EFFECTS OF COMBINED LIME AND FLY ASH STABILIZATION ON THE ELASTIC MODULI OF MONTMORILLONITIC SOILS

(FINAL REPORT)

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IMPLEMENTATION STATEMENT

Results of this study show that when fly ash is used with lime for stabilization of bentonite cementitious products developed within the mix are more abundant than those developed when only fly ash, or lime is used. The availability of these products determine the strength and durability of the mixtures, therefore, it is recommended that lime be added to soil-fly ash mixtures when stabilization (e.g. shoulders, sub-bases, etc.) is required. also that fly ash be used as an additive for lime stabilization of soils when higher strengths are desirable.

Results of this study shows that soil-lime-fly ash mixtures, when cured at 50°C for 24 hrs., or any combination thereof, produce similar cementitious products and, therefore, similar strengths to those cured for 28 days at 23°C.

Also, this study verifies that the reaction products of soil-lime-fly ash mixtures are similar to reaction products obtained from the hydration of portland cement, thus, it is recommended that testing laboratories adopt curing of soil-lime, soil-fly ash, soil-lime-fly ash or soil cement specimens for 24 hrs. at 50°C as a procedure parallel to the presently used 28 day curing at 23°C for a period of no less than one year.

Data from curing at 50°C for 24 hrs. and 28 day curing at 23°C should be recorded and sent to LTRC for correlation. If laboratory data corroborates the findings of this study then the 24 hrs. curing at 50°C should be adopted for routine testing. A suggested form for recording this data is attached.

Stress-strain relationships of lime-fly ash stabilized soils exhibit rather rigid characteristics, thus, in designing pavements, particularly flexible one on soft subgrades, this property of stabilized mixtures should be thoroughly considered.

SOIL STABILIZATION CURING TIME & TEMPERATURE STUDY

Name of Laboratory Performing the Tests:

Name of Person(s) Performing Tests:

Phone No.:

Soil Classification:

Liquid Limit:

Plasticity Index:

Sample Identification:

Sample Dimensions: Diameter____________ Height__________

Specimen No.	Compressive Strength of Samples Cured	
	@ 50°C - 24 hr.	@ 23°C - 28 days

Remarks:

Please make copies of this form for your use. Mail completed copy of this form to: Ara Arman, Director, Louisiana Transportation Research Center, P. O. Box 94245, Baton Rouge, Louisiana 70804.

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ABSTRACT

A laboratory study using bentonite to simulate the montmorillonite component of soils common to Louisiana was undertaken to evaluate the effects of combined lime and fly ash additions on stabilization reactions. Samples containing bentonite (75 weight percent), Class C - fly ash (20 weight percent), and calcitic lime (5 weight percent) were mixed, compacted, and cured at either 23^{o}C or 50^{o}C for periods of time as long as 180 days. This investigation integrates the test results obtained from single specimens rather than to utilize one specimen for physical testing and others for mineralogical and micromorphological analyses in order to develop a better understanding of how the formation of new cementitious minerals affects the texture and increases the strength of the stabilized material. Test methods employed included X-Ray powder diffraction, scanning electron microscopy, compressive strength measurements, and the calculation of the elastic modulus for all specimens.

The cementitious products are more abundant when bentonite was treated with fly ash and lime than when only one additive was used. Ettringite, C-S-H gel, and afwillite form after curing for various lengths of time and the increased relative abundance of these minerals corresponds to curing times when major increases in elastic modulus and compressive strength occur. Ettringite crystals are a source of early strength increases (just as in portland cement hydration) and then they become less abundant through continued reaction with the soil resulting in the

formation of major cementitious compounds, calcium silicate hydrates.

The unconfined compressive strength of the treated bentonite exceeds 2000 - 3000 kPa after 180 days of curing. The elastic modulus of the samples cured for 90 days exceeds 600,000 kPa (17X greater than untreated bentonite) and then decreases to approximately 400,000 kPa after 180 days of curing. A comparison of the values obtained at different temperatures indicates that reactions are occurring more rapidly in the 50°C cured samples. One day of curing at 50°C produces results comparable to those obtained after 28 days of 23°C, thus resulting in a considerably shorter time for the testing procedure. The combined effects of lime and fly ash are greater than when either one is used alone with the bentonite.

The increased rigidity and compressive strength of the fly ash-lime stabilized bentonite can be related to changes in the microstructure. Acicular crystals of ettringite and C-S-H span the pores providing more points of contact between fly ash spheres and particles of bentonite. As the cementitious network becomes more extensive, the particles are held in place and do not move freely in response to increased stress. This framework is best developed after approximately 90 days of curing. Then continued reaction of the lime, fly ash, and bentonite results in the dissolution of some fly ash spheres and a slightly lower modulus of elasticity because part of the network has been destroyed. These general observations should be applicable to natural soils rich in montmorillonitic clays.

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INTRODUCTION

Fly ash and lime, alone or in combination, are used for the stabilization of soils in the construction of bases and subbases for pavements. In Louisiana, fine grained soils are abundant and good quality aggregates are becoming scarce resulting in the need to utilize in situ soils modified by stabilizing agents such as lime. Partial or complete substitution of lime by self-cementitious fly ash has been considered for stabilization of fine grained soils, but little is known about the chemical stability of cementitious minerals that form in the soils. Pavement structure analysis and design require an understanding of changes taking place in the physical properties of the fly ash stabilized soils. The elastic modulus is one of the mechanical properties that can be determined from physical tests. Numerical pavement design methods are sensitive to the modulus of elasticity of the pavement system. An understanding of the micromorphological development of the soil related to changes in the elastic modulus therefore is important to explain and to project the effect of fly ash-lime stabilization to longer curing times and to other soils.

The main objective of this study is to determine the changes occurring in the mineralogy and morphology of a fly ash-lime stabilized pure clay (a bentonite composed primarily of montmorillonite) with increased curing time and to relate these to changes in the elastic moduli, and strengh development of stabilized mixtures. A laboratory study was undertaken using bentonite to simulate the montmorillonite-rich soils of Louisiana and to eliminate variables introduced by naturally mixed soils. Locally produced self-cementitious fly ash and a calcitic lime, were used with the bentonite to answer the following questions:

1- How does adding fly ash and lime to bentonite affect the elastic modulus and compressive strength?

