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Cementitious stabilization of soils in the presence of sulfate

Lan Wang

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**CEMENTITIOUS STABILIZATION OF SOILS
IN THE PRESENCE OF SULFATE**

A Dissertation

Submitted to Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
Requirements for the degree of
Doctor of Philosophy

in

The Department of Civil & Environmental Engineering

By

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ACKNOWLEDGMENTS

The evolution of Civil Engineering has tremendously accelerated in the last several decades. We are tempted to speak, in the language of our newspapers, of an “explosive” advance in the field of scientific and technological investigation.

One aspect must be mentioned concerning the development of Civil Engineering is the incorporation of multiple disciplines. Innovative solutions to civil engineering problems not only require basic techniques developed within the discipline but also demand an advanced knowledge of material science and testing, chemistry, mechanics and geology. “Cementitious stabilization of soils in the presence of sulfate” is one of such complex projects and its successful completion is based on the appreciation and application of the learning from many subjects.

It is needless to say that this achievement must be attributed to my Ph.D advisory committee, chaired by Dr. Roger K. Seals, Professor of Civil & Environmental Engineering. Dr. Seals is a great advisor and educator. The present dissertation would not have been possible without his elaborate guidance and full encouragement. He is really a venerable professor.

With the greatest appreciation I wish to express my obligation to Dr. John Metcalf, another international authority on pavement design and a Professor of Civil & Environmental Engineering, for his strong support and constructive suggestions.

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I also wish to express his thanks and appreciation to all other individuals who provides earnest assistance for this research work.

My final special thank will go to my family. What I would like to mention is the love, concern, understanding and support always brimming over there. I feel indebted and dedicate this dissertation to my wife Wu Shi and my son Wang An.

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ABSTRACT

Winn Rock (anhydrite, CaSO_4) comes from a quarry in Winn Parish in north Louisiana. Gravel from the quarry has been used extensively as a surface course on local parish and logging roads. Stabilization of these roads with Type I Portland cement followed by an overlay by asphaltic concrete sometimes resulted in heaving. The causes for heaving and possible solutions were investigated.

In the laboratory 2" x 4" molds of Winn Rock containing soil were prepared and cured in water bath at 40°C, sealed plastic bag at room temperature, and air. Molds were prepared with 5% to 20% cementitious material. The cementitious materials were Type I Portland cement, lime, and supplementary cementing materials (SCM) such as granulated blastfurnace slag (BFS), Class C fly ash (CFA), and an amorphous silica (AS). The expansion of the molds over time was monitored. Mineralogical and micro-structural analysis of the molds was also performed over time and correlated to expansion. The characterization methods included X-ray diffractometry, thermal analysis and scanning electron microscopy. A set of molds was also prepared with soil from a well-characterized site west of Baton Rouge (the Accelerated Loading Facility site), free of any sulfate minerals, to distinguish the effect of internal and external sulfates.

The Winn Rock gravel partially weathered in the soil to gypsum which was detected in all size fractions. The highest amount of expansion occurred in Winn Rock soil stabilized by lime cured at 40°C in water bath. The magnitude of the expansion is directly proportional to the amount of Type I portland cement, the amount of available moisture, and the curing temperature. Replacement of a part of the Portland cement by BFS reduced the expansion by almost an order of magnitude even at the highest moisture content. No expansion was detected when CFA and AS were used as replacement. The average length and amount of ettringite crystals, in general, inversely correlated with the magnitude of expansion.

A three-stage expansion model was developed to explain increased sulfate attack resistance provided by the SCMs, attributable to their consumption of calcium hydroxide and a morphology change of ettringite crystals.

CHAPTER 1. INTRODUCTION

1.1 Statement of the Problem

Soils can be stabilized by the addition of a small percentage of cement or lime. Such stabilization processes enhance many of the engineering properties of the treated soils and produce an improved construction material.

The concept of stabilization can be dated back to 5000 years ago. McDowell (1959) mentioned that stabilized earth roads were used in ancient Mesopotamia and Egypt, and that the Greeks and Romans once used soil-lime mixtures. The first tests involving soil stabilization were carried out in the United States in 1904 (Clare and Cruchley 1957). Cement was first used as a stabilizing agent of soil when a street in Sarasota, FL, was constructed in 1915 (ACI 1997), and lime was first used in modern construction practice in 1924 on short stretches of highway (McCaustland 1925). With the expansion of roads to cater for the growth of vehicle traffic in the 1930s, the use of soil stabilization began to increase. Today, stabilization of soil by incorporation of cement or lime is a technique widely used throughout the world, especially in road construction to improve bases and subbases. It is estimated more than 100,000 miles of equivalent 24 ft wide pavement have been constructed to date in the U.S.A using a stabilized soil base.

However, during the past few decades a number of cases have been reported where pavement bases stabilized by cement or lime underwent a significant amount of heave leading to pavement failure (Mitchell 1986; Hunter 1988; Little et al.1989, Perrin 1992; Kota et al. 1996; Ksaibati et al.1999; Rollings et al.1999). The literature also indicated that heave is due to the formation of a highly expansive crystalline mineral, namely, ettringite, which is the product of sulfate attack on stabilized soils.

Sulfate attack of conventional Portland cement concrete is a widely recognized phenomenon, and appropriate methods of protection against sulfate attack have been established as a function of the sulfate exposure level (ACI 1982; DePuy 1994), but the actual chemical reactions and products involved have not been completely understood. Similarly, the potential for sulfate attack on both cement- and lime- stabilized soils was established in the 1960s (Sherwood 1962). However, only limited research work has been carried out on this subject and little constructive guidance on how to deal with the problem is available.

1.2 Winn Rock Case

Sulfate attack on stabilized soil base, or sulfate-induced heave, has received much national attention (Mitchell 1986, Little et al. 1989). On the basis of the extent of sulfate-laden soils in the United States, one can expect an increased number of reported sulfate-induced heave problems in the future. A recent case of pavement deterioration reported by Louisiana Transportation Research Center (LTRC) was a typical example and stimulated this research work.

Winn Rock, quarried in Winn Parish in Louisiana, is a chemically active crushed stone. It consists mainly of anhydrite, or calcium sulfate (CaSO_4). Winn Rock has been used extensively as a crushed aggregate for the local construction of logging roads, parking lots, industrial haul roads, and secondary public and private roads. Several

parishes near the Winn Rock quarry used the aggregate as a surface course building material for their public roads and the Louisiana Department of Transportation and Development (DOTD) used it as a shoulder surface course material on some rural highways. In general, there had been no reports of unsatisfactory performance.

Some of these parish roads were taken into the DOTD owned and maintained system. Many of these roads were later overlaid with asphalt concrete or received asphalt surface treatment as a means of improvement. The rehabilitation process entailed stabilizing the existing base course with Portland cement and constructing an asphalt concrete overlay. Some bases, which contained Winn Rock experienced heave after Portland cement stabilization process. Remediation costs for the project that suffered sulfate-induced heave damage were very high and, in one instance, a stretch of a road several miles long had to be abandoned.

1.3 Research Objectives and Scope

As a result of the Winn Rock experience and other documented cases of sulfate-induced heave in cement- and lime- stabilized soil, an experimental study was conducted. The primary objectives for this study were:

- define the mechanical and chemical properties of the Winn Rock soil mixture. Index and mechanical properties including soil classification, particle size distribution, density and compaction, compressive strength, and chemical properties including its phase composition, of the Winn Rock were determined.
- determine the mechanical properties of the Winn Rock soil stabilized by several kinds of cementitious materials. Portland cement and blended cements incorporated with ground granulate blast furnace slag (GGBS), fly ash (FA) and amorphous silica (AS) were used stabilization. The mechanical properties of the stabilized soils were evaluated and compared.
- identify the chemical and mineralogical properties of the Winn Rock soil stabilized by several kinds of cementitious materials. Corresponding to the determination of its mechanical properties, the chemical and mineralogical properties including phase composition, microstructure, of the specimens were investigated and compared through instrumental analysis.
- determine the general conditions, both compositional and environmental, that may lead to the occurrence of sulfate expansion. A local silty sand soil bearing no sulfate was stabilized with Portland cement and subjected to internal and external sulfate attack. Its sulfate expansion properties were assessed and the important parameters for sulfate expansion were identified.
- assess the possibility of mitigating the external sulfate attack on the cement stabilized soil. Research work on the silty sand soil stabilized by Portland cement incorporated with FA and AS were conducted and its sulfate attack resistance was evaluated.

The results experimental study described above forms the basis for this dissertation. The dissertation research can be divided into three main parts: an exhaustive literature review concerned all aspects of the issue; a principal laboratory testing program designed to investigate the cause of a particular sulfate expansion case concerning the Winn Rock soil mixture (soil containing Winn Rock aggregate) and the means to avoid or mitigate this typical problem; and a secondary laboratory testing designed to investigate the general sulfate expansion problem and develop possible protective methods.

In first part, the literature research was concentrated on the background of the issue, including pavements with a stabilized soil bases, the stabilization mechanism, the mechanism of sulfate attack and case history review, possible methods of improvement of sulfate resistance, etc. This task was essential to the process of developing a theoretical framework upon which further experimental research work could be based.

The second part of the research consisted of two phases. Phase one was conducted to identify the properties of pure Winn Rock as well as the Winn Rock soil mixture. Representative specimens were subjected to mechanical, mineralogical and microstructure analyses. Phase two was to simulate the expansive process in the laboratory and was for alternative method research. Portland cement was used for the Winn Rock soil stabilization and the sulfate expansion as well as other properties was determined. As the final goal of the research project was to eliminate or mitigate the problem concerning the stabilization of Winn Rock, different kinds of stabilizers (including mixture of cement and ground granulated blast furnace slag (GGBS), fly ash (FA) and amorphous silica (AS) were tried.

The third part of the research was for further elucidation of sulfate attack on soil cement and the relationship between the amount of expansion and other factors, such as the source of sulfate, the concentrations of sulfate, the content of cement, temperature, curing conditions and time, etc. was established. The mechanism of resistance of soil cement incorporated with pozzolans to external sulfate attack would be interpreted.

Overall, successful completion of the research work would lead to a better understanding of the problem, a qualitative model describing the mechanisms of expansion and development of a cost effective method to solve or mitigate the problem.

CHAPTER 2. BACKGROUND AND LITERATURE REVIEW

2.1 Pavement with Cementitious Stabilized Soil Base

A pavement is a structure consisting of superimposed layers of selected and processed materials placed on a subgrade, whose primary function is to support the applied traffic loads and distribute them to the basement soil. The ultimate aim is to ensure that the transmitted stresses are sufficiently reduced that they will not exceed the supporting capacity of the subgrade.

2.1.1 Pavement Base

Pavement includes several layers. A typical profile of pavement is shown in Figure 2-1. The materials for the surface, base, and subbase layers are generally selected according to standard specifications. The quality of the subgrade soil is also a consideration.

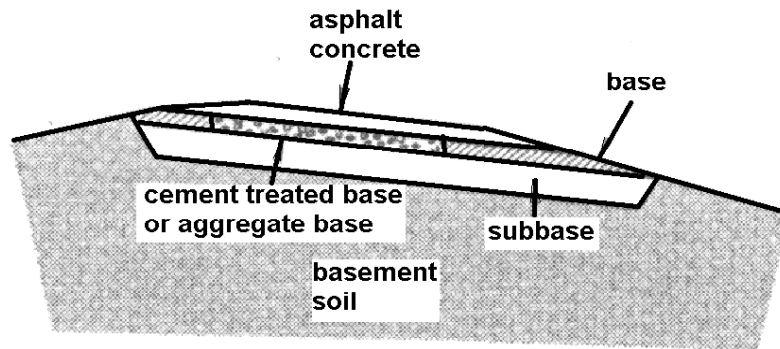


Fig. 2-1 Typical asphalt concrete pavement section (from Huang 1993)

The base course is the layer immediately under the wearing surface. Because the base lies close under the pavement surface, it is subject to severe loading. As some soil materials alone would be unsatisfactory as base, the cementitious stabilization process is often applied to improve the engineering properties of the soil. With the addition of cement or lime, cation exchange initiates the stabilization process very quickly, and it is followed by flocculation and agglomeration. Cementitious hydration and pozzolanic reaction develop strong bonds between soil particles, forming the products into a high-strength mass.

In fact, the important pavement design parameters include the strength and thickness of base layer. With cement or lime stabilization the supportive strength of base will increase and the thickness can be decreased correspondingly.

Pavement distress is another important factor of pavement designs. Distresses connected to the deficiencies of base consist of alligator cracking, longitudinal and transverse cracking, rutting for flexible pavement and corner break, faulting of transverse joints and cracks for rigid pavement. These distresses can also be mitigated or avoided

with stabilized base. For example, under concrete pavement, soil stabilized with cement can be used as a base to prevent pumping of fine-grained soils under wet conditions and heavy traffic. Furthermore, it provides a uniform, strong support for the pavement, which will not have excessive permanent deformation caused by traffic and will offer additional load transfer at pavement joints.

However, cementitious stabilized soil base may be subject to sulfate attack that will possibly lead to a heave and damage of pavement.

2.1.2 Cementitious Stabilization

Because of the significant improvement in soil properties, cementitious stabilized soil has been used as base underlying asphalt or concrete pavement surfaces on an even-increasing scale during the last half century. Other benefits of cementitious stabilization include possibly using borderline base materials and avoiding the generally more expensive process of transporting large quantities of granular fill.

Material

Soil materials

Almost all types of soils can be stabilized. Some exceptions include organic soils, highly plastic clays, and poorly reacting sandy soils. Typically, soils containing between 5 and 35% passing a No. 200 sieve produce the most economical stabilized soil. Types of soil used include silty sand, processed crushed or uncrushed sand and gravel, and crushed stone.

Soils containing more than two percent organic material are usually considered unacceptable for cement treatment. Fine-grained soils generally require more cement or lime for satisfactory hardening and, in the case of clays, are usually more difficult to pulverize for proper mixing.

Cementitious materials

For most applications, Type I or Type II Portland cement is normally used. Cement requirements vary depending on desired properties and type of soils. Cement contents may range from as low as 4% to a high of 16% by dry weight of soil. Generally, as the clayey portion of the soil increases, the quantity of cement required also increases.

Cement kiln dust, which can be considered as semi-product of cement, can be used as a soil stabilizer, as it often has high content of free lime. Nicholson (1983) once developed a product mainly from cement kiln dust as a base material.

Lime is a rather broad term for a variety of calcium bearing compounds. Various kinds of lime have been successfully utilized as stabilizers, including products with various degrees of purity. The amount of lime added should be related to the clay mineral content of the soil. According to Ingles (1987), a good rule of thumb in practice is to allow 1% by weight of lime for each 10% of clay in the soil.

Fly ash with high calcium oxide content or that mixed with lime has also been used for soil stabilization (Misra 1998, Shirazi 1999). Ground granulated blast furnace slag can also be incorporated in lime-stabilized soil (Wild et al. 1996 and 1998). The use of these materials may be due to economic considerations or for a special purpose, such as for resistance of sulfate resistance or shrinkage prevention.

Water

Water is necessary in a stabilized soil to help obtain maximum compaction and for the hydration of Portland cement or lime. Moisture contents of soil with cement or lime treated are usually in the range of 10 to 20% by weight of dry soil/stabilizer mixture.

Properties

The properties of stabilized soil are influenced by several factors, including the type and proportion of soil, the type and proportion of cementitious materials, water content, compaction, uniformity of mixing, curing conditions, and age of the compacted mixture. Because of these factors, a wide range of values for specific properties may exist. Important properties include density, compressive strength, stiffness, durability, permeability, and volume stability.

Density and compaction

Density of treated soil is usually measured in terms of dry density. Adding cementitious materials to a soil generally causes some change in both optimum moisture content and maximum dry density for a given compaction effort. However, the direction of this change is not usually predictable. The flocculating action of the cementitious materials tends to produce an increase in optimum moisture content and decrease in maximum density (Lees 1982). However, for cement, its high specific gravity relative to the soil tends to produce a higher density. In general, for given cementitious material content the higher the density, the higher the compressive strength of the stabilized soil mixtures (Shen 1966).

Compressive strength and stiffness

Unconfined compressive strength is the most widely referenced property of a soil treated with cementitious materials and is usually measured according to ASTM 1633. It indicates the degree of reaction of the soil-cement (or lime)-water mixture and the rate of hardening. Compressive strength serves as a criterion for determining minimum cement requirements for proportioning soil cement. Soaked specimens prior to testing is recommended since most soil-cement structures may become permanently or intermittently saturated during their service life and exhibit lower strength under saturated conditions. Curing time has the effect on the strength gain differently depending on the type of soil. The strength increase is greater for granular soil cement than for fine-grained soil cement. Ranges of unconfined compressive strengths of soil-cement are shown in Table 2-1.

Table 2-1 Unconfined compressive strength of cement stabilized soil (from ACI 1997)

Soil Type	Soaked compressive strength, (psi)	
	7-day	28-day
Sandy and gravel soils	300-600	400-1000
Silty soils	250-500	300-900
Clayey soil	200-400	250-600

The strength development of soil stabilized with lime also follows the similar pattern as that with cement. The strength increases rapidly at first, generally during the first 7 days of curing. Depending on the type of soil, the 28 day unconfined compressive strength can reach up to 700 psi.

Flexural-beam test (ASTM D 1635) can be used to evaluate flexural strength. In the test, a beam specimen is subjected to repeated flexural loads. Because of the repetitive nature of the test, the resultant damage accrued to the specimen increases with number of load applications resulting in a stiffness value, which is about one-fifth to one-third of the unconfined compressive strength.

Durability

Durability may be defined as the capability of maintaining the serviceability of a construction over a specified time. In many soil cement applications, both strength and durability requirements must be met to achieve satisfactory service life. ASTM D 559 and D 560 are standard test methods to determine, for a particular soil, the amount of cement needed to hold the mass together permanently and to maintain stability.

Permeability

Permeability of most soils is reduced by the addition of cement. For sandy soils the coefficient of permeability can decrease from about 50×10^{-6} m/sec to 1×10^{-6} m/sec with cement treatment. Some research work also indicated a decrease in permeability with time, possibly due to shrinkage cracks in the soil-cement filling with sediment and the tendency for the cracks to self-heal.

Volume stability

Shrinkage or expansive forces occurred in the field may lead to volume change of soil cement. Soil cements undergo shrinkage during drying. The shrinkage and subsequent cracking depend on cement content, soil type, water content, degree of compaction, and curing conditions. Methods suggested for reducing or minimizing shrinkage cracks include keep the soil cement surface moist beyond the normal curing periods and placing the soil cement at slightly below optimum moisture content. Expansive forces may present in soil cement matrix due to the occurrence of expansive clay mineral and sulfate attack. Precautions including application of blended cement may be used to mitigate expansion.

Mix Proportioning and Construction

The principal structural requirements of a hardened soil-stabilizer mixture are based on adequate strength and durability.

Proportioning

Various criteria are used by different organizations to determine acceptable mix proportions. The durability and strength requirements developed by USACE for Portland cement stabilization are given in Table 2-2 and 2-3, respectively.

In many cement stabilized soil applications, both strength and durability requirements must be met to achieve satisfactory service life. It is common practice, however, to use compressive strength to determine the minimum cement content.

Table 2-2 USACE durability requirements

Type of soil stabilized	Maximum allowable weight loss after 12 wet-dry of freeze-thaw cycles, percent of initial specimen weight
Granular PI <10	11
Granular PI >10	8
Silt	8
Clays	6

Table 2-3 USACE minimum unconfined compressive strength criteria

Stabilized soil layer	Minimum unconfined compressive strength at 7 days, psi	
	Flexible pavement	Rigid pavement
Base course	750	500
Subbase course, select material or subgrade	250	200

For lime stabilized soil, it is normally not necessary to add more than 8% lime, because it is exceptional for the clay content of a soil to exceed 80%.

Construction

In the construction of cementitious stabilized soil base, the objective is to obtain a thoroughly mixed, adequately compacted, and cured material.

The mixtures should be placed on a firm subgrade, without segregation, and in a quantity that will produce a compacted layer of uniform thickness and density conforming to the design grade and cross section. Compaction begins as soon as possible and is generally completed within 2 hr of initial mixing for the use of cement. As compaction nears completion, the surface of the mixture material is shaped to the design line, grade, and cross section. Proper curing of stabilized soil is important because strength gain is dependent upon time, temperature and the presence of water.

2.1.3 Cementitious Stabilizer - Soil Reaction Mechanism

The improvement in engineering properties of cement treated soils is believed to be due mainly to the hydration and hardening of cement. On the other hand, clay minerals can't be regarded as a chemically inert component. They can react with calcium hydroxide released by cement hydration or by solution of lime, which can generate additional cementitious materials and lead to the strengthening of the bonds between the soil grains.

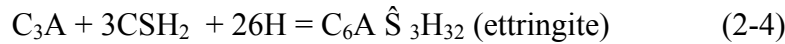
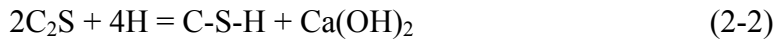
Source of Calcium

The most important factor in the initial timely stabilization of clayey soils is the ability of the stabilizer to supply an adequate amount of calcium. Both Portland cement and lime can supply this necessary ingredient, and both, when used properly, can

effectively stabilize clay soils. However, Portland cement and lime are inherently different materials, and the calcium provided by each is supplied to the soil-stabilizer system in a somewhat different manner.

Cement hydration

Portland cement is a finely divided material that results from intergrinding clinker and gypsum. The manufacturing of clinker is a pyro-process and includes a series of complex chemical reactions which take place in a special kiln. The clinker is a heterogeneous material composed of four major oxide phases: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) (According to nomenclature used in cement chemistry $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$, $\hat{S} = SO_3$). The reactions between cement and water can be described as following:



where C-S-H is a series composition with $C/S = 0.5-2$ and $S/H = 1-2$.

With regard to soil stabilization, the two calcium silicate phases are the most important. Upon hydration, these two phases produce calcium hydroxide which provides available calcium for cation exchange, flocculation and agglomeration, and stabilizes the clayey soil. These two phases also provide calcium silicate hydrate (C-S-H), which produce strength and structure in the soil matrix.

The reaction of cement hydration is much more complex than the equations given earlier, especially in soil cement system. When mixed with water, cement hydration is initiated and calcium concentration in the soils builds up quite rapidly, and the solution becomes immediately saturated with calcium hydroxide. As calcium ions (Ca^{2+}) are released in solution, they are available for stabilization. Initial absorption of calcium by clay is rapid and then is slow as it becomes increasingly diffusion dependent. Hydration can continue at an ever-slowng pace over many years, and therefore calcium hydroxide is produced during this time. This helps maintain the high pH level. Maintaining a high pH in a soil cement system is also important because high pH is necessary for long-term pozzolanic reactions to occur.

Lime dissolution

Lime, as a stabilizer, is manufactured in various forms including hydrated high-calcium lime ($Ca(OH)_2$), hydrated dolomite lime ($Ca(OH)_2 \cdot Mg(OH)_2$), quicklime (CaO), and dolomitic lime ($CaO \cdot MgO$). The availability of lime varies in accordance with its composition and solubility. The rate of dissolution of lime depends principally on particle size, with finer gradation going into solution faster because of the higher exposed surface area. Small concentrations of lime increase the pH of neutral water from 7 to 11 or more. Maintenance of the high pH environment is especially important for a lime-stabilized

system because cementitious material is formed only through long-term pozzolanic reactions and not through formation of cementitious compounds during hydration, as occurs in cement.

Soil as well as Clay Minerals

For engineering purposes, soil is defined as uncemented aggregate of mineral grains and decayed organic matter with liquid and gas in the empty spaces between the solid particles. Soils are generally called gravel ($>2\text{mm}$), sand ($>0.075\text{mm}$), silt ($>0.002\text{mm}$), or clay ($<0.002\text{mm}$), depending on the predominant particle size in the soil. Clay minerals are complex aluminum silicates.

Soil formation and constituents

Most soils have been formed by the disintegration of rock as a result of either mechanical or chemical weathering processes.

Any sample of soil will be found to contain some or all of following phases: solid, liquid and gas. The solid phase of a soil may contain various amounts of crystalline clay and non-clay minerals, non-crystalline clay mineral, organic matter, and precipitated salts. The crystalline minerals comprise the greatest proportion. Clay minerals in a soil usually influence properties in a manner far greater than their abundance.

Clay minerals

The clay minerals found in soils belong to the mineral family termed phyllosilicates. Their structures are made up of combinations of two basic units, the silicon tetrahedron and the alumina octahedron. The different clay mineral groups are characterized by the stacking arrangements of sheets of these units and the manner in which two successive two- or three-sheet layers are held together.

Of the three important clay minerals as shown in Fig.2-2, kaolinite consists of repeating layers of element silica tetrahedron, which is linked to form a silica sheet, and aluminum octahedral, which is usually linked to form a gibbsite sheet. The layers are held together by hydrogen bonding. Illite consists of an alumina octahedral sheet bonded to two silica tetrahedral sheets. The illite layers are bonded by potassium ions. The negative charge to balance the potassium ions comes from the substitution of aluminum for some silicon in the tetrahedral sheet. Montmorillonite has a structure similar to that of illite and there is isomorphous substitution of magnesium and iron for aluminum in the octahedral sheets. Large amounts of water can be attracted into the space between the layers.

In the clay minerals, some of the tetrahedral and octahedral spaces are occupied by cations other than those in the ideal structure. This isomorphous substitution in clay minerals, with the breaking of the structure at their edges, gives clay particles a net negative charge. To preserve electrical neutrality, cations are attracted and held between the layers and on the surfaces and edges of the particles.

When the clay is placed in water, some of the attracted cations will go into solution. Because the adsorbed cations produce a much higher concentration near the surfaces of particles, they try to diffuse away in order to equalize concentration throughout. The escaping tendency due to diffusion and the opposing electrostatic attraction lead to ion distributions adjacent to a clay particle in suspension as shown in Figure 2-3.

The charged surface and the distributed charge in the adjacent phase are together termed the diffuse double layer. The double layer may have some important influences on soil structure and its stability.

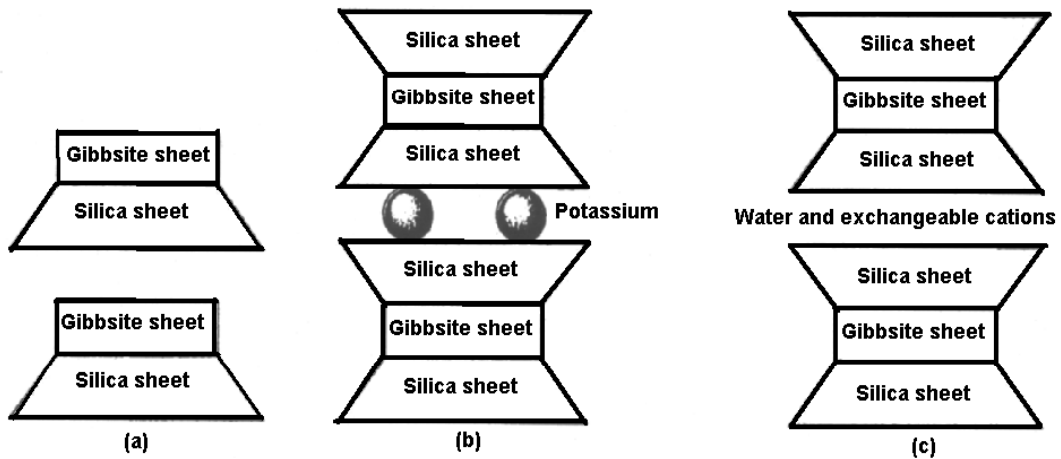


Fig.2-2 Diagram of the structure of (a) kaolinite; (b) illite; (c) montmorillonite (from Das 1997)

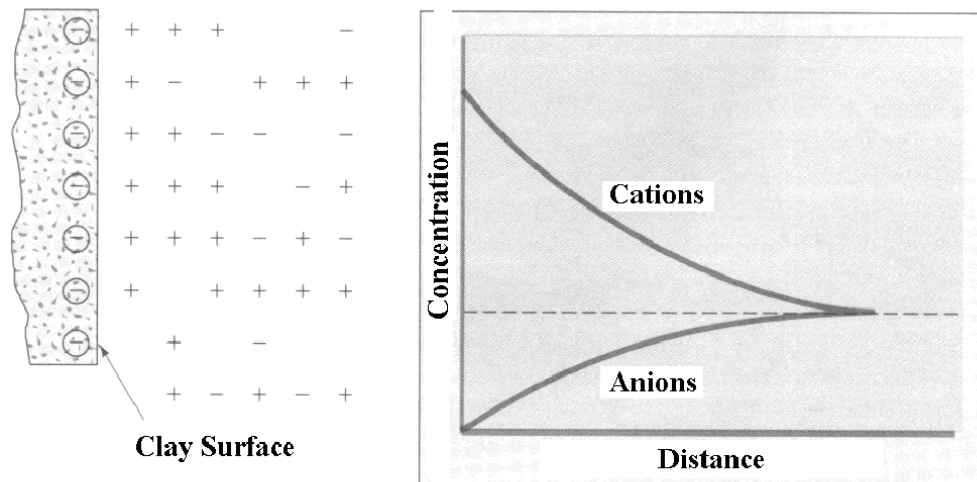


Fig.2-3 The concept of the diffuse double layer (from Das 1997)

Stabilization Processes

Cementitious materials stabilize soils and modify their properties through cation exchange, flocculation and agglomeration, and pozzolanic reactions. Additionally, cement provides hydration products, which increase the strength and support values of the base materials as well as enhance the performance of the treatment.

Cation exchange

Cation exchange initiates the stabilization process very quickly, and is followed by flocculation and agglomeration.

Clay will absorb cations of specific type and amount to form a double layer. Exchange reactions can occur in response to changes in the environmental conditions, and important changes in the physical and physicochemical properties of the soil may result. For example, the monovalent cations can be readily exchanged with cations of higher valence such as calcium. Upon ion exchange, the higher charge density of divalent or trivalent ions results in a significant reduction of the double-layer thickness, and reduction of the activity and plasticity.

Flocculation and agglomeration

Flocculation and agglomeration change the clay texture from that of a plastic, fine-grained material to that of a granular soil. Flocculation is the process of clay particles altering their structure from a flat, parallel structure to a more random orientation. Agglomeration is thought to occur as the flocculated clay particles begin to form weak bonds at the edge-surface interfaces of the clay particles, because of the deposition of cementitious material at the clay-particle interfaces.

Pozzolanic reaction

Pozzolanic reaction is a secondary process of soil stabilization. One prerequisite for the formation of additional cementing materials is the solution of silica and alumina from clay components. The high pH environment of a soil cement system increases the solubility and reactivity of the silica and alumina present in clay particles. The degree of the crystallinity of the minerals and particle size distribution are some factors influencing solubility. It is postulated that calcium ions combine with silica and alumina dissolved from the clay lattice to form additional cementitious material (C-S-H and C-A-H).

Cementitious hydration

Cement hydration produces cementitious material, as indicated in Equations 2-1 to 2-5. C-S-H and C-A-H form a network and serve as the "glue" that provides structure and strength in a cement treated soil. The most rapid strength increases occur between one day and one month; smaller gains in strength (due to continued hydration and formation of cementitious material) continue to occur for years.

2.2 Sulfate Attack on Cementitious Stabilized Soil Base

Early in the 19th century, it was established that Portland cement mortar and concrete could be attacked by seawater (Candlot 1890). Although sulfate, no doubt, plays a role in deterioration of concrete in sea water, its action is often more pronounced if concrete is exposed to sulfate-rich water and soil. It has been known for a long time that the alumina content in Portland cement plays a major role as far as the durability of concrete in a sulfate environment is concerned. The deterioration of concrete as a result of sulfate attack is usually associated with ettringite formation and expansion.

Sulfate attack on stabilized soil has also been a recognized problem in the United States since it was reported by Mitchell in 1986, even though some research work was

conducted earlier (Sherwood 1958). The mechanism of the problem is almost identical for both cement system and cement (or lime) soil system. However, the physical and chemical changes in the latter system are more complex.

2.2.1 Occurrence of Sulfate in Soils

The United States is the leading gypsum producing country with 15% of the world total (Kota et al. 1996). Figure 2-4 shows the locations of mined gypsum in the United States. The locations of gypsum mines usually indicate the presence of rich quantities of gypsum in the local soil and possible use of sulfate bearing aggregate as building materials. On the basis of the extent of sulfate-bearing rocks and soils in the United States, one can expect an increased number of reports of sulfate-induced heave problems in the future.

Origin and Transition of Sulfate

The origin of sulfates can be traced to evaporitic deposits (Zanbak et al. 1986). They formed by precipitation of salts from salt lakes and seas. Anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are the most prominent minerals in evaporitic deposits. Precipitation of evaporitic minerals is usually generated either by direct evaporation of brine or by an indirect manner; i.e., through dissolution, transportation and reprecipitation of primary evaporitic deposits by water circulating in the upper crust. In some areas, alternating layers or mixtures of evaporite and clay and other fine-grained clastic sediments formed during cyclic wet and dry periods.

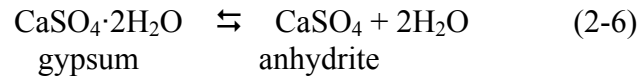


Fig. 2-4 Location of soils with gypsum and its mines in the United States (from Nettleton 1982)

Dissolution is one form of interaction of water with the rock-forming evaporitic minerals. Geochemical transition between sulfate minerals and water is another form of interaction. For example, anhydrite may hydrate into gypsum or gypsum may dehydrate into anhydrite depending upon the changes in the geochemical conditions. Temperature, pressure and salinity of liquids are the most prominent factors controlling the phase transitions.

Seawater consists of approximately 3.6% gypsum-anhydrite. When seawater is evaporated to one third of its original volume, gypsum and anhydrite precipitate. Based on the interpretations of laboratory and field studied by Blatt et al. (1980), it may be concluded that gypsum was the original mineral.

Even if anhydrite were to be the original mineral, it would be converted into the more stable form of calcium sulfate, gypsum, after precipitation. In fact, the gypsum-anhydrite transition is a reversible dehydration reaction as shown by:



for which:

$$K_{\text{eq}} = a_{\text{H}_2\text{O}}^2 \quad (2-7)$$

Thus, the equilibrium constant for the reaction, K_{eq} , depends only on the activity of water, $a_{\text{H}_2\text{O}}$. Any process, which decreases the activity of water, such as increases in temperature or in electrolyte concentration, will cause the reaction to proceed to the right (dehydration) in proportion to the square of the water activity.

Transportation of Sulfate

Gypsum and anhydrite are soluble and can enter into chemical reactions with compounds present in set cement, causing sulfate attack damage.

The absolute dissolution rates of gypsum and anhydrite have apparently not been recorded in the literature. Liu and Nancollas (1971) have shown that small gypsum crystals dissolve according to first order kinetics:

$$dM/dt = KA(c_s - c) \quad (2-8)$$

and Fabuss, et al. (1969) appear to have shown that anhydrite dissolves according to second order kinetics:

$$dM/dt = KA(c_s - c)^2 \quad (2-9)$$

where M is the mass of calcium sulfate dissolved at time t,
 c_s is the concentration of substance in saturated solution;
 c is the concentration of substance in solution at time t;
A is the area of mineral surface exposed to aqueous solution;
K is the rate constant.

James et al. (1978) developed a method for dissolution rate analysis and determined the K values of 2.9×10^{-6} m/sec and 5.4×10^{-8} m/sec for gypsum and anhydrite, respectively.

The equations indicate that the rates of dissolution of gypsum and anhydrite are likely to be controlled primarily by the surface area in contact with water and the flow velocity of water associated with unit area surface of the substance. For example, fragmented thin bands of gypsum (of high specific surface area), in contact with a rapidly flowing stream of water can be expected to dissolve faster than a massive deposit of gypsum in contact with a virtually stagnant and limited supply of water.

