sulfates from soil and using a fine porosity filter paper to remove suspended particles. The efficacy of using these simple techniques for the colorimeter used in AASHTO test methods needs to be further evaluated based on laboratory investigations with known sulfate concentrations. A comparison of available test methods for measuring sulfate concentrations in soil is given in table 2.

Table 2. Comparison of available test methods for measuring sulfate concentrations in soil.

Test Methods	Tex-620-J	Tex-146	CL-2103	Tex-145	AASHTO T 290-95 (method A)	AASHTO T 290-95 (method B)
Mechanism	Gravimetric	Conductivity	Colorimetry	Colorimetry	Gravimetric	Colorimetry
Sulfate identification	Precipitated $BaSO_4$	A proxy for sulfate content	Turbidity due to $BaSO_4$ precipitate	Turbidity due to $BaSO_4$ precipitate	Precipitated $BaSO_4$	Turbidity due to $BaSO_4$ precipitate
Particle size	Passing 425 µm sieve (No. 40 sieve)	Passing 425 µm sieve (No. 40 sieve)	Passing 425 µm sieve (No. 40 sieve)	Passing 425 µm sieve (No. 40 sieve)	Passing 2 mm (No. 10) sieve	Passing 2 mm (No. 10) sieve
Dilution ratio	1:10	1:20	1:10	1:20	1:3	1:3
Significant difference	Soil, distilled water, and reactants heated to near boiling	Distilled water used in measuring conductivity	Distilled water and $BaCl_2$ used, dissolution time of 16 hr @140°F	Distilled water and $BaCl_2$ used, no heat treatment, dissolution time of 12 hr	Soil, distilled water, and reactants heated to near boiling	No heat treatment, $BaCl_2$ used with reagents NaCl and stabilizing solution
Effects	Boiling cause interference from other soil constituents	Unable to distinguish different ionic types	Favors dissolution of anhydrides along with gypsum	Only soluble minerals go into solution	Possible interference from other soil constituents	Only soluble minerals go into solution
Remarks	Accuracy dependent on sample size, addition and treatment of $BaCl_2$, operator skills, and temperature	Good screening tool, but overestimates sulfate content in soils due to other salts present		Good and repeatable if performed under exact conditions		

CONCLUSIONS

Ettringite Formation

- Sulfate-bearing soils stabilized with calcium-based stabilizers may form ettringite and/or thaumasite if thermodynamic conditions are favorable.
- In order to form ettringite, a source of calcium, a source of aluminum, a source of sulfates, and water are required. The pH of the system must be maintained at about 10.5 or higher, according to most literature, although some literature confirms the stability of ettrigite at much lower pH values. Thaumasite is comprised of calcium, silica, and carbonates and is usually considered to form due to isostructural substitution of silica and carbonate in the ettringite crystal template. Periods of relatively low temperature are required for thaumasite to form, and its formation is normally associated with a reduction in volume compared to ettringite and a weakening of the structure.
- Molar volume calculations, based on cement chemistry, demonstrate that when the only water available for ettringite crystal growth is water within the system, the formation of ettringite from the constituents (tricalcium aluminate, gypsum, and water) results in a negative volume change, but when the source of water is external to the system, then the molar volume of ettringite is 137 percent greater than that of the constituents (tricalcium aluminate and gypsum).
- Stoichiometrics demonstrate that the water used in construction and during mellowing is far to little to dissolve all of the sulfate contained in the amount of gypsum required to provide a level of as low as 2,000 ppm water soluble sulfate, the quantity specified by many as a lower limit associated with deleterious sulfate-induced damage.
- The efficacy of using as much water as possible during the mellowing process and of extending the mellowing period as much as possible is validated, not based on the ability of the water of construction to solubilize all sulfates, but based on the probability of more water forming more and better dispersed ettringite nucleation sites. These dispersed sites with high surface area would tend to react with sulfate ions more rapidly and via a more homogeneous distribution of nucleation sites promote a higher probability that the ettringite crystals could be accommodated within the void structure of the system rather than forming larger crystal agglomerates that cannot be accommodated by voids. This may be considered somewhat analogous to the dispersion of pozzolans (sources of soluble silica) in concrete to counter alkali-silica reactions. In this case the idea is to disperse a large number of fine silica particles through the concrete matrix so there will not a sufficient amount of alkali metal ions to cause complete reactions of all particles and expansion will be reduced and not localized sites with high expansion will develop.

Sources of Sulfates

- Soluble sulfates in soils primarily occur in the form of gypsum, but other forms can occur as well with variable solubilities. In addition to evaporates such as gypsum, pyritic sulfur can oxidize to form gypsum, and this form of sulfate must be considered.

Defining Problematic Sulfate Levels

- Thermodynamic phase diagrams as well as analytical methods including differential scanning calorimetry (DSC) have proven to be useful in defining the threshold levels of soluble sulfate in the soil that supports the growth of quantities of ettringite that cause unacceptable levels of damage.
- Thermodynamic phase diagrams and DSC measurements on a variety of soils has demonstrated that different soils with different mineralogical compositions have different sensitivities to ettringite/thaumasite formation, and this belies the idea of a common threshold of soluble sulfates that is responsible for sulfate-induced damage in all soils treated with calcium-based stabilizers.
- Phase diagrams and DSC measurements have, however, validated the empirically based threshold of about 3,000 ppm and that below this level of soluble sulfates, deleterious sulfate-induced damage is not significant. However, this assumes that sulfate ions do not migrate into the treated layers after construction.