2- How does fly ash-lime stabilization of bentonite compare with only fly ash or only lime stabilization in terms of observed reaction products and changes in elastic moduli?

3- What type of cementitious minerals are forming? Where do they form and how do they relate to increases in strength and elastic modulus?

4- What is the effect of increased curing temperature (50°C) on the morphological development of cementitious minerals, compressive strength and elastic modulus of fly ash-lime stabilized bentonite? Do the same cementitous minerals form at 23°C and 50°C?

5- How can the information obtained from this study be applied to natural soils and to pavement design?

The literature contains many references related to mineralogical or physical changes in stabilized soils. Most of the work is limited to either mineralogical or physical changes in stabilized soils and the two approaches are rarely combined. This study provides an integrated investigation of the three major aspects of stabilization: mineralogical, micromorphological and physical. The data are used to explain the changes in elastic modulus values.

LITERATURE REVIEW

Introduction

" Soil stabilization is the collective term for any physical, chemical or biological method or any combination of such methods employed to improve certain properties of a natural soil to make it serve adequately an intended engineering purpose (35)". The most common application of soil stabilization is the strengthening of the soil components of highway and airfield pavements. Its chief advantages are (24), it:

1- Allows the in-situ soil to be used in construction.

2- Reduces the pavement thickness by improving subgrade conditions.

3- Allows use of low cost materials, instead of more expensive material in the pavement cross section.

4- Allows a byproduct (fly ash) of coal combustion to be used in highway construction.

In general, fine-grained soils rarely have adequate strength and durability for use as base or sub-base courses in the pavement cross-section. In order to improve the durability and strength of soils, various chemical additives such as, portland cement, lime and lime-fly ash are used in addition to mechanical stabilization. These additives improve the engineering behavior of the soils through two mechanisms (24):

1- Modification of soil by decreasing plasticity index, decreasing volumetric shrinkage and improving drainage characteristics.

2- Improvement of strength and durability most probably due to resulting cementitous products.

Cement Hydration

A summary of the hydration of portland cement is instructive (although only fly ash and lime are used in this study) because the reaction products for soil-lime and fly ash-lime mixtures are similar to those that occur in cements. Portland cement is a mixture of four principal compounds; tricalcium silicate (C_3S, 50 to 70 %); beta dicalcium silicate (C_2S, 20 to 30 %); tricalcium aluminate (C_3A, 5 to 12 %) and tetracalcium aluminoferrite (C_4AF, 5 to 12 %). Upon hydration, these materials form new cementitions compounds (31).

The most prominent phase detected by X-Ray powder diffraction techniques from a fully hydrated C_3S paste is calcium hydroxide. The other constituent is calcium silicate hydrate, which is almost amorphous and gives only two very weak and diffuse peaks, at about 3.1A and 1.8A. In cement pastes, calcium silicate hydrates (C-S-H) and calcium hydroxide are also the major products (31).

The Al^{3+}, Fe^{3+} and $SO_4{}^{2-}$ ions provided by the cement are incorporated partly in crystalline phases containing Al^{3+} or Fe^{3+}. Three main types are (31):

1- AFt (Al-Fe-tri) phases typfied by ettringite, $C_6AS_3H_{12}$. These form prismatic or acicular crystals of hexagonal cross section. Primary ettringite occurs as relatively long (4 to 5 micrometers) narrow rods with parallel sides. Secondary ettringite, produced by sulphate attack from external sources of sulfate, tends to be shorter, thicker, and have a hexagonal cross-sections.

2- AFm (Al-Fe-mono) phases, typfied by monosulphate or mono-sulphoaluminate C_4ASH_{12} . These compounds form platey hexagonal crystals.

3- Hydrogarnet phases, belonging to the solid solution series of C_3AH_6, C_3FH_6, C_3AS_3, C_3FS_3. They form roughly equidimensional crystals of cubic symmetry.

The microstructural changes that occur during hydration of cement were reviewed by Taylor (31). He stated, "The relatively large grains of unhydrated cement are replaced by the smaller particles of hydration products, which are formed partly in space originally occupied by water. The products form initially as coatings on the surfaces of the cement grains, from which they both grow outwards and eat inwards. Within a few hours, the coatings begin to join up, and the paste stiffens or sets. On further reaction, the gel becomes denser, and the paste hardens. This happens on a time scale of weeks and longer; if the paste is continously kept wet, the strength continues to increase over a period of years."

C-S-H is present in cement pastes in a variety of morphologies. "The most prominent type of C-S-H gel, especially at early ages, is elongate material usually radiating outward from cement grains. These particles have been called "spines", " acicular particles" " aciculae ", " prismatic or rod shaped crystals", "fibrous crystals", " tubular crystals ", "rolled sheet or acicular projections" and various other names (8)". They are prominent in C_3S and beta-C_2S pastes (33) and are refered to as "Type I" particles (3). Fibrous CSH Type I particles may be from 0.5 to 2 micrometers long, and usually less than 0.2 micrometers across. They have pointed ends and they often branch into two or more portions at the outer tip. Lathlike and rolled sheet type crystals are also reported (28).

C-S-H Type II (8) is composed of small cement grains enmeshed in a network. Fibrous crystals (same size as C-S-H Type I) with branches every half micrometer intersect with each other and coalesce forming a network (8). This network has been called "reticular network", " interlocking structure " , "honeycomb morphology ", etc. (8). "Barnes (3) reported a variant to this structure in which the 3-D character of the interconnecting network is preserved, but in which individual "rods" are replaced by nearly equant grains typically about 0.5 micrometers in length and almost the same in transverse directions. This habit is designated as a "Type IIA" structure."

Type III C-S-H gel consists of small, irregularly equant or flattened particles, less than 0.3 micrometers on each side (8). "Type IV C-S-H gel has a dimpled appearance, with either regular pores or close packed equant grains . The grain size is typically about 0.1 micrometer (8) ".

Calcium hydrate, monosulphate hydrate, and C_4AH_{13} have hexagonal platey microcrystals. The plates are several micrometers across but are only about 0.1 micrometers thick, and tend to show a characteristic edge-to-face contact at fracture surfaces (8). Calcium hydroxide forms relatively massive crystals. The crystals grow within surrounding pores and in some cases completely engulf partially hydrated grains. The crystals may grow up to 0.1 mm in size in the paste (2).