Figure 2-5 shows the initial dissolution rates of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) plotted with their specific surface area values, according to the Eqs. 2-8 and 2-9. The figure indicates the surface area has a significant influence on their initial dissolution rates. Anyway, a solution of small proportions of gypsum (or anhydrite) can contaminate soil and ground water, and produce materials which are potentially very dangerous to set cement.

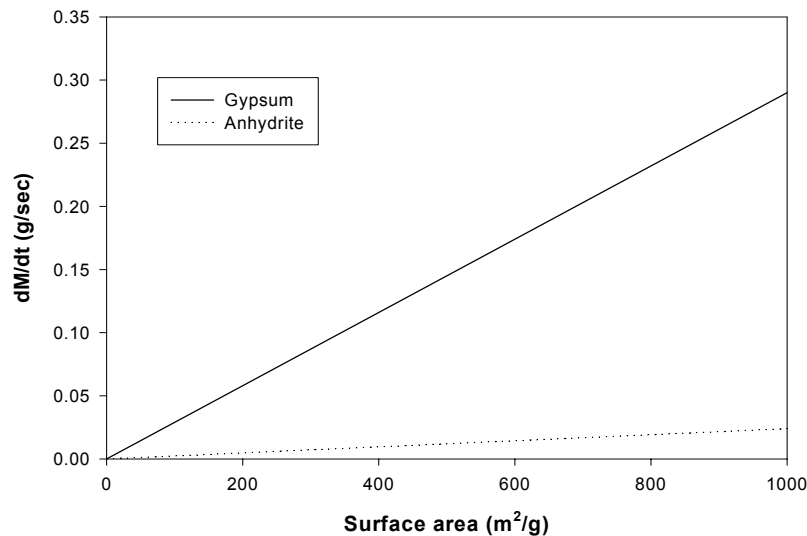


Figure 2-5 Initial dissolution rates of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4)

2.2.2 Sulfate Attack

Numerous research works were conducted on sulfate attack of conventional Portland cement concrete. However, only limited literature is available on the issue of sulfate attack on cementitious stabilized soil base. Guidance (Little et al. 1989 and 1992, ACI 1998; Rollings et al. 1996) does recognize the problem, but it provides little constructive guidance on how to deal with the problem.

The Formation, Structure and Properties of Ettringite

Sulfate attack occurs when calcium, alumina, and sulfate combine to form ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). It was indicated (Taylor 1997) that the molecular volume of ettringite is 714 mL, and the volume of water molecules of ettringite is 576 mL. It

means that the volume of ettringite may be over 200% that of the original constituents (disregarding the water), which may result in massive swelling and cracking when sufficient ettringite forms. Review of its composition, structure and properties is helpful to the understanding of the mechanism of sulfate attack.

Formation of ettringite

As discussed previously, Portland cement contains several primary clinker mineral phases. The hydration of the aluminate and aluminoferrite phases is somewhat more complex and goes through several possible stages depending upon the amount and solubility of the calcium aluminate and calcium sulfate phases present. In the presence of sulfate (e.g., gypsum), the reaction (2-3) is a dominant one of C₃A hydration, and the product is ettringite. As a small amount of gypsum is always added to cement during manufacturing to regulate cement setting, part of the aluminate will react with it to form ettringite. The ettringite formed during the initial hydration does not cause expansion as the cement paste is still in plastic state. Due to the shortage of sulfate, the rest of aluminate will react into monosulfate and aluminate hydrates. However, both hydrated aluminate and monosulfate may react with sulfate available from other sources (soil and/or water) to form ettringite again when the matrix is hardened. This will cause expansive damage and is termed sulfate attack.

For cement-stabilized soils, the situation is similar to cement concrete. However, there appears to be two possible mechanisms for sulfate attack. The Type I mechanism refers the conventional sulfate attack, analogous to attack on conventional Portland cement concrete, where the Portland cement hydration products provide the calcium and alumina to react with sulfates to form ettringite. The Type II mechanism is clay-based sulfate attack where the Portland cement hydration products provide calcium and the clay minerals in the soil provide alumina to react with sulfates, when it is present, to form ettringite.

Sulfate-resistant cements that are low in C₃A may provide protection against the Type I sulfate attack, but they will be completely ineffective against the Type II sulfate attack where the alumina is provided by the clay minerals in the soil. The application of lime can also cause the formation of ettringite and result in expansion.

Structure of ettringite

The crystal structure of ettringite was elucidated by Moore (1970) and Taylor (1974), and it was reported that it consists of columns containing (Al(OH)₆)³⁻ octahedra which are linked to each of their neighbors through groups of three Ca²⁺ ions, the coordination polyhedra of which are completed by water molecules. Each Ca²⁺ is thus eight-coordinated, by four H₂O molecules and four OH⁻ ions. These columns have an empirical formula of (Ca₃(Al(OH)₆)·12H₂O)³⁺. The channels between columns contain sulfate ions and water molecules. For each two units of the above empirical formula, there are four channel sites of which three contain SO₄²⁻ and one contains up to two water molecules, giving the formula (Ca₆(Al(OH)₆)₂·24H₂O)(3SO₄)(2H₂O) or, in more familiar terms, C₃A·3CaSO₄·32H₂O. Approximate calculations based on the composition of ettringite also indicate 1 mass percent of calcium oxide will lead to the formation of about 7.5 mass percent ettringite; 1 mass percent alumina will lead to the formation of 12.5 mass percent ettringite; and 1 mass percent gypsum will lead to the formation of 2.5

mass percent ettringite. The configuration of ettringite is shown in the Figure 2-6. There are three distinct types of water molecules in the ettringite structure, which are water within the channel, water bound to the columns, and water as hydroxide ions of the columns. It is expected that the conditions for dehydration and the structural changes associated with dehydration with differ significantly for each type of water.

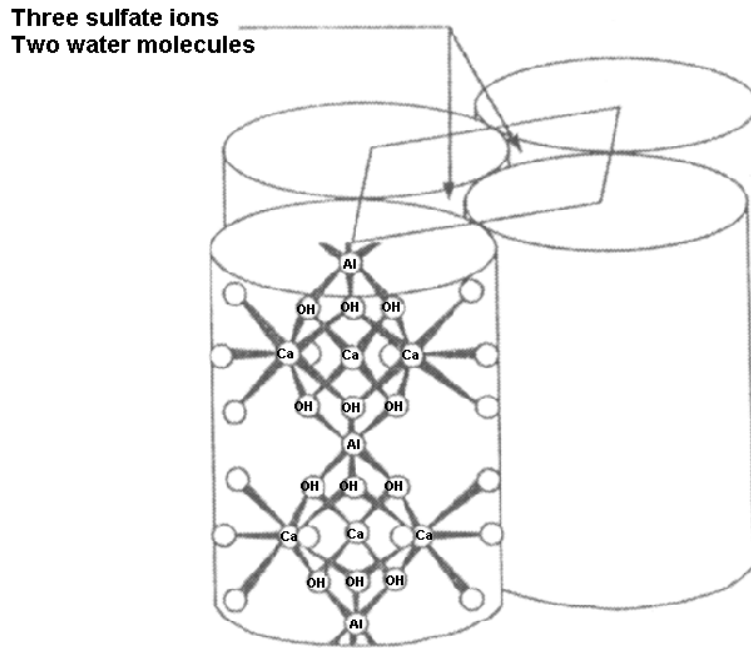


Figure 2-6 The structure of ettringite (from Morre 1970)

The thermal and chemical stability of ettringite, under varying conditions of pH value, have been evaluated by a number of investigators (Ghorab 1985 and 1986; Gabrisova 1991). Ettringite is the stable phase at room temperature and with pH value larger than 10.7. It is stable at sulfate concentrations above 3×10^{-6} mol per liter.

Properties and expansion mechanism

Important properties of ettringite are always connected to its expansion. The mechanisms of expansion were investigated by a number of investigators (Lafuma 1952, Mikhailov 1960, Mehta 1974). Numerous theories and models aimed at explaining the mechanism of formation of ettringite and expansion due to ettringite have been suggested and can be divided into two major schools of thought (Cohen 1983): the crystal growth theory and the swelling theory.

According to the first school, it was concluded that expansion begins when reaction zones of ettringite formation contact others, continue growing, and mutually exert pressure. According to the second school, expansion is caused by the swelling of the ettringite particles which are of colloidal size.

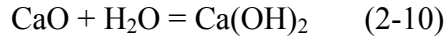
Even though the mechanisms of expansion are not fully understood, some phenomena are obvious. Specifically, the size of ettringite crystals and the presence of

lime affects expansion; in the presence of lime, sulfates, water and alumina, ettringite is formed as small crystals and their formation contributes much to expansion; and in the shortage of lime, the sulfates and water hydrate with expansive particles to give large ettringite crystals which contribute less to expansion (Cohen 1983).

Sulfate Attack on Soil Cement

Sherwood (1958) is the one of the early investigators who first noticed the problem concerning sulfate attack on soil cement. He conducted an experiment (Sherwood 1962) to determine the effect of the presence of sulfate ions in soils on the durability of cement- and lime-stabilized soils. The method of investigation consisted of observing the behavior of specimens of stabilized soil when totally immersed in water. When tested in this way cement- or lime-stabilized clay mixtures containing calcium, magnesium, or sodium sulfates disintegrated within a few days of being immersed, whereas cement-stabilized sand mixtures containing the same proportions of sulfates were unaffected even after being immersed for one year. This suggested that the effect was related to the clay content of the soil. It is proposed that sulfate attack on cement-stabilized soils is due principally to the reaction involving clay minerals and that the relatively slow combination of the sulfates with the cement is of secondary importance. Cordon (1962) conducted a similar laboratory test concerning sulfate attack resistance of soil cement. Different kinds of cements, Type I, Type II and Type V, and a coarse-grained soil and a fine-grained soil were used for specimen fabrication. Subsequently, the specimens were immersed in a sulfate solution. A photographic record, taken at different time intervals, was used as a method of demonstrating the progress of the sulfate attack. Major conclusions included that soil cement is subject to sulfate attack much in the same manner as cement concrete, but the deterioration in soil-cement is more rapid than in cement concrete; soil cement specimens fabricated with Type V and Type II cements are more resistant to the sulfate attack than soil cement specimens fabricated with Type I cement; and soil cement specimens made with fine-grained soils deteriorate more rapidly.

Mitchell (1986) brought attention to the engineering phenomenon of sulfate-induced heave in treated soils. An investigation was carried out concerning a section of major arterial street with lime treated expansive soil base in Las Vegas, Nevada. The completed construction appeared of good quality and initial performance was excellent. However, two years after construction, signs of distress began to appear in the form of surface heaving and cracking. The investigation of the failed pavement also indicated that the failure was not traffic-induced and that the structural design of the pavement section was adequate. It was proved that the soil in the failed zones had a much lower density and higher water content than the intact treated soil. Further testing provided the following information: the soil contained significant amounts of soluble sodium sulfate (up to 1.5 percent by weight); samples taken from intact and unfailed zones would swell if exposed to water; clay minerals were present in the soil; significant amount of ettringite was indicated by X-ray diffraction in both the failed and unfailed zones. These findings taken together led to the following hypothesis for the event leading to the unexpected swelling and pavement failure. When quicklime and soil are initially mixed in the presence of water, the quicklime hydrates according to



Some calcium goes into solution and exchanges with sodium on the clay, and suppresses the swelling tendencies of the expansive clay minerals when the treated soil is exposed to water at a short time after compaction. The result is a compacted soil that exhibits negligible swell and a high strength after soaking. Some of the strength increase may be attributed to the reduction in water content caused by the hydration of CaO. In the presence of sodium sulfate, however, the available lime is partially depleted according to



If the pH rises to 12.4, then silica (SiO_2) and alumina (Al_2O_3) will dissolve from the clay, or they may be present in amorphous form initially. These compounds can then combine with the calcium and sulfate present in the soil to form ettringite. If then the treated material is given access to water, a large amount of swell may occur. The water probably gained access through joints between the asphalt concrete pavement and gutter and curb.

Petry and Little (1993) reviewed a background on sulfate-induced heave in lime- and cement- treated clay soils and some examples of projects affected by this phenomenon. According to the literature, even though the total reaction and favorable environment for formation of expansive minerals resulting from the interaction of lime and sulfate-bearing clay soils or Portland cement and sulfate-bearing soils are not completely understood, the most often found expandable mineral resulting from these reactions is ettringite. Therefore, the formation of ettringite is necessary for the sulfate heave phenomenon to occur, and curtailment or elimination of its formation would dramatically reduce the volume increases noted. When lime or cement is added in sufficient quantities to clay, the pH is raised. Once the pH exceeds 10.5, dissolution of the clay surface occurs, and siliceous and aluminous elements are released. If sulfates, either in solid or groundwater form, are present in sufficient quantity, they may confound the reaction between the calcium and the pozzolans (silica and alumina released from clay minerals) to form significant quantities of ettringite or monosulfate hydrates. Mehta and Klein (1966) determined that the formation of monosulfate hydrates is favored in high alumina environments, but the formation of ettringite is favored in low alumina environments. They also indicated that monosulfate hydrates are favored in 1:1 type clay minerals like kaolinite, while the formation of ettringite would be favored in 2:1 type clay minerals such as smectite. They also describe ettringite as substantially expansive upon wetting, while monosulfate hydrate is not.

Swell testing has been utilized by researchers (Mitchell and Dermatas, 1990) to predict the nature of the volume increase caused by hydration of ettringite. The method of predicting behavior, if performed correctly, should reflect the physical and chemical influences of field conditions. Based on the evidence that shear planes were found and the material in the humps appeared to have been shoved one part over another, or buckled, Petry and Little (1993) introduced a type of swell test that may be used to indicate the nature of the problems. The test utilizes a cylinder specimen and compacted using standard Proctor energy level. The specimen is then placed on a porous stone and wrapped in filter fabric. This assemblage is then placed inside a triaxial membrane and sealed, except for porous stone and filter fabric which are allowed to absorb water as the

assemblage is placed into a bowl. Long-term swell tests are conducted as the height and circumference of the specimens are monitored daily. Simulations of field behavior were believed to be very successful by the investigators. When these specimens were inspected and sampled for testing, they appeared to be nearly identical to the field samples of the stabilized layer. Alternatively, lime or cement treated cylinder bars may be prepared, cured, and tested according to ASTM C 157 and ASTM D 1633. Bars exhibiting over 0.1 percent expansion were considered to have failed (Huntington et al.1995).

Factors Affecting Sulfate Attack

Similar to cement concrete, the pH value, moisture availability, temperature, sulfate levels, and clay mineralogy may all affect sulfate attack of cement-stabilized soils. These factors should therefore be determined when stabilized soils are susceptible to sulfate attack.

Sulfate concentration

Sulfate level is always an important factor and a necessary ingredient for ettringite formation. As stated by Ferris et al. (1991), the sulfate content is the most important single property indicating the extent to which ettringite will form. The greater the soluble sulfates, the greater the potential for the growth of ettringite. In addition, Mitchell and Dermatas (1990) explained that it does not depend on the form of sulfate present. The sources can include oxidation of pyrite. The levels of so-called soluble sulfates discussed as potentially problematic differ from one publication to another. Petry (1994) suggests that sulfate levels of 2,000 mg/kg (0.2%) have the potential to cause swelling in lime-stabilized materials and levels of 10,000 mg/kg (1.0%) have the potential to cause serious damage to lime-stabilized materials. This is consistent with Hunter's (1988) findings that 10,000 mg/kg (1.0%) clearly established a condition for sulfate attack of lime-stabilized material was likely. Mitchell and Darmatas's work (1992) work found that ettringite formed at sulfate contents as low as 0.3%, which also provides support for the limits proposed by Thomas et al. (1989) and Perrin (1992). Based on laboratory work, McCallister (1997) suggested appreciably lower limits for sulfate attack on lime-stabilized soils: sulfate contents of 100-5,000 mg/kg (0.01-0.50%) posed a low-to-moderate risk of heave; 5,000-12,000 mg/kg (0.50-1.2%) posed a moderate-to-serious risk of heave; and greater than 12,000 mg/kg (1.2%) posed a very serious risk of heave. Sherwood (1962) reported strength loss for lime-stabilized London clay was approximately 24% at sulfate contents as low as 0.25% and was approximately 67% at a 2.0% sulfate content. The problem with interpreting the sulfate data may be that different test methods will give significantly different numerical values for soluble sulfate content of soils, but the recommendations from the aforementioned researchers all suggest sulfate attack on lime-stabilized material can occur at relatively low levels of sulfate content.

For Type I sulfate attack on a coarse-grained soil without significant clay content, conventional published guidance (Neville 1981) on exposure levels and protective measures for Portland cement concrete would seem reasonable. Dunlap et al. (1975) suggested that for sulfate contents greater than 0.09%, sulfate-resistant cements should be used for protection against sulfate attack of cement stabilized coarse-grained soils, but there has been no experimental verification of this limit. There are several complicating

factors for using conventional Portland cement concrete sulfate attack guidance for cement stabilized soils. For instance, cement stabilized materials are more permeable than conventional concrete, which would tend to make them more susceptible to attack. On the other hand, cement stabilized soils have more voids than conventional concrete and may be able to accommodate ettringite growth without destructive swelling. Sherwood (1962) found that the compressive strength of sand specimens without clay minerals that were stabilized with 10 percent ordinary Portland cement generally were unaffected by immersion in calcium and magnesium sulfate solutions varying from 0.25 to 3.0 percent sulfate (SO_3). Some of the immersion periods were up to one year. These results suggest that it is unlikely that Type I sulfate attack actually will occur on cement-stabilized soils without significant clay content. However, more testing is needed to verify Sherwood's (1962) results before such a sweeping conclusion is warranted.

Type II sulfate attack where alumina is available from the clay minerals in the soil is a much more significant threat to cement stabilized soils. Sherwood (1962) found that sulfate contents as low as 0.2 percent resulted in losses of strength of more than 59 percent in a clay stabilized with 10 percent cement. It appears that cement stabilized soils containing clay minerals are particularly susceptible to sulfate attack. However, at present, inadequate data are available to draw any type of reasonable limits on allowable sulfate exposure for cement-stabilized soils containing clay minerals.

Clay content and clay minerals

In assessing tolerable sulfate levels for stabilized materials, the clay content of the soil is also a major factor. Hunter et al. (1998) found that only minor swelling of lime stabilized soils occurred when clay size particles were less than 10 percent even at sulfate levels as high as 25,000 mg/kg. Sherwood (1962) observed that clay content had a significant impact on sulfate attack of cement stabilized sand-clay mixture. Specimens were prepared that consisted of sand and 0, 25, 50, 75, and 100 percent London clay stabilized with 10 percent Portland cement. The compressive strength of the 100 percent sand specimens essentially was unaffected by immersion in sulfate solutions, but strength loss was dramatic in all specimens containing London clay. The amount of strength loss was related directly to the percentage of clay in the specimen with percent loss increasing as the percent clay increased for immersion at any given level and type of sulfate.

Conceptually, alumina-rich clay minerals such as kaolinite that can give up more alumina in high pH environments to participate in ettringite formation are potentially more susceptible to sulfate attack than clay minerals such as montmorillonite with lower alumina content. Mitchell and Dermatas' (1992) investigation of swelling lime stabilized specimens of sand mixed with kaolinite or montmorillonite provided experimental support for this concept. However, Mehta and Klein (1966) reached a conclusion that clay minerals with lower alumina content would experience a higher sulfate expansion. The disagreement may be due to different reaction conditions. Nevertheless, more research is needed to understand more clearly and correctly the role of clay mineralogy on the reaction.

pH value

Lime and Portland cement stabilization typically raises the soil pH value to above 12. When the pH value increases above approximately 9 (Rollings et al. 1999), solubility of

silica and alumina increase exponentially as a function of pH. This is a crucial factor in freeing material from the clay particles to participate in the pozzolanic reactions, but it also produces the chemically active alumina necessary for formation of ettringite during sulfate attack on stabilized materials. The high pH environment that frees alumina for ettringite formation will always exist in conventional Portland cement or lime stabilization.

The pH value is also an important factor to determine the formation and expansion of ettringite. In an ettringite stability study, Gabrisova et al. (1991) demonstrated the boundary for the disappearance of ettringite is $\text{pH} = 10.7$. Therefore, at pH value below 10, only gypsum and aluminum sulfate are the stable phases. On the other hand, Wang et al. (1986) reported that NaOH accelerates the formation and expansion of ettringite. As the NaOH concentration increases, the CaO concentration decreases, and both the ettringite content and expansion of the paste increase. This indicates that expansion depends more on pH rather than CaO concentration.

Moisture

Moisture is a necessary ingredient for formation of ettringite, and generally ample moisture from rainfall infiltration, water vapor movement, etc., is available in a pavement structure to support this reaction. The amount of observed expansion and water accumulation associated with poor drainage, ponding or utility cuts have been correlated on some projects suffering from sulfate attack on stabilized materials (Mitchell 1986, Hunter et al. 1988; Perrin 1992). It appears that the relatively high permeability of the materials encourages swelling, even though it is not a necessary condition for the expansive reactions to occur.

Temperature

The formation of ettringite is temperature dependent (Mehta and Klein 1966; Mitchell and Dermatas 1992). Usually, the temperature regimes ($20 - 40^{\circ}\text{C}$) found in pavements are adequate to allow these products to form, and their rate of formation with resulting expansion would be the greatest in warm weather.

2.2.3 Case Review

Although reports of sulfate attack on stabilized materials are relatively uncommon, when such attacks do occur they are highly destructive and result in major repair or replacement costs. Several cases have been reviewed and all indicated that the formation of ettringite is highly expansive and is the cause of the expansion observed in sulfate attack on cement-stabilized material.

Georgia Case

In the spring of 1992, unexplained bumps began to appear in the Bush Road pavement (Rollings et al. 1999) within 6 months after construction. As the initial bumps began forming, additional bumps followed quickly. These bumps varied from barely noticeable up to 3.1 m wide and 63 mm high. The bumps developed erratically along the length of the road and often were associated with discontinuities such as construction

joints. Excavation of the bumps found apparent expansion and cracking in the base course material had caused the visible bumps on the pavement surface.

The soil used in the cement stabilized base course was predominately a sand material with some fines and was described as clayey sand. The material was stabilized with 5 or 6% Portland cement. Laboratory examination of samples from an area showing distress revealed the presence of ettringite due to sulfate attack on cement stabilized soil base. It was concluded that the formation of ettringite caused severe expansion. The source of the sulfur was identified as the well water that was used to mix the cement soil base. This sulfate attack of cement-stabilized soil was highly destructive and the whole base course had to be excavated and re-constructed.

Texas Case

Several roads, airfield pavement, and parking lots in Texas have also suffered severe pavement damage due to expansive minerals formed from the reactions of calcium-based materials used to stabilize sulfate-bearing soils. Perrin (1992) summarized the findings of investigations on three projects, where these reactions caused considerable damages. On these projects, heaves caused linear ridges or bumps as much as 300mm high in both the transverse and longitudinal directions on the roads or parking lots. Generally, the damage appeared to be most severe in areas of poor drainage. Shear planes observed at the damaged areas confirmed that the heaving was caused by horizontal expansion resulting in buckling and not concentrated vertical heaves. Soluble sulfate was traced from mixing water or gypsum seams near the surface.

Since sulfates were suspected in the native soil from the preconstruction investigation, experimental test sections were planned with both lime of 6% and cement of 4% as alternate stabilizers for the high PI natural clay (Kota et al. 1996). Laboratory tests indicated that the natural soil had as high as 24,700 ppm of soluble sulfates based on a 1:10 soil water ratio. Several months after construction, heaving was observed in the form of transverse ridges in both lime-stabilized and cement-stabilized sections of the roadway. Damage became apparent within a few days after initial rains following construction. The transverse ridges were found to be 50 to 100 mm high and are spaced at distances of 4.5 to 7.6 m. The distress in the lime-stabilized section was more severe than the distress observed in the cement treated section.

2.3 Methods To Avoid Or Mitigate the Problem

A limited amount of work (Ferris 1991, Wild et al. 1996) has been done to investigate ways to control sulfate attack on stabilized soil. Most often these methods are costly, and if they are not properly evaluated before use in the field, the damage can occur and may be severe. For example, sulfate resistant cements might provide protection against Type I sulfate attack, but will be useless against Type II attack. In general, stabilization is cost effective on the basis of initial construction costs. However, if the pavement survives only for a short period, its cost can greatly exceed nonstabilized methods.

2.3.1 Low-calcium Stabilizers

Calcium-based stabilizers such as lime, cement, and fly ash have a well-established record of success in stabilizing soils. However, it is clear that if sulfate-bearing soils are stabilized with different stabilizers, the stabilizer that supplies more calcium will form more ettringite. Since lime has more calcium than cement or fly ash, one would expect more ettringite to form in the lime stabilization of sulfate bearing soil. For this reason, it appears that lime is more severe than low-alumina cement or fly ash in causing sulfate-induced heave. A practical example (Kota et al. 1996) indicated more ettringite will be produced and cause more heaving with the use of lime. For that reason, low-calcium stabilizers seem to be suitable candidates for stabilization of sulfate-bearing soils. Conceivably, it also may be possible to use mixture of pozzolans and Portland cement or lime as low-calcium stabilizers to counter the formation of ettringite as it is sometimes successful with Portland cement concrete. These pozzolans include ground granulated blast furnace slag (GGBS), fly ash (FA), silica fume (SF), etc.

In fact, research work on the mixture of GGBS and lime as stabilizer was conducted (Wild et al. 1996,1998) and demonstrated that partial substitution of lime with GGBS may be effective for sulfates-bearing clay soil stabilization. This initial study revealed that small additions of GGBS to sulfate-bearing soils substantially reduce the damaging expansion and have positive effect on strength development.

2.3.2 Other Possible Methods

Except for the application of low-calcium stabilizers, other possible methods may have to be examined in detail prior to construction of pavements on soils with soluble sulfates. Following are some of the alternatives.

Double Application of Lime

The concept of double application of lime (Ferris 1991) is based on the assumption that the first application of lime allows formation and subsequent expansion of ettringite, whereas the second application helps complete the pozzolanic reaction and the formation of cementing agents to bind the soil particles and often increases the strength. The delay period between the first and second treatments is vital to this technique. If sulfates in the soil are only partially soluble during the double application of lime, a low-sulfate form of calcium-sulfate-aluminate-hydrate may form. However, upon release of a high level of sulfates, such as from a subsequent rain, the low-sulfate form may transform into a high-sulfate form of calcium sulfate aluminate hydrate, which can produce substantial later expansion (Little et al. 1992). If sulfates are present in the soil, they may increase sulfate concentrations due to oxidation.

A double application of lime may be effective if the natural soil has a low level of soluble sulfates and the soil does not have sulfate minerals. However, a double application of lime will be effective only if used with sufficiently long delay periods between the two applications, with more than an optimum amount of water in the first application, and when low percentages of lime are involved. If all the foregoing

conditions are met, it appears that soils with soluble sulfates up to 7,000 mg/kg (based on 1:10 soil-water) may be effectively stabilized with a double application of lime.

Non-calcium-based Stabilizers

Since calcium is necessary to form the expansive materials, it appears that stabilizers with no calcium may prove successful since this will entirely eliminate the formation of ettringite. Petry (1992) remarked that the formation of ettringite is necessary for the sulfate heave phenomenon to occur, and curtailment or elimination of its formation would dramatically reduce the volume increases noted. There are several non-calcium-based soil stabilizers available on the market, such as sodium chloride (Singh et al. 1999) but they lack field performance history. A careful evaluation of these products on soils with high levels of soluble sulfates might be a good starting point in progressing toward a solution to this problem.

Geotextile/Geogrid Materials

A combination of geotextiles and geogrids can be considered as an alternative for highly plastic soils with soluble sulfates (Perrin 1992). The purpose of a geotextile is to separate the layers of the pavement from the natural subgrade and also to prevent infiltration of clay into the layers above due to the dynamic action of traffic loads. If the natural soil is not a highly plastic clay, a geogrid alone can be used. Perrin (1992) also mentioned one instance where geogrid was used successfully on very high sulfate soil. Although the structural contribution of the geogrid is not evident at present, it was at least successful in avoiding the problems that would have been caused by lime stabilization of the sulfate-bearing soil.

Stabilizing the Top Portion of Select Fill

Soils with no sulfates can be brought in from different locations to use as a select fill material immediately above the subgrade. Stabilizing the top 150 to 200 mm of this select fill material can be considered equivalent to stabilizing the top 150 to 200 mm of the natural subgrade. However, the main benefit is to avoid the sulfate-induced heave. Although the select fill material may not contain soluble sulfates, it is possible that soluble sulfates may slowly infiltrate the stabilized layer from the sides or from capillarity action from the underlying materials. However, the extent to which sulfates from external sources can enter the pavement is unclear. This method could be a viable alternative for soils with moderate levels of soluble sulfates.

Pretreatment with Barium Compounds

Ferris (1991) suggested using barium compounds to pretreat the soil and stabilize with lime later. Barium reacts with soluble sulfates and forms a low-soluble barium sulfate. Since the sulfates are tied up with barium sulfate, subsequent application of lime will be successful in stabilizing the clay without forming the expansive minerals. Although the barium compounds are found to be effective in laboratory studies, Ferris

(1991) was skeptical about their application in the field due to their impact on the surrounding environment.

Asphalt-stabilized Base

Construction of an asphalt stabilized base directly on the natural subgrade can be an alternative for soils with low plasticity. If the natural subgrade is a high PI clay, then placing a select fill of low PI material between the natural subgrade and asphalt-stabilized base is recommended.

Compacting to Lower Densities or Regulating Particle Size Distribution

It may be possible to reduce horizontal expansions by compacting the stabilized layer to a lower density. Increased pore space at the lower densities provides more room for the growth of expansive minerals and results in less overall expansions.

Yoder and Witczak (1975) developed a model to describe density of soil-aggregate mixtures, as given in Figure 2-7. An aggregate that contains little or no fines (Figure 2-7a) usually has a relatively low density and high void ratio, and may accommodate some expansion. An aggregate that contains sufficient fines to fill all the voids between the aggregate grains (Figure 2-7b) has a high density, but cannot accommodate any expansion. The situation is same when a material contains a great amount of fines (Figure 2-7c) and the aggregate merely “floats” in the soil. However, its density is low. Nevertheless, it is proposed that suitably regulating particle size distribution may control expansion effectively.

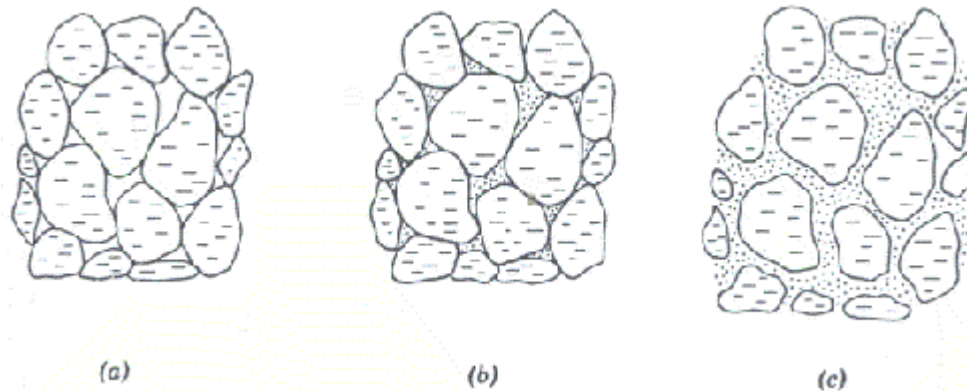


Figure 2-7 Physical states of soil-aggregate mixtures (from Yoder and Witczak 1975)

CHAPTER 3. EXPERIMENTAL DESIGN AND METHODOLOGY

3.1 Experimental Design

Based on the research objectives and scope as well as information from the literature review, an experimental program was organized into the following components: identification of the Winn Rock, its weathering products and the properties of the Winn Rock soil mixture; experimental studies of Winn Rock soil stabilized using different kinds of cementitious materials in order to develop cost effective methods to mitigate sulfate attack damage; and a general experimental investigation of factors influencing internal and external sulfate attack on soil cement.

The specific objective of the research work was to acquire basic information of the problem of the Winn Rock sulfate expansion case, and develop a cost effective method to solve or mitigate this problem. The broad objective was to develop a general understanding of the mechanisms responsible for sulfate-induced heave, important factors and the effectiveness of various mitigation methods.

The scope of the three components of the project is summarized below.

3.1.1 Winn Rock Soil: Its Mechanical and Chemical Properties

Mineral aggregates are the basic materials of pavement construction. They support the main stresses occurring within the pavement. The manner in which they do so depends upon the inherent properties and qualities of the individual aggregate particles and upon the means by which they are held together, i.e., by interlocking, by cementitious binders, or by both. Aggregates may be used in pavement construction. However, in low-cost roads, where it is desirable to make the most use of locally available materials, natural gravel aggregates or crushed aggregates mixed with soil frequently form the entire pavement structure. This is the case for the application of Winn Rock.

To develop a better understanding of the mechanism that led to the heave of soil containing Winn Rock and stabilized with cement, the mineralogy and the microstructure of Winn Rock and its weathering products were studied. The engineering properties of Winn Rock soil mixture, such as particle size distribution, plasticity index, compaction and strength, were also evaluated.

3.1.2 Winn Rock Soil Stabilized with Different Kinds of Cementitious Materials

Since the primary goal of the research project was to eliminate or mitigate the problem concerning the stabilization of Winn Rock soil, different kinds of stabilizers (including cement, blended cements incorporated with ground granulated blast furnace slag, GGBS, fly ash, FA, etc.) were selected for investigation and a comprehensive study was carried out including mineralogical and microstructure analysis and mechanical properties test. The sulfate attack resistant properties of each cementitious material would be assessed and compared with each other, involving their linear expansion, compressive strength and variations of their microstructures. In addition, the mechanism of resistance to sulfate attack was interpreted in detail.

3.1.3 Sulfate Attack on Soil Cement

The experiment was to simulate the expansive process of soil cement subjected to sulfate attack. Instead of Winn Rock, research on local soils bearing no sulfate and stabilized with cementitious materials was conducted.

Various conditions were set up to simulate the process of internal and external sulfate attack with different concentrations of sulfate and other conditions and to identify its primary factors that would lead to the sulfate expansion. Potential protective methods were also analyzed and assessed.

3.2 Methodology

Sulfate-induced heave is a complex issue. Understanding the phenomena requires application of concepts from civil engineering, chemistry, materials science, and geology. Various experimental methods were used for this research work, and these methods can be categorized as instrumental analytical techniques and laboratory soil testing.

3.2.1 Instrumental Analytical Techniques

Analysis techniques including X-ray diffractometry (XRD), thermal analysis (TA), electron scanning microscopy (SEM), et al., were used for research. The working principles and applications of each instrument are introduced briefly as follows.

X-ray Diffractometry

In the study of cement, soil, and other materials, X-ray powder diffraction (XRD) methods are the most powerful and commonly used as they can provide information about phase identification, chemical composition, crystal size. They can also be used for quantitative analysis of phase compositions.

When a narrow beam of monochromatic X-rays penetrates the face of a crystal, reflection will occur. The condition for “reflected” beam is given by the relation:

$$n\lambda = 2d\sin\theta \quad (3-1)$$

Where n = an integer, the order of the reflection;

λ = the wavelength of the X-rays;

d = the interplanar spacing between successive atomic planes in the crystal;

θ = the angle between the atomic plane and both the incident and reflected beams.

This fundamental relation (Figure 3-1) is known as the Bragg equation or Bragg law. The values of d and the number and types of atoms in each plane are unique for every mineral. The reflections are limited to those angles where X-rays “reflected” by a series of hkl planes are in phase. This analogy based on the distinct geometry of each mineral forms the basis for qualitative analysis by XRD. The angles at which peaks are expected can be calculated from basic cell parameters.