Treating Sulfate Rich Soils

- When the soluble sulfate content of the soil is less than about 3,000 ppm, then traditional construction techniques should be acceptable. However, if any sulfate content is measured, it is important to use as much water as possible in the mixing and mellowing period in an attempt to form as much ettrigite as possible during mellowing.
- If the soluble sulfate content is greater than about 3,000 ppm, special steps must be taken during construction. It is not possible to provide enough water to solubilize all sulfates, but it is important to use as much water as possible and to mix as thoroughly as possible in order to homogeneously distribute sulfates and force the formation of well-dispersed ettringite nucleation sites. This will promote a formation of ettringite early and uniformly in the pre-compacted treated soil.
- It is also important to extend the mellowing period as long as possible to allow as much crystal growth of ettringite as possible in the mellowing period. This may require adding additional water several times during the mellowing period to keep the moisture level high and to continue to solubilize sulfate. Sulfate in the treated soils used to form ettringite during mellowing will not be available for forming ettringite after compaction.
- Soils with soluble sulfate contents in excess of about 8,000 ppm may not be able to be successfully treated. However, it is possible to use additives to force the formation of minerals with lower Gibbs free energy. One such additive that has proven successful is soluble silica. A silica rich environment tends to favor nonswelling calcium-alumino-silicate minerals other than ettringite. But the efficacy has to be confirmed by laboratory testing of soil in question prior to field applications.

Evaluation of Sulfate Test Methods

Sulfate content in soils should be determined prior to construction, and techniques outlined for specific sulfate levels should be used to reduce the risk of post-compaction ettringite

formation. Colorimetric techniques are fast and economical when compared to other available methods for measuring sulfate concentrations in soil. The efficacy of method AASHTO T 290 may be improved by incorporating a few changes in techniques used for sample preparation. These changes include.

- The rate of dissolution of gypsum is directly related to the surface area of particles. The AASHTO method recommends using soil particles passing the 2 mm (No. 10) sieve for sulfate testing. Further reducing the size of soil particles used in testing will facilitate a faster and more complete dissolution of available sulfates in soil. Hence it is recommended that the soil fraction passing the 4.75 mm (No. 4) sieve be crushed to a particle size passing the 425 μm (No. 40) sieve before sulfate extraction with water.
- Solubility of sulfate particles in soil is linearly dependent on the dilution ratio used in extraction. The AASHTO method recommends a 1:3 soil to water dilution ratio for sulfate extraction. Use of a lower soil to water extraction ratio may underestimate the amount of available sulfates in the soil, as the solubility is limited by saturation conditions of the solution. Hence a minimum 1:10 dilution ratio should be used to extract available sulfates from the soil.
- Dissolution of minerals is time dependent. Although a higher dilution ratio and a smaller particle size can enhance sulfate release into solution, time required for complete dissolution depends on the concentration of sulfates in the soil. Based on satisfactory performance of sulfate test methods followed by TxDOT and CDOT, it is recommended that the soil-water mix be left idle for at least 12 hours prior to filtration to facilitate complete dissolution of sulfates in soil. Since gypsum is the major sulfate source in soil, as the temperature dependency of gypsum solubility is insignificant when compared to other calcium sulfate forms like anhydrite and hemi-hydrate, the extraction may be performed at standard room conditions. The effect of adding chemical reagents to stabilize the suspension and minimize interference during AASHTO testing are not considered to be a problem, but a complete assessment of their effects would require a laboratory sensitivity study.

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Standard Recommended Practice for

Stabilization of Sulfate-Bearing Subgrade Soils

AASHTO Designation: R Draft (2008)

American Association of State Highway and Transportation Officials
444 North Capitol Street N.W., Suite 249
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INTRODUCTION

In-place treatment of clay-rich soils using calcium-based stabilizers can address strength deficiencies, moisture instability, and problematic shrink/swell behavior. During stabilization, distresses can occur seemingly at random when soils rich in sulfate-bearing minerals are encountered. Stabilization of sulfate-rich soils with lime, Portland cement, or fly ash may lead to the formation of expansive minerals such as ettringite and/or thaumasite, which can cause distress in the pavement structures due to the volume change associated with their formation. The distress mechanisms associated with the precipitation of these minerals are complex and may vary among soils due to differences in soil composition, construction methods, availability of water, ion migration, and how these minerals grow within the void structure in stabilized layers.

The economic benefits of stabilization of these problematic soils are sufficient to require engineers to consider the use of stabilizers such as lime, Portland cement, and fly ash. However, the engineer must also understand and be able to identify when conditions warrant restraint in using certain chemical stabilizers and when or if the risk associated with their use is tolerable. This recommended practice provides guidance on when and how to use lime as a stabilizer with a tolerable level of risk when sulfate-bearing soils are encountered.

SCOPE

This recommended practice details the basic mechanism of ettringite formation in soil; describes methods to assess the risk potential before stabilization; outlines methods to follow during stabilization; and details the use of different techniques to reduce the risk involved in construction operations. Because experience in stabilizing sulfate-bearing soils has been primarily with lime treatment of such soils, this recommended practice relies most heavily on that experience, but also addresses the differences related to the impact of the different chemical compositions of stabilizers other than lime on the stabilizer-soil reactions.