Soil-Lime Reaction

The reaction products in lime stabilized soils are generally either calcium silicate hydrates (C-S-H) or calcium aluminate hydrates (C-A-H) because silica, alumina and calcium are the most abundantly available ions in the soil-lime system. There are two mechanisms reported for the formation of these cementitious crystals: a) solution, or b) hydration-crystallization. Eades and Grim (30) reported that the edges of the clay particles are attacked first and the whole clay mineral structure deteriorated without the formation of any substantial new crystalline phase. Contrary to Eades and Grim's belief, Stocker (30) found that only a small portion of the clay was involved in the cementitious reactions . He showed that even strongly cemented clay preserved its original crystal ine structure. Ormsby and Boltz (27) suggested the possibility of formation of cementitious crystals directly on the surface of the clay. A complete deterioration of clay structure is not likely, however an alteration of the clay structure is possible. The reaction details depend on the type of clay mineral present.

Montmorillonite-Lime Reaction Products

Goldberg and Klein (15) stabilized bentonite with up to 8 percent hydrated lime but they could not detect any new X-Ray diffraction peaks after curing. Eades and Grim (11) used slurries and compacted samples of bentonite and hydrated lime to determine the reaction products of stabilization. A non-crystalline reaction product was evident, but in the bentonite and lime samples that Eades and Grim (11) cured at 60°C for 60 days its identification was not conclusive. They reported that the non-crystalline mineral was probably C-S-H gel.

Hilt and Davidson (17) used montmorillonite and lime mixtures cured for 30 days at 23°C and found new X-Ray diffraction peaks at d-spacings of 8.11A, 10.0A, 7.1A. They isolated a reaction product that was isostructural with tetracalcium aluminate hydrate. Glenn and Handy (13) prepared slurries of pure bentonite and hydrated lime and cured them at 22°C for two years. The reaction products were calcium silicate hydrate, 10A tobermorite, alpha-C_4AH_{13}, beta-C_4AH_{13} and unidentified new diffraction peaks of 7.6A, 3.79A and 2.54A. A 7.95A hexagonal platey product was isolated from this mixture.

Other studies by Diamond et al. (9), Croft (4), Kronert and Wetzel (22), Stocker (30), Sabry (29), Joshi et al., (20), detected various forms of C-S-H and other minerals. The reported montmorillonite-lime reaction products varied from one study to the other considerably without a recognizable trend, depending on the mixture proportions, sources and types of materials used, curing temperature and time, and whether slurries, pastes or compacted samples were used. In most cases, C-S-H (I) is the most widely reported reaction product. In some cases the cementitious minerals may have formed but were not detected because determination of the cementitious minerals using X-Ray diffraction techniques is very difficult due to the poorly crystalline nature of the minerals. The reported cementitious minerals at 50°C were generally the same as those in the room temperature cured samples. At $60^{o}C$, other minerals were detected. Fifty degrees appears to be the upper limit for curing samples in laboratory studies that can be correlated directly with field results.

Lime-Fly Ash Reaction Products

Fly ash chemically reacts with calcium hydroxide at ordinary temperatures to form compounds possesing cementitious properties. Leonard and Davidson (23) investigated the pozzolanic reaction products of a slurry of hydrated lime and fly ash cured at $23^{o}C$ for one year. They reported new X-Ray diffraction peaks at 17.3A, 12.6A, 3.08A. For other mixtures which were cured at elevated temperatures of 40^{o}, 50^{o}, 60^{o} C , they reported no new peaks. The initial product was non-crystalline, after which there was slow crystallization to C-S-H (I), similar to tobermorite.

Minninck (26) studied hydrated lime and fly ash samples cured at $140^{o}C$, or autoclaved, and reported new X-Ray diffraction peaks at 3.31A, 3.05A, 2.97A and 2.77A. In another study Minnick (25) indicated that the major cementing compounds formed in lime fly ash mixtures were calcium silicate hydrates and possibly ettringite. Low sulphate sulfoaluminate might also be formed. Croft reported the formation of calcium silicate hydrate I and hydrated calcium aluminate in the form of C_4AH_{13} (5). The first indications of crystalline reaction products began to appear after 28 days at a curing temperature of 50°C. A combination of montmorillonite clay with lime and fly ash produced no reaction products other than those present in the lime-fly ash mixtures alone. It may be concluded that C-S-H (I) is the cementitious reaction product which is consistently reported by different researchers. Ettringite and C_4AH_{13} are also present.

Particle Hydration

There have been many studies of the hydration of fly ash on an individual particle basis. Idorn (19) lists three mechanisms of particle hydrations:

1- The particle reacting with calcium hydroxide is surrounded by an integrated layer of C-S-H gel (21).

2- The fly ash particles are completely inert fillers within the surrounding cement paste (8).

3- The fly ash particle dissolves and resulting (C-S-H and calcium aluminate hydrates) products precipitate leaving a space between the remaining portion of the fly ash particle and cement paste (30). A combination of all the above mentioned mechanisms can be found together, because of the chemical variability of the fly ash (7).

Grutzeck et al., suggested a hydrating hollow cenosphere model and explained the morphology at various stages of hydration (16). At early stages "Pull out " features, in which the fly ash particle has been cleanly removed or " pulled out " when the sample was broken for observation, were observed. An equal number of smooth surfaced voids and spheres were visible at this stage. At later stages a crust of radiating C-S-H fibers surrounded the dissolving fly ash sphere and fewer pull out features with rough surfaces were observed. Once a sphere was completely consumed, the mottled interior surface remained as a remnant of the original sphere.

Diamond et al., (6) reported a duplex film on fly ash grains similar to that observed by Barnes et al., (1) in a cement paste. The cementitious reactions should occur through this film by diffusion, but they also noted that the film could be a precipitate on an inert sphere (6). Ghose et al. (12) observed similar double films covering fly ash spheres. Some of the fly ash spheres did not react at all. Diamond (7) stated that depending on the chemical compositions, many fly ash spheres might not react and inert fly ash spheres might not be detrimental to strength.