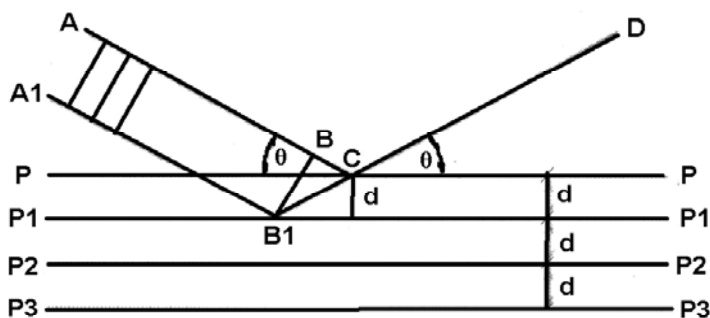


Fig.3-1 The principle of X-ray reflection

Experience with applications of the simple geometric relationships obtains from the Bragg Analogy and unit cell parameters for different minerals reveals that the intensity of XRD peaks varies. The intensity of diffraction varies because atoms with different scattering efficiencies for X-rays are situated throughout the volume of the unit cell. The intensity is the summation of the scattering by all atoms with a correction for phase interference differences due to their position. In general, crystalline materials of high symmetry tend to give strong patterns containing relatively few peaks, while materials of lower crystal symmetry give weaker pattern and a greater number of lines.

Quantitative X-ray power diffraction analysis is often necessary for phase quantitative identification. The basic principal and procedure is same as for qualitative analysis, but much attention must be paid for sample preparation and selection of testing conditions.

Thermal Analysis

Thermal analysis methods can be defined as a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. The physical property measured and the corresponding thermal analysis techniques are tabulated in Table 3-1.

Table 3-1 Physical properties measured in thermal analysis

Physical Property	Derived Techniques	Abbreviation
Mass	Thermogravimetry	TG
dm/dt	Derivative Thermogravimetry	DTG
Temperature	Differential Thermal Analysis	DTA
Temperature	Differential Scanning Calorimetry	DSC

Thermogravimetry

The thermal analysis technique of thermogravimetry (TG) is one in which the change in sample mass (mass-loss or gain) is determined as a function of temperature and/or time. The resulting mass-change verse temperature curve provides information

concerning the thermal stability and composition of the initial and intermediate compounds.

Quantitative measurements of the mass-changes are possible by determination of the distance, on the curve mass axis, between the two points of interest or between the two horizontal mass levels.

Derivative thermogravimetry

In derivative thermogravimetry (DTG), the derivative of the mass-change with respect to time, dm/dt , is recorded as a function of time (t) or temperature (T). The area under the DTG curve is directly proportional to the mass-change; the height of the DTG peak at any temperature gives the rate of the mass-change at that temperature.

When overlapping reactions occur, it is sometimes difficult to locate an unambiguous point on the TG curve where one reaction ends and the other starts. By using the minimum in the DTG curve, an extrapolation procedure can be used to determine approximately where the second reaction begins.

The TA Instruments Hi-Resolution technique is another alternative. It differs from previous control techniques in that the heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposition of the sample so as to maximize weight change resolution.

Differential thermal analysis

Differential thermal analysis (DTA) is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of the sample, inert material, or furnace temperature as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, crystalline structure inversions, dehydration reaction, dissociation or decomposition reactions, and other chemical reactions. The temperature changes occurring during these chemical or physical changes are detected by a differential method. If the sample and reference temperatures are T_s and T_r , respectively, then the difference in temperature, $T_s - T_r$, is the function recorded.

Differential scanning calorimetry

In DTA, reactions are observed by measuring the deviation of the sample temperature from the temperature of the reference material. This deviation causes thermal fluxes which complicate the theoretical description of the curves and decrease the sensitivity. It would be advantageous to keep the sample and reference at the same temperature and to measure the rate of heat flow into each that is necessary to maintain the constant temperature. This is achieved by placing separate heating elements in the sample and reference chambers; the rate of heating by these elements can be controlled and measured as desired. This is the basis of differential scanning calorimetry (DSC).

Electron Scanning Microscopy

The interaction of an electron beams with a solid can generally result in a variety of signals that can produce important information on structural, compositional, and other

properties of the materials. The major signals produced by the interaction of the primary electrons with a solid are illustrated in Figure 3-2.

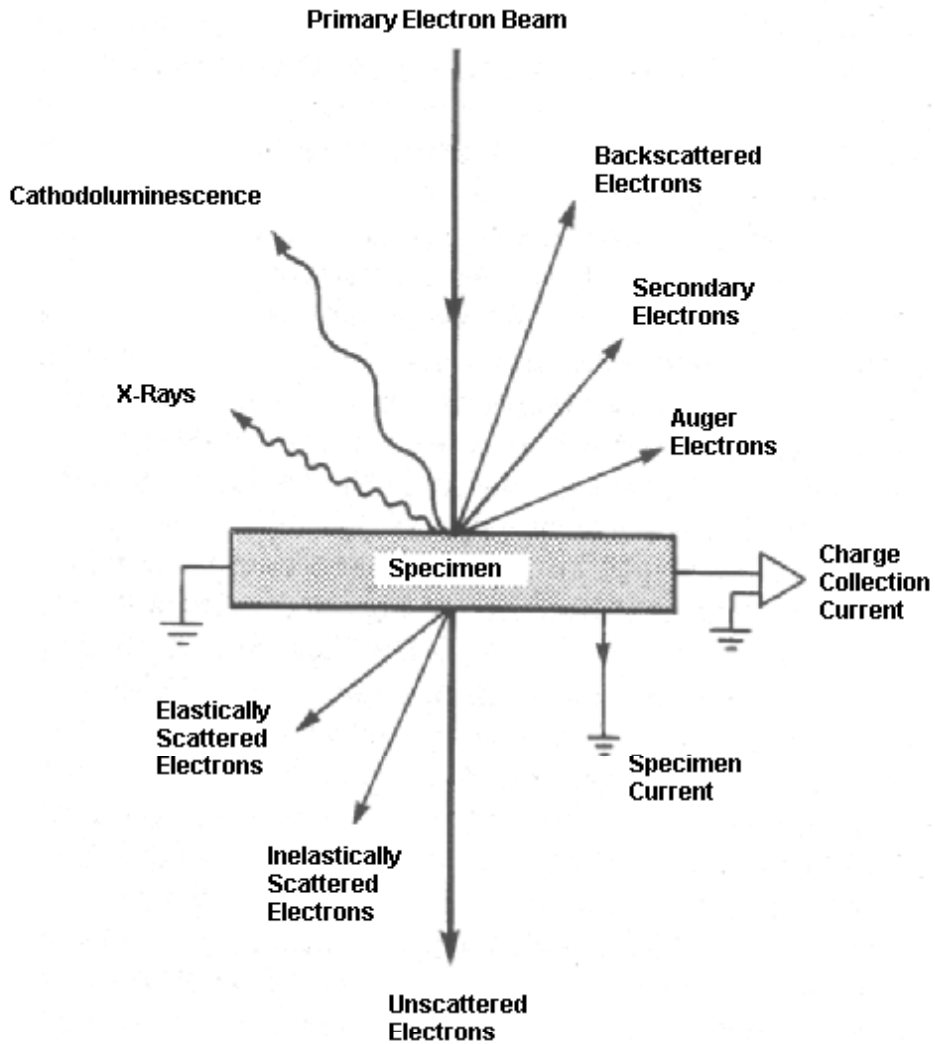


Fig. 3-2 The major signal produced by the interaction of the primary electrons (from Christian and O'Reilly 1986)

Useful signals are the low-energy secondary electrons, the high-energy backscattered electrons and X-rays. Secondary electrons, which provide the most widely used SEM technique, are those emitted with energies less than 50 eV and they produce topographic contrast with much better resolution and depth of the field than do optical microscopies.

The electron beam can be focused to a small spot, and scanned across the specimen to generate the signals that control the local intensity of the image on the view screen, thus the primary uses of the SEM lie in its direct observation of surface topography from the secondary reflected electrons.

Backscattered electrons are emitted with energies close to that of the incident (primary) electron beam. Backscattered electrons can provide information on the specimen topography, as well as atomic number contrast since regions of higher atomic number Z backscatter more primary electrons. Areas that appear brighter are regions with a larger average atomic number, and thus, this type of contrast can provide qualitative information on compositional uniformity. A flat sample is usually needed in order to discriminate between the topographic information, and the compositional information as well as phase identification.

The X-rays can be analyzed with a suitable detective system – energy dispersive spectrophotometer (EDS), giving a chemical image. The X-ray image of the surface may be qualitative, and with suitable calibration of X-ray production, quantitative.

3.2.2 Laboratory Soil Testing

A dozen of tests are available concerning the materials characterization of stabilized soils. Among them soil classification, density and compressive strength are the basic and most important properties. These properties identify or relate to other engineering properties including stiffness, durability, etc., and lead to a routine laboratory soil testing procedure for stabilized soils. The present research work was focused on these basic tests.

Soil Classification

Soil classification categorizes soils according to their probable engineering behavior. By knowing the soil classification, a fairly good idea is obtained of the way the soil will behave during construction and service. According to ASTM D 2487 or AASHTO M 145, laboratory tests for soil classification comprise grain size analysis and Atterberg limit tests.

The particle-size distribution involves two tests, which determine the percentages of individual particle sizes present in a soil. These two methods are sieve analysis for particle sizes larger than 0.075 mm in diameter, and hydrometer analysis for particle sizes smaller than 0.075 mm in diameter. If significant quantities of both coarse- and fine-grained particles are present in the given soil, the results of both tests may have to be combined to give the particle-size distribution. The results of a particle-size analysis are presented to make a plot of the sieve or particle size versus the percentage passing the given sieve. The results of this test are of most value when used for soil classification purposes. It is often found that the larger the particle size, the better will be the engineering properties of the soils for pavement construction.

By consistency is meant the property of a soil which is manifested by its resistance to flow. As such it is a reflection of the cohesive resistance properties of the soil rather than of the intergranular ones. These properties are considerably affected by the moisture content of the soil. The behavior of soil can be divided into four basic states: solid, semisolid, plastic, and liquid. The moisture contents defining the transition from the state to another are defined by three limit values. Among them, two of these limits, the liquid limit (LL) and the plastic limit (PL) are used in the engineering classification systems.

The liquid limit of a soil is the moisture content, expressed as a percentage by mass of the oven-dry soil, at the boundary between the liquid and solid states. This boundary

was arbitrarily defined by Atterberg as being the moisture content which caused the soil to begin to flow when lightly jarred against the heel of the hand. The plastic limit of a soil may be defined as the moisture content of the soil at the boundary between the plastic and semi-solid states. This boundary was also defined by Atterberg as the moisture content at which a sample soil begins to crumble when rolled into a thread under the palm of the hand. A value usually used in conjunction with the liquid and plastic limits is the plasticity index. The plasticity index (PI) of a soil is the arithmetic difference between the liquid and plastic limits.

The most common application of the Atterberg limits test results is for the purpose of soil classification. Both the liquid limit and the plasticity index can be used to a certain extent as a quality-measuring device for pavement materials, in order to exclude soil materials with too many fine-grained particles that have cohesive plastic qualities.

Density and Compaction

Density is an elementary soil property which characterizes the state of a soil. Soil density can be altered by compaction to control and improve other engineering properties such as compressibility and strength.

Wherever soil is used for pavement construction purposes, it is placed in a loose state and then compacted by rolling or vibrating until the desired degree of compaction is achieved. Field moisture-density tests provide a means by which compaction of the soil is controlled on site. The moisture-density test is designed specifically to aid in the field compaction of soil. The assumption is that the stability of a given soil increases with increasing dry density. It is therefore common practice to specify the compaction required for a soil or soil-aggregate mixture as a percentage of that achieved in the laboratory when compacted at the moisture content which produced the maximum density for the applied effort. A most important factor to be noted about this test is that the presence of a certain amount of water is needed in order to achieve the desired dry densities. Water facilitates the compaction process. However, as the moisture content is increased, a point is reached at which only a small amount of air remains trapped in the soil; this is the point at which maximum density is achieved. Any increase in moisture content above this level simply results in soil being replaced by water, with a consequent reduction in dry density. Thus the laboratory test not only defines the maximum dry density but also suggests how much water should be used during the compaction if this density is to be achieved. However, the laboratory compaction method does not generally duplicate field compaction processes.

Strength

Unconfined compressive strength is one of the most widely referenced properties of stabilized soils. Because strength is directly related to density, this property is affected in the same manner as density by degree of compaction and water content. For strength testing, specimens are generally tested at their maximum dry density and optimum moisture content. However, somewhat more conservative fabrication conditions can be used. Soaking specimens after properly cured is recommended prior to testing since most

soil-stabilized structures may become permanently or intermittently saturated during their service life and exhibit lower strength under saturated conditions.

The unconfined compressive strength test may be classed as a shear strength test, since it is essentially a triaxial test with zero lateral pressure. For soil stabilization work, the test serves much the same purpose as for concrete work. Particular uses of the test are to determine the suitability of the soil for stabilization with a given stabilizer and to compare different mixture to specify the stabilizer content to be used in construction, and to provide a standard by which the quality of the field processing can be assessed. The measured strength value is not used for design purposes, nor is the modulus of the elasticity that can be determined from the stress - strain curve. Rather, the unconfined compressive strength data are principally significant for control purposes and are as indicator of durability.

CHAPTER 4. WINN ROCK SOIL MIXTURE: ITS BASIC PROPERTIES

4.1 Introduction

The potential of sulfate attack on soil cement was established in the early 1960s (Sherwood 1962). This early study concluded that under certain conditions sulfates present in a cement-stabilized soil could lead to its disintegration. Mitchell (1986) brought attention to field problems of sulfate attack on stabilized soils and indicated if sulfates were present in soil, then the use of Portland cement as a stabilizer should be approached with great caution. With the increasing reports of cases (Kota et al. 1996, Huntington et al. 1995, Rollings et al. 1999), the issue of sulfate attack on soil cement has received wide special recognition.

Sulfates of various kinds occur naturally and the main sulfate sources that cause sulfate attack are from soil and water. However, sulfate bearing aggregate can also lead to sulfate attack and this is much more elusive. A recent case that sulfate-induced heave caused by weathering of Winn Rock aggregate occurred in the soil mixture was documented by Louisiana Transportation Research Center (LTRC 2000) and provided the stimulation for this research work.

Winn Rock is a kind of sulfate bearing aggregate and was widely used as pavement construction aggregate material regionally. As the rehabilitation process was carried out, which entailed stabilizing the existing base course with Portland cement, some bases containing the Winn Rock aggregate experienced severe heaving. Remediation costs for the project that suffered sulfate-induced heave damage was very high, and in one instance a stretch of a road several miles long had to be abandoned.

The present work reports the mechanical properties and mineralogical compositions of the Winn Rock soil mixture. Tests including gradation, Atterberg limits, compaction and unconfined compressive strength were conducted. Based on the gradation and Atterberg limits test results, the Winn Rock soil mixture was classified using AASHTO method. Mineralogical compositions of the Winn Rock and the soil mixture were determined with instrumental analysis methods. Attention was paid to the analysis of mineralogical phases of Winn Rock aggregate itself and assessment of the content of sulfates in the soil, since the sulfate concentration is one of the most important parameter that will determine the degree of sulfate attack on the soil cement. Besides, the sensitivity of the mixture to sulfate attack was assessed with lime stabilization.

4.2 Materials And Experimental Program

4.2.1 Materials

Winn Rock mined from the Winn Parish quarry and that separated from the Winn Rock soil mixture (the soil containing Winn Rock aggregate) sampled from the construction site as well as the sampled Winn Rock soil mixture were used for mechanical properties and mineralogical compositions analyses.

Winn Rock mined from the Winn Parish quarry, LA, is considered as fresh and intact rock, which has not experience weathering and can be used for comparative purposes. Winn Rock sampled from the construction site, the shoulder of US 71 near

Campti, Winn Parish, LA, would be expected to undergo some phase change and needs to be thoroughly analyzed. In addition, clay minerals might be introduced by the soil in situ and would influence sulfate expansion of the mixture, further mineralogical compositions analysis is necessary for better understanding of the sulfate attack phenomenon occurred in the soil mixture matrix.

Calcium oxide, as a pure chemical agent supplied by Mollinckzodt Chemical, Inc., KT, was also used as a calcium-bearing stabilizer for tentative stabilization of the Winn Rock soil mixture.

4.2.2 Experimental Analysis of the Winn Rock Soil Mixture

Mechanical Properties Investigation

For mechanical properties analyses, experiments comprising soil classification, compaction as well as unconfined compressive strength testing were conducted according to AASHTO M 145, ASTM D3282, ASTM D558, ASTM D1633 and ASTM D 2166, respectively.

Soil classification system as indicated in AASHTO M 145 takes into consideration the particle-size distribution and consistency. The particle size distribution of the Winn Rock soil mixture was determined with sieve analysis and hydrometer analysis according to ASTM D 422, with a natural specimen. Specific gravity of the mixture was measured according to ASTM D 854. Atterberg limits tests were conducted for the consistency of the Winn Rock soil mixture specimen.

The compaction test was used to determine proper moisture content and density to which the soil mixture is compacted. The standard Proctor compaction effort was utilized throughout the study. In the Proctor test, the soil is mixed with varying amounts of water and then compacted in a mold with a volume of 943.3 cm³. For each test, the moisture content can be determined and the dry density can be calculated. The relationship between dry density and moisture content would reveal the maximum dry density and optimum moisture content.

The procedure used for preparation of unconfined compressive strength test was similar to that used for the compaction tests. However, the specimens for strength testing were compacted at their corresponding maximum dry density and optimum moisture content values. United Compression Model SFM-30E load frame was used for the test.

Mineralogical and Microstructure Analysis

For mineralogical analyses, XRD and SEM analyses were carried out to identify the phase compositions of Winn Rock and its weathering product. XRD and TA analyses were also conducted to identify the phase compositions and sulfate concentrations of the Winn Rock soil mixture.

For XRD analysis, powder samples were prepared by manual grinding in a porcelain mortar pestle to powder form. The powder samples were kept in a desiccator with P₂O₅ for drying. XRD analysis was carried out on a Siemens diffractometer D5000, using a Cu K α radiation at 40 kV and 30 mA, with a Solid State Detector KSI alongside a monochromatic incident ray. The scanning speed is 0.02°, 2 second counting at each step,

the angle scanned was $5-70^\circ 2\theta$. The diffraction pattern for each sample was matched with the standard patterns prepared by the Joint Committee of Powder Diffraction Data Service (JCPDS) with Diffract AT V3.1 Software System. Only qualitative evaluation was conducted to determine the type of the various minerals present in the samples.

SEM analysis was carried out using Jeol (JSM-840), which performs morphological and micro-structural assessment and gives a full elemental description using the energy dispersive spectrophotometer (EDS) if needed. Each particle sample was first freezing dried and then held in an aluminum sample holder and sputter coated with a film of carbon or gold.

TA analysis was also carried out using each portion of Winn Rock soil mixture and much attention was paid to the quantitative analysis of gypsum content. A TA Instrument 2950 was used. About a 25mg powder sample was placed in a crucible. The temperature was raised from 40 to 1000°C at a rate of $50^\circ\text{C}/\text{min}$, with a resolution of 6, which means overlapping peaks will be resolved to a high degree.

Tentative Sulfate Attack Assessment

In order to assess the sensitivity of the Winn Rock soil mixture to sulfate attack, 9 percent calcium oxide was added to and mixed with the mixture. Cylindrical specimens were fabricated with the dimension of $\phi 50 \cdot 100$ mm at 95 percent of maximum dry density and optimum moisture content of the soil mixture. For comparison, a controlled specimen without the addition of lime was also fabricated and cured for linear expansion measurement. The specimens were kept in 100 percent relative humidity and maintained at 40°C . Linear expansion was measured at intervals. Phase composition and microstructures of the lime-treated soil mixture were also traced by XRD and SEM analyses.

4.3 Results and Discussion

4.3.1 Mechanical Properties

Determination of the specific gravity of the Winn Rock soil mixture gives the value of 2.64. For analysis of particle size distribution of Winn Rock soil mixture, the result of sieve analysis of the specimen is shown in Figure 4-1.

The particle size distribution curve shows that the range of particle sizes present in the specimen is between 4.75mm to 0.05mm, and indicates a well-graded distribution. Percentages passing No.10 sieve (2.00mm), No. 40 sieve (0.425mm) and No.200 sieve (0.075mm) were about 80 percent, 40 percent and 15 percent, respectively. Hydrometer analysis indicated that approximate 2 percent of the soil mixture is less than 0.001 mm. As expected for this gravel soil, consistency testing showed it was non-plastic (NP). According to the American Association of State Highway and Transportation Officials (AASHTO M 145) classification system, the mixture specimen is classified as A-1-b group.

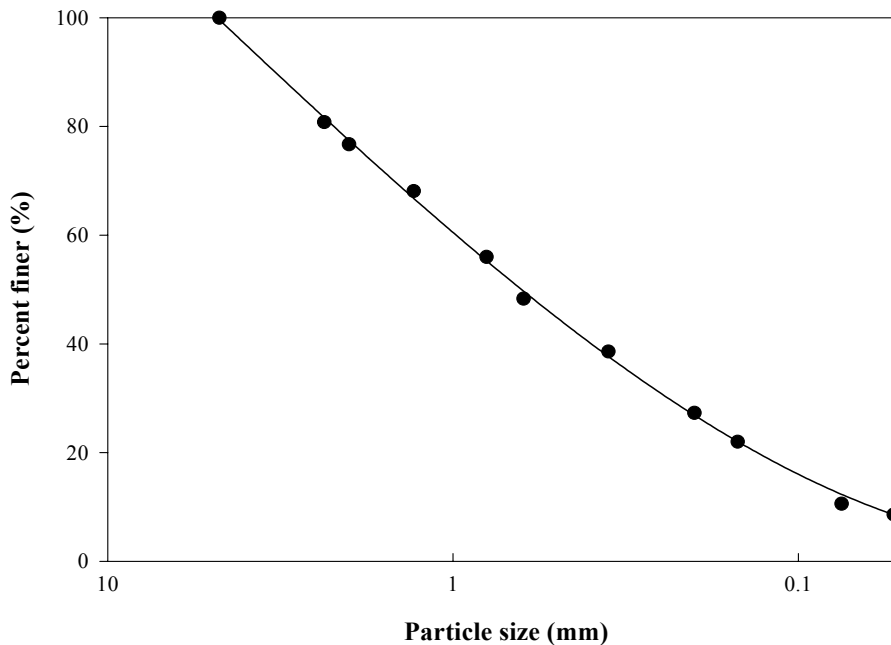


Fig. 4-1 Particle size distribution of Winn Rock soil mixture

The values of dry unit weight γ_d determined from a series of compaction tests is plotted against the corresponding moisture contents (Figure 4-2) to obtain the maximum dry density and the optimum moisture content for the specimen, which are 18.42 kN/m³ and 14.2 percent, respectively.

Unconfined compressive strengths (UCSs) were determined for specimen cured in moist room at 20°C for 7 days and 28 days. Three specimens were tested for each age. Variation analysis was conducted and the average values are listed in Figure 4-3. The unconfined compressive strength of the specimens is quite low, averaging 18 psi at 7 days and 78 psi at 28 days.

Soil classification itself will not yield sufficient information to permit an accurate prediction of true soil behavior. However, it serves a useful purpose and will permit a qualitative estimate of the behavior of the soil. From mechanical point of view, the Winn Rock soil mixture, which is classified as A-1-b, is suitable as pavement base material. It has a certain amount of compressive strength and is easily mixed with cement to produce a soil cement to provide capacity. The well-graded distribution curve of the mixture means that it has a dense soil structure, which is defined as the geometric arrangement of soil particles with respect to one another. Such a gradation will result in a dense structure and a correspondingly high dry density and stability, as aggregates that contain some fines to fill all the voids between the aggregate grains will gain its strength and shear resistance from grain contact. However, it must be indicated that this dense structure may aggravate sulfate expansion, as decreased pore space provides less room for the growth of expansive minerals and may result in less overall expansions (Kota et al. 1996).

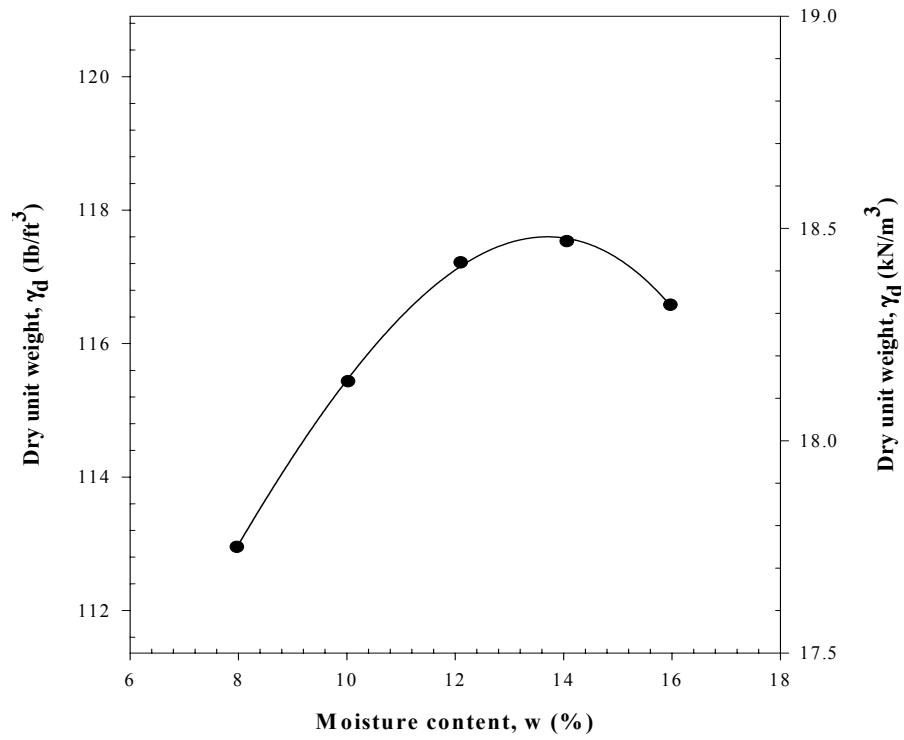


Fig. 4-2 Standard Proctor test results for Winn Rock soil mixtures

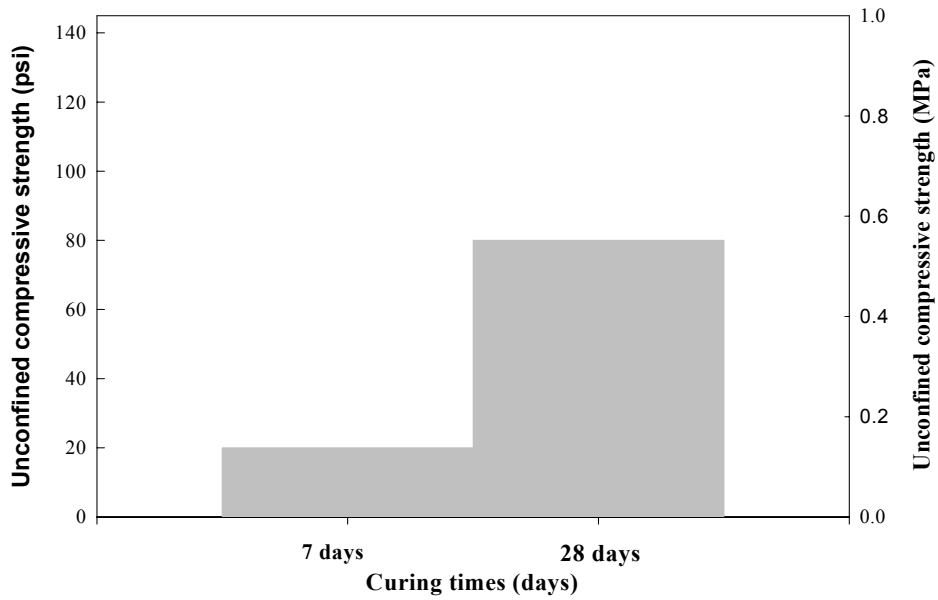


Figure 4-3 UCSs of Winn Rock soil mixture cylinders

4.3.2 Phase Composition and Microstructures

Winn Rock and its Weathering Product

Immediate visual observation of fresh Winn Rock mined from the quarry shows that it is a rock with rough surface texture and dark gray color. However, the surface of some Winn Rock particles sampled from the construction site was covered with a thin layer of efflorescence.

Observations of the fresh Winn Rock aggregate particles kept in moist condition for several months indicated the formation of efflorescence on the surface of these aggregate particles. This efflorescent material can also be easily observed occurred in the fresh Winn Rock aggregate separated from the specimen sampled in situ and was identified as gypsum with XRD analysis as shown in Figure 4-4. The XRD patterns also indicate that the main phase composition of pure Winn Rock is anhydrite.

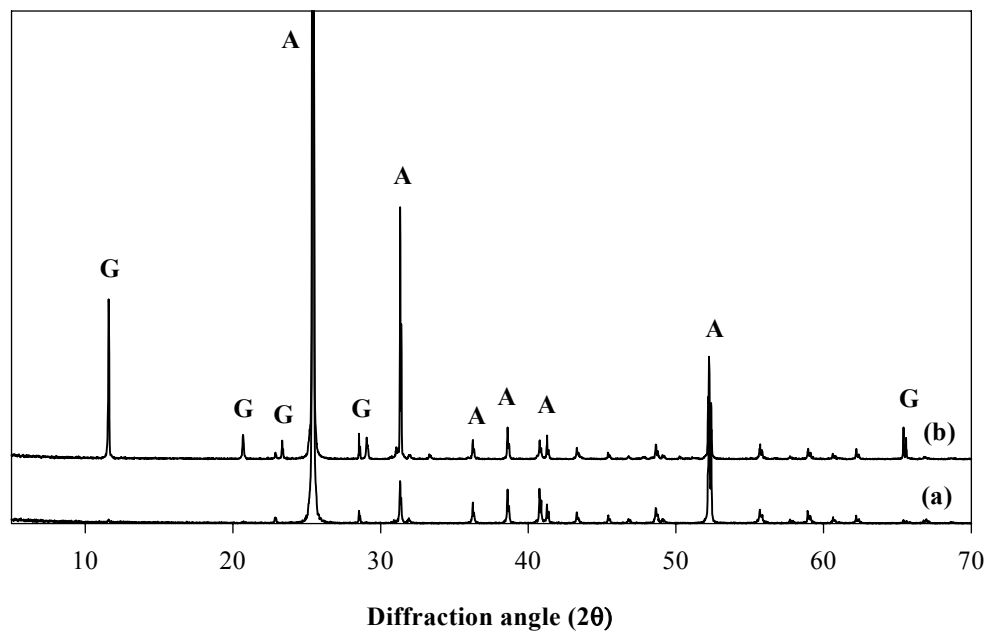


Fig. 4-4 XRD diffraction patterns of Winn Rock and its weathering products
(a) fresh Winn Rock; (b) the weathered products: A-anhydrite, G-gypsum

The SEM micrograph of fresh Winn Rock demonstrates the visual presence of minerals in the sample and shows a dense crystalline microstructure with stacked crystal particle size of about 20 nm (Figure 4-4), and EDS spectrum (Figure 4-5) in conjunction with SEM identifies the elements present in the mineral and also reveals that the major elements of fresh Winn Rock are nearly equal amount of Ca and S. On the other hand, fully developed lath-like crystals of gypsum are found on the surface of weathered Winn Rock (Figure 4-6). These gypsum crystals are present in either long or short laths and are visibly aggregated in separate colonies.

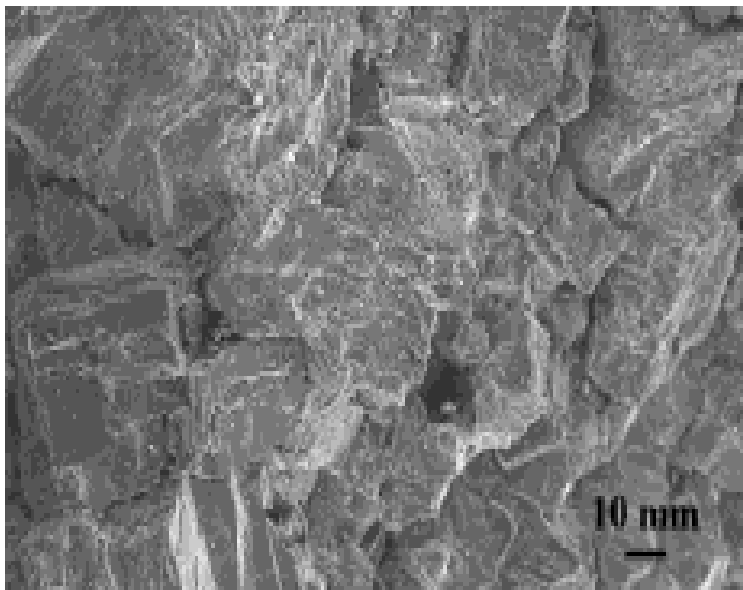


Fig. 4-4 SEM micrograph of fresh Winn Rock

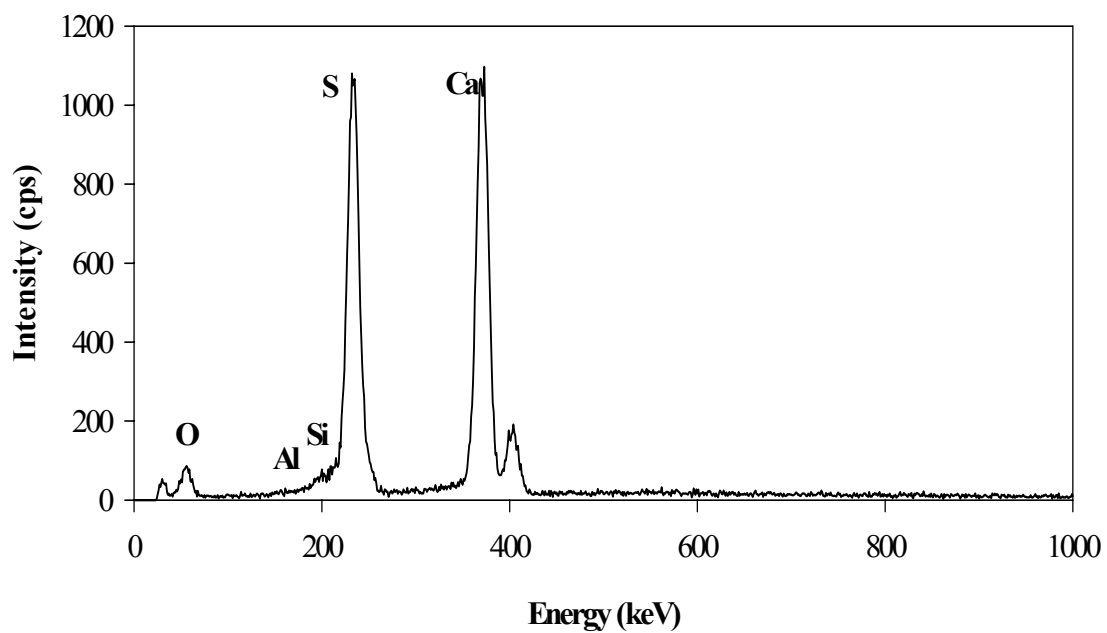


Fig. 4-5 EDS spectrum of fresh Winn Rock

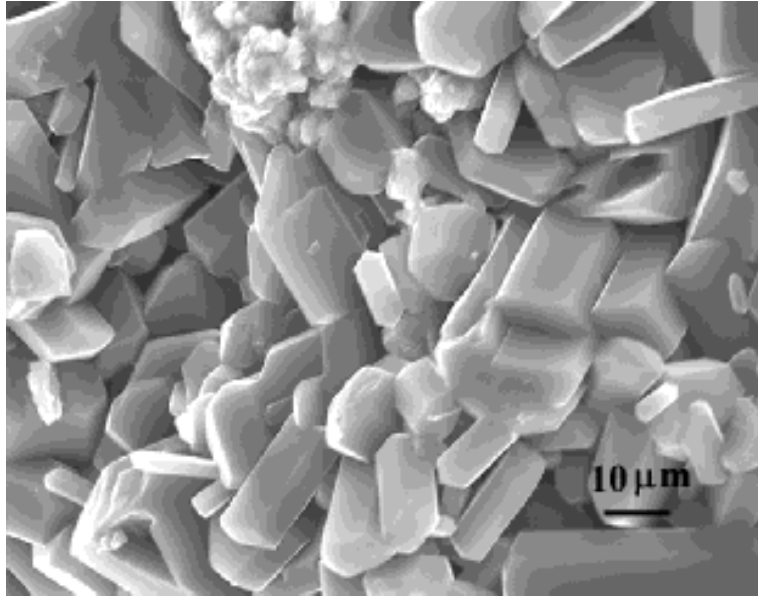


Fig. 4-6 SEM micrograph of weathered Winn Rock

Winn Rock is composed of anhydrite rock and has a dense microstructure, as indicated by XRD and SEM analyses. However, it is an unstable phase and will convert into the more stable form of calcium sulfate, gypsum under favorable conditions. Temperature, pressure and availability of water are the most prominent factors controlling the geochemical phase transitions (Zanbak 1986). At temperatures below about 70°C, anhydrite will react sluggishly with water to form gypsum. The application of Winn Rock as base construction aggregate supplied such an open system, which is defined as an environment where free water may enter into the system and start the hydration process leading to the formation of gypsum. XRD and SEM analyses correlate this observation.