This standard may involve hazardous materials, operations and equipments. This standard does not address all the safety problems associated with their use. It is the duty and responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

REFERENCED DOCUMENTS

AASHTO Standards:

- M 145, Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes
- R 13, Conducting Geotechnical Subsurface Investigations
- T 248, Reducing Samples of Aggregate to Testing Size
- T 290, Determining Water-Soluble Sulfate Ion Content in Soil
- R(Draft), New AASHTO standard for subgrade stabilization

ASTM Standards:

- D 3877, Standard Test Method for One-Dimensional Expansion, Shrinkage, and Uplift Pressure of Soil-Lime Mixtures

Non-AASHTO/ASTM Standards:

- TEX 146-E, Conductivity Test for Field Detection of Sulfates in Soil
- TEX 124-E, Determining Potential Vertical Rise

TERMINOLOGY

- Mole - Gram atomic or gram molecular weight
- Reactant - Component that participates in chemical reaction
- Stoichiometry - Quantitative relationship between reactants and products in a chemical reaction
- Limiting reagent - Component of a chemical reaction that determines how far the reaction will proceed; for the current standard this is the reagent with the lowest stoichiometric concentration
- Kinetics - Rate of progress of a chemical reaction
- ppm - Parts per million or milligram per liter (also equivalent to mg/kg); concentration of solute, sulfates, in milligrams per liter of solvent, water
- Threshold sulfate levels - Sulfate concentrations above which significant ettringite growth occurs in soil
- CaO - Calcium oxide
- $Ca(OH)_2$ – Calcium hydroxide
- Al_2O_3 - Alumina
- SO_4^{2-} - Sulfate ions

SIGNIFICANCE AND USE

Even though stabilization improves engineering properties of clay-rich soils, problems can arise when calcium-based stabilizers are used in soils rich in sulfate-bearing minerals. Stabilization of these soils in the presence of excess moisture may lead to the formation of minerals such as ettringite and/or thaumasite and can cause distress in or even destruction of pavement structures due to heaving. Engineers are required to understand the fundamental mechanisms associated with the formation of these minerals in soils in order to assess the efficacy of using calcium-based stabilizers in treating sulfate-bearing soils. This recommended practice provides the pertinent information needed for decision making and details the techniques to be followed in successfully modifying or stabilizing sulfate-bearing soils. Modification or stabilization of sulfate-bearing soils requires a clear understanding of the following:

Mechanisms of precipitation of ettringite in soils and the extent of expansion associated with the mineral formations.

Techniques to be followed in risk assessment of soils prior to soil exploration and sampling.

Techniques for quantifying sulfate concentrations in soil.

Level of risk associated with lime stabilization based on the concentration of available sulfates in the soil.

Amelioration strategies for successfully stabilizing sulfate-bearing soils.

Construction techniques to be followed to reduce the extent of deleterious reactions associated with precipitation of ettringite in lime treated soils.

Quality Assurance tests to be conducted during the construction process.

This recommended practice is not meant to be an inflexible description of treatments or investigation requirements, but an outline of processes that may be effective in successfully stabilizing sulfate-bearing soils. Other techniques may be applied as appropriate.

BACKGROUND

Sulfate-induced distress can occur in pavement sections due to the formation of hydrous calcium aluminum sulfate minerals, ettringite and thaumasite, that can cause volumetric transformations in stabilized layers. The formation of ettringite is typically accompanied by expansive reactions, whereas thaumasite formation often results in a softening of the stabilized soil matrix and a reduction in the load-carrying capacity of pavement layers.

Ettringite precipitates in high-pH environments with high activities of Ca^{2+}, $Al_{(aq)}$, and SO_4^{2-}. The precipitation of thaumasite can be sustained in the matrix at low-temperature conditions, generally considered below 15°C, with intensive carbonation and with available sources of soluble silica. Under these conditions, soluble silica is mostly derived from the decomposition of C-S-H formed during cementing reactions in treated soils. Unreacted calcium silicates in cement or soluble silica from clays or microcrystalline silt fractions in soil can also provide the required quantity of silicates in treated soils.

Constituents needed to form ettringite are made available partly from the additive used in stabilization and partly from the soil minerals. Calcium ions are provided by the stabilizer: lime, Portland cement, or fly ash. Aluminum is supplied by dissolution of clay minerals and other soluble aluminum-bearing phases in soil, and sulfates are supplied by dissolution of gypsum, oxidation of sulfide, or ion migration of

sulfate ions as water diffuses through the matrix. For one mole of ettringite to form, 6 moles of CaO, 1 mole of Al_2O_3, 3 moles of SO_4^{2-}, and 32 moles of water are required.

The amount of ettringite that precipitates in soils may vary depending on the availability of stoichiometric proportions of the components needed for formation.

The extent of swell or distress associated with these mineral precipitations may vary depending on factors such as the strength of the stabilized soil matrix and the spatial arrangement of ettringite and/or thaumasite crystals within the matrix. Observed volume changes may also vary depending on whether the source of the components used in mineral precipitation are external or internal to the matrix.

The presence of water is critical to the formation of ettringite and/or thaumasite, and the measurable expansion in stabilized layers may vary with the source of water consumed in mineral formation. If ettringite forms solely from water added during initial treatment of the soil, then the formation of ettringite may cause a volumetric shrinkage of the matrix. This is because the molar volume of ettringite is less than that of the stoichiometric quantities of constituents required for it for form (i.e., CaO, Al_2O_3, SO_4, and H_2O). However, when external water migrates into the stabilized soil to participate in the formation of ettringite, a considerable volume increase of up to 1.37 times the initial volume of the reactants can occur. This is because the molar volume of ettringite is 1.37 times greater than the molar volume of the constituents other than water (i.e., CaO, Al_2O_3, and SO_4). The source of this external water can be surface infiltration, lateral movement, capillary movement, or moisture diffusion under a temperature or partial pressure gradient.