Changes in Elastic Moduli

The addition of fly ash and lime to stabilize a base course, changes the stress strain properties of the stabilized soil. The marked effect of addition of lime, to the compressive stress strain properties of fine grained soils is shown in Figure 1. The failure stress (strength) is increased, and the ultimate strain of the stabilized soil is decreased relative to that of the natural soil. Improvement in stress/strain characteristics occurs immediately and improvement continues with an increase in the curing time (32).

"As a result of studies conducted with representative Illinois soils stabilized with lime (32) it has been possible to develop a generalized compressive stress/strain relation for cured soil lime mixtures. These mixtures appeared to be strain susceptible , and the ultimate strain at maximum compressive stress was approximately one percent, regardless of soil type and curing period. The compressive modulus of elasticity at a confining pressure of 105 kPa was estimated (32) from the unconfined compressive strength of the lime soil mixture according to the following relation.

$$E = 70 + 0.124\ q \qquad \ldots\ldots (1)$$

In which E is the compressive modulus of elasticity in MPa and q is the unconfined compressive strength in kPa. The elastic modulus obtained from triaxial compression tests can be used to determine the thickness of pavements.

METHODS AND MATERIALS

Various studies of lime, fly ash, and portland cement stabilization have been reported in the last three decades. Many were performed only on their engineering properties while others emphasized the importance of chemical reactions between stabilizing agents and soil. X-Ray diffraction, differential thermal analysis, and electron microscope studies of the isolated reaction products have been employed. However very few mineralogical studies are reported using compacted samples.

In this study we have attempted to combine these approaches and use the same specimens for engineering tests, mineralogical analyses, and micromorphological examinations. A flow chart illustrating our methods is presented in Figure 2. A bentonite fly ash-lime mixture was compared with hydrated fly ash and binary mixtures of fly ash with bentonite or lime and bentonite with lime in order to determine whether the changes were unique to the ternary mixture and to simplify some of the mineralogical identification tasks.

Mixture Design

The amount of lime to stabilize the bentonite was determined by Eades and Grim's pH method (10) and Hilt and Davidson's plastic limit method (18). Bentonite-lime slurries with one to eight percent lime by dry weight were prepared and their pH was measured after one hour. The increase in pH with increasing lime percentage is presented in Figure 3. The optimum lime addition for this bentonite is four percent by dry weight.

Hilt and Davidson's (18) method uses the plastic limit to determine the optimum lime content. The lime percentage at which the increase in plastic limit is negligible is the quantity required for stabilization. The plastic limit corresponding to three percent lime by dry weight is 45 and it increases to 56 with the addition of 5.5 percent lime (Figure 3). The plastic limit slightly increases to 57 with 6.5 percent lime by dry weight and levels off. The optimum lime content for stabilization of bentonite by this method appears to be about six percent. Five percent lime by dry weight of bentonite, the average of the two estimates, was used in this study.

To determine the amount of fly ash to be added to the bentonite-lime mixture, different percentages of fly ash were added (8.5 to 30 percent by dry weight of the total mixture) and samples were compacted at 33 percent water content and cured for one day at 23°C after which unconfined compressive strengths were determined. The results are presented in Figure 4. A sharp increase in unconfined compressive strength to 1147 kPa (166.1 psi) was observed when the amount of fly ash was increased from 12.3 to 21.9 percent. The dry densities of these mixtures increased from 1.19 to 1.32 Mg/m^3 (74.3 to 82.4 pcf). It is expected that the strength and density will continue up to a point, to increase with the addition of more fly ash but using very high percentages of fly ash (above 25, 30 percent) is impractical in soil stabilization. Twenty percent fly ash was arbitrarily chosen for this study because of the large relative change in compressive strength that occurred at this value. A summary of the proportions of solids in the five test mixtures is listed in Table 1.

TABLE 1

THE MIXTURE PROPORTIONS

Mixture	% Bentonite	% Fly ash	% Lime
1. Bentonite-Fly Ash-Lime	75	20	5
2. Bentonite-Fly ash	79	21	0
3. Bentonite-Lime	94	0	6
4. Fly ash-Lime	0	80	20
5. Fly Ash	0	100	0

Determination of Compaction Water Contents

The water contents were determined individually for each mixture by monitoring the changes in unconfined compressive strength and dry density with increasing water content using the Harvard compaction device. A typical curve (Figure 5) illustrates the changes observed for bentonite-fly-ash-lime samples after curing for one day at 23°C. It is difficult to select an optimum water content in the classical sense because of the scatter in the analytical results and become the cementitions reactions are taking place at variable rates in different quantities of water. The water content corresponding to the maximum compressive strength was selected because it is thought to promote the optimum development of cementitions products at densities close to the minimum. Values used in the experiments are listed in Table 2.

TABLE 2

THE COMPACTION WATER CONTENTS OF MIXTURES

Mixture	Water Content (%)	Dry Density (Mg/m^3)
Bentonite-Fly ash-Lime	34	1.25
Bentonite-Fly Ash	24	1.40
Bentonite-Lime	40	1.15
Fly ash-Lime	20	1.65
Fly ash	11	1.90

Triaxial and Unconfined Compression Tests

A Harvard miniature compaction device with 89 N spring was used to mold the samples. The mold has an inside diameter of 3.334 cm (1.313 in) and a height of 7.153 cm (2.816 in). A minimum of 5 layers and 10 tamps, at a rate of 10 tamps per 15 seconds, were employed to obtain reproducible results according to the procedure recommended by Wilson (34).

Constituents for one sample at a time were weighed, mixed and compacted to minimize the possibility of reactions occuring before the test samples were made. After extrusion, the compacted samples were wrapped in cellophane film and placed in plastic bags which in turn were placed in the humidity room for 23°C curing or in an oven for 50°C curing.

The samples were tested by using an ELE loading frame, ELE triaxial cell, ELE constant pressure cell, 7 kN load cell , Transtek model 3132 LVDT and a Hewlett Packard data acqusition system. The strain rate used was 0.25 mm/min. Because low confining pressures are involved with stabilized base and sub-base material, a confining pressure of 100 kPa (14.5 psi) was used.

Three tests with zero kPa and three tests with 100 kPa confining pressure were conducted for each curing period and temperature for the bentonite-fly ash-lime mixture. A total of three samples was tested for each curing time and for each temperature for bentonite-fly ash, and bentonite-lime mixtures, two with no confining pressure and one with 100 kpa confining pressure.