Winn Rock Soil Mixture

Winn Rock is used as aggregate and added to soil to form a soil aggregate mixture. Instrumental analyses are necessary to determine its phase compositions. From chemical point of view, the finer portion of mixture is much more active, so XRD and TA analyses were carried out using the portion of the Winn Rock soil mixture with the particle sizes less than 0.6 mm (sieve No. 30).

The XRD pattern (Figure 4-7) of the Winn Rock soil mixture shows that the occurrence of nonclay and clay minerals except for anhydrite and gypsum.

Figure 4-8 depicts the results of the thermal analysis of the finer fraction (<0.6mm) of Winn Rock soil mixture. The weight loss with an increase in temperature, as given by the TG curve, indicates that there is a slight reduction in weight due to small amount of loss in water at low temperature. However, a major reduction took place at a temperature of 100°C, nearly setting the upper bound of gypsum stability. This temperature is associated with phase transformation of gypsum-anhydrite. Complete dehydration of gypsum, which terminates at 120°C, is accompanied by a total reduction in mass of 7%,

indicating 33 percent gypsum present in the soil fraction less than 0.6 mm. This would represent about 12 percent gypsum present in the soil mixture. Beyond 120°C, the curve shows gradual weight loss up to a temperature of 620°C as adsorbed or interlayer water is removed. This is a good indicator of the presence of clay, possibly kaolinite, in the sample. The second largest endothermic peak and the corresponding reduction in mass of 8% between 620°C and 730°C are associated with the decomposition of carbonate. The third endothermic peak between 800°C and 900°C is probably due to the decomposition of some complex sulfate phase.

Thermal analyses also showed that gypsum contents occurred in fractions with a particle size larger than 4 mm and smaller than 0.053 mm are 29.1 percent and 10.4 percent, respectively. It must be indicated that the amount of gypsum in Winn Rock soil mixture is not constant, but depends on the degree of weathering and other environmental conditions. The gypsum content will increase significantly with moisture and time.

XRD analysis indicated the occurrence of a clay mineral, kaolinite, present in the soil mixture, and they may supply alumina for the formation of ettringite. Gypsum is another ingredient for the formation of ettringite and substantial amount of gypsum present in the soil mixture was identified by TA analysis. Based on laboratory work, McCallister and Tidwell (1997) suggested appreciably lower limits for sulfate attack on lime-stabilized soils: sulfate contents of 1.20 percent posed a very serious risk of heave. 4 percent of sulfate as SO₃ will constitute an expansion risk of Portland cement. The value of sulfate content in this Winn Rock soil mixture exceeded this upper limit and constitutes a real threat of sulfate attack on the soil cement.

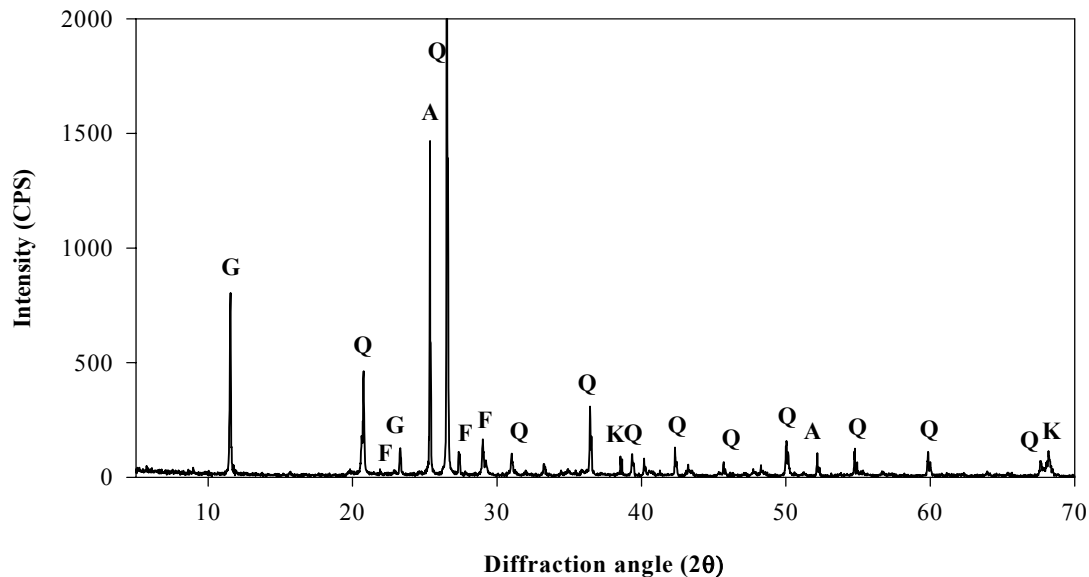


Fig. 4-7 XRD pattern of Winn Rock soil mixture:
G-gypsum, Q-quartz, F-feldspar, A- anhydrite, K-kaolinite

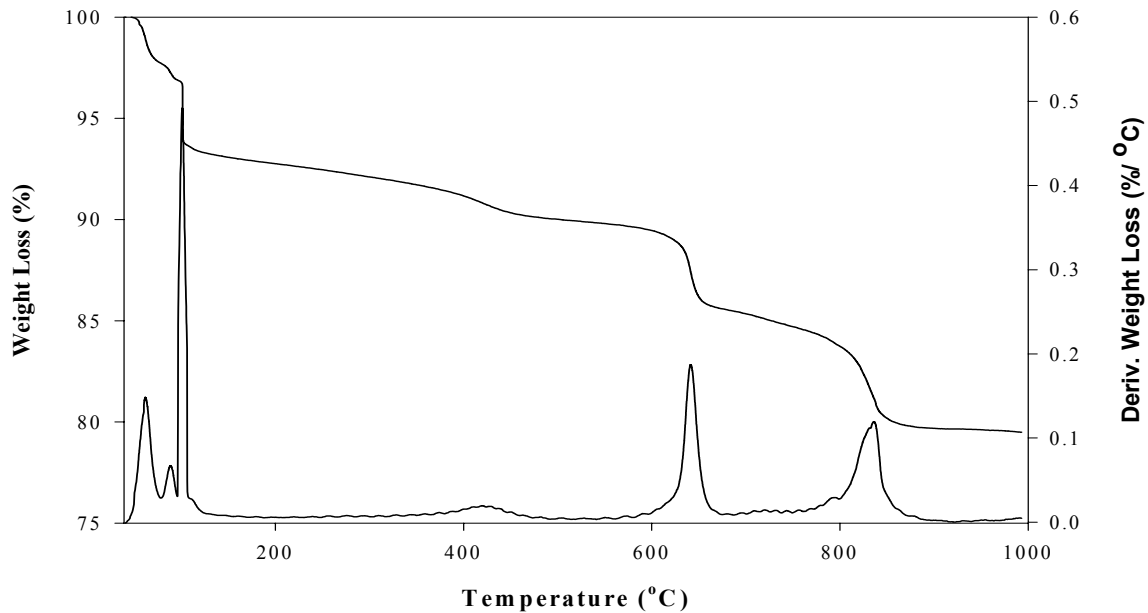


Fig. 4-8 Thermal analysis of Winn Rock soil mixture

4.3.3 Sulfate Attack Assessment

In order to evaluate the potential of sulfate attack on the Winn Rock soil mixture, linear expansion of cylindrical specimens, one treated with 9 percent of lime and one plain soil, were measured at intervals. The measurements demonstrated that the expansion reaches 5.1 percent within the first curing day and 7.7 percent within the second curing day, and remained essentially stable thereafter. Then it terminated forever, whereas the untreated specimen underwent no expansion. As no alumina can be derived from lime, the expansion is due to Type II sulfate attack on soil cement, as the alumina is supplied by clay minerals for ettringite formation.

The XRD pattern and SEM micrographs of the specimen cured for 2 days are given in Figures 4-9 to 4-11.

The XRD pattern exhibits the peaks of gypsum with strong intensity. Calcium hydroxide peaks as well as carbonate peaks can also be identified, but no obvious ettringite peaks can be identified. XRD pattern between $8.5 - 9.5^\circ$ is given in Figure 4-10, which will show a peak of ettringite with $d = 0.9753$ nm, if it occurs, but no peak is traced. On the other hand, small ettringite crystals with approximate dimensions of less than $1 \mu\text{m}$ in length were revealed in high abundance through SEM observation (Figure 4-11). Direct measurement of the dimensions of each ettringite crystal present in entire vision of SEM micrograph (Figure 4-11) reveals the average length of ettringite crystals is about $0.8 \mu\text{m}$.

Kota et al. (1996) noticed the same phenomenon, that is, ettringite in lime-treated soil could not be identified by XRD, but SEM tests demonstrated the visual presence of substantial amounts of needle-shaped crystals. It was speculated that either some of the ettringite minerals were lost in sample preparation or the overall amount of ettringite in

the sample used for XRD is less than 10 percent. Anyway, further research work is needed in order to understand this phenomenon.

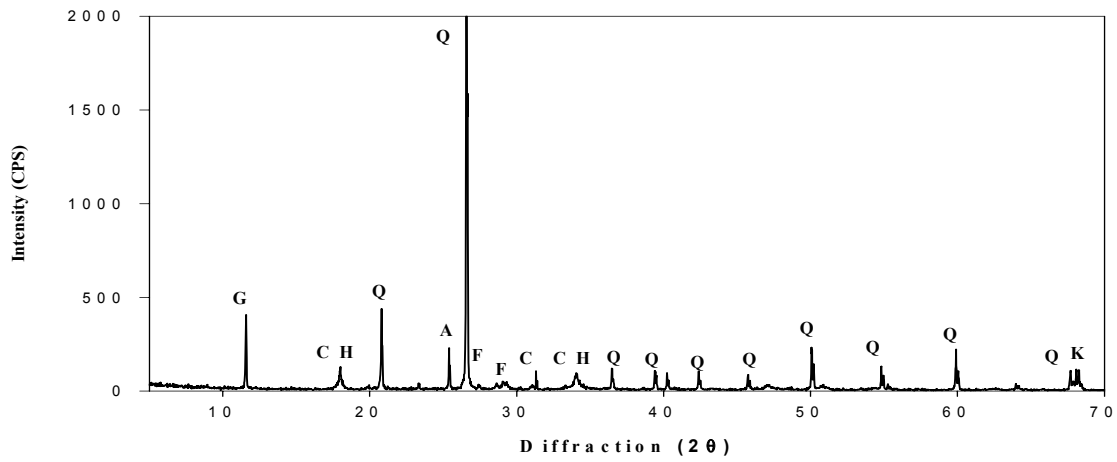


Figure 4-9 X-ray diffraction analysis of lime treated Winn Rock soil: Q-quartz, F-feldspar, A-anhydrite, K-kaolinite G-gypsum, CH-Ca(OH)₂, C-carbonate

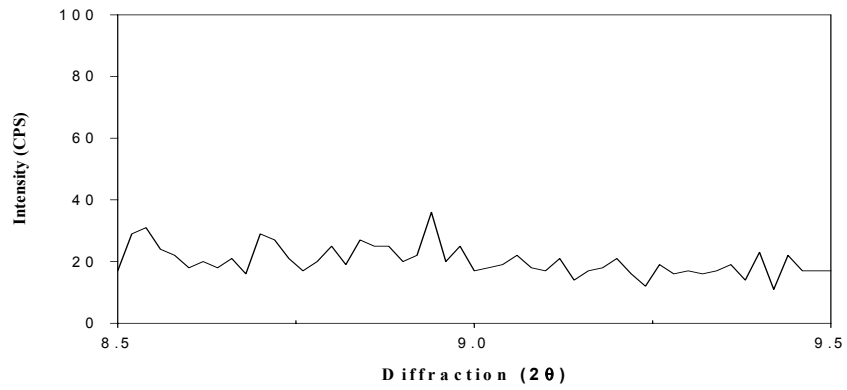


Figure 4-10 Partial X-ray diffraction analysis of lime treated Winn Rock soil

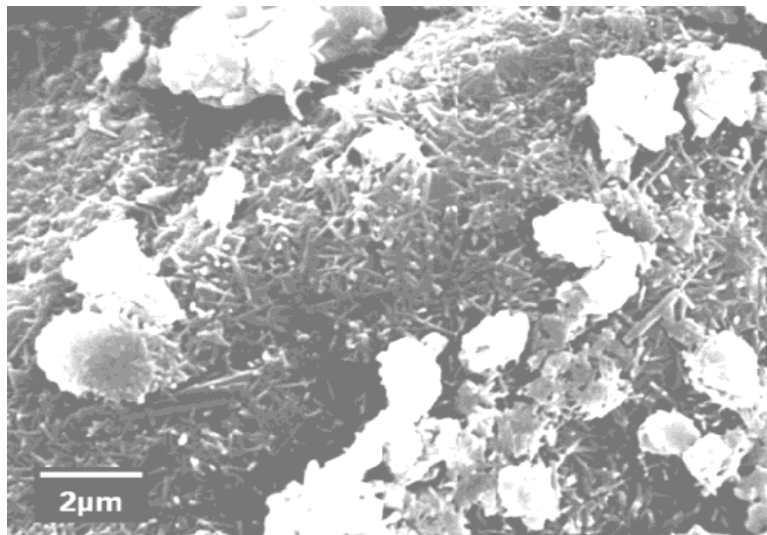


Figure 4-11 SEM micrograph of lime treated Winn Rock soil cured for 2 days

4.4 Summary

Based on the results from this study, some conclusions could be drawn as follows:

1. Fresh Winn Rock aggregate is an anhydrite mineral. It is a unstable phase with respect to gypsum under the ambient weather. It will convert to gypsum during hydration. The application of the Winn Rock as pavement construction aggregates offered such an environment for its transformation, as water may penetrate into the pavement base.

2. Winn Rock soil mixture can be classified as A-1-b group soil. The maximum dry density is 18.42 kN/m^3 at optimum moisture content of 14 percent. It exhibits an unconfined compressive strength of 78 psi at 28 days.

3. Winn Rock soil mixture contains kaolinite and more than 10 percent gypsum for one particular soil specimen, and this poses a very serious risk of sulfate expansion when stabilized with cementitious materials. The well-graded particle size distribution of the mixture may make some contribution to expansion.

4. Initial tentative experiment conducted on lime-treated Winn Rock soil mixture demonstrates that it is highly sensitive to sulfate attack. 7.7 percent linear expansion occurred within two days when 9 percent lime was used for the specimen cylinder fabrication. SEM observations reveal there exists an abundant amount of ettringite crystals with an average length of $0.8 \text{ }\mu\text{m}$, but XRD cannot identify the occurrence of ettringite in the soil matrix.

CHAPTER 5. EVALUATION OF MECHANICAL PROPERTIES OF CEMENTITIOUS STABILIZED WINN ROCK SOIL

5.1 Introduction

Soil cement has been used as a base material for pavement construction in Louisiana State, U.S.A., for several decades. Soil cement bases are relatively easy to design and construct. A wide variety of soil types can be successfully used to make soil cement. Over the years, soil cement performed well and provided economic service life. However, soil cement is vulnerable to sulfate attack. A recent case is sulfate expansion caused by the presence of sulfate rich aggregate – Winn Rock in soil, which was widely used for pavement construction locally. As the rehabilitation process was carried out, which entailed stabilizing the existing base course with Portland cement, some bases containing Winn Rock aggregate experienced severe heave. Previous analysis (Chapter 4) showed that the soil mixture contains a large amount of gypsum derived from the weathering of Winn Rock. This sulfate attack on soil cement bases is highly destructive and, in one instance, a stretch of a road several miles long had to be abandoned. This raises imperative requirement that cost effective stabilization agents for soils containing the Winn Rock aggregate must be developed as soon as possible. It may be possible to use ground granulated blast furnace slag (GGBS) and other supplementary cementitious materials such as fly ash to control sulfate expansion in soil cement as it is sometimes successful with Portland cement concrete (Frearson 1986, Fraay et al. 1987, Schiessel et al. 1994). This speculative concept provides a starting point for developing a protective method for soil cement incorporated with Winn Rock aggregate.

Blast furnace slag is a by-produce of the metallurgical industry. It consists essentially of glassy silicates and aluminosilicates of calcium. It can be ground separately or with Portland cement clinker in various proportions. For typical applications, it provides enhanced durability, including high resistance to sulfate attack. The well-established sulfate resistance properties imported to cement concrete by blending it with GGBS suggests that the mixture may transfer similar sulfate resisting properties to soil cement. Earlier investigations (Wild et al. 1996, Higgins 1998) confirmed some beneficial effects associated with the use of GGBS to reduce sulfate expansion in lime-stabilized bases. These studies also revealed that small addition of GGBS to sulfate-bearing soils substantially reduces the damaging swelling and has no significant deleterious effect to strength development.

Pozzolan includes all those inorganic materials, either natural or artificial, which harden in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement). Fly ash is a kind of pozzolan, which is widely used as a supplementary cementitious material. It is a mineral by-product that is produced by burning pulverized coal in power stations. In addition to its widely known pozzolanic properties, fly ash has been found to have a positive effect in reducing sulfate expansion of cement concrete. Some fly ashes, designated as Class C, have a high calcium oxide content, are characterized by their self-cementing property and have been used for soil improvement. Stabilization characteristics of clay soils blended with Class C fly was assessed and discussed by Misra (1998).

Amorphous silica (AS) residue can also be classified as a pozzolan. It is a waste material from the technological process used in the manufacture of AS products. Initial work (Wang, Roy and Seals 2001) indicated that AS residue has a remarkably high pozzolanic activity. It can react with calcium hydroxide released by the hydration of cement to form C-S-H gel quickly and increase the strength of cement paste and mortar significantly. Such a material is likely to be beneficial to improve resistance to sulfate attack.

The use of the mixture of blended Portland cement with supplemental cementitious materials for sulfate-bearing soil stabilization is generally a novel process and needs to be evaluated thoroughly and carefully. Hence, the aim of this study is to investigate the mechanical properties of Winn Rock soil mixture stabilized by cement incorporated with supplementary cementitious materials. The effect of sulfate attack on soil cement and soil cement incorporated with cementitious replacement materials was assessed with linear expansion measurement and other engineering properties. The feasibility of application cement-supplementary cementitious material mixture for sulfate-bearing soil – Winn Rock soil mixture stabilization was assessed and discussed.

5.2 Materials And Experimental

5.2.1 Materials

Winn Rock Soil Mixture

Winn Rock soil mixture used in this research was sampled from the construction site, the shoulder of US 71 near Campti, Winn Parish, LA, and then crushed until no materials were retained on the No. 4 sieve (4.75 mm). No dry treatment was applied, as heating would change the phase compositions of the soil mixture. Initial research (Chapter 4) classifies the soil mixture as A-1-b soil group, and its index properties are listed in Table 5-1.

Table 5-1 Index properties of Winn Rock soil mixture

Property	Winn Rock soil mixture
Passing sieve No. 4 (%)	100
Passing sieve No. 10 (%)	80
Passing sieve No. 40 (%)	40
Passing sieve No. 200 (%)	15
Clay content (%)	2
Liquid limit (LL) (%)	NP
Plastic limit (PL) (%)	NP
Plastic index (PI)	NP
Optimum water content (%)	14.2
Maximum dry density (kN/m ³)	18.4
Classification (AASHTO)	A-1-b

Cement

Type I Portland cement manufactured at the Lone Star Industries, Inc., Plant in Cape Girardeau, MO, was used to prepare stabilized samples. This cement contains 51.4 percent tricalcium silicate (C_3S) and 5.7 percent tricalcium aluminate (C_3A).

Supplementary Cementitious Materials

Several kinds of supplementary cementitious materials including GGBS, FA and AS were used in this study, and selected chemical and physical properties are given in Table 5-2. The GGBS was supplied by the Lone Star Industries, Inc., the FA meeting ASTM C-618 was supplied by the Bayou Ash Co., Erwinville Co., LA, and the AS was supplied by the Silica Products Division of PPG Industries, Lake Charles, LA, respectively.

Table 5-2 Properties of the supplementary cementitious materials

Composition (%)	GGBS	FA	AS
SiO ₂	34.5	47.5	95.0 – 98.0
Al ₂ O ₃	9.5	20.6	0.12
Fe ₂ O ₃	1.3	5.2	0.06 – 0.21
CaO	39.6	16.2	0.06 – 0.30
MgO	10.9	2.5	0.02 – 0.04
K ₂ O	1.26	0.7	0.01 – 0.06
Na ₂ O	0.48	0.3	0.65 – 3.29
Special Surface Area (m ² /kg)	380*	350*	95000**

*From Taylor (1997), ** From Wang et al. (2001)

5.2.2 Experimental Program

Two kinds of specimen cylinders were prepared: one for compaction and unconfined compressive strength test and the other for linear expansion test.

For the compaction and unconfined compressive strength test, the Winn Rock soil mixture, denoted as A, was thoroughly mixed with 5 or 9 percent cementitious materials. Their composition is given in Table 5-3. The calculated amount of water according to the values of compaction tests was then added and the material was mixed again to achieve a homogeneous material. The compaction test was conducted with Standard Proctor method (ASTM D 558). For the unconfined compressive strength test, specimen cylinders with maximum dry density and optimum moisture content were kept in wet room with 100 percent relative humidity at 20°C, and before test, they were submerged in water for 4 hours. For each test, three specimen cylinders were fabricated. The unconfined compressive strength test was conducted according to ASTM D 2166-91 with a United Compression Model SFM-30E load frame.

For the linear expansion test, that calculated amounts of soil incorporated with 5 or 9 percent cementitious materials and water were mixed and wholly accommodated in mold of $\phi 50 \cdot 100$ mm and compressed to reach an exact volume with 95 percent of maximum dry density and at optimum moisture content as determined by the compaction test series. The specimen cylinders fabricated for linear expansion test, denoted as B, were subjected

to different curing conditions as listed in Table 5-4. Their linear dimensions and corresponding weight changes were measured and recorded at intervals.

Table 5-3 Specimen cylinder preparation matrix

No.	Composition (weight %)				
	Winn Rock soil	cement	GGBS	FA	AS
A0	100	-	-	-	-
A1	95	5	-	-	-
A2	91	9	-	-	-
A3	91	4.5	4.5	-	-
A4	91	2.25	6.75	-	-
A5	91	4.5	-	4.5	-
A6	91	4.5	-	3.375	1.125

Table 5-4 Curing conditions of specimen cylinders for linear expansion test

Symbol	Curing procedure
H40	Kept in zip bag for 1 day, then cured in a bath with 100% relative humidity and 40°C
H20	Kept in zip bag for 1 day, then cured in a wet room with 100% relative humidity and 20°C
M20	Kept in zip bag for 1 day, then cured in a zip bag and at about 20°C
L20	Kept in zip bag for 1 day, then expose to air and maintaining about 20°C

At present, there is no standard method for the linear expansion measurement of soil cement. ASTM Test Methods C 157 and C227, which are designed for length change of hardened hydraulic cement mortar and concrete and for potential alkali reactivity of cement aggregate, can be used as reference. When specimen cylinders were fabricated, they were demolded immediately and kept in a plastic bag for 24 hours. After that, the first value of cylinder length L_0 was measured. The cylinders were then kept in different curing conditions and their lengths L_i were measured at intervals. The percent ratio of increased length ($L_i - L_0$) to the original length L_0 is defined as linear expansion. During the test, much attention would be paid to obtain accurate data by a vernier micrometer with precision of 0.1 mm and the average value measured from three specimen cylinders was used as the linear expansion magnitude. Weight changes of the specimen with 9 percent cement were followed in a similar way.

5.3 Results and Discussion

5.3.1 Engineering Properties Evaluation

Winn Rock Soil Stabilized by Portland Cement

The values of dry unit weight γ_d of specimens A1 and A2 determined from the compaction test are plotted against the corresponding moisture contents (Figure 5-1). The plot of a plain specimen, designated as A0 (seeing Chapter 4), is also listed for

comparison. These plots revealed that the maximum dry unit weight for specimens A0, A1 and A2 are 18.4 kN/m^3 , 18.7 kN/m^3 and 18.8 kN/m^3 , respectively.

Adding cementitious materials to a soil changes in both the optimum moisture content and the maximum dry density for a given compaction effort. The flocculating action of the cementitious materials tends to produce an increase in optimum moisture content and decrease in maximum density (Lees 1982). However, as indicated in Figure 5-1, the addition of cement increases the maximum dry density of the specimens A1 and A2. This may be attributed to the high specific gravity of cement relative to the soil mixture and its small size particles easily filled in the voids of the soil mixture.

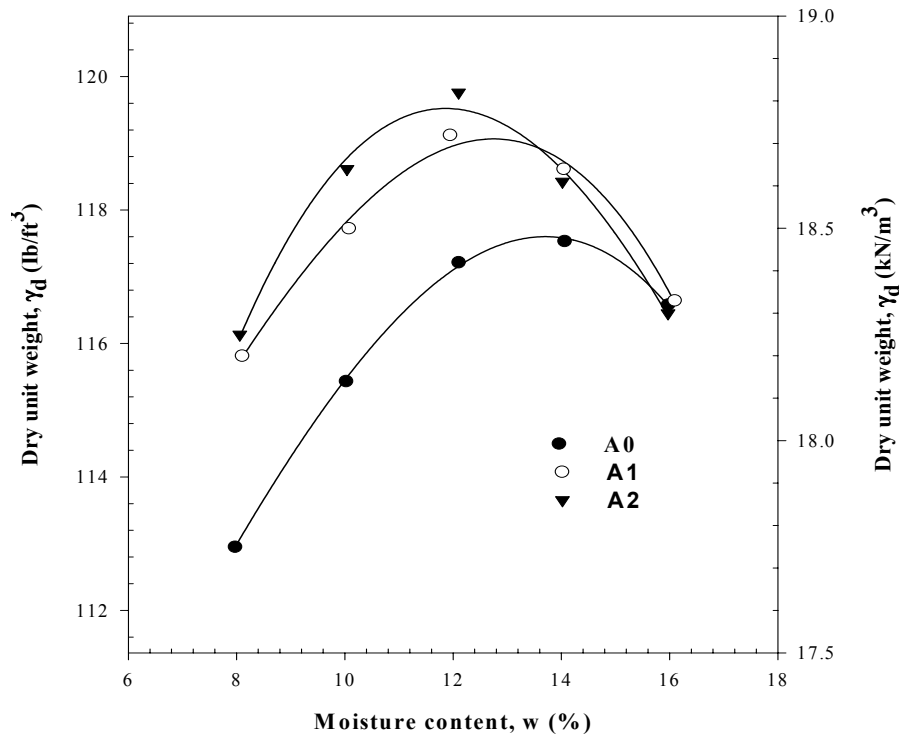


Fig. 5-1 Standard Proctor test results for Winn Rock soil cement mixtures A0, A1 and A2

Unconfined compressive strengths (UCSs) were determined for specimen cylinders of A0, A1, A2 and cured for 7 days and 28 days as listed in Figure 5-2. The unconfined compressive strength of specimens increased with increasing cement content and curing time.

However, although the strength increased with cement stabilization, the strength gain is lower than expected (ACI 1998). Typical unconfined compressive strength values of sandy and gravelly soils stabilized with 5 to 9 percent cement may be up to 300-600 psi for 7 day curing and 400-1000 psi for 28 day curing. It is proposed that the limited gain of strength growth of the Winn Rock soil mixture is due to sulfate attack, as significant expansion and cracking occurred in the specimens A1 and A2 used for the strength testing. At present, the relationship between sulfate attack and strength loss has not been established because only inadequate data are available. Nevertheless, Sherwood

(1962) found sulfate contents as low as 0.2 percent resulted in losses of strength of more than 50 percent in clay stabilized with 10 percent cement.

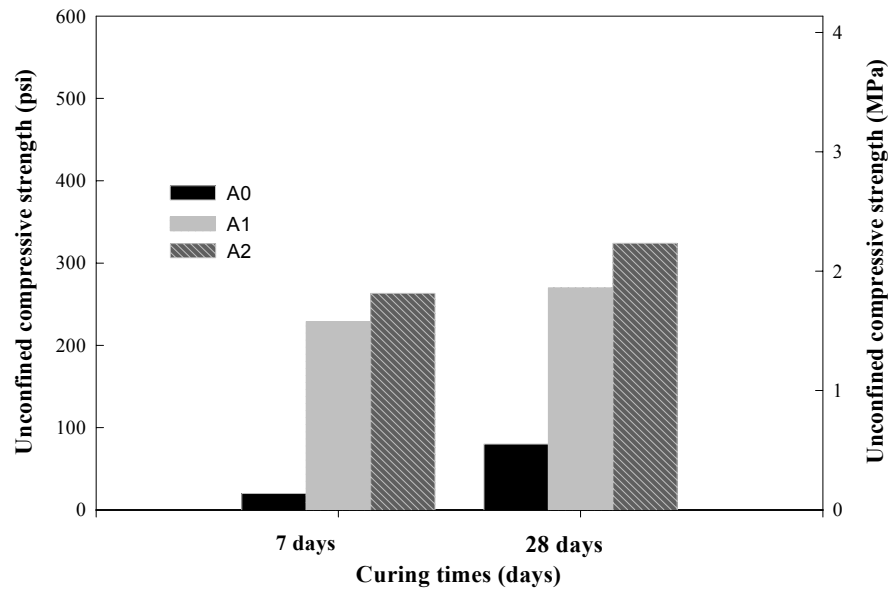


Figure 5-2 UCSs of Winn Rock soil cement mixture cylinders

Winn Rock Soil Stabilized by Slag - Portland Cement

Compaction tests revealed the relationship of dry density and moisture content of each mixture of the Winn Rock soil stabilized with slag cements (Figure 5-3). The values of maximum dry unit weight of the specimens A3 and A4 are 18.7 and 18.7 kN/m³, respectively. There are no basic differences in compaction behavior as comparing the soil – Portland cement mixture with the mixtures of the soil – slag cements.

In Figure 5-4, the unconfined compressive strength values of specimens A3 and A4 is plotted against curing time. Interestingly, the unconfined compressive strength shows a significant increase as compared with that produced by Portland cement.

GGBS is a cementitious material. It reacts more slowly with water than Portland cement, but it can be activated chemically (Daimon 1980). Activators can be either alkaline activators such as lime, or sulfate activators such as calcium sulfates. They will lead to the formation of C-S-H gel and ettringite phase. Both cement and gypsum present in Winn Rock soil mixture can function as “activators” for the hydration of GGBS. Generally speaking, the strength of GGBS cement is lower than that of Portland cement, especially in the early stage of hydration (Syolczyk 1980). On the other hand, GGBS is acknowledged to have a higher resistance to sulfate attack (Locher 1966, Wischers 1980). Considering both the factors, the high strength value of specimens A3 and A4, compared to specimens A1 and A2, must partially be attributed to this sulfate attack resistant property. It is worthwhile to indicate that specimen A4 with only 2.25 percent Portland cement content reached 450 psi at 7 days, suggesting that GGBS has a profound effect on the strength development of the sulfate-bearing soil cement matrix. In other words, the presence of a significant amount of gypsum present in the Winn Rock soil mixture, plus

calcium hydroxide released by cement, activated the latent hydraulic activity of GGBS and led to a high strength development.

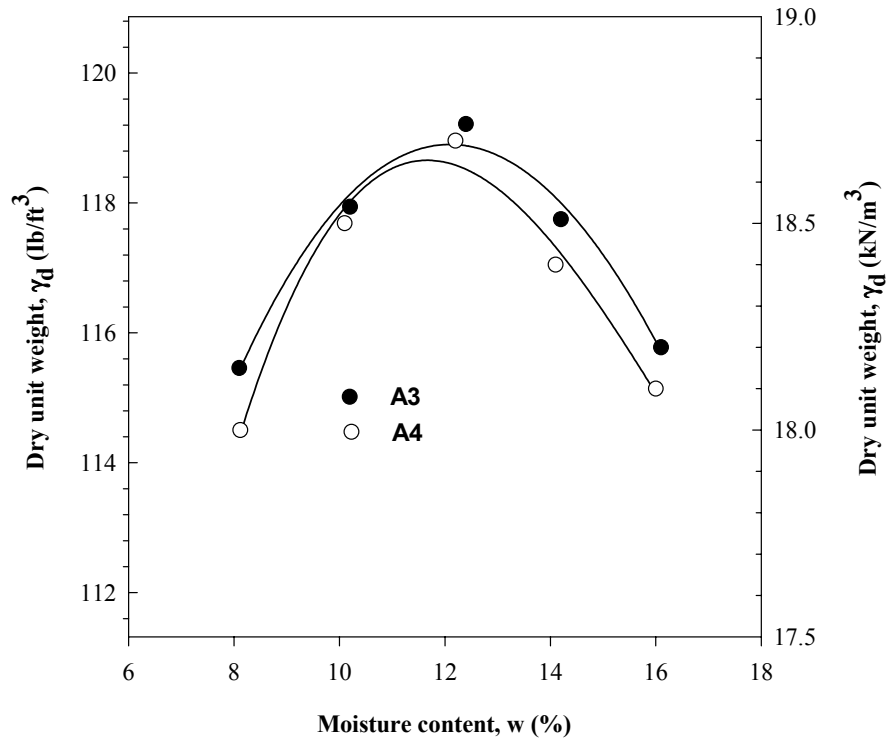


Figure 5-3 Effect of slag cement on the compaction of the Winn Rock soil

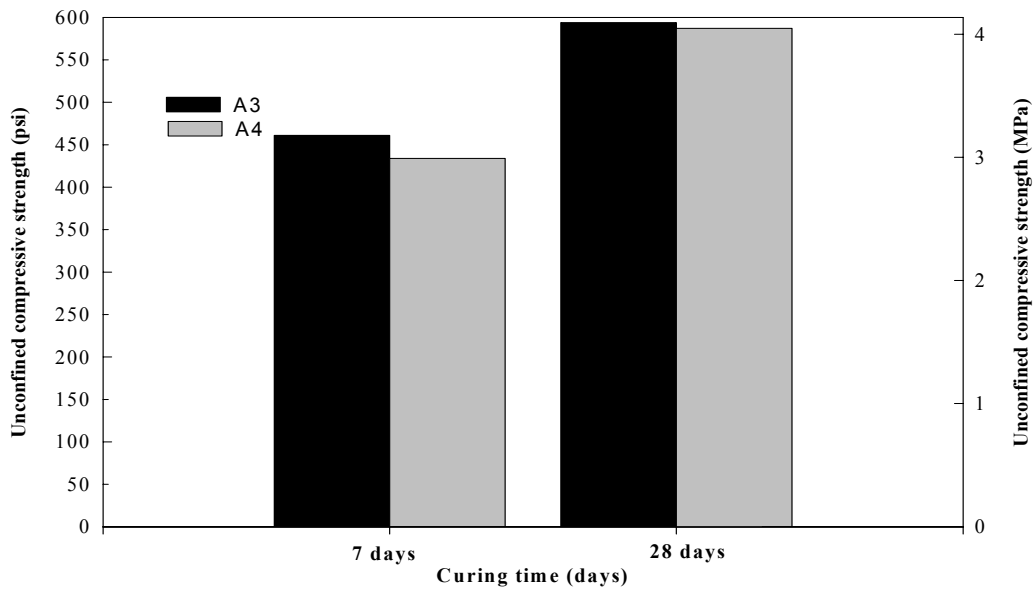


Figure 5-4 Effect of slag cements on the UCSs of the Winn Rock soil

Winn Rock Soil Stabilized by Portland Cement with FA and AS

Compaction test results also revealed the relationship of dry density and moisture content of each mixture of the Winn Rock soil stabilized by Portland cement plus FA and AS (Figure 5-5). The values of maximum dry unit weight of specimens A5 and A6, which were incorporated cement plus FA and cement plus FA as well as AS, are 18.7 and 18.5 kN/m³, respectively.