Certain misconceptions that exist among practitioners regarding stabilization of sulfate-bearing soils are addressed below.

Because lime is most often used to treat clay soils, it is often considered to be the only stabilizer that causes ettringite formation in sulfate-bearing soils. But most calcium-based stabilizers, including lime, Portland cement, and class C fly ash have the potential to produce free lime and raise the pH of the system to a level that can solubilize alumina and maintain a high enough pH to support the formation of ettringite. The lime derived from Portland cement or class C fly ash is produced primarily during the hydration of calcium silicates. Therefore, any calcium-based stabilizer that can support a high pH environment can cause sulfate-induced distress.

Sulfate-resistant cement is believed to be effective in reducing ettringite formation in soils. A limited concentration of alumina in sulfate-resistant cement probably has a

very limited effect on ettringite formation. This is because a virtually unlimited source of aluminum is available from the clay soil in most systems, and if the pH environment is high enough to solubilize alumina then ettringite can form.

Based on the resources needed for ettringite formation, it is logical to believe that low-calcium fly ash, if used alone in stabilization, would not contribute to ettringite formation. However, being a pozzolan with little or no calcium oxide, class F fly ash typically requires activators like lime or Portland cement to initiate stabilization reactions. Hence stabilization of soil using low-calcium fly ash may also cause deleterious mineral formations.

MECHANISMS INVOLVED

If the stoichiometric proportions, detailed in Section 5.3, of constituents needed for ettringite formation are available in solution, the kinetics of precipitation is rapid. This is the case during hydration of Portland cement. However, other practical issues may impact the rate of ettringite growth in soils.

Ion availability in soils is determined by dissolution of soil minerals, which in turn is affected by the surface area of particles. A larger surface area translates into a higher reactivity. Agglomerates of soil particles formed during early stages of lime application, i.e., after initial flocculation/agglomeration reactions, have a substantially smaller surface area, lower reactivity, when compared to processed Portland cement particles. Soil minerals also have a well-defined crystal structure and are more heterogeneous when compared to Portland cement. Hence the extent of ions available in solution is limited in stabilized soils when compared to hydrated cement pastes. Therefore, it is highly improbable for significant concentrations of ettringite to form rapidly, within minutes or hours, in stabilized soils as they do in the hydration of Portland cement.

The limited solubility of gypsum, the major source of sulfates in most soils, in the water available for mixing and compaction also restricts the rate of formation of ettringite and the quantity of ettringite that forms during the early hydration periods.

Ettringite precipitation/crystal growth may occur at the solid-solution interface or through a solution mechanism, where the products precipitate randomly from the liquid phase. The precipitation conditions may vary depending on geo-chemical conditions existing in the matrix.

Since it is likely that only small amounts of ettringite will form during the initial hydration periods, it is highly probable that these precipitation locations may act as nucleation sites for future crystal growth when limiting reagents become available.

Observed distortion or heaving in pavement layers may either be due to precipitation and anisotropic crystal growth of ettringite in the matrix or due to water absorption by ettringite crystals resulting of further expansion of these crystals. An arbitrary combination of these mechanisms may also initiate heaving in stabilized layers.

The extent of measurable expansion depends on the time and location of mineral formation and also on how well the minerals are accommodated inside voids in stabilized layers. The source of water consumed in the formation of ettringite is also critical in determining the extent of expansion, as detailed in Section 5.6.

It is possible for a pavement layer containing ettringite to expand and heave but also retain a stiff and strong structure. On the other hand the expansion may cause the layer to fracture due to the internal stresses that develop.

Distribution of nucleation sites created during the initial stabilization period may also influence the extent of damage in soils. A uniform distribution of nucleation sites may promote more rapid and uniform mineral growth causing limited expansion, whereas a random distribution of nucleation sites resulting in a high concentration of crystal growth can create non-uniform or localized expansions that are significant.

RISK IDENTIFICATION

Risk assessment prior to soil exploration can be used to develop effective soil exploration techniques and sampling protocols, to define the scale of testing needed, and to help define the steps to be taken to limit deleterious expansions during construction. Identification of problematic locations is based on careful consideration of certain selected features as listed and discussed in the following sections and subsections.

Soils characteristics including clay content, carbonate content and sulfate content can impact the potential for development of deleterious reactions, or "hot spots," along the roadway. Identification of areas with high concentrations of these constituents needed to form ettringite will help provide an initial estimate of risk associated with lime stabilization.

U.S. Geological Survey maps of the location should be used as a part of risk assessment to identify the soil formations that overlap the alignment of the roadway. These soil formations can be identified by overlaying the alignment drawings of the project on appropriate geological maps.

Estimates of the soil compositional characteristics can then be determined from pedological profiles, engineering property databases, and aerial photographs from the

National Resources Soil Conservation Service (NRSCS) county soil survey reports.

Clay-size particles are generally the most reactive minerals in soils, due partially to their very high surface area. Clay minerals are also the major source for aluminum needed for ettringite formation. Therefore, identifying soils carrying higher clay contents, based on AASHTO M 145, will help define soils with a higher reactivity when treated with lime.

Identifying the soil types based on soil classification can further be used to refine the locations with the potential for ettringite formation. Matrix suction in soil can draw water into the pavement layers, which can cause sulfate movement in and through the soil and can also aid in the supply of external water for the formation of ettringite. Low hydraulic conductivity, high capillarity, and high suction properties can create sulfate reservoirs in subgrade sections that need to be considered as part of risk assessment. These properties are typically associated with clays and shales.