Additional samples were tested in a Cox and Sons, Inc. compression device (Cox and Sons, Inc.) with a 223 kN (50000 lb) Strainsert brand load cell, at a strain rate of 0.25 mm/min (0.01 in/min). A total of 24 samples of fly ash-lime and 16 samples of fly ash were tested with no confining pressure. All tests were conducted at room temperature.

Sample Preparation for SEM and XRD

The sample from the compressive strength test was placed on a plexiglass plate and ten, 0.5 to 1.0 cm subsamples were obtained by bending and fracturing. Large chunks were first broken with the help of a knife and they were further crumbled into smaller pieces by hand. Representative pieces were put into 15 ml vials and sealed for freezing and vacuum drying. Care was taken not to pick up any portion of the sample disturbed by the knife. Fracture surfaces correspond most closely with the original undisturbed state because there are fewer steps in their preparation relative to techniques such as embedding in resin, sectioning, polishing and etching (13). However, fracture surfaces are not random sections, they are biased to areas with lower tensile strenghts. The remaining portion of the sample was placed into an oven at 105°C for water content determinations. After drying, the samples were placed in plastic bags, sealed and stored for further evaluation by X-Ray diffraction and plastic limit tests.

In this study freeze drying, with liquid nitrogen as the freezing agent, was used to dry the samples prior to SEM examination. The use of liquid nitrogen for freezing also served to stop the reactions after compression tests. Small pieces (approximately one cm^3) of each sample were dipped into liquid nitrogen for 2 minutes. Frozen samples were immediately transfered to a desiccator and 30 miliTorr vacuum was applied to dry the specimens. After 24 hours the samples were removed and places into 15 ml vials, sealed, and stored before coating. Most of the samples were gold coated by using a sputter coater, but selected samples were carbon coated by the evaporation technique to facilitate EDS analyses.

One problem with the SEM is establishing the representative nature of photos because the operator may tend to photograph the most unusual features. To avoid this, the whole sample was surveyed at a magnification of 350 and a portion of the sample with minimal topographical change was selected and photographed. The magnification was increased to 2000 and a minimum of 20 frames within the selected area were studied. Energy dispersive X-Ray analyses were conducted on special interest areas. Representative scanning electron micrographs are presented later in this report in the results section. Low magnification refers to those taken at 350X magnification and intermediate magnification refers to ones taken at magnifications from 2000 to 3500X. High magnification ones are those taken above 5000X. Bar scales on all photomicrographs permit the direct comparision of crystal sizes.

Characteristic X-Ray Spectral Analysis

There are two types of equipment commonly used for X-Ray chemical determinations: Wavelength dispersive spectrometers (WDS) and energy dispersive spectrometers (EDS) . The wavelength dispersive spectrometers identify the characteristic X-Rays by diffraction from crystals. The energy dispersive spectrometers segregate X-Rays according to their energy.

EDS is useful in obtaining rapid qualitative analysis of a sample while WDS is prefered for quantitative information and analysis of light or trace elements. In this study, the energy dispersive spectrometer was used. Ca/Si and Al/Si ratios were obtained from EDS analyses and the data are presented in the results section. The wavelength dispersive spectrometer was used to obtain the chemical compositions of individual fly ash grains. The results are presented in the materials section.

To conduct an X-Ray analysis, considerations must be given to count rate, geometry, take-off angle, specimen topography and specimen preparation. In a typical EDS analysis, a total of thousands to hundreds of thousands of X-Ray counts are accumulated . If the count rate is too low, a long period of analysis is required and the electron beam damages the specimen. Sixty second counts were employed in this study. If the take off angle is low, the X-Rays generated within the specimen must travel a greater distance through the specimen to reach the detector, resulting in the increased absorption of X-Rays, a lower count rate, and variable intensity ratios. During all SEM analyses, the lowest possible specimen height settings were used to maximize the take-off angle (27). In this study the Ca/Si and Al/Si ratios were used for identification purposes even though they varied widely in the same specimen. The fractured surfaces exhibited high relief so the element ratios are only approximate.

X-Ray Diffraction Methodology

A Philips APD-3720 X-Ray diffractometer with Cu K-alpha radiation and a diffracted beam monochromator was used. Finely ground, representative powders were loaded in a specimen holder by using a side loading technique to obtain random orientation and uniform density of packing. The X-Ray diffractograms were recorded from two degrees to 70 degrees two-theta. Peak overlap, poor crystallinity of the newly formed cementitious minerals, and the low weight percentages of reaction products complicated the automated identification routines, so manual procedures were followed after stripping the montmorillonite peaks from the diffractograms.

MATERIALS

Bentonite

The bentonite, (brandname: Aquagel), was supplied by NL Industries Company of Houston, Texas in powder form. A representative X-Ray powder diffractogram with the major peaks labeled, is shown in Figure 6. The major mineral constituents are montmorillonite (M) and quartz (Q). Calcite (K), feldspar (F), biotite (B) and hematite (H) are also present. Small unidentified peaks are present with d-spacings of 2.33A (1), 1.87A (2), 1.79A (3), 1.78A (4), and 1.62A (5). As seen from the high background in the 20 to 30^{o} two-theta region, amorphous material is also present. Other peaks located by the automated routine were considered too small to be included in the interpretation.

Figure 6. Powder X-Ray Diffraction Patterns of Bentonite, Fly Ash, and Hydrated Lime. Q=quartz, M=montmorillonite, F=feldspar, K=calcite, H=hematite, A=anhydrite, L=Lime, T=tricalcium aluminate, R=portlandite, I=alite, P=periclase. For d-spacings presented by numbers refer to the text.

Fly Ash

Fly ash was obtained from the Cajun Electric Company Power Plant, near New Roads, Louisiana. Three, five gallon containers were filled with fly ash and sealed. In the laboratory these three containers were mixed and placed into one gallon air-tight tin cans lined with air-tight plastic bags to prevent the further reaction of the fly ash with atmospheric moisture. The physical and chemical properties of this fly ash are presented in Table 3. It is an ASTM Type C fly ash containing 22.3 % lime (CaO).