It is apparent that the addition of FA or FA and AS to soil cement changes its compaction characteristics to some extent. However, the general compaction behavior is essentially the same as that of the soil cement mixture A1. Specimen A5 acquired high maximum dry density at low optimum moisture content. This may be probably attributed to its dispersion effect of FA, as it can act as a lubricant. In contrast, with limited amount of AS added, the mixture exhibited a low maximum dry density. This may be due to the high pozzolanic activity of AS that leads to a strong flocculating action.

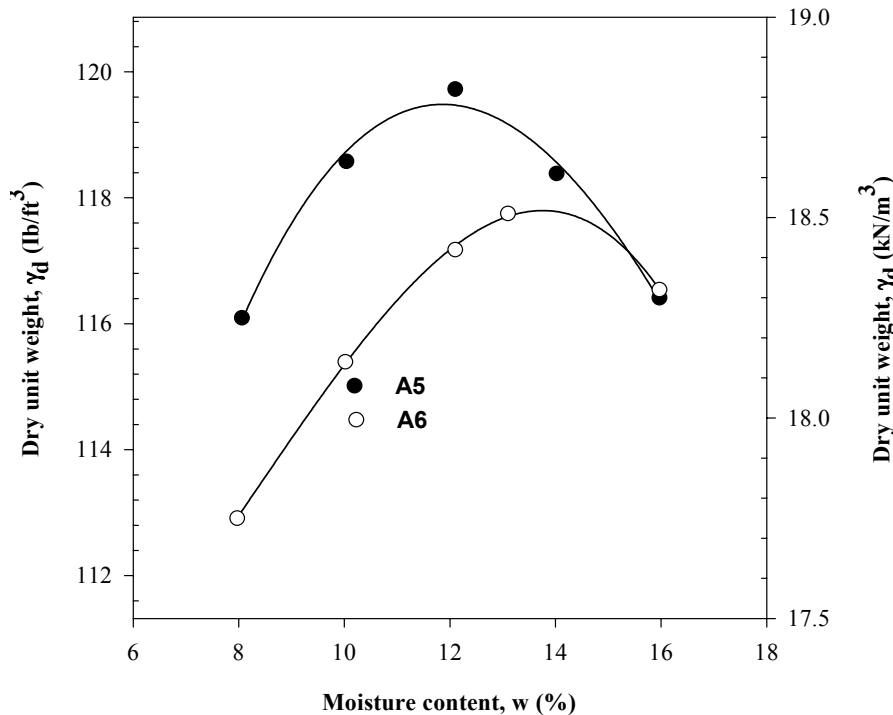


Figure 5-5 Effect of cements incorporated with FA or FA plus AS on the compaction of the Winn Rock soil

The addition of FA (the specimen A5) or FA and AS (specimen A6) also produced an increase in strength. However, a pronounced difference between them is noteworthy. The strength increased about 30 percent with incorporation of 1.125 percent AS instead of FA, as indicated in Figure 5-6. This dramatic improvement must be attributed to the high pozzolanic properties of AS (Wang, Roy and Seals 2001). Since it has a high pozzolanic activity, AS will react with calcium hydroxide, released by the hydration of cement, to form C-S-H gel and lead to an increase in strength. At the same time, as

calcium hydroxide is converted to C-S-H gel, the risk of sulfate attack is reduced, for little calcium hydroxide is available for the formation of ettringite. This is also beneficial to maintain the high strength of the soil cement.

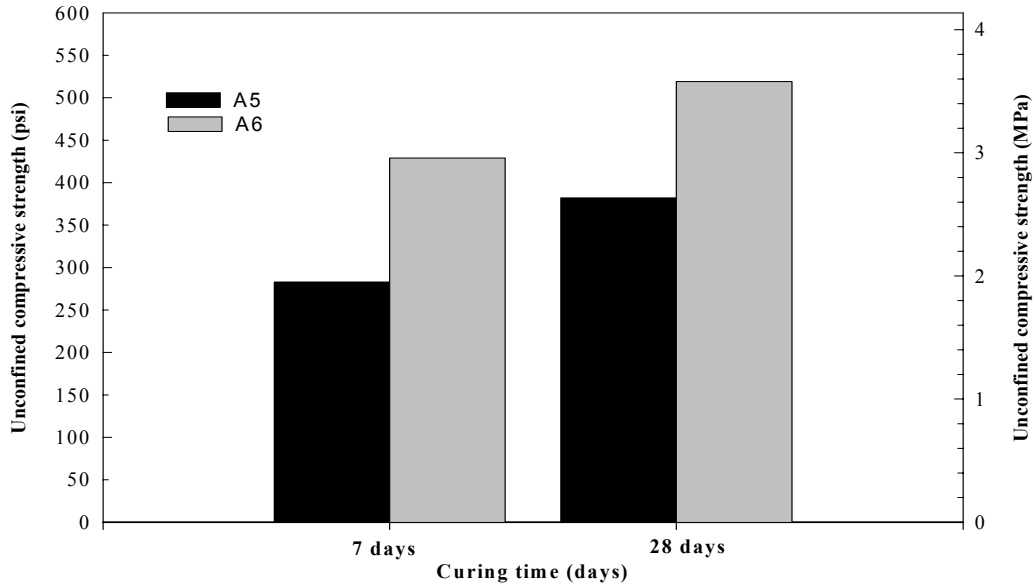


Figure 5-6 Effect of cements incorporated with FA or FA plus AS on the UCSs of Winn Rock soil

5.3.2 Linear Expansion Evaluation

Sulfate attack on the stabilized Winn Rock soil mixture is assessed with the linear expansion measurement of each specimen. However, no standards are available to indicate an acceptable limit value and severity of sulfate expansion for soil cement. For cement concrete, Lerch (1961) and Stark (1982) visually evaluated the performance of test specimens by using a numerical rating system with a range from 1.0 to 6.0 (with 1.0 indicating no evidence of deterioration and 6.0 indicating failure). Smith (1959) defined failure as 0.5 percent expansion. Samarai (1976) recommended 0.1 percent expansion as a safe margin for determining the maximum sulfate expansion percentage that can be introduced into mixtures without causing any deterioration. Crammond (1984) used 0.1 percent expansion after six months as the limit above which expansion becomes significantly deleterious. Referred to these suggestions, an arbitrary criterion for soil cement is set as given in Table 5-5.

Table 5-5 Severity of sulfate attack on soil cement

Linear expansion (%)	Severity
0	zero expansion
0 to 0.1	negligible
0.1 to 0.5	light
0.5 to 1.0	medium
1.0 to 2.0	high
Larger than 2.0	very high

Winn Rock Soil Incorporated with Portland Cement

The results of linear expansion tests for the Winn Rock soil mixture stabilized by Portland cement, are presented in Figures 5-7 and 5-8, showing that expansion occurred with the addition of cement. Both Figures indicate that the expansion of all specimens A1 and A2 cured in different conditions increases over time and reaches constant values within 3 months. Cement content and curing conditions influence and control the magnitudes and rates of expansion. Increase of cement content, temperature and humidity can significantly promote the sulfate expansion. The maximum value of expansion of specimen A2-H40 with 9 percent cement and curing at 100 percent relative humidity and 40°C reached 3.5 percent and this is more than twice that of specimen A1-H40 with 5 percent cement at same curing condition. On the other hand, specimen A2-H40 obtained its maximum expansion with two weeks, which was maintained at 40°C, whereas the same specimen A2-H20 maintained at 20°C took about 3 months to reach a constant expansion value. Relative low humidity also limited the expansion as shown with specimen A1-M20 and A2-M20. When exposed to air, no expansion was observed for specimens A1-L20 and A2-M20. This may be due to the evaporation of moisture from the specimens, and therefore little water is available for the formation and expansion of ettringite.

Corresponding weight changes of the specimens A2 with 9 percent cement was also plotted with curing time and listed in Figure 5-9. It is clearly indicated that linear expansion is concurred with the increase in weight due to water absorption. This total absorbed water may be partially used for ettringite.

Taking the specimen A2-H40 for further analysis indicates the specimen absorbed 55.5 g water and produced an increase of volume of about 68.7 cm³. The absorbed water volume is approximately equal to the increased volume. However, elaborate experiments must be conducted to establish and verify this relationship.

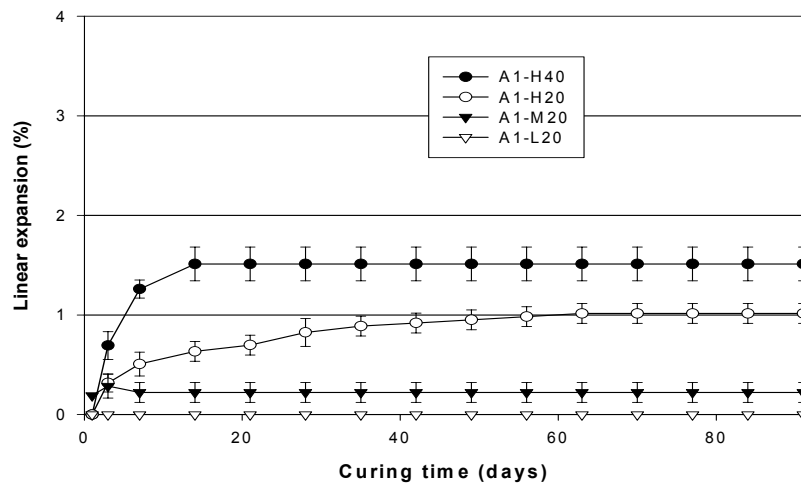


Fig. 5-7 Percent linear expansion of the Winn Rock soil stabilized with 5% cement

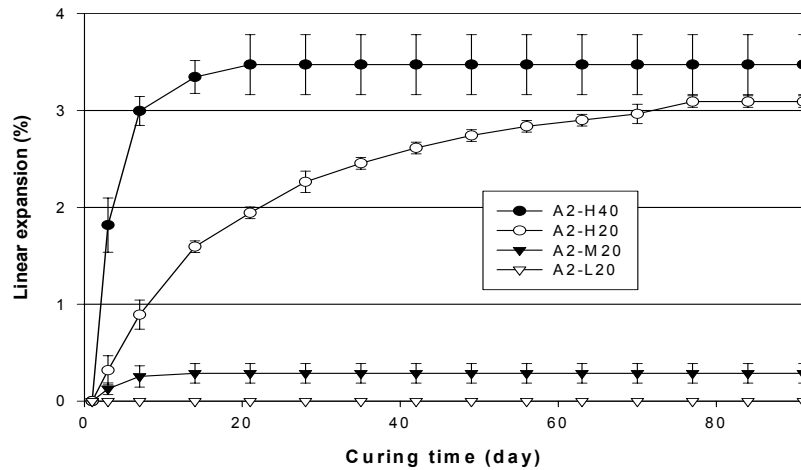


Fig. 5-8 Percent linear expansion of Winn Rock soil stabilized with 9% cement

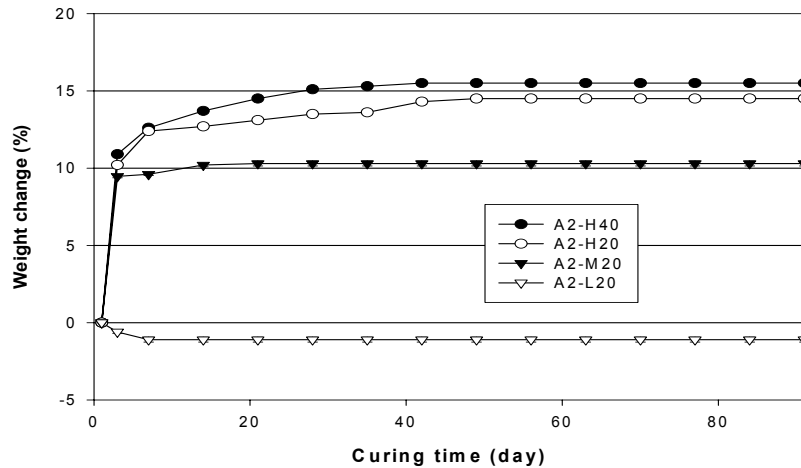


Fig. 5-9 Percent weight changes of Winn Rock soil stabilized with 9% cement

Winn Rock Soil Incorporated with Slag - Portland Cement

Figure 5-10 shows linear expansion of each specimen A3 and A4 cured at 100 percent relative humidity and maintained at 40°C, plotted against curing time up to 3 months. The addition of GGBS reduces the expansion significantly. With half of cement content replaced by GGBS, the expansion magnitude decreased from 3.5 percent to about 0.2 percent. Increasing the content of GGBS up to 75 percent of the cementitious material (specimen A4) would reduce the linear expansion to about 0.1 percent.

Winn Rock Soil Incorporated with FA – AS - Portland Cement

Figure 5-11 shows linear expansion of each specimen (A5-H40 and A6-H40), incorporated with cement plus FA or cement plus FA and AS, plotted against curing time up to 3 months. Even though the effect of FA is not remarkable, it reduced the expansion to 0.5 percent, which is about one-third of that of specimen A1-H40 with 5 percent

cement. It is of interest to note that the expansion of specimen A6-H40 was totally eliminated with limited amount of AS (1.125 percent by the weight of all solid materials, or 12.5 percent by total cementitious materials).

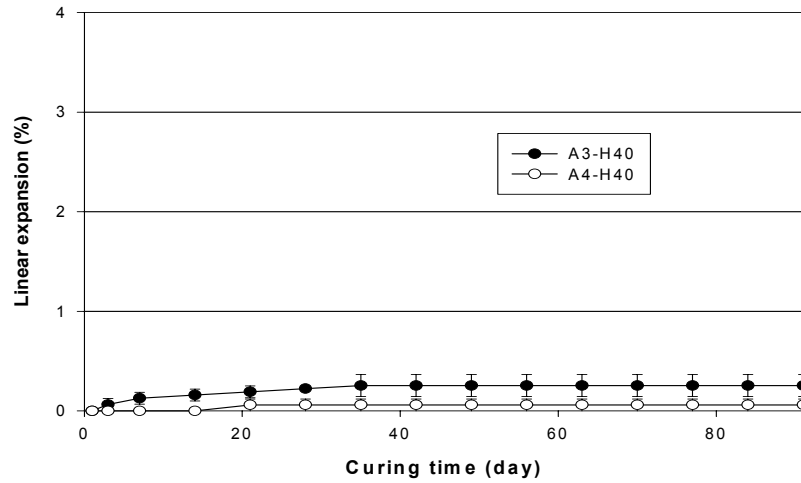


Figure 5-10 Linear expansion of Winn Rock soil stabilized with slag cements

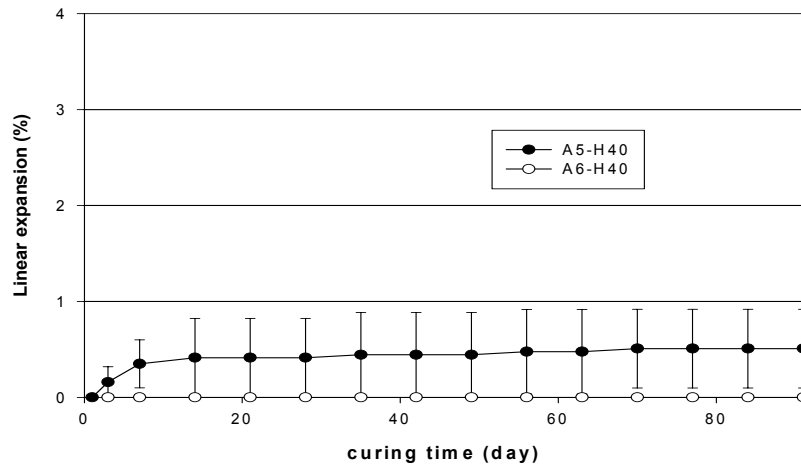


Figure 5-11 Linear expansion of Winn Rock soil stabilized with cements plus FA and AS

According to the criterion given in Table 5-5, the severity of sulfate attack on each specimen is listed in Table 5-6.

Table 5-6 Severity of sulfate attack on soil cement

Specimen	Severity
A1-L20, A2-L20, A6-H40	zero expansion
A4-H40	negligible
A1-M20, A3-H40	light
A5-H40	medium
A1-H40, A1-H20	strong
A2-H40, A2-H20	very strong

5.4 Summary

Based on the results from this study, some conclusions can be drawn:

1. When incorporated with cementitious materials, Winn rock soil mixtures exhibit normal compaction properties. The compressive strength of the mixtures varies depending on the kinds of the cementitious materials added. It is proposed that the expansion leads to a significant loss of unconfined compressive strengths of specimens.
2. Several factors influence the sulfate expansion of the Winn Rock soil stabilized by cementitious materials. Increase of cement content from 5 percent to 9 percent doubled the expansion magnitude. Raising the curing temperature increases the rate and magnitude of expansion. Water availability is also important, and it seems that the expansion of ettringite is mainly due to water absorption from outside of the material matrix.
3. Partial substitution of cement with GGBS, FA and AS for soil stabilization dramatically improves its resistance to sulfate attack. Linear expansion of specimens incorporated with pozzolans all shows significant reduction compared to specimens only added with Portland cement. In particular, GGBS is more effective than FA in mitigating sulfate attack; whereas addition of small amount of AS can prevent sulfate attack.

CHAPTER 6. INVESTIGATION ON THE MINERALOGICAL COMPOSITION AND MICROSTRUCTURE OF CEMENTITIOUS STABILIZED WINN ROCK SOIL

6.1 Introduction

Soil cement, or cement-stabilized soil, is a densely compacted mixture of Portland cement, soil/aggregate, and water. It is used primarily as a base material for pavement. The improvement in engineering properties of cement-stabilized soils is believed to be due mainly to the hardening of Portland cement. Additional cementitious material could be generated with reactions between hydrating cement and clay components, leading to the strengthening of the bonds between the soil grains themselves and between soil and cement particles.

For soil cement mixture, cement contents may vary depending on desired properties and type of soils, and usually range from 5 to 9 percent by dry weight of soil. Water, approximately in the range of 10 to 16 percent, is also necessary to help obtain maximum compaction and for hydration of Portland cement.

The soil/aggregate particles are bonded by cement paste as in cement concrete, but the individual particle is not completely coated with cement paste because of its lower content. Besides, compared with cement concrete there exists higher void ratio and permeability in soil cement, even though compaction increases its density significantly. Both of the facts indicate that soil cement seems more vulnerable to chemical attacks by some destructive agencies, such as sulfate attack.

Sulfate attack on conventional Portland cement concrete is a well-recognized phenomenon (Mehta and Klein 1966, Neville 1981, DePuy 1994) and occurs when cement hydrates of calcium hydroxide and calcium aluminate hydrates react with sulfate to form sufficient ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), which results in massive expansion and cracking.

The potential for sulfate attack on soil cement was established in 1950s and 1960s (Sherwood 1962, Cordon 1962). In recent years, the number of literature reports (Little et al. 1989, Huntington 1995, Rollings 1996 and 1999) of sulfate attack on soil cement was increased, as soil cement has become one of the most widely used forms of soil stabilization for pavement construction. A recent case of sulfate-induced heave is documented by LTRC (LTRC 2000). Aggregates of sulfate-bearing Winn Rock, used for pavement base construction material, caused substantial expansion when stabilized by cement. Research work to identify the properties of Winn Rock soil and to explore the possibility of partial substitution of cement with pozzolans for sulfate-bearing soil stabilization have been successfully conducted (Chapters 4 and 5). Linear expansion of the Winn Rock soil mixture stabilized with 9 percent Portland cement or lime under 100 percent relative humidity and at 40°C reached 3.5 percent and 7.7 percent, respectively, indicating the mixture was subject to very strong sulfate attack. On the other hand, partial substitution of cement with some kinds of cementitious materials reduces the expansion approximately to zero. However, the mechanism of sulfate attack on soil cement and the mechanism of sulfate attack resistance of soil cement incorporated with pozzolans have not been elucidated.

The object of this paper is to present the results of studies to investigate the basic mechanism responsible for sulfate attack and sulfate attack resistance. Specimens of Winn Rock soil stabilized with Portland cement and blended cement plus pozzolans were analyzed with XRD and SEM, and the microstructures of the specimens were observed, and the underlying mechanisms were discussed in greater lengths.

6.2 Materials and Experimental

Details of the experimental investigation program such as the materials, proportioning, mixing, specimen fabrication, and curing conditions have been presented in Chapter 5.

For Portland cement stabilized Winn Rock soil, the specimens with 9 percent cement and cured in different conditions were studied with XRD and SEM analyses. For specimens stabilized with supplementary cementitious materials, only those cured in 100 percent relative humidity and 40°C were selected for XRD and SEM analyses.

A special drying method was used to prepare specimens for analysis. Lumps of the samples were placed in a freeze dryer for 1 to 3 days at -40°C and high vacuum condition. In that way, a treated sample could be coated properly for SEM observation.

XRD and SEM analysis procedures have also been described in Chapter 4. Powder samples were prepared by manual grinding of the specimen in a porcelain mortar pestle. After conducting the XRD tests, phase compositions were analyzed automatically with the standard patterns prepared by the Joint Committee of Powder Diffraction Data Service (JCPDS) with Diffract AT V3.1 Software System. SEM analysis was carried out using a Jeol (JSM-840) Model, which performs morphological and micro-structural assessment.

6.3 Results and Discussion

6.3.1 Winn Rock soil stabilized by Portland cement

When stabilized by Portland cement, the Winn Rock soil mixture exhibited substantial expansion. Typical specimens were selected and XRD and SEM analyses were carried out to identify the changes of the phase composition and microstructure.

Figure 6-1 shows partial X-ray patterns of specimens A2 cured in three different conditions for 3 months. All patterns show the peak of ettringite, even though there appears to be a slight difference in intensity. Measurement of full width of half maximum (FWHM) of the ettringite peak with $d = 0.9753$ and between 8.5–9.5° reveals that they are approximate 0.10°, 0.12° and 0.12° for specimens A2-H40, A2-H20 and A2-M20, respectively, indicating no significant difference between them. Usually the smaller the width, the better the crystallinity of the mineral.

SEM tests demonstrated the visual presence of substantial amounts of ettringite crystals (Figures 6-2 to 6-6). Although the SEM technique is subjective in terms of quantifying the mineral, it is evident that certain morphology is predominant.

The SEM micrographs of specimen A2-H40 show that ettringite crystals are abundant in cluster with needle-like shape. The cluster of needle-like shape indicates the ettringite crystals grow outward from alumina-bearing or sulfate-bearing particles (Schwiete 1966, Mehta 1976). Direct measurement of the dimensions of each ettringite

crystal present in entire vision of SEM micrograph (Figures 6-2 and 6-3) reveals the average length of ettringite crystals is about 2.1 μm . Same patterns of ettringite were also observed in specimen A2-H20 and A2-M20 (Figures 6-4, 6-5 and 6-6). The dimensions of the ettringite crystals present in specimen A2-H20 reach about 5.5 μm in length. However, ettringite crystals in specimen A2-M20 (Figure 6-6) exhibit needle-like morphology with a dimension of 7.8 μm in length. Another remarkable difference lies in the abundance of ettringite crystals presented in each specimen. Significant amounts of ettringite crystals were observed in specimens A2-H40 and A2-H20, but scarcity in specimen A2-M20.

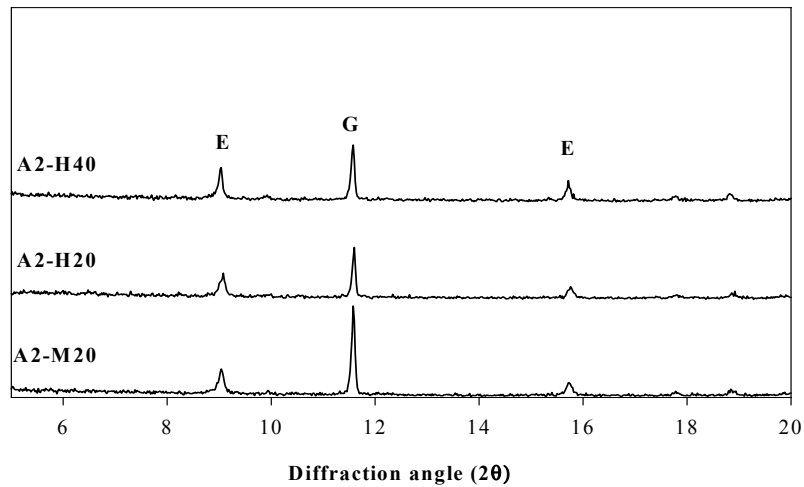


Figure 6-1 Partial X-ray patterns of specimen A2-H40, A2-H20 and A2-M20 cured for 3 months: E-ettringite, G-gypsum and Q-quartz

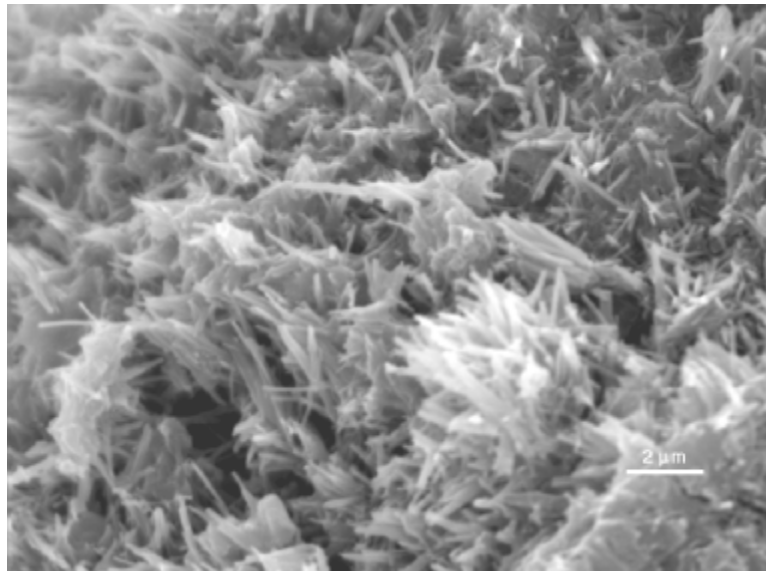


Figure 6-2 The SEM micrograph specimen A2-H40 cured for 3 months

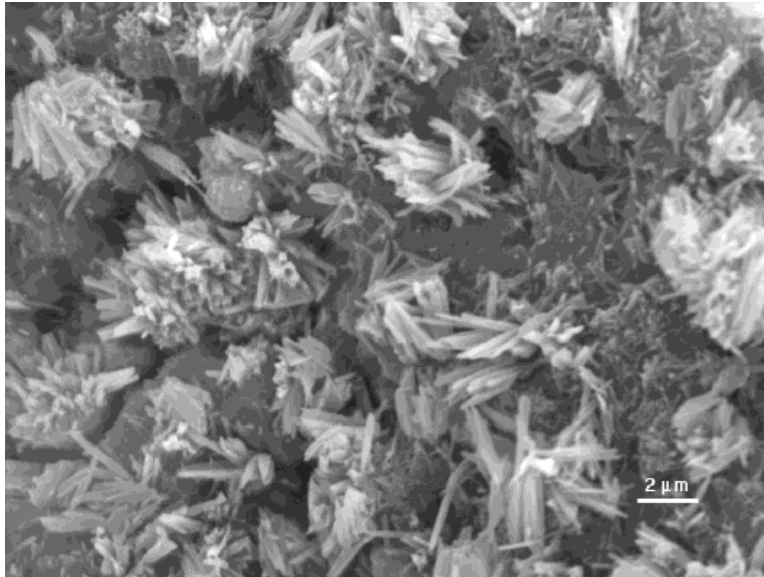


Figure 6-3 The SEM micrograph specimen A2-H40 cured for 3 months

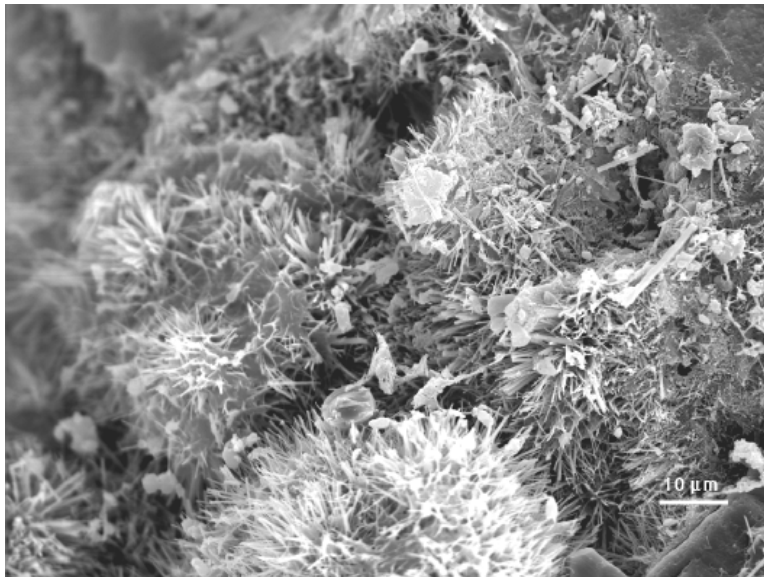


Figure 6-4 The SEM micrograph specimen A2-H20 cured for 3 months

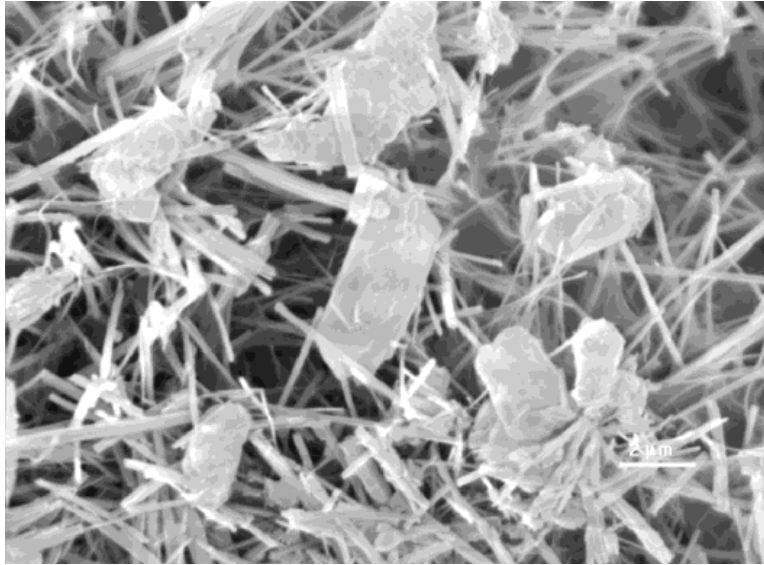


Figure 6-5 The SEM micrograph specimen A2-H20 cured for 3 months

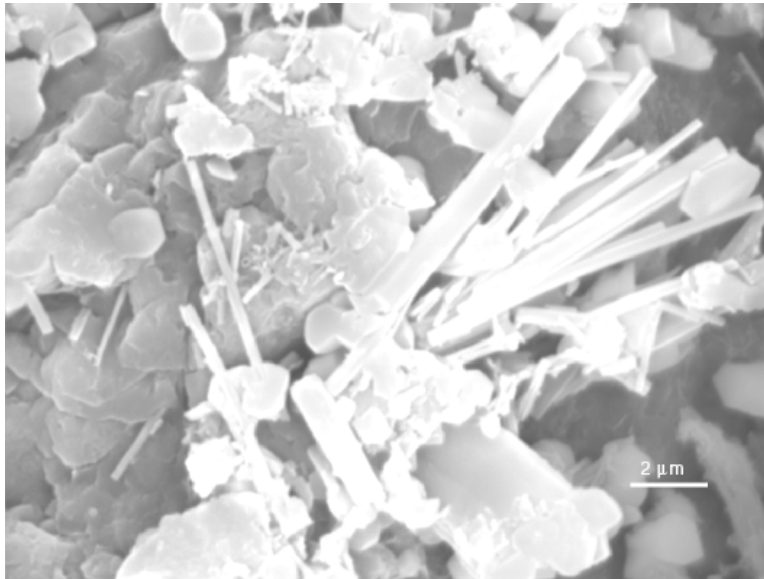


Figure 6-6 The SEM micrograph of specimen A2-M20 cured for 3 months

The effects of temperature and humidity on the sulfate expansion have been illustrated in Chapter 5. The formation and expansion of ettringite are temperature dependence (Mehta and Klein 1966). When cured at 40°C and high humidity, linear expansion of specimen A2-H40 incorporated with 9 percent cement reached 3.5 percent. When cured at 20°C and high humidity, that of specimen A2-H20 obtained 3 percent in 3 months. This difference may be possibly traced to the different morphologies of both specimens revealed by SEM analysis. Corresponding to the high rate and magnitude of expansion of specimen A2-H40, the SEM micrographs of Figures 6-3 and 6-4 revealed abundant small crystals of ettringite (2.1 μm in length). SEM micrograph (Figures 6-4 and 6-5) demonstrated that the dimension of the ettringite crystals (5.5 μm in length) is larger than that present in specimen A2-H40. Charlotte and Taylor (2001) indicated any expansion caused by ettringite formation would be due mainly to the growth of small crystals. It was proposed that the formation of ettringite consists of two steps: nucleation and growth (Fierens and Verhaegen 1976, Mehta 1973). At high temperature of 40°C, the formation of ettringite is accelerated and a lot of nuclei of ettringite are developed with small dimensions. Whereas at low temperature of 20°C, as the rate and number of ettringite nuclei formation is limited, they would grow up into a mature ettringite crystal with larger dimensions. Limited expansion of specimen A2-M20 may be due to the limited amount of large ettringite crystals present in the matrix, as water is not available quickly for the formation of abundant small ettringite crystals.

6.3.2 Winn Rock Soil Stabilized by Slag – Portland Cement

Figures 6-7 to 6-9 illustrated the XRD pattern and SEM micrograph of the specimens A3-H40 and A4 H40. Both specimens incorporated with 9 percent slag cement with 50 percent and 75 percent slag, respectively. Ettringite phase can be identified clearly in both specimens A3-H40 and A4-H40.