Besides clay soils, additional sources for alumina in soils include feldspars, oxy-hydroxides, and amorphous forms of alumina. Identifying the relative concentration of reactive soil minerals from soil survey reports will help target problematic locations along the alignment.

Information acquired from maps and soil characteristics, as discussed in the earlier sections, should be used only for preliminary identification of potentially problematic areas. Physical testing for sulfates based on AASHTO T 290 or equivalent is required to verify the presence of sulfates and to quantify their concentrations.

Climatic characteristics should be considered in deciding the depth of sampling and testing intervals in problematic locations. In arid areas, sulfate deposits are likely to be found in near-surface environments due to evaporation processes, whereas water infiltration can carry sulfate ions into deeper strata in wet and humid areas, which can be transferred back to the surface due to capillary action.

Drainage characteristics of the location can influence the redistribution of sulfates in soil and should be considered during risk assessment and while developing sampling plans.

Topographic slope influences hydrologic processes, including overland flow and subsurface flow and therefore has a strong influence on residual sulfate concentrations in soils. Slopes shaped by erosion can move sulfate ions to locations far from the parent source and into pavement sections where these flow channels are intercepted. These locations, if present, should be identified as a part of risk assessment and included as potential sampling sites.

In rolling terrains, significant sulfate concentrations may accumulate in low-lying areas due to surface runoff, creating sulfate hot spots in the soil. The frequency of

sampling in these locations should be increased in accordance with recommendations in Section 8.1.4.

Water from surface runoff, rainfall, fluctuations in water table, surface infiltration, or capillary suction can cause dissolution of sulfate minerals in soil and also become the source of water needed for ettringite formation after lime treatment. Hence chances for water movement should be taken into account as a part of risk assessment.

Visual inspection should be performed along the project alignment and at borrow sources, if used, to locate any visible sulfate crystals. Gypsum can exist in soils as visible diamond-like crystals along constructed slopes and excavated areas or in top soil as white powdery efflorescence especially during dry seasons.

Sulfate heaves sometimes occur in small, localized areas and along isolated locations within the stabilized section. This is partly due to spatial heterogeneity of sulfate distribution in soil as they often exist in seams and stratified pockets in the soil. Therefore, field conductivity measurements should be performed following TEX 146-E or equivalent test methods as a part of field investigation to identify isolated sulfate pockets along the alignment.

Special care should be taken in locations where engineering techniques can invert the natural stratigraphy of the soil and expose subsurface layers to the surface for lime treatment. Soil horizons that are exposed during grading operations must be carefully evaluated as such sections may yield sulfate crystals or may expose minerals that can change upon exposure to free oxygen. This is the case when pyrite oxidizes to form gypsum. Sulfate testing in these locations should follow the protocol in Section 8.1.5.

SULFATE QUANTIFICATION AND THRESHOLD SULFATE LEVELS

Due to spatial heterogeneity of sulfate distributions in soil, identifying the sampling locations for sulfate testing is a critically important step.

Sources for sulfates in stabilized soil vary from surface bedrocks and sulfate salts present in soil to oxidation of sulfide groups and ion migration with water movement from underlying soils. Because of the heterogeneity in the distribution of sulfates within the soil, it is imperative to consider soil geology (topography, stratigraphy, pedology, and mineralogy), soil chemistry, and climatic conditions in developing a sampling plan, as detailed in Section 7, for the detection of sulfates.

Observations from conductivity testing as detailed in Section 7.7 can be used in targeting sampling locations along the alignment.

Sampling depths and testing intervals should be adjusted depending on climatic conditions in the project location as detailed in section 7.3.

For soil investigations in sulfate-laden soils, the minimum recommended frequency for drilling and logging test holes is every 500 feet on alternating sides of the width of the road bed.

For cut sections, test holes should be drilled to a depth corresponding to the final grade elevation of the subgrade in order to capture samples for sulfate testing.

Sample collection and storage should be done following AASHTO R 13.

Representative fractions should be selected following AASHTO T 248.

Test method AASHTO T 290 (modified test method), or equivalent, should be followed in testing sulfate levels in soil.

Sulfate contents are generally expressed either in ppm (parts per million), or in percent dry weight of soil (mg/kg).

Due to a limited solubility of gypsum in natural water, a minimum soil-to-water dilution ratio of 1 to 10 should be used to extract sulfates from soil.

Preliminary risk assessment for soils can be based on empirical sulfate thresholds in soil and is given in table below:

Risk Involved	Soluble Sulfate Concentrations	
	In Parts Per Million (ppm or mg/kg)	In Percent Dry Weight
Low Risk	Below 3,000	Below 0.3
Moderate Risk	3,000 to 5,000	0.3 to 0.5
Moderate to High Risk	5,000 to 8,000	0.5 to 0.8
High to Unacceptable	Greater than 8,000	Greater than 0.8
Unacceptable Risk	Greater than 10,000	Greater than 1.0

Identifying the exact threshold sulfate level required to form a deleterious quantity of ettringite in a specific soil is difficult and complex as it depends on all the factors described in Section 5.3. The expansion potential of a lime or Portland cement treated sulfate-bearing clay soil is related to the water-soluble sulfate content, the threshold soluble sulfate levels, whether the treatment process will provide a pH level high enough to release alumina from the soil, and whether a sufficient source of water is available for the mineral formation to occur.

The only way to directly assess swell potential at present is to perform a swell test on a stabilized soil to monitor the volume changes over a specified period of time. This can be estimated based on one-dimensional swell test (ASTM D 3877) or a three-dimensional swell test.