The fly ash is composed of varying diameter spheres and finely crystalline powdered material. The smallest crystals are most probably anhydrite and other soluble phases. The chemical compositions of the spheres vary. Microprobe analysis of 40 fly ash grains revealed that although the chemical compositions of the spheres vary they are grouped in four categories. Bar diagrams illustrating their variable compositions are presented in Figures 7 and 8. The first category has a $SiO_2 + Al_2O_3$ content of more than 75 percent. The second category has a $SiO_2 + Al_2O_3$ content between 50 and 75 percent. The third category has $SiO_2 + Al_2O_3$ content between 50 and 30 percent. The second and third categories of fly ash spheres have considerable quantities of CaO. The fourth category has less than five percent $SiO_2 + Al_2O_3$ and it is mostly composed of FeO. A representative X-Ray powder diffractogram of the fly ash is presented in Figure 6. The identified mineral constituents are quartz (Q), tricalcium aluminate (T), periclase (P), anhydrite (A), lime (CaO) (L), alite (I), hematite (H) and magnetite (MA). Amorphous material is evident by the high background between 20 to 30 ° two-theta.

The presence of tricalcium aluminate, anhydrite and lime is the major reason for the self-cementitious behavior of this fly ash. The unidentified peaks, 3.75A (1), 2.64A (2), and 2.02A (3), are probably some form of calcium aluminum silicate hydrate.

Hydrated Lime

The hydrated lime was supplied by the Pelican State Lime Company, Baton Rouge, Louisiana. A chemical analysis of the hydrated lime yielded 99.5 percent CaO and MgO (calcitic lime). A representative X-Ray powder diffractogram of lime is presented in Figure 6. The major component is portlandite (R). Periclase (P) and calcite (K) are also present.

TABLE 3

THE CHEMICAL AND PHYSICAL PROPERTIES OF THE FLY ASH USED IN THE STUDY

Test Property	Value
Type	Bayou
Tested for Class	C
Physical Properties:	
Fineness, % Ret. #325	17.2
PAI With Cement, 28 Days, % of Control	106.2
Water Requirement, % of Control	90.2
Autoclave Expansion, %	+0.05
Specific Gravity	2.66
Sp. Gr. Uniformity, % Var. From Avg.	1.1
Fineness Uniformity, Pct. Pts. From Avg.	2.1
Chemical Properties:	
Loss on Ignition, %	.85
Sulfur Trioxide, %	1.6
Total Oxides, %	69.5
Calcium Oxide, %	22.3
Magnesium Oxide, %	4.2
Alkalies, %	.72

RESULTS

In this chapter the results of physical and mineralogical tests will be presented in the order: fly ash, fly ash-lime, bentonite-fly ash, bentonite-lime, bentonite-fly ash-lime. Results for samples cured at 23°C will be discussed first in each section. For each mixture, the stress-strain curves will be discussed and then the micromorphology of the mixture at different curing periods will be presented with a set of micrographs. Finally, an interpretation of the X-Ray powder diffraction patterns will be presented.

Fly Ash (Cured at 23°C)

The changes in the unconfined compressive strength (UCS) of hydrated fly ash are illustrated in Figure 9. After 28 days of curing the UCS increases from 10237 kPa (1482.3 psi) to 18367 kPa (2659.5 psi). A smaller increase to 19745 kPa (2859.1 psi) is observed between 28 and 90 days. The 180 day-cured sample has an unconfined compressive strength of 26030 kPa (3769.1 psi). These values are one order of magnitude greater than the highest unconfined compressive strength values obtained for bentonite-fly ash, bentonite-lime, and bentonite-lime-fly ash mixtures. The increased compressive strength is attributed to the formation of cementitious compounds between fly ash spheres during curing.

Figure 10A shows the unreacted fly ash in powder form. Fly ash spheres have diameters ranging from 0.5 to 20 micrometers. Larger spheres up to 100 micrometers in diameter may also be present. Note that the spheres are very distinct and there are no fine cementing crystals between the fly ash spheres. With the addition of water and curing for varying lengths of time some materials are dissolved and reprecipitated to form cementitious compounds in the voids. At low magnifications the fly ash particles appear to be embedded in a continuous cement matrix (Figure 10B, one day cured). The matrix after 90 days of curing (Figure 10C) appears to be more densely packed than the matrix in the one day cured sample (Figure 10B). At intermediate magnifications (Figure 10D), C-S-H Type I needles (N) protrude into the pore walls in some areas as a result of crystallization from the amorphous appearing cementitious matrix (M).

The detailed morphology of the cementing crystals is illustrated in Figure 11. The dominant features are C-S-H Type I and Type II needles. The C-S-H Type I needles, protruding into the pores are approximately three micrometers long. The faces of these crystals are roughly parallel but they narrow toward their outer ends. Type II C-S-H crystals (N) are similar to those of type I but they form a three dimensional interlocking network composed of 0.5 to 1.5 micrometer long needles (Figure 11A, one day cured). The fly ash spheres are less distinct because some have begun to react and others are covered with cementitious products.

After 28 days of curing, hexagonal plates (P1, P2) are seen in the pores (Figure 11B). They are very thin and less than five micrometers across. They may form roughly parallel or randomly oriented aggregates which fill the pores between the particles and act as braces in the pores. Their development and orientation seem to depend on the availability of open pore space. The aggregate in the larger circular pore space (P1) is randomly oriented and composed of smaller crystals than at (P2) where the roughly parallel plates are found along the walls of an elongated pore. The plates are five to seven micrometers across and less than 0.2 micrometers thick. XRD methods suggest they are tetracalcium aluminate thirteen hydrate (C_4AH_{13}). Needles morphologically similar to C-S-H Type I and C-S-H Type II co-exist with these plates.

Figure 11C shows the C_4AH_{13} plates (P) after 90 days of curing. These plates are six to ten micrometers across and less than 0.2 micrometers thick. They are randomly oriented. EDS anlyses of these plates yield a Ca/Si ratio of 1.25 and an Al/Si ratio of 1.47 . After 180 days of curing the plates are ten to twenty micrometers across and less than 0.3 micrometers thick (Figure 11D). EDS analyses produced a Ca/Si ratio of 2.76 and an Al/Si ratio of 1.47 . Increased curing time results in thicker plates with a higher Ca/Si ratio.