The XRD analysis in Figure 6-7 shows significant different patterns between specimens A3-H40 and A4-H40. The ettringite peaks of specimen A3-H40 is less intensive than that of specimen A4-H40. On the other hand, measurement of full width of half maximum of the ettringite peak with $d = 0.9753$ and between $8.5\text{--}9.5^\circ$ reveals that they are approximate 0.09° and 0.06° for specimens A3-H40 and A4-H40, respectively. It was suggested that the area of peaks of a mineral is approximately proportional to the content of the mineral (Moore and Reynolds, 1989). Odler (1984) found that the intensity of the XRD peaks belonging to ettringite is to a great extent sensitive to variation of its crystallinity. Usually, well-crystalline (or large crystals) minerals produce sharp XRD peaks and poor-crystalline (or small crystals) minerals produce dispersive XRD peaks. With this discussion and referred to Figure 6-7, it is proposed that the average size of ettringite crystals present in specimen A3-H40 is smaller than that in specimen A4-H40.

SEM observation (Figures 6-8 and 6-9) revealed certain amount of ettringite present in the specimens A3-H40 and A4-H40 and offered another evidence that the ettringite crystals present in specimen A3-H40 is larger than that in the specimen A4-H40. The dimensions of largest ettringite crystals in specimen A3-H40 is 5 μm in length and 2 μm in width, whereas that in A4-H40 is 10 μm in length and 5 μm in width. Statistical analysis of direct measurement of the dimensions of each ettringite crystal present in entire vision of SEM micrograph (Figures 6-8 and 6-9) reveals the average length of

ettringite crystals is about 4.7 μm in length in specimen A5-H40 and 8.2 μm in length in A6-H40.

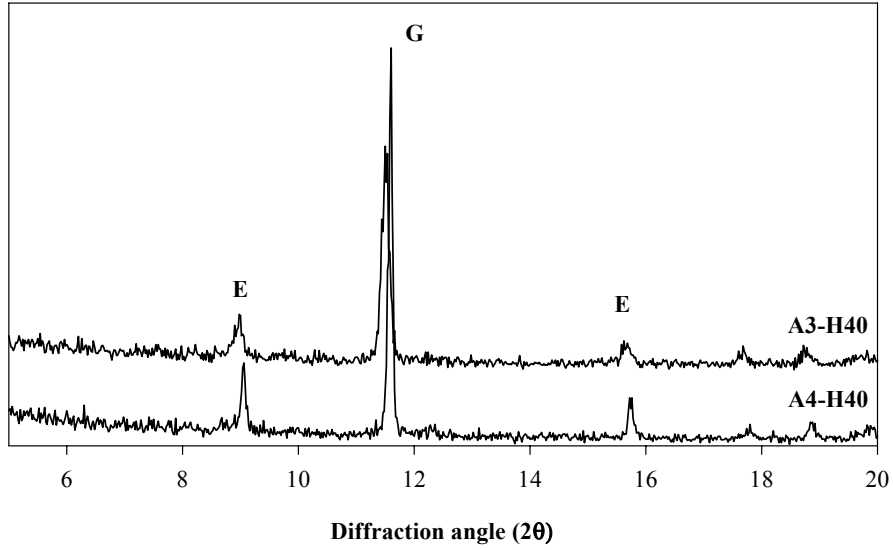


Figure 6-7 The XRD patterns of the Winn Rock soil stabilized by slag cements: E-ettringite, G-gypsum

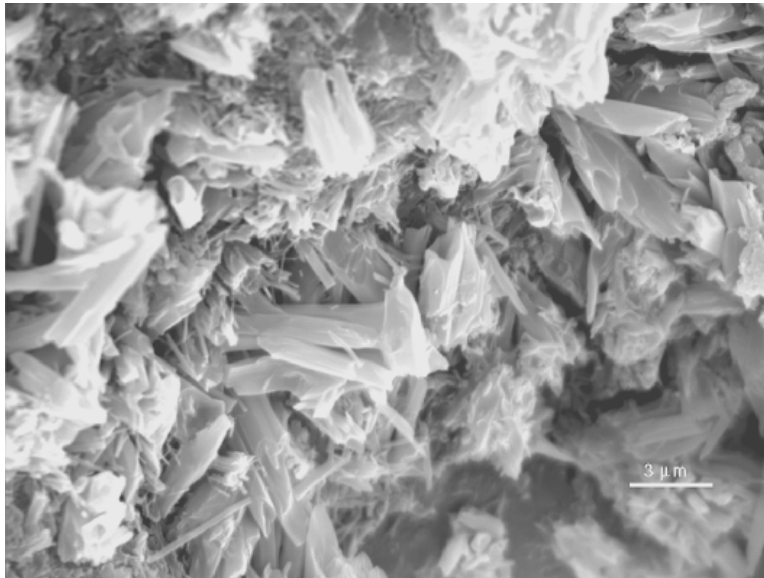


Fig. 6-8 The SEM micrograph of specimen A3-H40 cured for 3 months

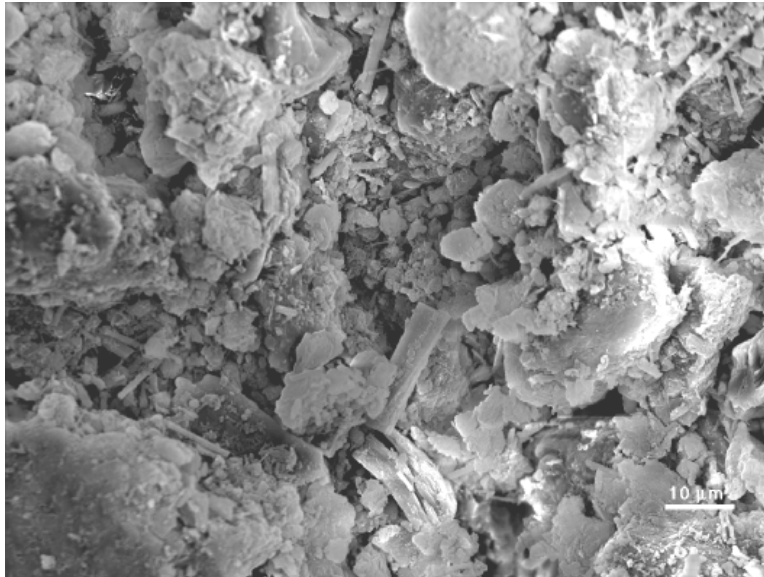


Fig. 6-9 The SEM micrograph of specimen A4-H40 cured for 3 months

Linear expansion tests (Chapter 5) indicate that application of slag cement can improve sulfate attack resistance. However, substantial ettringite was identified in soil slag-cement matrix and this seems conflicted with the results of expansion test and cast the doubt in the feasibility of application of pozzolans for sulfate attack resistance. However, the presence of ettringite is not directly related to sulfate expansion. A recent investigation (Charlotte and Taylor 2001) illustrated ettringite needles have formed throughout the microstructure without causing any damage. This conclusion is in agreement with the SEM observations in the present study. With the incorporation of slag, the morphology of ettringite converted from densely compact needle-like crystals with small dimension (Figures 6-2 and 6-3) to separated ones with a little large dimension (Figures 6-8 and 6-9). This may be a reason that the incorporation with slag can improve the resistance to sulfate attack.

6.3.3 Winn Rock Soil Incorporated with Portland Cement plus FA as well as AS

Figures 6-10, 6-11 and 6-12 illustrate XRD patterns and SEM micrographs of the Winn Rock soil stabilized by cement plus FA and AS. The mineralogy analysis with XRD and SEM shows patterns similar to those stabilized with slag cements.

Corresponding to sulfate expansion test (Chapter 5), the XRD patterns also indicate that ettringite crystals present in specimen A5-H40 are smaller in size than that present in specimen A6-H40, as indicated by measurement of full width of half maximum of the ettringite peak with $d = 0.9753$ and between $8.5\text{--}9.5^\circ$ reveals that they are approximate 0.09° and 0.07° for specimens A5-H40 and A6-H40.

SEM observation also revealed that the ettringite crystals are approximate $4.9\ \mu\text{m}$ in specimen A9-H40 and $5.3\ \mu\text{m}$ in specimen A6-H40. With the addition of AS (specimen A6-H40), the ettringite crystals is presented in separate ones with micron dimensions

(Figure 6-12). This may also be a reason that the incorporation with AS can significantly improve the resistance to sulfate attack. Nevertheless, further elaborative discussion is necessary for reliable diagnoses.

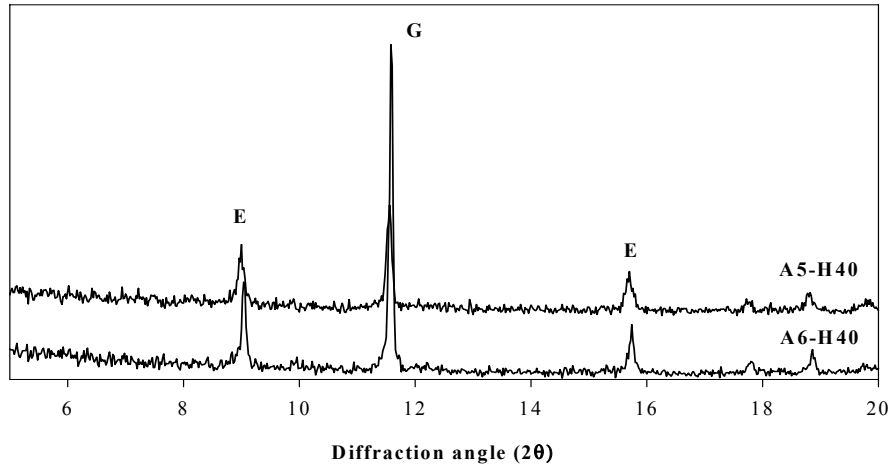


Figure 6-10 The XRD patterns of the Winn Rock soil stabilized by cements plus FA and AS: E-ettringite, G-gypsum

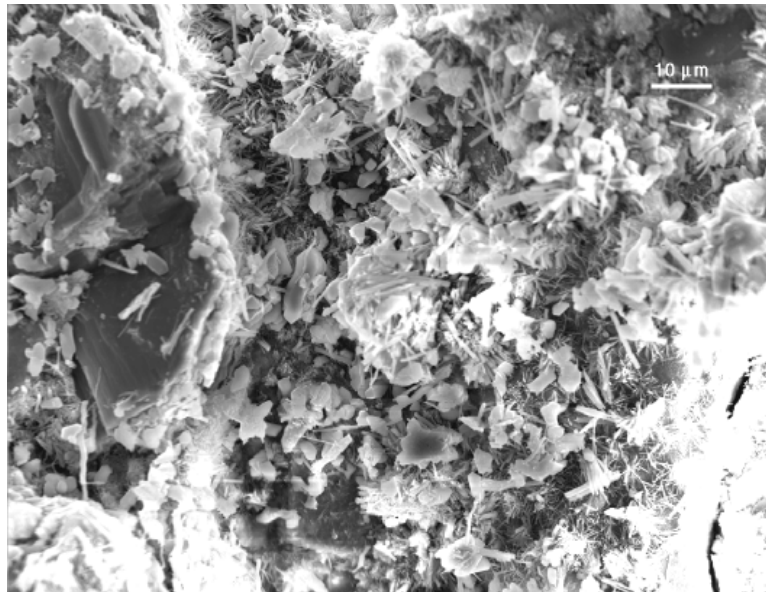


Fig. 6-11 The SEM micrograph of specimen A5-H40 cured for 3 months

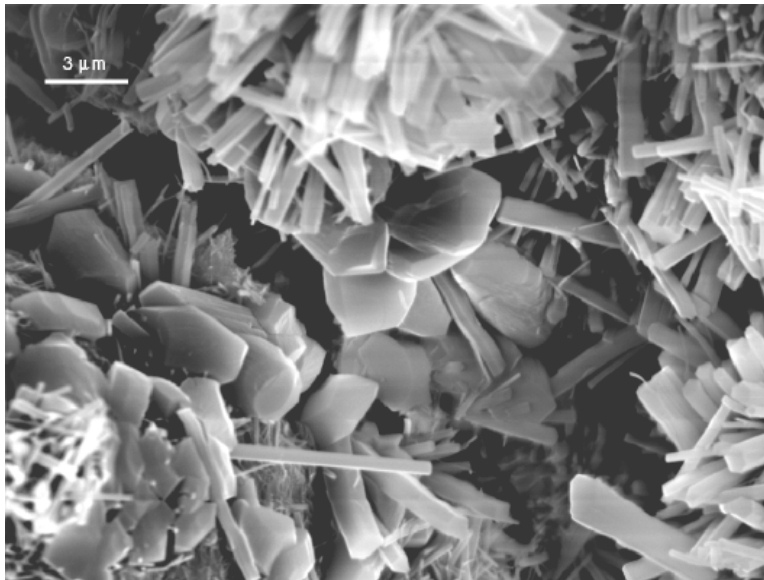


Fig. 6-12 The SEM micrograph of specimen A6-H40 cured for 3 months

6.4 Comprehensive Discussion: Sulfate Attack and Sulfate Attack Resistance

6.4.1 Hypotheses of Sulfate Attack and Sulfate Attack Resistance

Sulfate attack is one of most important issue of cement chemistry. Research work may be dated back to 19th century that Candlot (1890) connected this phenomenon to the occurrence of ettringite. However, even though expansion caused by ettringite formation is the most widely recognized mechanism of sulfate attack, the mechanism underlying ettringite expansion has not been fully understood (Cohen 1983). Numerous theories and models are aimed at explaining the mechanism of formation of ettringite and expansion due to ettringite and they can be divided into two major schools of thought: the Crystal Growth Theory and the Swelling Theory.

According to the first school, expansion is caused by the growth of ettringite crystals, which form on the surfaces of the expansive particles or in the solution. The growth of these crystals, commonly referred to as crystal growth, is responsible for the crystallization pressure and, hence, expansive force. According to the second school, expansion is caused by the swelling of small ettringite particles (about 1 μm), which are of colloidal property. These particles are commonly referred to as gel. This gel has a large specific surface area and takes up water to produce overall expansion by swelling. The formation of this gel occurs by a through-solution mechanism due to reaction between the expansive particles and the surrounding solution. Moreover, if $\text{Ca}(\text{OH})_2$ exists in the solution, then ettringite particles will be colloidal in size. But if $\text{Ca}(\text{OH})_2$ is absent, then ettringite particles will be larger in size. It is only in the former case, i.e., ettringite crystals forms in colloidal size when $\text{Ca}(\text{OH})_2$ is presented, that expansion can occur.

With respect to sulfate attack resistance, cement concrete containing GGBS or FA are acknowledged to have a higher resistance to sulfate attack than Portland cement

concretes. Much published data are available to substantiate these conclusions (Locher 1966, Regourd 1980, Dikeou 1970, Pierce 1982).

The increased resistance of slag cements to sulfate attack is generally associated with the lower content of free calcium hydroxide present in cement paste. Obviously the amount of alumina from C₃A available for conversion to ettringite is reduced because of the smaller Portland cement content. Frearson (1986) found that the sulfate resistance of blended cements increased as the slag increased and that mortars with 70 percent slag content showed a better resistance than sulfate-resisting Portland cement. Regourd (1977) found that in slag cements, the kinetics and the mode of crystallization of ettringite are different from those of Portland cement. Ettringite occurs by a relatively slow process of the passage into the solution, and this leads to a diffuse distribution of big needle-like crystals.

The beneficial effect that FA imparts in sulfate attack resistance is believed to be brought about with direct and indirect effects (Swamy 1986). The direct effect to reduce the potential for sulfate attack results from the straightforward dilution of the alumina content, and from FA reacting with Ca(OH)₂. The indirect effect is to reduce the permeability of cement concrete and thereby controlling the ingress of sulfate ions into concrete matrix.

6.4.2 Summary of the Present Research Work

Relative research results (including Chapters 4 and 5) concerning sulfate attack and sulfate attack resistance of the stabilized Winn Rock soil mixture were summarized in Table 6-1.

Table 6-1 Summarization of the phenomena of sulfate attack on and sulfate attack resistance of the Winn Rock soil mixture stabilized by cementitious materials

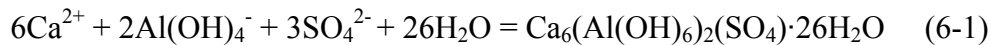
Stabilizer 1		Stabilizer 2		Max. expansion (ME) (%)	Curing time to ME (day)	Curing condition	FWHM of ettringite XRD peak (°)	average ettringite dimension in length (∞m)
kind	%	kind	%					
lime	9	-		7.7	2	H40	no peak	0.8
cement	9	-		3.5	21	H40	0.10	2.1
cement	9	-		3.1	77	H20	0.12	5.5
cement	9	-		0.3	7	M20	0.12	7.8
cement	4.5	slag	4.5	0.3	42	H40	0.09	4.7
cement	2.25	slag	6.75	0.1	2	H40	0.06	8.2
cement	4.5	FA	4.5	0.5	56	H40	0.09	4.9
cement	4.5	FA+ AS	3.38+ 1.13	0	-	H40	0.07	5.3

As indicated in Table 6-1, there exists some relationship between the value of FWHM and the average length of ettringite crystals, when cured in same conditions. Specimens containing large ettringite crystals show small value of FWHM, and specimens containing small ettringite crystals show high value of FWHM. Presence of large crystals is corresponded to small expansion, whereas presence of small crystals is corresponded to large expansion. Largest expansion with highest rate occurs when lime is used. Substantial expansion also occurs when cement is used and the expansion may be mitigated with incorporation of supplementary cementitious materials.

6.4.3 Ettringite Formation and Expansion

Ettringite Formation

The formation of ettringite can be described according to Eq. (6-1):



It is obvious that calcium, alumina, sulfate and water are required ingredients for the formation of ettringite. Calcium can be supplied by lime and cement. The dissolution of lime can offer calcium ions at a high concentration immediately. The release of calcium ions from cement will depend on the degree of its hydration, even through Ca^{2+} concentration of the liquid phase reaches supersaturation during early stages of hydration (Barnes 1983). The final content of calcium hydroxide in a typical mature cement paste matrix is about 13.2 percent (Taylor 1987). This means up to 1 percent calcium hydroxide is possibly available when 9 percent Portland cement is used for stabilization. Alumina can be derived from cement or clay minerals.

Rollings et al. (1996) suggested there exist two types of sulfate attack on stabilized soil according to the sources of alumina. The Type I attack indicates that alumina is provided by cement hydration. The Type II attack indicates that the alumina is provided by clay minerals in the soil. The cement used for the Winn Rock soil mixture stabilization contains about 5.7 percent tricalcium aluminate, or about 2 percent of Al_2O_3 , meaning that only 0.2 percent Al_2O_3 is introduced into the soil stabilized with 9 percent cement. As indicated in Chapter 4, about 2 percent clay minerals present in the Winn Rock soil mixture. Suppose they are illite, this will introduce another 0.7 percent Al_2O_3 into the stabilized soil. Based on the assumption that clay mineral is kaolinite, Al_2O_3 introduced will be about 0.9 percent.

Sulfate is an important ingredient for ettringite formation. Experiment conducted in Chapter 4 also indicates that more than 10 percent gypsum exists in the soil mixture, much higher than the limits of series risk of sulfate expansion (McCallister and Tidwell 1997).

This simple analysis clearly suggests that the amount of ettringite and the severity of sulfate attack are controlled by alumina content, especially from clay minerals, as water is available for the reaction. Sherwood (1962) also observed that clay content had a significant impact on sulfate attack of cement stabilized sand-clay mixtures.

Ettringite Expansion

The formation of ettringite does not always lead to expansion. In fact, some cementitious systems can give high early compressive strength and permanent volume stability, the major hydrate of which is also ettringite (Wang and Glasser 1986). Important factors on ettringite expansion consist of ettringite content, its morphology (Ogawa and Roy 1982, Mehta 1973 and 1982), the sources of its ingredients (Odler 1999, Chengsheng 1988) and when and where they are deposited and developed (Lobo 1992,

Fu 1996), the microstructure of the matrix (Charlotte and Taylor 2001), its confining condition (Ghosh 1983), etc.

The source of ingredients for ettringite formation

The sources of ingredients for ettringite can effect the formation and expansion of ettringite. Sources of sulfate ions in soil cement matrix may be internal or external (Chengsheng 1988). The internal sulfate attack is immediate, while the external sulfate attack will depend on the penetration of sulfate ions. In this study, as high content of gypsum has been identified present in the Winn Rock soil mixture, sulfate attack can be considered to occur when the mixture is mixed with cementitious materials and water. Calcium ions can be provided by dissolution of lime or hydration of cement. The availability of calcium ions has a foundational influence on the formation and expansion of ettringite. Calcium itself is a necessary composition for ettringite formation. The high Ca^{2+} concentration and pH could initiate attack of clay particles and also cause breakdown of amorphous silica and alumina which could combine with calcium to form secondary cementitious materials (Herzog 1964). Lambe (1960) also suggested that strong bases formed during the hydration of cement dissolve silica and alumina from clay, and that calcium ions liberated during the hydrolysis of cement react with dissolved silica and alumina forming cementitious materials. This will lead to a stabilization of clayey soil treated with lime. The dissolution of clay minerals also provides alumina, a composition of ettringite. Significant sulfate expansion of the Winn Rock soil mixture treated by lime clearly indicates that the alumina is derived from clay minerals. Sherwood (1962) suggested that the sulfate expansion of soil cement is related to the clay content of the soil, and that sulfate attack on cement itself is only secondary importance. Mitchell and Dermatas' investigation (1992) got same conclusion. Compared the behaviors of the Winn Rock soil treated with lime and cement in this study, it seems that alumina dissolved from clay minerals contributed much to sulfate expansion.

The content and morphology of ettringite as well as its expansive mechanisms

When other conditions are identical, sulfate expansion is obviously related to the content of ettringite. However, a satisfactory method to identify ettringite quantitatively is unavailable until recently (Ludwig 1993, Luke 1995).

Ettringite crystals may present in various morphologies as demonstrated by SEM observation in this study. The important effect of the morphology of ettringite crystals on their expansion property has been recognized (Mehta 1973, Cohen 1983, Charlotte and Taylor 2001).

An interesting phenomenon is that calcium hydroxide may determine the morphology of ettringite crystals and further determine the expansion property of ettringite. In studying the hydration of expansive cements with and without quick lime, Mehta (1973) examined the microstructural development and came to the same conclusions as those drawn by Okushima (1968) concerning the ettringite crystal sizes. SEM observation indicated that in the presence of lime, ettringite crystals were about 1 μm in length and 0.25 μm in width. In the absence of lime, they were larger, about 6 to 8 μm in length and 1 μm in width. Ettringite with smaller dimension obtained higher expansion. This description of ettringite dimensions and its expansion property is identical to the SEM observation conducted in the present research.

The mechanism that Ca^{2+} concentration controls the morphology may be tentatively elucidated as follows. When mixed with soil and water, lime or cement particles dissolve in the liquid phase quickly and Ca^{2+} concentration reaches and exceeds the saturation level quickly (Young and Tong 1977). At the same time, gypsum dissolves into the liquid phase. As the presence of adequate amounts of gypsum and the supply of sulfate ions is uninterrupted, the liquid phase remains rich in calcium ions and crystallization of $\text{Ca}(\text{OH})_2$ is limited (Barnes 1983). However, when alumina is dissolved from dissolution of clay minerals or from hydration of cement, numerous ettringite nuclei form in solution and precipitates mainly on the surface of clay minerals or C_3A grains, as its high concentration is localized, close to the surface of the clay minerals or C_3A grains (Corstjanje 1973). Mehta (1973) suggested that the mode of formation of ettringite follows a through-solution mechanism, whereas many investigators (Schwiete 1966, Bentur 1974) reported that ettringite crystals are formed topochemically on the surfaces of alumina-bearing grains. Both suggestions may be corresponding to different steps of ettringite formation. On the other hand, if Ca^{2+} concentration is low, limited amount of ettringite nuclei will form and develop into big well-crystalline crystals

The relationship of the morphology of ettringite with its expansion property was first noticed by Mehta (1973). It was proposed the presence of saturated calcium hydroxide causes the ettringite crystals to be gel-like and colloidal in size. Since colloidal particles have a large specific surface area, water molecules will be adsorbed on the surfaces of ettringite particles. This will generate strong swelling pressures leading to an overall expansion of the system. Research results summarized in Table 6-1 support the assumption to some extent. Substantial expansion is really due to the presence of saturated calcium hydroxide and the occurrence of small ettringite crystals. As indicated with lime treatment, the Winn Rock soil mixture obtained about 8 percent linear expansion and SEM observation revealed the occurrence of small ettringite crystals. Kota (1996) conducted a similar test and noticed that expansive mineral (ettringite) in lime-treated soil could not be identified by XRD, but SEM tests demonstrated visual presence of substantial amount of needle-shaped crystals. So a speculation was suggested that either some of the expansive minerals were lost in the process of subsampling and sample preparation or the overall amount of expansive mineral in the subsample used for XRD was less than 10 percent. As the same specimen of lime treated Winn Rock soil was used for XRD and SEM analysis in this study, it was impossible to lose the expansive mineral. On the other hand, less than 1 percent can be identified with XRD (Ludwig 1993). The reasonable explanation is that ettringite crystals in lime treated soil mixture presents in small size and gel-like or poor-crystalline state, and cannot be identified by XRD. These small poor-crystalline crystals are mainly responsible for substantial early expansion as proved by experiment on lime treated Winn Rock soil mixture. This conclusion is basic in agreement with the mechanism of expansion suggested by Mehta (1973). Charlotte and Taylor (2001) also pointed out the importance of small expansive crystal of ettringite.

Mehta et al. (1978,1982) observed that an increase in the amount of adsorbed water corresponds to an increase in volumetric expansion, thus providing support for his hypothesis that the expansion characteristic is attributed to the larger specific surface area of the fine ettringite crystals, adsorbing more water. Kalousek and Benton (1970) stated that ettringite can cause expansion simply because the volume increase value (ratios of the volume of the hydrates phase to the volume of the anhydrous phase) being positive

and means an increase in volume, exerts an expansive stress against the surrounding particles.

Both of these suggestions may establish an early-term expansion mechanism, but some hypothesis may be proposed according to the research on the sulfate expansion of the Winn Rock soil mixture and referring to the literature concerning the mechanisms of ettringite expansion. The occurrence of small ettringite crystals can cause substantial expansion as indicated with the lime-treated Winn Rock soil mixture. This expansion may be attributed to that small crystals can absorb water as some clay minerals behave, or simply attributed to the volume increase linked to ettringite formation. However, it must be mentioned that the magnitude of ettringite is related to its confining condition (Ghosh 1983). When treated with cement, cement hydrates will form a network and serve as the “glue” that provides structure and strength in soil cement matrix. This binding force will limit ettringite expansion to some extent. When treated with lime, no cementitious materials are available immediately. Pozzolanic reaction between calcium hydroxide and clay minerals in soil, which may provide additional cementitious materials, is usually quite slow. Since no such binding force exists in the matrix, ettringite can obtain free expansion. This may be one of reasons that in this study the linear expansion of lime treated soil is much more swift and more than twice that of cement treated. Cordon (1962) noticed raising cement content is apparently an important method in producing sulfate resistant soil cement when other ingredients for ettringite formation are limited.

It is obvious that the mechanism of ettringite expansion becomes a little more complicated when cement is use. Compared with lime, the release of Ca^{2+} from cement hydration into liquid phase is a long-term and stepwise process, depending on the degree of hydration. In the initial stage of cement hydration the formed $\text{Ca}(\text{OH})_2$ dissolves in the liquid phase and Ca^{2+} concentration may reach or exceed the saturation level (Taylor 1984). This high Ca^{2+} concentration can be reduced quickly due to the formation of nuclei of ettringite. The formation of ettringite nuclei is then limited, as the availability of Ca^{2+} will depend to further hydration of cement. Further expansion will depend on the growth of the nuclei of ettringite crystals.

Much literature (Budnikov and Kravchenko 1968, Richards and Helmuth 1977) indicated that expansion occurs when the growth of crystals, which grow at a “linear speed”, moves the obstacles apart. In their option, expansion depends on the number of crystallization nuclei in the unit of volume and also on the growth speed of the crystals. In addition, expansion will also be larger if the growth of crystals is more prolonged. This may be the middle-term expansion mechanism of ettringite expansion and the case when cement is used and when initial expansion due to the formation of ettringite nuclei is terminated. With the hydration of cement, Ca^{2+} is released continuously. When other ingredients are available, the growth of ettringite is initiated and further expansion occurs. This may be the reason that expansion continues after a couple of days when mixed with water. However, expansion magnitude reduced during middle-term expansion process. The reason may be that a nucleus will not grow where it has to exert pressure if it can grow equally well where it does not have to exert pressure (Charlotte and Taylor 2001). This means ettringite crystals prefer to grow up in voids or cavities, which will not contribute much to expansion. Charlotte and Taylor (2001) conducted a SEM observation on cement concrete and revealed that ettringite needles have formed in air voids and other cavities without causing any significant damage. It is further explained the extent to

which the growth of a solid phase in a porous material causes expansion depends on the magnitude of the stresses that can be produced, and on the ability of the material to resist them. Stubby ettringite crystals of submicrometer size growing in small pores could exert substantial pressure, whereas the long needles growing in open cracks or other cavities produce less pressure (Scherer 1999). The extent to which the growth of a solid phase can cause damage also depends on the ability of the material to withstand the stresses produced. The formation of solid products becomes slower and finally ceases if the expansive forces are insufficient to disrupt the surrounding material.

Referred to this discussion, interpretation of ettringite expansion of cement treated soil can be suggested as follows. Initial high Ca^{2+} concentration leads to the formation of substantial amount of ettringite nuclei and relative high expansion according to early-term expansion mechanism. With the decrease of Ca^{2+} concentration, the nuclei of ettringite crystals may develop to mature crystals according to middle-term expansive mechanism and produce moderate expansion, which is also limited as the strong bound mass structure is formed. The crystals deposited near big pores or cavities may develop into large crystals, since ingredients for ettringite formation are easily available and the resistance to their development is low there. This may be defined as later-term expansion mechanism. During that time, the development of these large ettringite crystals contributes less to final magnitude of the expansion.

However, more experimental verification is needed to make a final conclusion concerning this three-term expansion mechanism.

6.4.4 Sulfate Attack Resistance

With incorporation of pozzolans, sulfate expansion of cement treated Winn Rock soil mixture is mitigated or prevented according to the amount and types of pozzolans used.

As indicated in Table 6-1, substitution of 50 percent cement with GGBS reduces the expansion to 0.3 percent, whereas substitution of 75 percent cement with GGBS, expansion is further reduced to less than 0.1 percent. Lea (1998) suggested slag cement is resistant to sea water only with the addition of more than 60 percent slag, indicating the content of GGBS has important influence on sulfate attack resistance. Research work in this study also demonstrated that ettringite crystals present in specimens with supplementary cementitious materials are different from that with lime or cement in morphologies. When cement was substituted with GGBS, the content of calcium hydroxide was reduced. It is proposed that the amount of ettringite nuclei is limited, so is the expansion. These crystals would develop into large crystal during later-term period, and they contributed less to total expansion. It needs to be mentioned the formation of large ettringite crystals may contribute much to the strength development of the cementitious materials (Smolczyk 1965), due to their interlocking action and densifying action.

As also indicated in Table 6-1, addition of FA and AS can mitigate sulfate expansion to some extent. Since the substitution of 50 percent cement with FA will straightforwardly dilute and reduce Ca^{2+} concentration through pozzolanic action, sulfate attack resistance of cement soil incorporated with FA is improved. However, pozzolanic reaction is a slow process and FA itself contains certain amount of calcium oxide, so

linear expansion of 0.5 percent occurs. Whereas significant change occurred when small amount of AS was added. Since AS is very highly active (Wang, Roy and Seals 2001), it would react with calcium hydroxide released by cement hydration. This reaction would exhaust calcium hydroxide quickly. Scarce ettringite nuclei may be formed and developed into large mature crystals, but they cannot cause any expansion.

6.5 Summary

Based on the results from this study, the following conclusions can be made:

1. When stabilized with Portland cement, the Winn Rock soil mixture experiences substantial expansion. Ettringite was identified in the soil cement mixture with XRD and SEM observations. These observations revealed the presence of substantial amount of ettringite crystals of submicrometer dimensions. Such morphology leads to a large expansion.

2. Several factors influence the sulfate expansion of the Winn Rock soil stabilized by Portland cement. Raising the curing temperature and relative humidity promote the formation of ettringite crystals with submicrometer dimensions and increases the rate and magnitude of expansion.

3. The mineralogy and microstructure analyses indicated the occurrence of ettringite in all soil cement mixture incorporated with or without supplementary cementitious materials. However, the morphology and size of ettringite crystals present in the specimens are significantly different. With the addition of pozzolans, ettringite converted from densely compact fine crystals with small dimension to separated ones with larger dimensions. This may be the reason that supplementary cementitious materials improve resistance to sulfate attack.

CHAPTER 7. SULFATE ATTACK ON SOIL CEMENT

7.1 Introduction

Sulfate expansion of cement concrete has been a long-time research objective and got extensive investigation. It has been known since 19th century (Candlot 1890) that the ettringite formation from Portland cement hydration plays a major role as far as the durability of concrete in a sulfate environment is concerned, and the deterioration of cement concrete as a result of sulfate attack is usually associated with ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) expansion.

Soil cement is a densely compacted mixture of Portland cement, soil/aggregate, and water and its primary use is as a base material under asphalt and concrete pavements. The potential of sulfate expansion of soil cement was established in the 1960s (Sherwood 1962), but it was not until the twentieth Terzaghi lecture (Mitchell 1986) brought attention to field problems of sulfate attack on stabilized materials that the issue of sulfate attack on stabilized soils received much more recognition. Several cases (Huntington et al.1995; Kota et al.1996; Rollings et al.1999) have been reported recently, and remediation costs for the projects that suffer expansion damage are always very high, because often the entire pavement with soil cement base may have to be removed and reconstructed.

Published guidance (ACI “State-of-the-art” 1998; Rollings et al. 1996) do recognize the problems of sulfate attack of soil cement, but provide little constructive guidance on how to deal with the problems. This makes evaluation of sulfate attack of soil cement important and necessary. However, it must be done with care because the mechanisms underlying the problem are not fully understood and sulfate attack on soil cement is much more complex than that on Portland cement concrete.

Three sources including aggregate, soil and water may provide sulfate ions and cause sulfate attack. Petry and Little (1993) discussed the effect of sulfate levels on sulfate attack in detail. Based on different sources of sulfate ions, the chemical attack is divided into internal and external attack. The presence of sulfate rich constituents in cement based mixtures, such as sulfate bearing aggregate, is referred to as the internal sulfate attack situation, whereas the case of cementitious mixtures exposed to sulfate rich environments (e.g., groundwater and soil) is described as the external sulfate attack. Both kinds of sulfate attack have reported occurred in soil cement.

Physical properties such as permeability, porosity, availability of moisture, water: cement: soil ratios as well as temperature, all are significant factors controlling sulfate expansion in soil cement matrix. The congenital high permeability of soil cement (DeGroot 1971) allows sulfate ions to penetrate the whole matrix quickly, thereby accelerating expansion reactions and magnitudes. High porosity may accommodate expansion to some degrees, and even a hypothesis that increased pore space at the lower densities provides more room for the growth of expansive ettringite and may result in less overall expansions has been evaluated (Kota 1996). Moisture is a necessary ingredient for formation of ettringite, and several cases of sulfate expansion reported (Kota et al. 1996, Rollings et al.1999) were relative to the availability of ample moisture from rainfall infiltration. The formation of ettringite is temperature dependent (Mehta and Klein 1966; Hunter 1988). The temperature regimes found in pavements are adequate to allow

ettringite to form, and the rate of formation with resulting expansion would be the greatest in warm weather.

In this study, research was conducted to identify the effects that control sulfate expansion of soil cement with emphasis on sulfate sources and sulfate level, moisture availability and temperature. Soil cement specimens were made with fine-grained soils, and various percentages of gypsum were mixed with soil cement at the time of fabrication, which was designated as I group would be subject to different curing conditions, or soil cement incorporated without gypsum, designated as E group, would be submerged in Na₂SO₄ solution. Linear expansion of each specimen was measured and recorded at intervals, and XRD and SEM analyses were conducted to examine the variation of phase compositions and microstructures.