For three-dimensional swell tests, test methods detailed in AASHTO standard for stabilization of subgrade soils and base materials to measure volume changes after lime stabilization of expansive soils should be followed. Swell tests may be performed at accelerated temperature to reduce testing time.

However, it is important to consider certain limitations of swell testing. First, swell tests are typically performed over a limited time, normally 30 days or less. This period may not be sufficient for the precipitation/growth of all ettringite crystals that can possibly form in the matrix as these processes are driven by the solution properties and mobilities of the minerals involved, especially alumina. Secondly, the effect of external sulfates, introduced by the water that enters the soil, is not normally considered as part of swell testing. However, this migration of external sulfate concentrations in the water supplied for the swell test can be used to mimic field conditions, but this adds another level of complexity to the predictive process.

CONTROLLING ETTRINGITE FORMATION IN SULFATE-LADEN SOILS: GENERAL

Ettringite formation in soils can be restricted by limiting the availability of one of the reagents needed for its formation. Among the factors detailed in Section 5.3, the only component that is external to the stabilized soil matrix, and that can practically be controlled, is external water, where external water is defined as post-stabilization water or water that was not used in the slaking, mixing, mellowing, or curing operation.

Providing a proper drainage gradient and surface drainage features can limit the movement of external water to a certain extent.

Another action to help control or mitigate post-compaction ettringite formation is to create conditions in the treated soil that favor the rapid formation of ettringite prior to compaction. This can be achieved by as much mixing water as possible in order to solubilize and mobilize sulfates present in the soil. Although the dissolution properties of minerals are a restrictive factor in the formation of significant ettringite concentrations during initial hydration periods, the promotion of as much ettringite formation as possible prior to compaction is a key to producing as many nucleation sites as possible for future growth. This is linked to availability of sufficient water for mixing, an extended mellowing period, and uniformity of mixing.

Sufficient water during the mixing and mellowing period prior to compaction helps ensure that mobile sulfate ions can migrate to points where soluble alumina exists. Under ideal conditions, ettringite is precipitated along these locations which may act as nucleation sites where additional crystal growth may occur when limiting reagents become available. Providing plenty of mixing water may also

promote additional mineral growth during the extended mixing/mellowing period.

Homogeneous mixing of soils after mellowing helps to improve distribution of the newly created nucleation sites. Crystal growth during post-compaction periods is now more likely to be dispersed among these many nucleation sites.

A proliferation of small nucleation sites will also consume available sulfate ions in solution rapidly and will form innocuous expansion as the sulfates ions are consumed uniformly over the many sites. An increased number of nucleation sites with high surface areas will aid in the dispersal of sulfate consumption rather than allowing sulfate to be consumed at a few concentrated locations. A random distribution of nucleation sites can create non-uniform or isolated ettringite formation, causing localized expansions in the stabilized layer.

STABILIZATION TECHNIQUES FOR SULFATE-LADEN SOILS: LABORATORY TESTING METHODS

An accepted mixture design protocol for soil stabilization with lime, Portland cement, or fly ash mixture design should be followed.

An additional step in the mix design for sulfate-bearing soils is to identify the appropriate amount of water for mixing and to determine the length of the mellowing period.

This can be accomplished by simply mixing as much water as is practical for construction, normally 3 to 5 percent above that determined to be the optimum moisture content for compaction. The water should be added together with the optimum amount of stabilizer determined from mixture design.

Note 1: Consider the time and effort required to reduce the moisture content of mellowed soil to optimum moisture level for compaction purposes while deciding the amount of water to be added to soil for mellowing.

The samples should be well mixed and left idle without compaction for extended periods. Extended mellowing periods of 1, 2, 3, 4, and 5 days are typically used. The higher moisture content is maintained throughout the mellowing period.

At the end of each mellowing period, the soluble sulfate content of the treated soils should be determined following AASHTO T 290 (revised) or equivalent test method.

The length of the mellowing period is ideally the time taken for soluble sulfate content to drop below 3,000 ppm. The combination of mellowing time and moisture content that achieves this goal in the time selected for mellowing.