Figure 10. Scanning electron micrographs of original and cured fly ash samples. A) Loose spheres and fine crystals characterize the unreacted fly ash. B) Fly ash spheres (S) are encased in a matrix (M) in samples cured at 23°C for one day. C) The further development of the matrix presented in B, is seen after 90 days of curing at 23°C. Plates (p) are bridging the pores. D) The fracture surface presented in B at higher magnification. The matrix (M) engulfs the fly ash grains (S) and needles (N) protrude into the pores.

Figure 11. Scanning electron micrographs of the cementitious crystals in fly ash cured at 23^{o}C. A) Fine crystals of original fly ash dissolved and formed a matrix and three-dimensional network of needles (N) supporting the fly ash grains (S) after one day of curing. B) Hexagonal plates (P1, P2) are bridging the pores after 28 days of curing. C) Matrix (M) and randomly oriented hexagonal plates (P) after 90 days of curing. Note the plates are getting larger. D) Randomly oriented hexagonal plates after 180 days of curing.

Figure 12A shows a fractured surface of the 180 day-cured sample at low magnification. A comparision of this fracture surface (Figure 12A) to the fracture surface of the one day-cured sample (Figure 10B) reveals that the pore-filling matrix between the fly ash spheres has become more densely populated with fine crystals and more reaction products are observed. Figures 12B and 12C illustrate representative portions of the cementitious matrix at intermediate magnification. In Figure 12B the imprint of a 55 micrometer diameter fly ash sphere is seen after 28 days of curing. The sharpness of the depression suggests that the fly ash sphere was not altered. A mat of one to three micrometer roughly cubic crystals (SC) connected with fibrous crystals (FC) lines the cavity. The crystals formed a coating on the sphere. The interparticle pores are approximately 0.5 micrometers in diameter. Other fly ash spheres below the mat have radiating needles (N) similar to C-S-H Type I material on them. EDS analyses of the mat give a Ca/Si ratio of 1.6. Figure 12C illustrates the same features after 90 days of curing. The sizes of the roughly spherical crystals (SC) are similar but there are more fibrous crystals (FC) connecting them. The hexagonal plates are supporting this mat. EDS analyses of the mat yield a Ca/Si ratio of 1.08 and Al/Si ratio of 1.38 . The chemical composition is very similar to the composition of the early-formed (Figure 11B) plates. The mat morphology is better illustrated (Figure 12D) at a

Figure 12. Scanning electron micrographs of fly ash samples cured at 23^{o}C. A) After 180 days of curing, the matrix has become more densely populated with fine crystals. Hexagonal crystals (P) are seen at low magnification. B) A representative portion of the cementitious matrix after 28 days of curing. The sharpness of the depression from the imprint of a 55 micrometer fly ash grain suggests that the fly ash sphere was not altered. A mat of roughly spherical crystals (SC) connected with fibrous crystals (FC), hexagonal plates (P) and needles (N) are present. C) Same features presented in B after 90 days of curing. The size of the roughly spherical crystals are the same but there are more fibrous crystals connecting them. D) The morphology of the mat at high magnification after 180 days of curing. Roughly spherical crystals (SC) are connected with a three-dimensional network of fibrous crystals (FC).

higher magnification for the 180 day-cured sample. The diameters of these sub-spherical crystals (SC) range between 0.5 to 1.5 micrometers and they are connected to each other with a three dimensional network of fibrous crystals (FC).

The rigid behavior of hydrated fly ash observed in this study may be related to the development of this network of roughly spherical crystals supported by plates (illustrated in Figure 11C). In this specimen, a grain was pulled out during fracture exposing its means of support. The grain was surrounded by plates at the bottom and by the crystal mat at the sides. There was no place for this grain to move so the failure occured at very low strains and, because of the supporting mat, the strength was improved considerably.

XRD patterns for the cured samples are presented in Figure 13. The major mineral is quartz (Q) and the peaks produced by it are labeled on the pattern for the one day cured sample. Comparision with the original fly ash (Figure 6B) reveals no change in the relative intensities of these peaks in the samples. Tri-calcium aluminate (T) is the second most abundant mineral. The minor mineral constituents of the original powder , anhydrite, lime, and alite are not easily recognized in the cured samples. The anhydrite (A) peak is present with a very low peak intensity after one day of curing and it disappears after 28 days of curing. The intensity of the lime (CaO) peak (L) is very low relative to the intensity in the powder form after just one day of curing. There is no further change in its intensity with longer curing time. The intensity of the tri-calcium aluminate (T) peak decreases with increasing curing time. The new cementitous minerals that are recognized are C-S-H Type I and tetracalcium aluminate thirteen hydrate (C_4AH_{13}). In the scanning electron micrographs the C-S-H Type I minerals are seen as needles and the C_4AH_{13} occurs as thin hexagonal plates. The 8.2A, 2.88A and 2.45A d-spacings are assigned to C_4AH_{13} (G). These peaks are not found in the unreacted fly ash, they appear after one day and the intensity of the 2.45A peak increases up to 90 days and then decreases between 90 and 180 days. A low intensity 3.02A calcite (K) peak is observed after 28 and 90 days of curing and is not seen after 180 days. The intensity of the 1.43A hematite (H) peak fluctuates without a recognizable trend. A decrease in the intensity of the 1.49A alite peak (I) is observed up to 28 days of curing. The intensity of the 2.10A periclase (P) peak does not change. There are other unidentified peaks which are tabulated below (Table 4). They represent minerals that could not be readily identified because of the absence of additional peaks, low peak intensities, or severe overlap by other minerals.

Figure 13. Powder X-Ray Diffraction Patterns of 1, 28, 90 and 180 Day Cured Fly Ash (Cured at 23^{o}C). Q=quartz, T=tricalcium aluminate, A=anhydrite, G=C_4AH_{13}, C= CSH I, P=periclase, H=hematite, L=lime, I=alite. For d-spacings represented by numbers refer to the text.

TABLE 4

UNIDENTIFIED PEAKS IN FLY ASH CURED AT 23^{o}C.

D-Spacing	Remarks
2.33 (1)	Is present in unreacted fly ash, its relative intensity increases at one day,decreases at 28 days and shows a sharp increase at 180 days of curing.
2.21 (2)	Its intensity decreased relative to the unreacted fly ash and then stayed constant.
2.02 (3)	Unchanged.
1.95 (4)	Its intensity is enhanced after 180 days.