7.2 Materials and Experimental

7.2.1 Materials

A silty sand sampled from Accelerated Loading Facility Site of LTRC at Port Allen, LA, was used for the study. This kind of soil is considered to be typical of soil material met in local pavement construction. The index properties of the soil are given in Table 7-1. The major mineral compositions of the soil obtained by x-ray diffraction analysis (Figure 7-1) include quartz, feldspar and illite.

Table 7-1 Index properties of the silty sand soil

Property	Silty sand
Passing sieve #200 (%)	39
Silt (%)	30
Clay(%)	9
Liquid limit (LL) (%)	NP
Plastic limit (PL) (%)	NP
Plastic index (PI)	NP
Specific gravity	2.69
Optimum water content (%)	15.0
Maximum dry density (kN/m ³)	17.2
Classification (AASHTO)	A-4

Type I low alkali Portland cement was supplied by the Lone Star Industries, Inc., Plant in Cape Girardeau, MO, was used to prepared stabilized samples. This cement contains 51.4 percent tricalcium silicate (C₃S) and 5.7 percent tricalcium aluminate (C₃A) and 2.7 percent SO₃.

Calcium sulfate, a chemical agent with 99.9 percent of gypsum (CaSO₄·2H₂O) supplied by Sigma Chemic Co., Mo, was used for the preparation of the specimens to simulate internal sulfate attack. Na₂SO₄ (a chemical agent supplied by Fisher Scientific Co., NJ) solutions with different concentrations were also prepared for some specimens to be cured in to suffer external sulfate attack. CaO, supplied by Mollinckzodt Chemical, Inc., KT, was used as a stabilizer to evaluate the potential of Type II sulfate attack, in which the clay minerals in the soil provide alumina for ettringite formation.

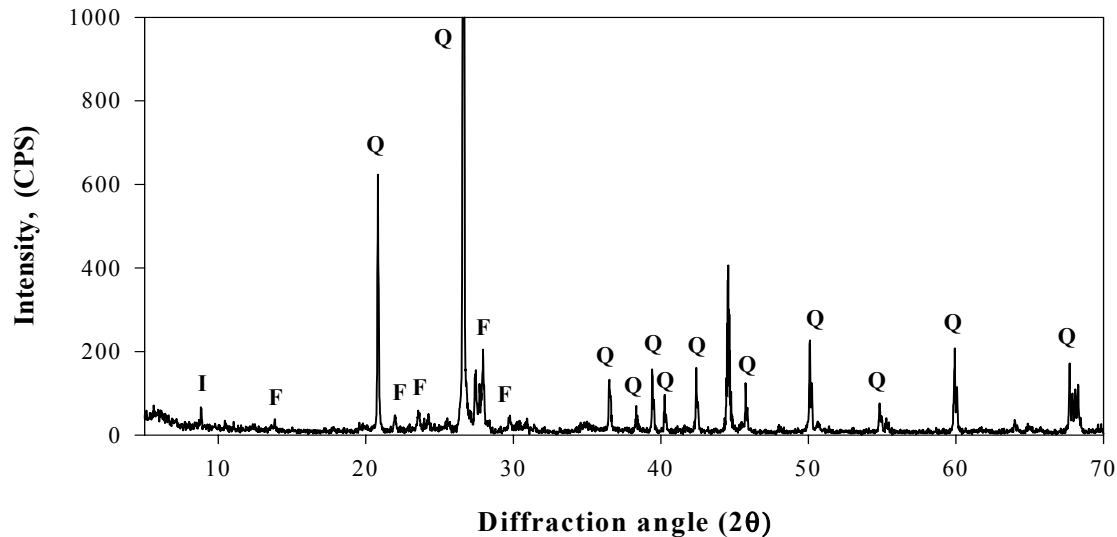


Figure 7-1 X-ray diffraction analysis of soil: Q-quartz, F-feldspar and I-illite

7.2.2 Sample Preparation and Curing

As cement was added, laboratory compaction test, specified by ASTM D-560, was conducted and revealed that the maximum dry density and optimum water content are approximately 17.7 kN/m^3 and 14.2 percent, respectively, for soil cement mixture with 9 percent cement, and 17.4 kN/m^3 and 14.4 percent, respectively, for that with 5 percent cement.

Two kinds of specimen cylinders (Groups I and E) were prepared, both with the same dimension of $\phi 50 \times 100 \text{ mm}$. Their components and curing conditions are shown in Table 7-2. They are designed for internal and external sulfate attack testing, and denoted as I group and E group, respectively.

The specimen cylinders for linear expansion measurements were prepared with following sequential steps: the required amount of soil, cement and gypsum (if needed) was added and mixed thoroughly, and then calculated quantity of water was added and the mixture was mixed again to a uniform consistency; and the mixture was then allowed to stand for several minutes to aid the dispersion of the moisture and to permit better adsorption of the water by the soil cement. The mixture was then placed in mold and statically compressed to reach an exact volume with 95 percent of maximum dry density as determined by compaction test. Four specimen cylinders were fabricated for each curing condition. After extruded and labeled, they were subject to different curing conditions according to designed curing conditions.

Sulfate level selection for this study is based on following considerations. When sulfate is derived from aggregate or soil, it usually presents in large quantity. Kota et al. (1996) mentioned that a subgrade soil contains gypsum quantity up to 30 percent. Previous study (Chapter 4) also revealed that there exists more than 10 percent gypsum. Besides, simple stoichiometric calculation indicates that approximately 5 percent gypsum is expected to react with alumina derived from 10 percent clay minerals for ettringite

formation. Corresponding to these facts, 6 to 18 percent gypsum was used for simulation of sulfate expansion in laboratory. For external sulfate attack, Mccallister and Tidwell (1997) suggested sulfate content (SO_3) between 0.5 to 1.2 percent poses a moderate to serious risk of heave; and sulfate content (SO_3) greater than 1.2 percent poses a very serious risk of heave. This is about 1 to 2.5 percent, respectively, when converted to equivalent Na_2SO_4 . Sulfate solution concentrations in the present study cover the range of possibly moderate to serious heave.

Table 7-2 Components of soil cement specimens and curing conditions

No.	Components (%)			Curing conditions
	Soil	Cement	Gypsum	
I-1	73	9	18	Kept in zip bag for 1 day, then in a bath with 100% relative humidity and 40°C
I-2	82	9	9	Kept in zip bag for 1 day, then in a bath with 100% relative humidity and 40°C
I-3	86	9	5	Kept in zip bag for 1 day, then in a bath with 100% relative humidity and 40°C
I-4	82	9	9	Kept in zip bag for 1 day, then in a wet room with 100% relative humidity and 20°C
I-5	82	9	9	Kept in zip bag for 1 day, then in a wet room with 50% relative humidity and 20°C
I-6	90	5	5	Kept in zip bag for 1 day, then in a bath with 100% relative humidity and 40°C
I-7	90	5	5	Kept in zip bag for 1 day, then in a wet room with 100% relative humidity and 20°C
E-1	91	9	-	Kept in polythene bag for 1 day, then cured in a solution of 50g Na_2SO_4/L and 20°C
E-2	91	9	-	Kept in polythene bag for 1 day, then cured in a solution of 20g Na_2SO_4/L and 20°C
E-3	91	9	-	Kept in polythene bag for 1 day, then cured in a solution of 10g Na_2SO_4/L and 20°C
E-4	96	5	-	Kept in polythene bag for 1 day, then cured in a solution of 50g Na_2SO_4/L and 20°C
E-5	96	5	-	Kept in polythene bag for 1 day, then cured in a solution of 20g Na_2SO_4/L and 20°C
E-6	96	5	-	Kept in polythene bag for 1 day, then cured in a solution of 10g Na_2SO_4/L and 20°C
I-0	82	9*	9	Kept in zip bag for 1 day, then in a bath with 100% relative humidity and 40°C

*instead of cement, lime was used as a stabilizer

As listed in Table 7-2, instead of cement, lime was used in a specimen designated as I-0, but other conditions for the specimen preparation and procedures for its analysis are the same as that of specimen I-2 subjected to.

7.2.3 Linear Expansion Measurements and Microstructure Analysis

Linear expansion of each specimen was measured according to the procedure given in Chapter 5.

Phase composition and microstructure changes of some specimens would be identified with XRD and SEM analyses. Sample preparation method and instrumental analysis parameters were all described in previous Chapters.

7.3 Results and Discussion

7.3.1 Potential of Type II Sulfate Attack

In order to evaluate the potential of Type II sulfate attack on the silty sand soil, linear expansion of specimen I-0, which was treated by lime, was measured at intervals. A plain cylinder was also fabricated and measured for comparison. The measurement of lime treated specimen I-0 demonstrated, following the expansion pattern of that of lime treated Winn Rock soil mixture, that the expansion reaches 3.7 percent within first curing day and 4.8 percent within second curing day. Then expansion terminated forever. On the other hand, on expansion is traced for plain specimen.

The XRD pattern and SEM micrographs of specimen I-0 cured for 2 days is given in Figures 7-2 to 7-5.

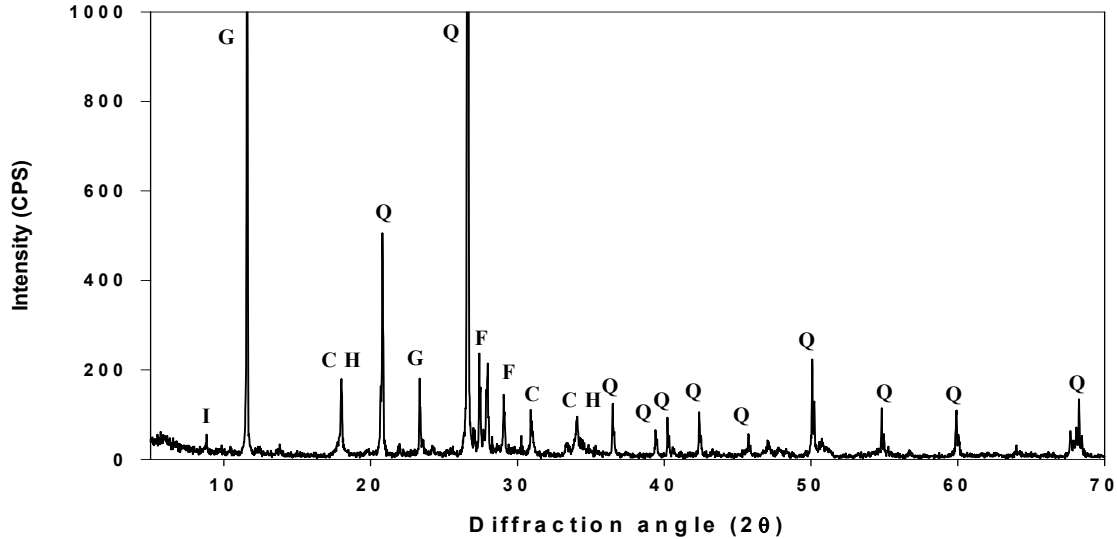


Figure 7-2 X-ray diffraction analysis of soil: Q-quartz, F-feldspar, I-illite, G-gypsum, CH-Ca(OH)₂, C-carbonate

The XRD pattern exhibits the peaks of gypsum with strong intensity. Calcium hydroxide peaks as well as carbonate peaks can also be identified, but no obvious ettringite peaks can be identified as indicated in Figure 7-3. On the other hand, small ettringite crystals with approximate dimension of 1 μ m in length were revealed through

SEM observation (Figure 7-4). Statistical analysis of direct measurement of the dimensions of each ettringite crystal present in entire vision of SEM micrograph (Figure 7-4) reveals the average length of ettringite crystals is about 1.2 μm . Besides, lath-like crystals of gypsum were also revealed as given in Figure 7-5.

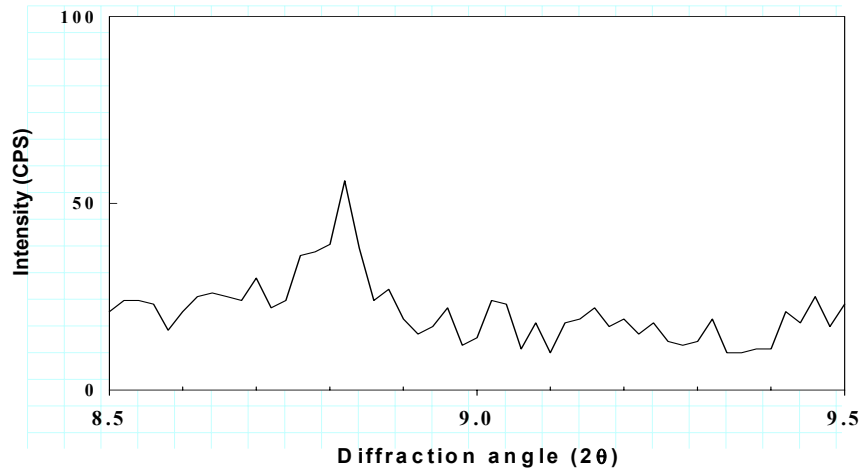


Figure 7-3 Partial X-ray diffraction analysis of lime treated silty sand soil

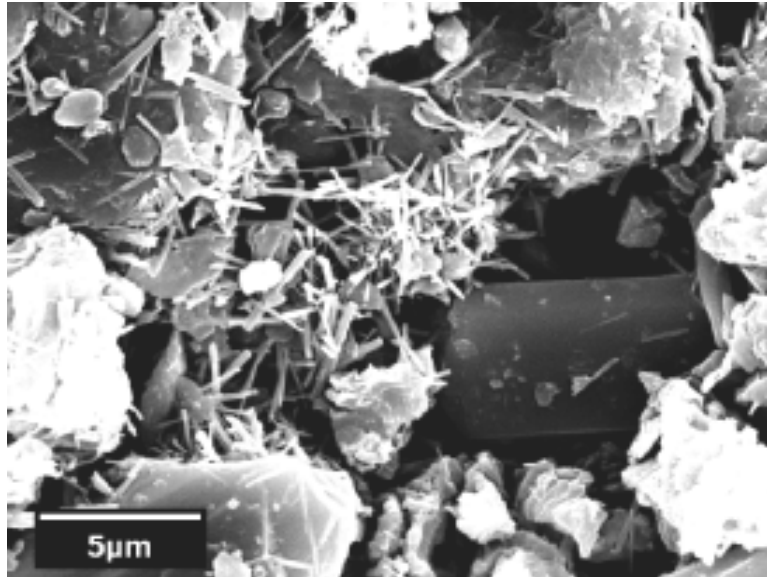


Figure 7-4 SEM micrograph of specimen I-0 cured for 2 days

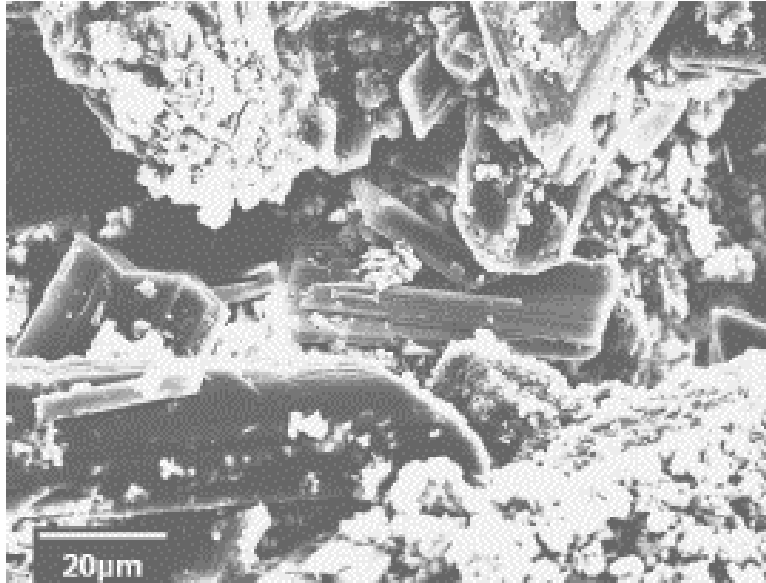


Figure 7-5 SEM micrograph of specimen I-0 cured for 2 days

Ettringite formation and expansion mechanism derived from experiment and discussion on the stabilized Winn Rock soil mixture can also be used to explain the behavior of the lime treated silty sand. Significant difference between them is that the expansion magnitude of lime treated Winn Rock soil is approximately twice that of lime treated silty sand. Several reasons may be proposed to be possibly responsible for the difference.

Since it consists of 9 percent clay, mainly illite, significant content of silica may be dissolved from the clay minerals. This high active silica can also react with calcium hydroxide and reduce Ca^{2+} concentration in liquid phase, and limit the formation and expansion of ettringite, as indicated in Figure 7-5 that ettringite crystals is not so abundant. Silica- rich clay mineral such as illite can give more silica to participate in pozzolanic reaction (Mitchell and Dermata 1992). Another possible reason is that gypsum (a chemical agent) added in the silty sand soil is less active than that derived from the weathering of Winn Rock. XRD and SEM analyses all demonstrate that abundant gypsum crystals remain in the treated silty sand soil. The most possible reason may be laid in the availability of water. Water is a necessary ingredient for ettringite formation and expansion (Mehta 1978). Typical value of hydraulic conductivity of gravel and coarse sand is about 0.1 cm/sec, whereas that for silty sand is about 0.001 cm/sec (Das 1997). This means that the ingress of water from outside the silty sand as well as the flow of water inside its matrix is more limited than that with the Winn Rock soil mixture.

Nevertheless, further research work is necessary to elucidate this phenomenon undoubtedly.

7.3.2 Linear Expansion Analysis

The primary purpose of the study was to determine the sulfate attack on soil cement under various conditions. Linear expansion measurement was conducted to demonstrate the process of such an attack. These measurements are shown in Figures 7-6, 7-7 and 7-8 for I group and in Figures 7-9 and 7-10 for E group, respectively.

Figure 7-6 shows the linear expansion of the silty sand stabilized with a constant cement content, but incorporated with different amounts of gypsum. The effects of increasing amounts of gypsum on the linear expansion are obvious. Specimen I-1 with 18 percent gypsum produced a linear expansion of 1.6 percent, whereas the magnitudes of linear expansion decreased to 1.2 percent and 1.0 percent as the contents of gypsum decreased to 9 percent and 6 percent, respectively. Three specimens incorporated with different amounts of gypsum all terminated the expansion process at about 3 weeks.

Both Figures 7-7 and 7-8 illustrated the influence of curing conditions on the linear expansion of the specimens. When cured in 100 percent relative humidity and at 40°C, specimen I-2 exhibited the largest linear expansion, reaching up to 1.2 percent, as compared with specimen I-4 cured in relative low temperature, and I-5 cured in relative low temperature and humidity. It is worthwhile to indicate that the variation in temperature within some range affects the linear expansion rate significantly, but not the final magnitude values, for specimen cured at 20°C reached 1.1 percent linear expansion. This is nearly equal to that cured at 40°C, but it took about 9 weeks to reach its maximum expansion value. On the other hand, low humidity limited the linear expansion effectively and the specimen I-2 cured at low relative humidity only obtained 0.2 percent expansion, much more lower than that cured in high relative humidity.

Compared the previous results given in Figures 7-7 and 7-8, it is noted that the cement content also affect the final value of linear expansion. When the cement content decreased from 9 percent (specimen I-2) to 5 percent (specimen I-6), the linear expansion decreased from 1.2 percent to 0.8 percent.

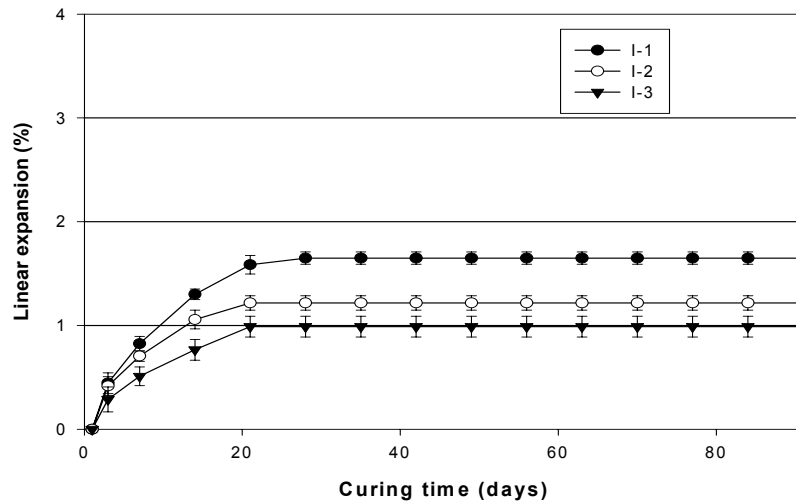


Figure 7-6 Linear expansion of specimens I-1, I-2 and I-3 cured at 100% relative humidity and 40°C

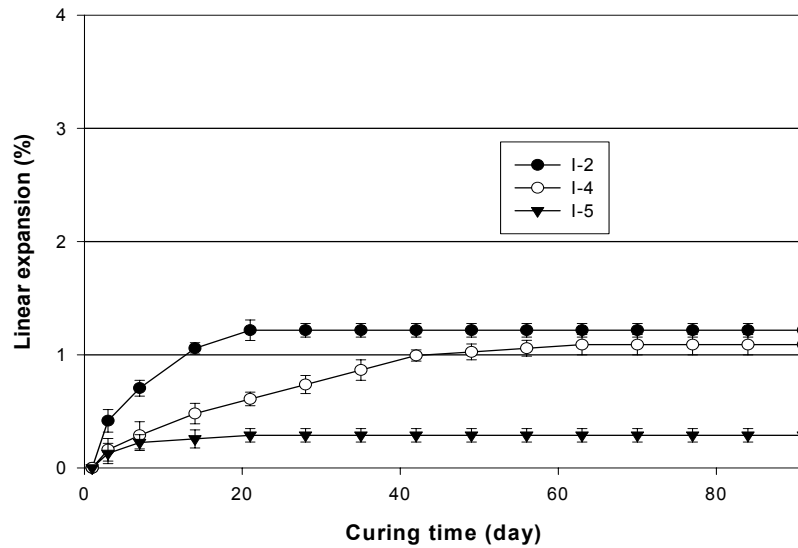


Figure 7-7 Linear expansion of specimens I-2, I-4, and I-5 cured in different conditions

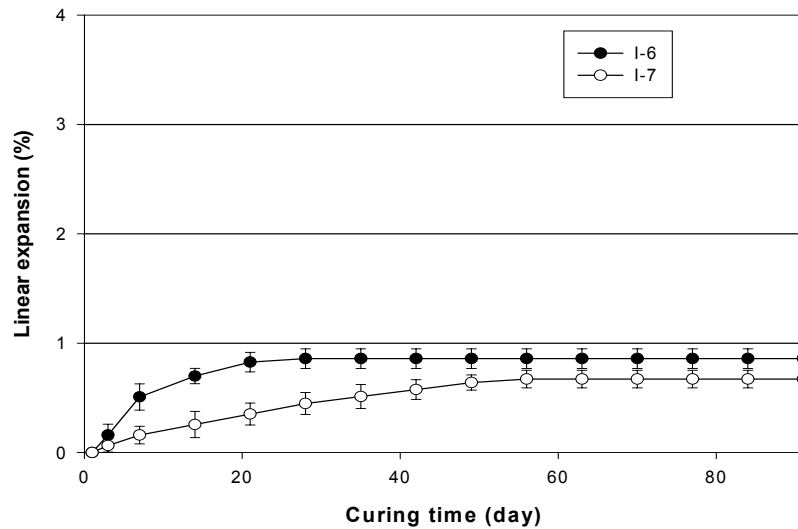


Figure 7-8 Linear expansion of specimens I-6 and I-7 cured in different conditions

When subjected to external sulfate attack, the specimens exhibited the same linear expansion patterns of the specimens (I group) subjected to internal sulfate attack. Both Figures 7-9 and 7-10 illustrate the expansion process and the effects of sulfate concentrations and cement contents on sulfate expansion of the specimens. As indicated in both Figures, the increase in sulfate concentration and cement content would lead to a higher expansion. The maximum value of specimen E-1 reached up to 0.8 percent at sulfate concentration of 50g Na₂SO₄/L at about 9 weeks.

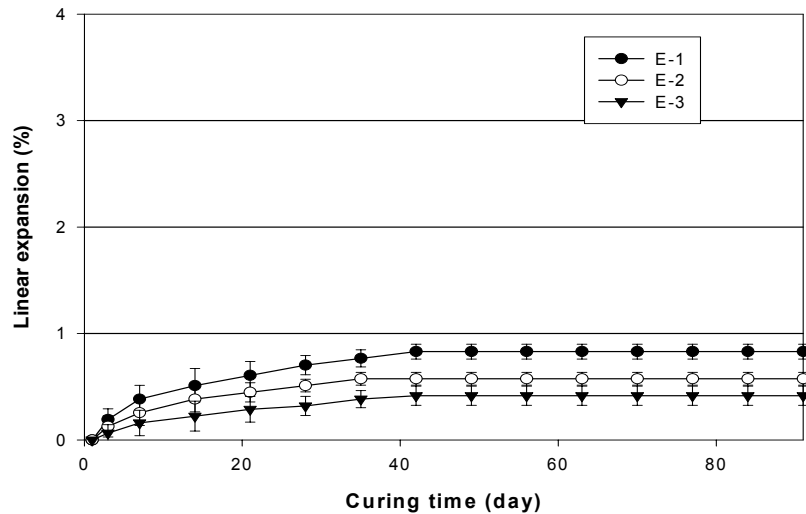


Figure 7-9 Linear expansion of E-1, E-2 and E-3 cured in different concentrations of Na_2SO_4 solutions

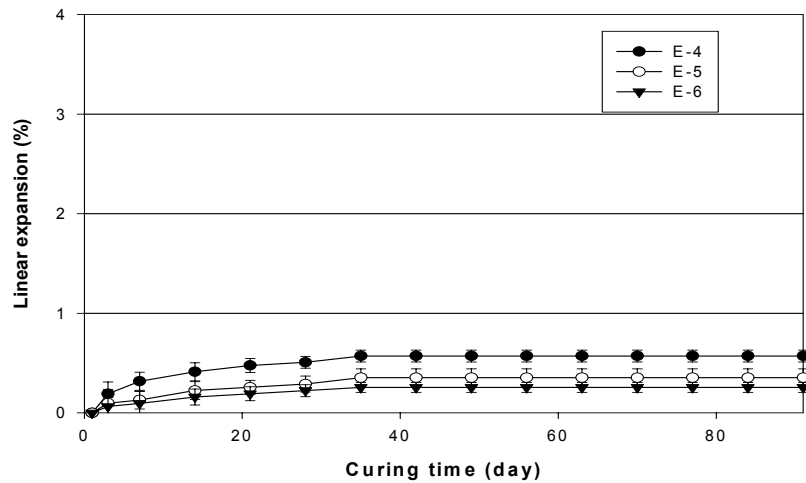


Figure 7-10 Linear expansion of E-4, E-5 and E-6 cured in different concentrations of Na_2SO_4 solutions

The results of linear expansion indicate that sulfate attack on soil cement varies with sulfate level, cement content and curing conditions. For cement concrete there may be some difference of sulfate attack corresponding to sulfate sources (Chengsheng 1988), i.e. the difference between internal sulfate attack and external sulfate attack, but this difference is not obvious for soil cement, considering that specimen I-4 reached its maximum expansion of 1.1 percent at about 6 weeks and that specimen E-1 reached its maximum expansion of 0.9 percent at the same time interval.

7.3.3 Phase Composition and Microstructure Analyses

The XRD patterns of the soil cement specimens I-2, I-4 and I-5 cured for 3 months are given in Figure 7-11.

It can be seen that all three specimens show the peaks of ettringite, except for some differences in intensity and dispersivity. As approximately illustrated by the comparison of the intensity of ettringite peaks of three specimens, the formation of ettringite in I-5 specimen seems limited, and this may be due to the lower humidity, and this is in agreement with its expansion behavior. On the other hand, the peaks of ettringite crystals present in specimen I-4 is a little more shape than that of specimen I-2, indicating a little better crystalline ettringite crystals formed corresponding to low temperature curing condition.

SEM observations were conducted to evaluate the typical microstructure of the specimens. These observations also provided important information on the microstructure of the specimens subjected to sulfate attack.

Figures 7-12 and 7-13 show the microstructure of specimen I-2. Ettringite abounds in the matrix and presents in quite small crystals with average length of about 1.6 μm . As discussed in Chapter 6, the formation of these small ettringite led to the expansion of the specimen I-2. Similar structures were observed in specimens I-4 (Figure 7-14) and I-5 (Figure 7-15). As in I-2 specimen, ettringite crystals are fibrous, or needle-like, but the dimensions of the ettringite crystals that occurred in specimen I-4 are in average length of 3.7 μm and those in specimen I-5 are 7.3 μm . This revelation is basically identical to that in the case of stabilized Winn Rock soil mixture (Chapter 6).

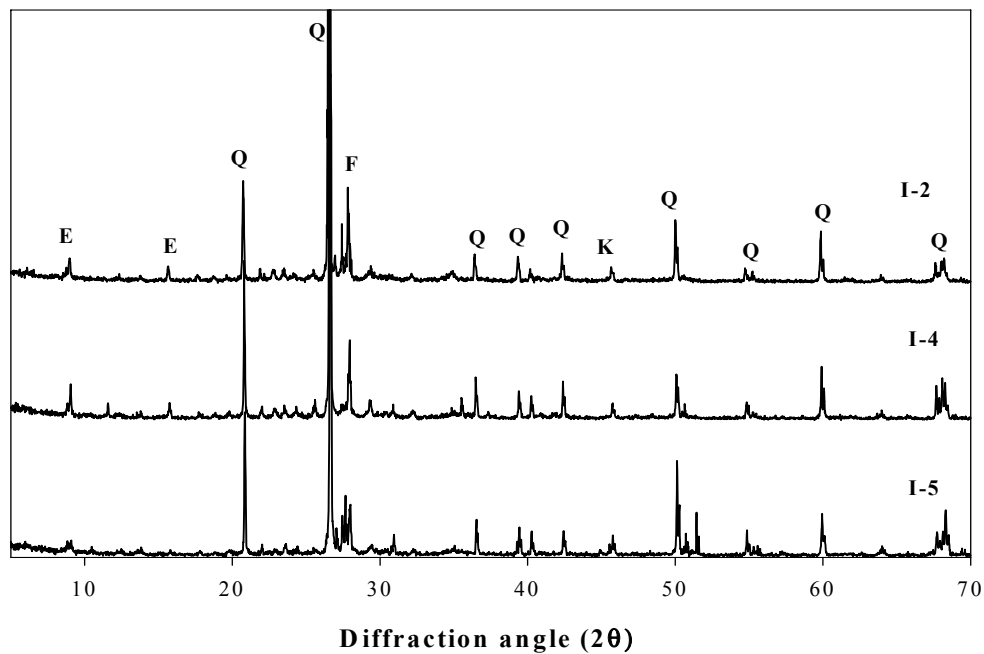


Figure 7-11 XRD pattern of silty sand soil cement specimens I-2, I-4 and I-5:

E-ettringite, Q-quartz, F-feldspar and K- kaolinite

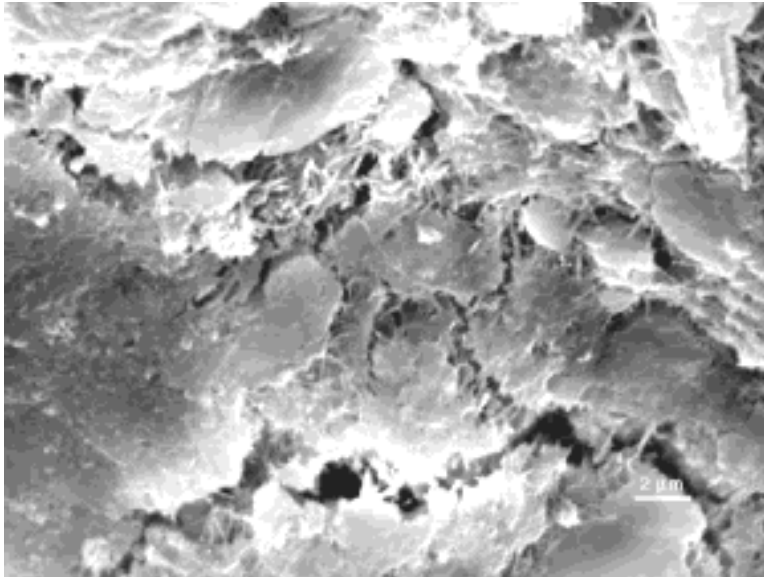


Figure 7-12 SEM micrograph of specimen I-2 cured for 3 months

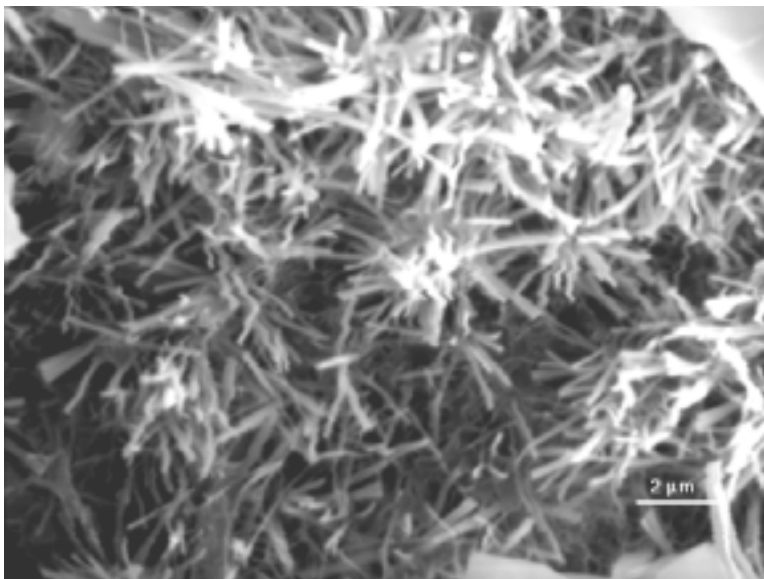


Figure 7-13 SEM micrograph of specimen I-2 cured for 3 months

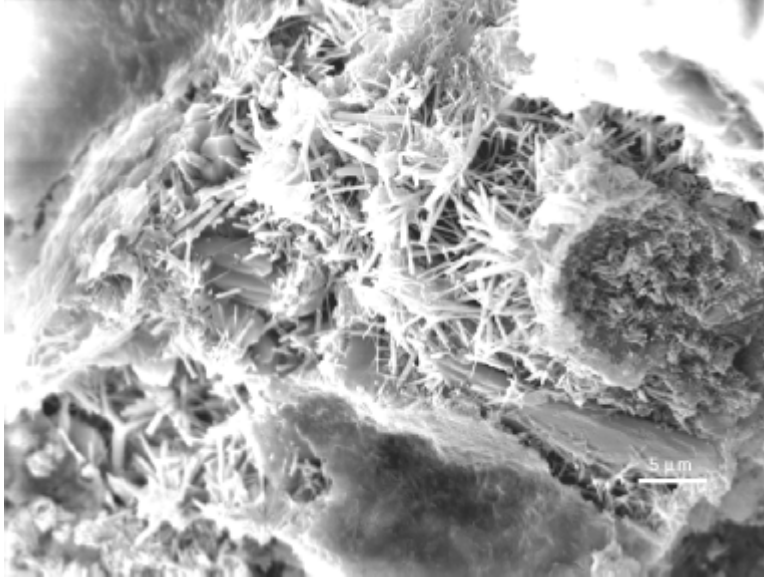


Figure 7-14 SEM micrograph of specimen I-4 cured for 3 months

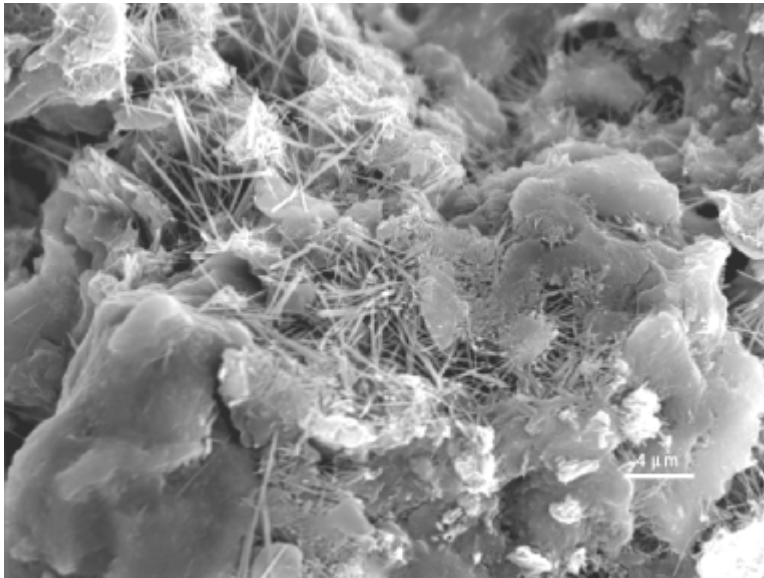


Figure 7-15 SEM micrograph of specimen I-5 cured for 3 months

XRD (Figure 7-16) and SEM (Figure 7-17) analyses of specimen E-1 demonstrated the same results as those of I group. However, the dimensions of ettringite crystals are much larger than those in I group, about 18.7 μm in average length. The crystals were found to cover the entire vision area, indicating sulfate ions penetrated easily into the inside matrix of soil cement specimen. However, these crystals of ettringite occurred in pores with sulfate solution between solid soil cement particles only cause relatively low expansion. Again as indicated by Charlotte and Taylor (2001), ettringite crystals with large dimensions present in voids or cavities contribute not much to expansion