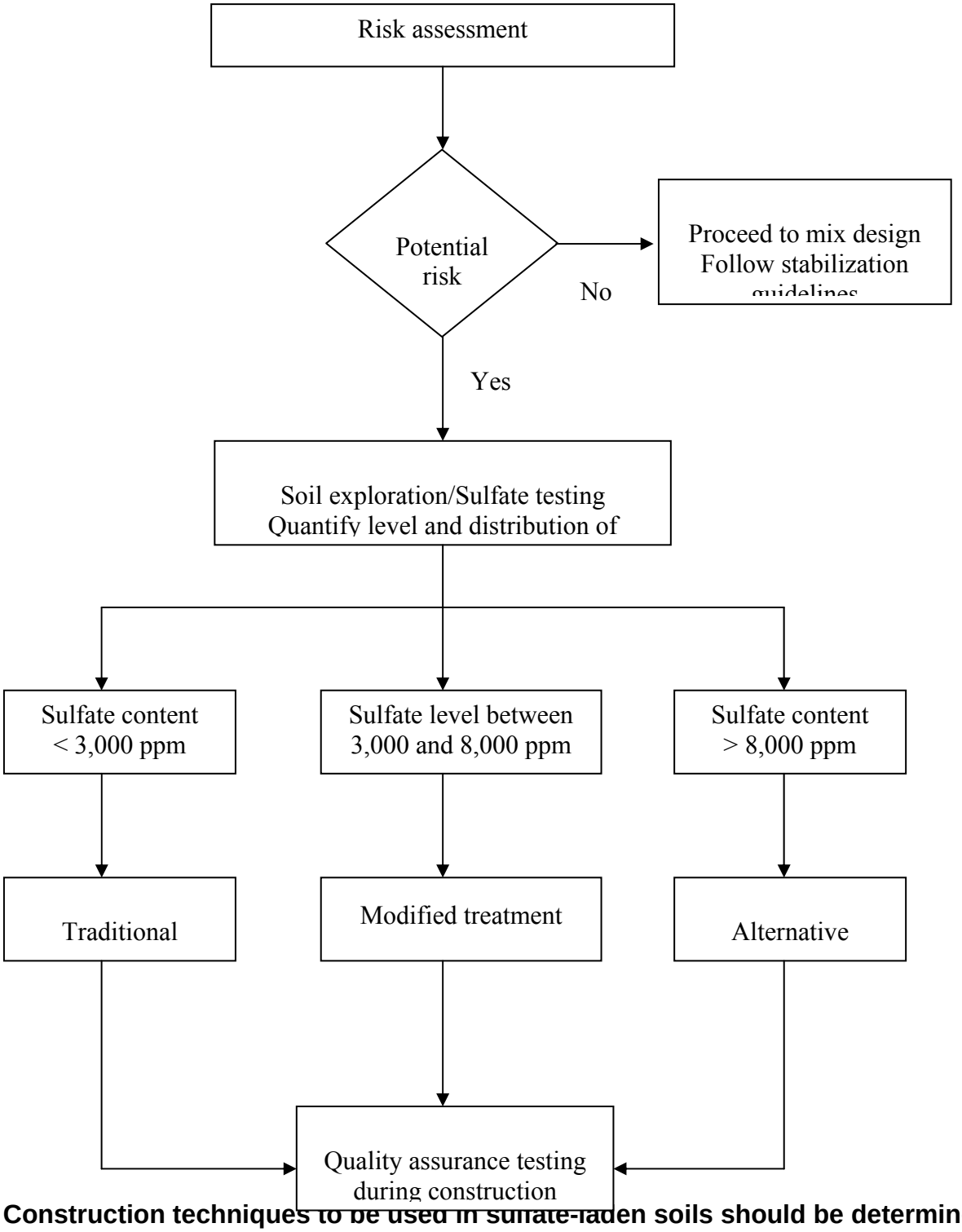
STABILIZATION TECHNIQUES FOR SULFATE-LADEN SOILS: CONSTRUCTION METHODS

A primary and practical engineering approach to reducing the risk of damage due to ettringite formation is to limit the infiltration of water from an outside source into the matrix.

Identification of sulfate sources in the soil is critical in defining treatment alternatives and construction techniques for sulfate-laden soils.

Identification of sulfate pockets is difficult and should be approached based on available resources, previous experiences in the region, data collected from adjoining projects, and other factors. Collecting expert opinions on the project location regarding the location and the depth where sulfate patches normally occur may be effective in locating sulfate hot spots. County soil survey reports may provide valuable information in this direction as described in Section 7.2. Including field conductivity measurements, in accordance with TEX 146-E or equivalent test method, as a part of field investigations may also be an effective method by which to identify sulfate pockets in soils. Risk assessment steps detailed in Sections 7.1 to 7.8 should be followed to identify locations with potential risk for ettringite formation. Measurable sulfate content in soils from these locations should be determined in accordance with Section 8.2. Site specific stabilization techniques, detailed in Section 11.4 through 11.9, should be selected based measured sulfate contents in the soils.

The following flowchart outlines the steps involved in achieving an economical stabilization of sulfate-laden subgrade soil to be used in highway construction.



Construction techniques to be used in sulfate-laden soils should be determined based on measured sulfate concentrations in the soil. Steps detailed in Section 8 should be followed in sulfate quantification and for decision making.

If soluble sulfates are detected, then lime slurry should be used instead of dry lime with adequate amounts of water (typically at least 3 percent above optimum) for mixing. This may help limit the amount of unreacted lime in stabilized soils that can create favorable conditions for post-compaction ettringite formation.

Level and distribution of sulfate concentration should be plotted along the length of the alignment and used to decide the technique to be used in stabilization. These sulfate distribution plots will help identify the locations and depths that require alternative material and pavement designs.

Material design and construction technique options should be decided based on the highest concentrations measured along the selected section.

Due to the high variability in sulfate distribution, selection of more than one construction technique or use of different stabilizers may be required along different sections of the pavement.

If the water-soluble sulfate levels in soil are below 3,000 ppm or 0.3 percent by dry weight of soil, lime stabilization should not be of significant concern. Traditional lime treatment may be followed in these soils. Use the mix design process for lime stabilization as recommended in the new AASHTO (Draft) recommended practice for lime stabilization.

Note 2: ***Sulfate levels below 3,000 ppm does not mean that there is no potential for heaving. Sulfate reactions may still occur in these soils, but detrimental expansions can be limited by using lime slurry, by adequate mixing, and by moisture treatment. Furthremore, if the migration of additonal sulfates can be prevented, the 3,000 ppm level of sulates should not be stoichiometrically sufficient to promote disruptive expansion. This means that a conscienious effort must be made to minimize the potential for post construction water movemenet into the stabilized layers. The source of such water movement may surface infiltration, capillary rise or suction, or lateral movement of a combination of all.***

Soils with soluble sulfate levels between 3,000 ppm (0.3 percent) and 8,000 ppm (0.8 percent) are deemed to be of moderate concern in terms of ettringite formation. Lime stabilization is a possible alternative but must be used with caution. Care must be taken during mix design to identify the proper treatment strategy including the efficacy of an extended mellowing period.