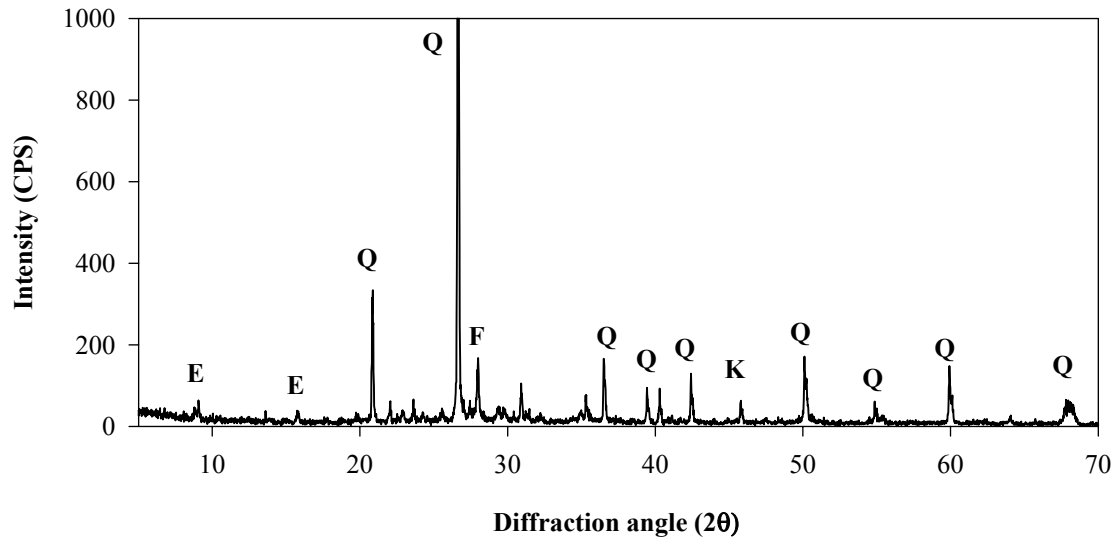


Figure 7-16 XRD pattern of silty sand soil cement specimens E-1 curing for 3 months

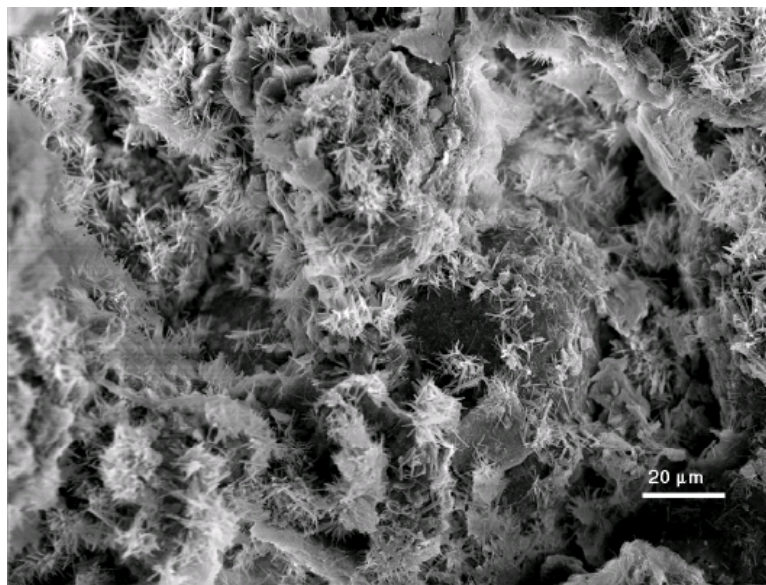


Figure 7-17 SEM micrograph of specimen E-1 cured for 3 months

7.4 Summary

This research work examined the internal and external sulfate attack on the soil cement. Linear expansion measurements were conducted for specimens cured in different conditions. XRD and SEM analyses were performed to determine the causes of the expansion. The following conclusions can be drawn:

1. Both internal and external sulfates can attack soil cement significantly. The sulfate expansion of the soil cement will be affected by several important parameters, including sulfate concentration, cement content, temperature and humidity.

2. Sulfate expansion will increase with the increase in sulfate concentration and cement content. Raising the curing temperature will accelerate the sulfate expansion, but has little influence on the final magnitude of the expansion. Relative humidity is an important affect that will determine the occurrence and magnitude of sulfate expansion.

3. There seems no remarkable difference between the internal and external sulfate attack on soil cement. This may be due to the easy penetration of sulfate ions into the soil cement matrix.

4. XRD and SEN analyses also revealed the presence of ettringite in the soil cement matrix. For internal sulfate attack, small ettringite crystals grew outward from the solid particles and caused expansion. For external sulfate attack, relative large crystals of ettringite developed in the voids between solid particles and also caused relatively small expansion.

CHAPTER 8. INFLUENCE OF POZZOLANS ON THE EXTERNAL SULFATE ATTACK RESISTANCE OF SOIL CEMENT

8.1 Introduction

Because of its successful engineering performance and low cost, soil cement has been used increasingly as a base course material in highway pavement construction. The improvement in soil properties is believed to be due mainly to the hydration of cement as well as possible pozzolanic reaction between cement hydrates and silica and alumina dissolved from clay minerals.

Portland cement is a finely ground material containing four major mineral phases: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetraxalcium aluminoferrite (C_4AF). The two calcium silicate phases are the most important with regard to soil stabilization. Upon hydration, these two phases produce calcium hydroxide for pozzolanic reaction, and calcium silicate hydrate ($C-S-H$), which provides strength and hardening matrix of soil cement. However, as sulfate attack is concerned, which has been realistically considered the cause of distress in many transportation facilities (Mitchell 1986, Petry and little 1993, ACI “state-of-the-art” 1998), both aluminate hydrates and calcium hydroxide plays a major role as in cement concrete.

Sulfate attack is one of cement concrete deterioration, and ettringite, which forms from the reaction of sulfate ions with aluminate hydrates and calcium hydroxide, has been connected to the phenomenon of sulfate attack for a long time. It is actually a complex process and the mechanism underlying sulfate expansion still remains a subject of debate (Cohen 1983, Charlotte and Taylor 2001).

On the other hand, the sulfate resistance properties of blended cement incorporated with supplementary cementitious materials have been recognized for long time (Berry 1980) and these materials including fly ash (FA) are widely used as protective measures against sulfate attack. The beneficial effect that FA imparts in sulfate attack resistance is brought about with direct and indirect effects (Swamy 1986). The direct effect to reduce the potential for sulfate attack results from the straightforward dilution of alumina content, and from FA reacting with $Ca(OH)_2$. The indirect effect is to reduce the permeability of cement concrete and thereby controlling the ingress of sulfate ions into concrete matrix.

This practically proved sulfate resistance properties of blended cement with FA suggest they may impart the similar properties to soil cement, and the beneficial associated with the application of pozzolans in soil cement to mitigate internal sulfate attack has been reported (Chapter 6). The aim of this study is to demonstrate the behavior of soil cement incorporated with supplementary cementitious materials and subject to external sulfate attack, as most problems associated with sulfate attack on soil cement are caused by the penetration of water containing sulfates. The influences of sulfate attack on soil cement and soil cement incorporated with supplementary cementitious materials was assessed with linear expansion measurement, and mineralogy and microstructure changes were traced with instrumental analyses. External sulfate expansion mechanism and resistance properties of soil - blended cement were evaluated and discussed.

8.2 Materials And Methods

8.2.1 Materials

The properties of the materials, including a silty sand, Portland cement, FA and AS, sulfate, have been described in Chapter 7.

Initial work (Wang, Roy and Seals 2001) illustrated that AS has very high pozzolanic activity due to its higher specific surface area and amorphous characteristics and can be used as supplementary cementitious material. The X-ray pattern and transmission electron photomicrograph (TEM) of the material are given in Figures 8-1 and 8-2. Low intensity XRD peak indicate that AS is an amorphous material, and TEM observation illustrates that its particle size is below 0.03 μm .

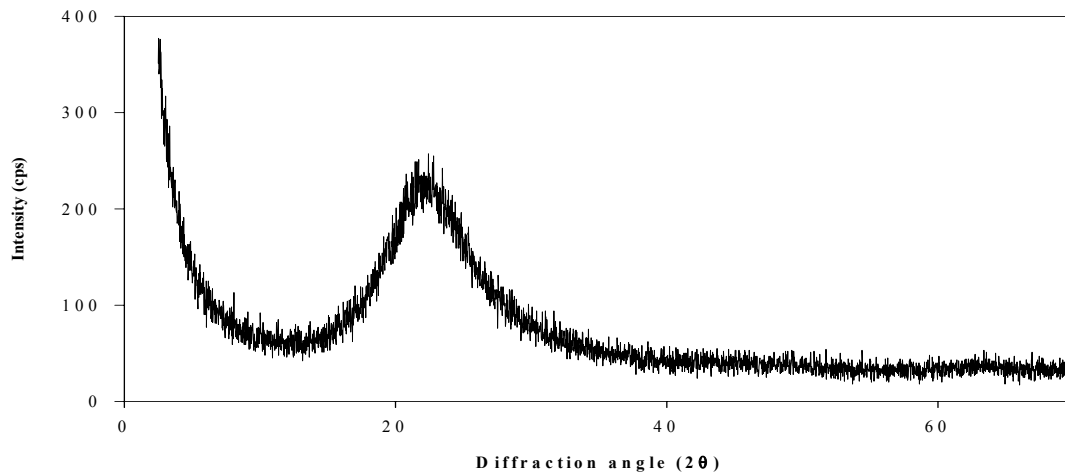


Figure 8-1 XRD pattern of AS residues

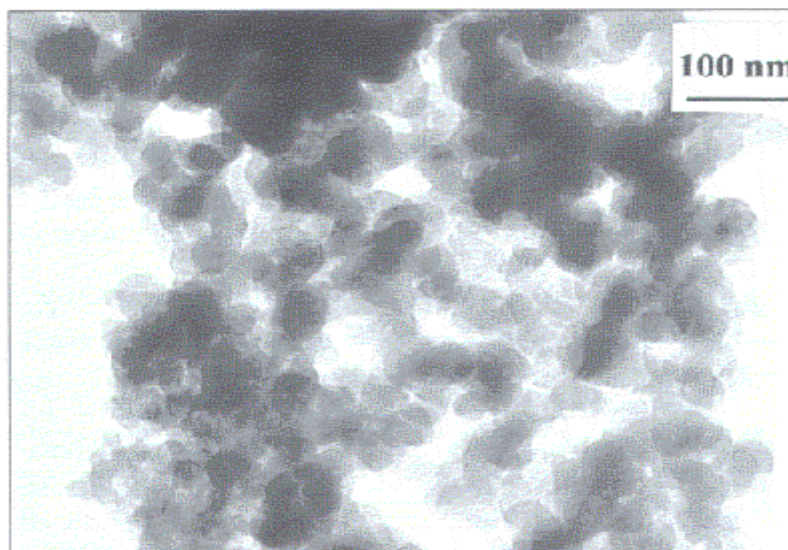


Figure 8-2 Transmission electron photomicrograph of AS residues

8.2.2 Laboratory Testing Methods

Generally, 4 to 9 percent cement is often employed for soil stabilization, depending on the properties of the soil. The current work includes both cement content levels. If supplementary cementitious materials are added, the cementitious material content was restricted to 9 percent as for comparison proposes. Compositions of the test specimens are listed in Table 8-1.

Table 8-1 Specimen cylinder preparation matrix

No.	Composition (by weight %)				
	Silty sand	cement	FA	AS	Water*
C5	95	5	-	-	14
C9	91	9	-	-	14
CF	91	4.5	4.5	-	14
CFA	91	4.5	3.375	1.125	14

*by the weight of dry mixture and based on compaction test

Specimen cylinders prepared for this test were designed for a dry density of 17 kN/m³ at 14 percent moisture content, so that calculated components of the mixture would be wholly accommodated in mold of $\phi 50 \times 100$ mm and compressed to obtain an exact dimensions.

After fabrication, the specimens were demolded and kept in moist room with 100 percent relative humidity and at 20°C for 7 days. The specimens were then submerged in a 5 percent Na₂SO₄ solution. Linear expansion was measured and recorded at intervals and fragments of broken specimens were tested with instrumental analyses for mineralogy composition and microstructure examination.

8.3 Results and Discussion

Figure 8-3 presents the linear expansion of each specimen plotted against curing time up to 3 months. During the first one week of normal curing period, none of the specimen exhibited expansion. However, when subjected to the sulfate solution, significantly different behaviors were exhibited by the specimens. As expected, the soil stabilized by Portland cement was most vulnerable to sulfate attack. Specimen C9 with 9 percent cement reached its maximum linear expansion of 0.6 percent within 5 weeks.

On the other hand, the effect of incorporation of supplementary cementitious materials is dramatic. The addition of FA increases the sulfate attack resistance and reduces the expansion of soil cement significantly. With half of cement content replaced by FA, the expansion magnitude decreased from 0.6 percent to about 0.2 percent. It is of interest to note that the expansion of specimen CFA was totally eliminated with addition of small amount of AS (1.125 percent by the weight of whole solid materials, or 12.5 percent by cementitious materials).

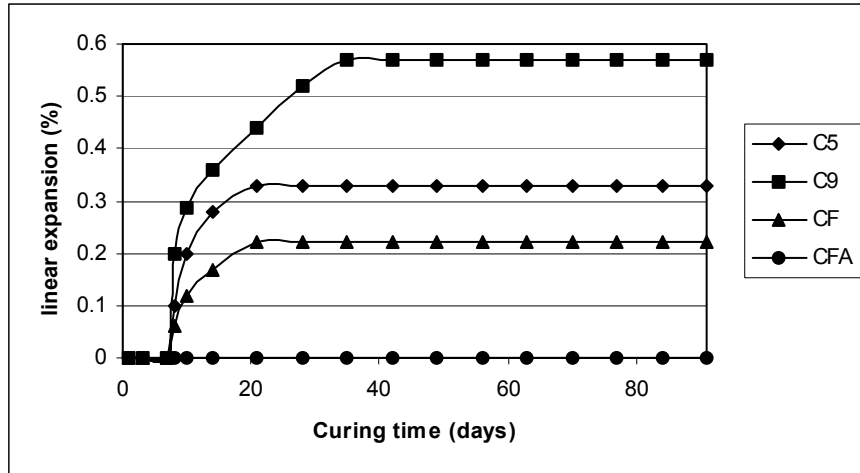


Figure 8-3 Linear expansion of specimens plotted with curing time

The XRD patterns and SEM micrographs of the specimens cured for 7 days are given in Figures 8-4, 8-5 and 8-6. Ettringite can be easily identified with all specimens. Actually ettringite is a normal product of cement hydration. As a certain quantity of calcium sulfate (usually gypsum) is added to cement for proper regulation of setting, ettringite forms and its XRD peaks can be even detectable with a few hours (Taylor 1997). It has long been known, however, that ettringite formed in the early stage of hydration does not result in expansion due to its limited amount and plastic state of the cement paste. Calcium hydroxide, another normal cement hydration product can also be detected in the XRD patterns, but only for specimen C5 and C9. Carbonate also occurs within soil cement matrix and even in the specimen incorporated with FA (specimen CF), through carbonation of calcium hydroxide with the presence of atmospheric CO₂ in the initial mixture and by following penetration. Significantly different pattern of XRD was illustrated by the specimen CFA incorporated with FA and AS. No calcium hydroxide and carbonate peaks show up in the corresponding XRD pattern. It has been demonstrated (Wang, Roy and Seals 2001) that AS has a remarkably high pozzolanic activity and can react with calcium hydroxide to form C-S-H gel. This result of the test conducted for soil cement incorporated with AS is identical with initial experimental conclusion.

SEM micrograph of specimen C9 (Figure 8-4) revealed that abundant ettringite crystals with an average length of 4.8 μm, whereas larger ettringite crystals with an average length of 10.2 μm present in the matrix of specimen CFA, which was incorporated with FA and small amount of AS. It is obvious that the addition of these pozzolans changed the morphology. As discussed in Chapter 6, this change is due to the addition of AS. AS can react with calcium hydroxide released by the hydration of cement to form C-S-H gel and reduce Ca²⁺ concentration. Under this condition ettringite crystals can grow up and present in large size.

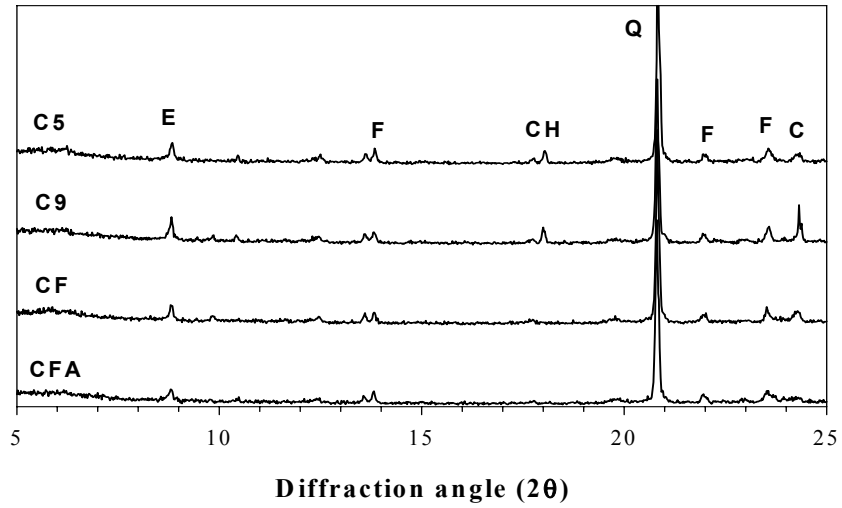


Figure 8-4 XRD patterns of specimens cured for 7 days: Q-quartz, F-feldspar, E-ettringite, CH-calcium hydroxide, C-carbonate

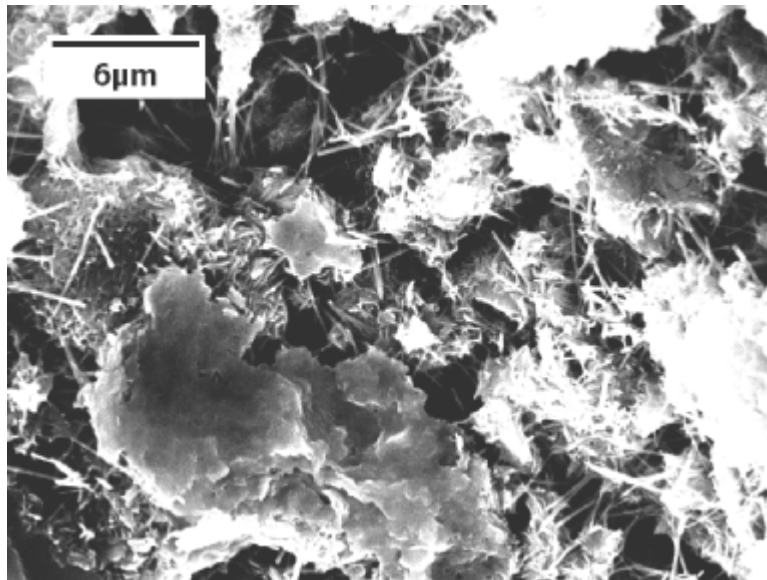


Fig. 8-5 SEM micrograph of specimen C9 curing for 7 days

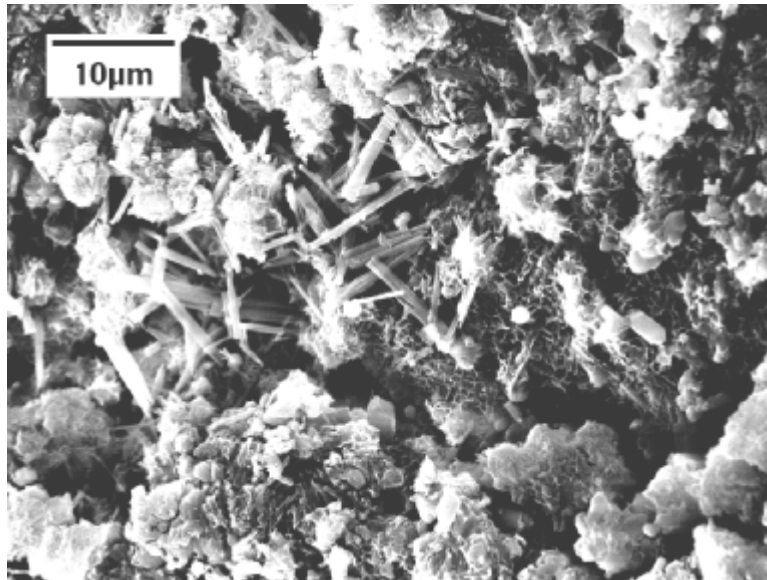


Fig. 8-6 SEM micrograph of specimen CFA curing for 7 days

After submerged in sulfate solution, ettringite peaks of all specimens can also be identified easily for as the XRD patterns indicated in Fig. 8-7, even though no obvious difference occurred as compared with the specimens that have not subjected to sulfate attack. However, the XRD peaks of calcium hydroxide of the specimens C5 and C9 are nearly undetectable. This deficiency of calcium hydroxide must be due to its reaction with other compositions for ettringite formation. The SEM micrograph presented in Figures 8-8 and 8-9 showed that substantial amount of ettringite crystals occurred in the specimen C9 when subjected to sulfate attack for a week. These slender, needle-like crystals grew from the reactant surface into cavities, and caused expansion. On the other hand, specimen CFA is high resistance to sulfate attack. As shown in Fig.8-11, no change of microstructure of the specimen is demonstrated when it is subjected to sulfate attack.

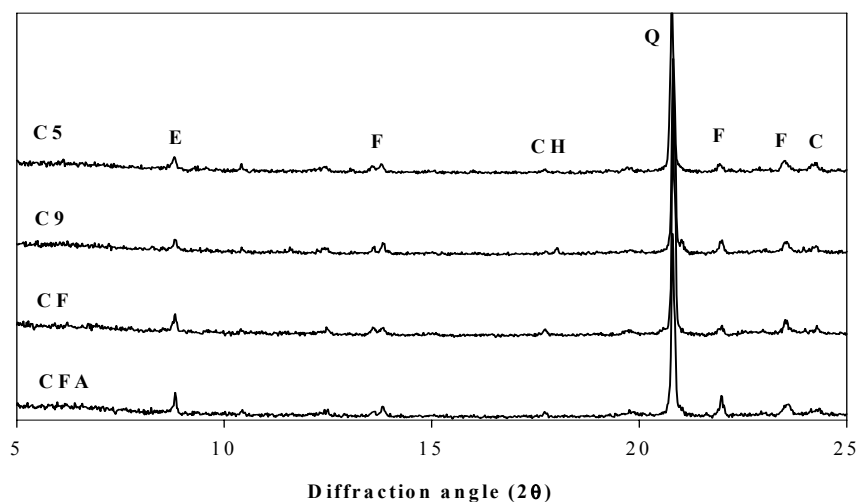


Figure 8-7 XRD patterns of specimens cured for 7 days and kept in sulfate solution for another 7 days: Q-quartz, F-feldspar, E-ettringite, CH-calcium hydroxide, C-carbonate

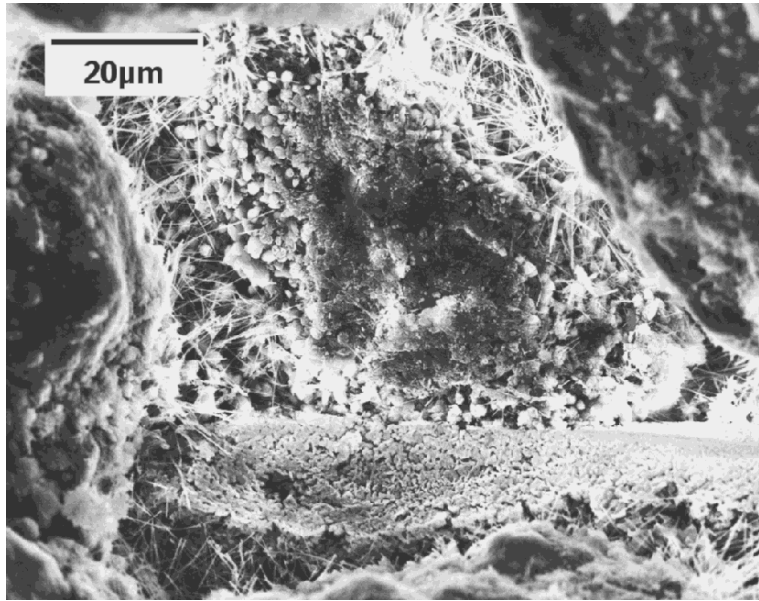


Fig. 8-8 SEM micrograph of specimen C9 curing for 7 days and kept in sulfate solution for another 7 days

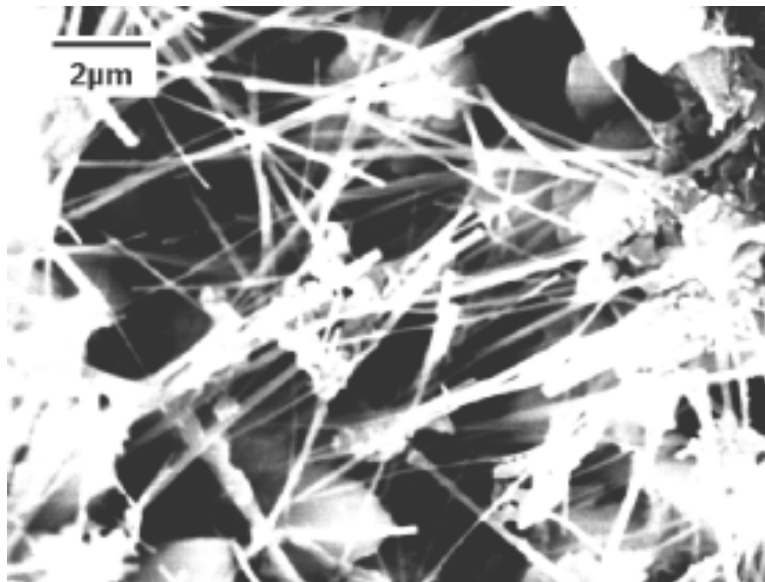


Fig. 8-9 SEM micrograph of specimen C9 curing for 7 days and kept in sulfate solution for another 7 days

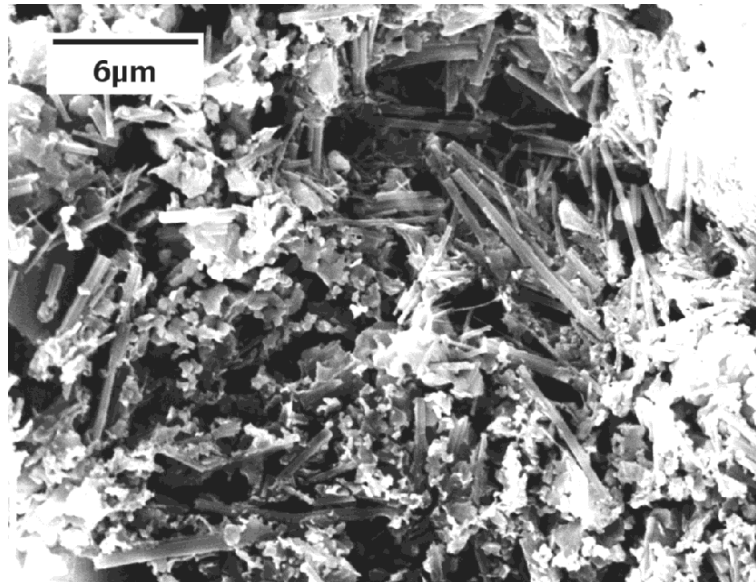


Fig. 8-10 SEM micrograph of specimen CFA cured for 7 days and kept in sulfate solution for another 7 days

The mechanism underlying the expansion of ettringite is an unsettled issue, and there exist a number of theories concerning ettringite formation and expansion. Cohen (1983) reviewed and summarized the various hypotheses, and grouped them as two schools: the crystal growth theory and the swelling theory.

Referred to these theories and based on the study presented in Chapters 4, 5 and 6, a tentative three-stage hypothesis of ettringite formation and expansion was developed. On an arbitrary basis, the process of ettringite formation and expansion may be divided into three stages: early-term, middle-term and late-term, which correspond to the formation of ettringite nuclei, the growth of ettringite and the development of mature crystals of ettringite. Ettringite nuclei are generally defined as particles smaller than 2 μm , whereas those grown ettringite and mature ettringite can be defined as particles between 2 – 5 μm and larger than 5 μm , respectively.

During early-term stage, if calcium hydroxide concentration maintains saturated, substantial amount of ettringite nuclei will form, which will lead to a significant expansion. If calcium hydroxide is low or cannot be kept saturated, limited amount of ettringite nuclei will form, leading to an initial moderate expansion and the beginning of middle-term stage. During middle-term stage, as calcium hydroxide is available, ettringite nuclei will grow up and push against the surrounding particles to produce expansion. However, the magnitude of expansion depends on where they occur. If they present in small voids, they will produce large expansion. If they present in large cavities, they will produce small expansion. During late-term stage, with the decreasing of calcium hydroxide concentration, only ettringite crystals present in large cavities can continue to develop into mature particles of large dimensions. As the resistance there to the growth of ettringite crystals is low, this development contributes little to total expansion.

The research results (Chapters 7 and 8) can be fairly elucidated with the three-stage hypothesis. When lime was used to treat the silty sand soil with the addition of gypsum, substantial amount of ettringite nuclei formed quickly, and led to significant expansion.

When cement was used to treat the silty sand soil with the addition of gypsum, calcium hydroxide was available for the formation of certain amount of ettringite nuclei, which led to an initial moderate expansion. The expansion continued for some time due to the growth of ettringite crystals. When subject to external sulfate attack, the growth of ettringite crystals occurred in large cavities, which led to the formation of large ettringite crystals and small expansion.

When incorporated with supplementary cementitious materials, especially with amorphous silica, calcium hydroxide released by cement hydration was consumed quickly to form C-S-H gel, creating a calcium hydroxide deficiency situation. Limited amount of ettringite nuclei formed and developed into mature particles in large size. No expansion occurred whether it was subject to internal sulfate attack or external sulfate attack.

8.4 Summary

The following principal points may be deduced from the results, with regard to the influence on pozzolans, i.e., FA and AS on the external sulfate attack resistance of soil cement.

1. Soil cement is sensitive to external sulfate attack. A 5 percent Na_2SO_4 solution can lead to a linear expansion of 0.6 percent for soil cement incorporated with 9 percent Portland cement cured for several weeks.

2. Partial substitution of Portland cement with supplementary cementitious materials can significantly reduce the linear expansion. With the addition of small amount of AS, external sulfate expansion can be totally prevented.

3. Supplementary cementitious materials, especially AS, can react with calcium hydroxide, so that the latter is not available as the reactor for the formation of substantial amount of ettringite crystals with small dimensions. This may be the reason that the addition of supplementary cementitious materials can increase sulfate attack resistance of soil cement.

CHAPTER 9. CONCLUSIONS

Stabilization of soil cement by lime or Portland cement is a technique widely used in road construction to improve bases and subbases. However, a number of cases have been reported where pavement bases stabilized by cement or lime underwent a significant amount of heave leading to pavement failure. Cementitious stabilization of Winn Rock-containing soil in north Louisiana is such an example. Following are the conclusions from this study:

Winn Rock is composed of anhydrite which weathered to gypsum in soil when used as aggregate. Gypsum is present in all size fractions. In one soil more gypsum is present in the finest fraction (50 μm) than in the coarser ones. The other minerals present in the soil are quartz and a minor amount of kaolinite. Additionally, the Winn Rock soil mixture can be classified as A-1-b group soil. Its maximum dry density is 18.42 kN/m^3 at the optimum moisture content of 14 percent. The compressive strength of the Winn Rock soil mixture reached 78 psi at 28 days after fabrication.

A Substantial amount of small ettringite crystals is identified in both lime treated and cement treated Winn Rock containing soil, which leads to a linear expansion of 7.7 percent and 3.5 percent, respectively, when the specimens are cured in 100 percent relative humidity and at 40°C , indicating the occurrence of Type II sulfate attack and the important effect of calcium hydroxide on the formation of ettringite and the subsequent expansion of the soil.

When stabilized by Portland cement with or without partial substitution by supplementary cementitious materials, including GGBS, FA and AS, the Winn Rock soil mixtures exhibits normal compaction behavior. The maximum dry density and optimum moisture content of the stabilized soil vary within a limited range. Their compressive strength shows significant difference, but all increase as compared with that treated by Portland cement only. In addition, the presence of a supplementary cementitious material dramatically improves the resistance of the stabilized soil to sulfate attack. Linear expansion of specimens incorporated with supplementary cementitious materials shows a significant reduction compared to specimens treated only with Portland cement. In particular, GGBS is more effective than FA in reducing expansion; whereas the addition of small amount of AS produces no expansion at all.

A three-stage hypothesis is developed for the explanation of the mechanisms of ettringite formation and expansion. In the initial stage, when the pore solution is saturated with calcium hydroxide, substantial amount of ettringite nuclei will form, which will lead to a significant expansion. During the middle stage, as calcium hydroxide is also available, ettringite nuclei will grow up and push against the surrounding particles to produce moderate expansion. In the late stage, with a decreasing of calcium hydroxide concentration, only ettringite crystals present in large cavities can continue to develop into mature particles of large dimensions, and this development contributes little to total expansion. Mineralogical and microstructural analysis generally supports this hypothesis.

Soil cement is vulnerable to both internal and external sulfate attack. There seems no remarkable difference between the internal and external sulfate attack on the soil cement. Supplementary cementitious materials, especially AS, is also effective in the mitigation of external sulfate attack. The three-stage hypothesis can be applied to explain the mechanisms of ettringite formation and expansion for this general case.

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