Design lime content and optimum moisture content of the soil should be determined as recommended in new AASHTO (Draft) recommended practice for lime stabilization but using a representative fraction of the sulfate-rich soil. The sample used in all testing should have a representative concentration of sulfates as measured during sulfate tests.

Mellowing time and water content to be used for mellowing should be determined following the procedures detailed in Section 10.

Engineering judgment must be exercised during field operations as the conditions of testing in laboratory vary significantly from field conditions. The target moisture level should be maintained by sprinkling water to counter losses due to evaporation. Light compaction will help seal the mixture and reduce oxidation of lime.

The soluble sulfate content in the soil should be verified at the end of the mellowing period. If the sulfate levels in soil are below problematic levels, remix the lime soil mixture and perform final compaction and placement.

Soils with soluble sulfate levels above 8,000 ppm are deemed to be at a high level of risk for formation of substantial amounts of ettringite resulting in significant damage. Successful stabilization of these soils is challenging, and treatments should be performed with utmost caution combined with proper engineering judgment. Alternative treatment techniques for these soils are discussed below.

The safest alternative is to remove high-sulfate soils from along the alignment and replace them with borrow soils that either do not require stabilization or with borrow soils that contain sulfates below problematic levels if the soils are to be treated with calcium-based stabilizers. The sulfate concentrations in borrow soils that are to be treated with calcium-based stabilizers must be tested in accordance with Section 8.2 prior to use as a substitute soil.

If the borrow soils require treatment with calcium-bases stabilizers, the possibility of sulfate migration into the borrow soil due to water movement from underlying layers should be assessed. A combination of high sulfate content in the underlying in-situ soil and a water table close to surface the surface may cause sulfate movement in to the low-sulfate borrow soil.

Instead of full replacement of a high-sulfate soil, the existing soil may be diluted with a soil that has a low sulfate content until the resultant sulfate content is acceptable for treatment with a calcium-based additive.

Instead of full replacement of the high-sulfate soil, the existing soil can be diluted with a non-plastic of low plasticity, granular soil. The blend ratio of the native soil and the granular soil should be determined based on the potential vertical rise (PVR) of the mixture measured in accordance with TEX 124-E. Blending non-plastic and granular materials like sand and gravel may also help reduce the swell potential and improve strength properties of natural soils. If the goal is solely to reduce plasticity and swell potential, then the blending approach alone is adequate. However, it is possible that the blended soil still requires stabilization to achieve target stiffness and strength values. If this is the case, then the sulfate content of the blended soil must be tested following Section 8.2. Mix design and optimum moisture content should be determined based on Section 11.8.1 and 11.8.2.

Lime-treated soil blends should be subjected to capillary soak in accordance with Section 8.3.2 to determine their swell potentials.

Three-dimensional expansion below 2 percent may be considered acceptable for lime-treated soil blends.

Maintaining proper mixing and moisture density requirements and increased density control testing, as detailed in Section 12, may be followed during construction to ensure uniformity of these mixes.

Extended mellowing and blending of soils may be used in combination with additives like soluble silica and ground granulated blast furnace slag (GGBFS) to limit expansive heaving in soils. These mixes should satisfy all required engineering properties including strength and shrink/swell, should have only acceptable sulfate levels after mellowing periods, and should have the required durability properties for acceptability in field application. Additives high in soluble silica may provide favorable thermodynamics to form calcium-silicate-hydrates rather than ettringite/thaumasite and therefore prevent damage induced by expansion.

QUALITY ASSURANCE TESTING DURING CONSTRUCTION

Conductivity of soils should be monitored in accordance with TEX 146-E or equivalent test methods. If presence of soluble salts is detected by conductivity measurements, soil samples may be further evaluated for the presence of sulfates. The minimum recommended frequency as mentioned in Section 8.1.4 should be followed in testing.

Colorimetric measurements need to be performed only on soils with conductivity measurements are above acceptable limits recommended in TEX 146-E or equivalent test method. Sulfate content in soils should be tested in following the modified AASHTO T 290 method.

If high sulfate concentrations are detected during field conductivity testing, increase the frequency of testing to determine the boundaries of sulfate pockets in the location.

Methods of treatment, construction techniques, and additive percentages, if any, must to be adjusted during construction in response to varying sulfate levels. This should be done in accordance with Section 11 guidance.

Uniformity of mixing of lime and soil should also be evaluated as a part of quality assurance program.

REPORT

The report for stabilization of sulfate-laden soils should include:

The details of locations identified to have a risk for ettringite formation when soils are stabilized with lime of other calcium-based stabilizers. The report should also include details of locations of test pits and bore holes, and details of all other sampling sources used for sulfate quantifications in soils.

A graphical presentation of the distribution of sulfate concentration along the length of the pavement. Sulfate levels (in ppm) should be plotted along the y-axis and distance along x-axis. The graphs should be used in deciding the stabilization technique and amelioration strategy for specific locations along the alignment.

A description of the investigation procedures, data tabulations for all field conductivity measurements, and laboratory test results for sulfate concentrations in samples collected from the field. Details of all additional testing conducted in field or in the laboratory prior to construction or during quality assurance programs in post-construction periods should also be included in the report.

PRECISION AND BIAS

This standard provides qualitative data only; hence, precision and bias are not applicable.

KEYWORDS

Ettringite; soil stabilization; mineralogy; sulfate-induced distress; ettringite formation

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