The X-Ray diffractograms showed that the major reactive components of the fly ash are tricalcium aluminate, anhydrite and lime. Tetracalcium aluminate thirteen hydrate and calcium silicate hydrate I are two new minerals that are detected in the X-Ray diffractograms. The low intensities of the peaks reveal that the new minerals are present in very small quantities and they are poorly crystalline. Other cementitious minerals may be present but their identities can not be determined by XRD techniques. The data obtained from the scanning electron microscopy complements the identification of the new cementitious minerals. For example, the C-S-H Type I needles seen in the micrographs confirm the assignment of the 3.07A peak to C-S-H I and the plates are typical of C_4AH_{13}.

Fly Ash (Cured at 50°C)

The changes in the unconfined compressive strength of the 50°C cured fly ash sample with time are presented in Figure 14. The unconfined compressive strength of the one day-cured sample is 10923 kPa (1582 psi) and it increases to 18877 kPa (2733 psi) after 28 days. After 90 days, the unconfined compressive strength is 26948 kPa (3902 psi) and it decreases to 22630 kPa (3276 psi) after 180 days. The 180 day UCS is slightly lower than that recorded for the 23°C cured sample. This decrease in strength is discussed later in this report. It is attributed to the deterioration of some of the fly ash spheres. It is expected that the strength of hydrated fly ash will be leveling off after about 180 days of curing with the completion of the deterioration of the fly ash spheres.

At the elevated temperature, the C-S-H I needles (N) are more numerous than the needles found in the 23°C cured samples (Figure 15A). Roughly spherical crystals are connected with fibrous crystals in the one day cured sample (not shown). After 28 days of curing, the fibrous crystals become more numerous and hexagonal plates are seen in the pore spaces. After 90 days the mat becomes more densely populated with roughly spherical crystals.

Figure 15. Scanning electron micrographs of fly ash samples cured at 50^{o}C. A) Needles (N) and the initial stages of plates (P) after one day of curing. Needles radiate from fly ash grains and they protrude into the pores. B) At higher temperatures the fly ash grains are more directly involved in the cementitious reactions. The reacted shell (R) of a representative fracture surface of the 180 day cured sample. The mat (M) engulfs the fly ash spheres and hexagonal plates (P) span the pores. D) Reacted crust (R) on a fly ash grain is readily apparent after 180 days of curing.

Figure 15B shows an imprint of a 22 micrometer diameter sphere. During fracturing the outer shell of the sphere broke and half of the impression is covered by the reacted shell (R). The other half is a typical mat . At higher temperatures, the fly ash spheres are more directly involved in the cementitious reactions. EDS analyses of the shell yield (R) a Ca/Si ratio of 1.53, and an Al/Si ratio of 0.86. The Ca/Si ratio of the mat is higher than the section without this mat.

The dominant features in the 180 day-cured sample are similar to the ones seen at other curing periods. These features are roughly spherical crystal mats, needles and plates (Figure 15C, intermediate magnification). The mat (M) engulfs fly ash spheres while the hexagonal plates (P) span the pores. The plates at (P) have a Ca/Si ratio of 2.4 and an Al/Si ratio of 0.69 . The compositions of the plates are different from the ones observed at the lower curing temperature. In Figure 15D there is an eleven micrometer fly ash sphere, half of it is covered with cementitous material (R) and the other half is not. EDS analyses on both parts showed a very low Ca intensity. For the covered part the Ca/Si ratio is 0.17 and the Al/Si ratio is 0.43 while for the uncovered part the Ca/Si ratio is 0.18 and the Al/Si ratio is 0.35.

X-Ray Diffractograms

The powder X-Ray diffractograms of the 50°C cured fly ash samples are presented in Figure 16. The X-Ray diffractograms are similar to those for the 23°C cured fly ash samples. The low intensity anhydrite peak that was present in the 23°C one day-cured sample is not seen in the 50°C one day-cured sample. C-S-H Type I (C) and C_4AH_{13} (G) are the new cementitious minerals. The intensity of the 1.43A hematite peak (H) increases with increasing curing time.

Fly Ash-Lime (Cured at 23°C)

The changes in the unconfined compressive strength with time for the fly ash-lime mixture are shown in Figure 17. A major increase in the unconfined compressive strength (UCS) from 7188 kPa (1041 psi) to 18265 kPa (2645 psi) is observed between one and 28 days. The UCS of the one day-cured fly ash-lime is lower than the UCS of the one day-cured fly ash. This is due to the dilution of the fly ash by the addition of 20 percent hydrated lime and due to the lower dry unit weight of the fly ash-lime mixture relative to the dry unit weight of the fly ash. The UCS for the fly ash-lime mixture reaches 26492 kPa (3836 psi) at 90 days and further increases to 32236 kPa (4668 psi) at 180 days. After 28 days the unconfined compressive strengths (UCS) of the fly ash-lime and fly ash mixtures are similar, but at 90 and 180 days the fly ash-lime mixture has higher unconfined compressive strength. This is due to the increased availability of hydrated lime for the formation of calcium silicate hydrates and calcium aluminate hydrates.

Figure 18A illustrates a fractured surface of the one day-cured sample. The matrix material (M) fills the pores between the fly ash grains. At this curing time the outlines of the fly ash spheres (S) are visible and the matrix has micropores. Figure 18B shows a fractured surface of the 90 day-cured sample, when a major strength increase was observed. The outlines of the fly ash grains are less distinct indicating more extensive cementation of the spheres. There are more fine crystals in this matrix than at shorter curing periods. A 100 micrometer diameter broken fly ash sphere is seen which is filled with smaller spheres and cementitious material. Pull out features are present. The matrix material (M) is seen at an intermediate magnification (Figure 18C for the 28 day-cured sample) to fill the pore space between the fly ash grains. All of the pores are spanned with plates (P). A 17.5 micrometer diameter fly ash sphere (S) covered with a reaction product is seen in Figure 18D. The tiny blades are one micrometer long, edge-to-face oriented relative to each other and their long axes are tangent to the surface of the fly ash sphere.

The detailed morphologies of the cementitious products are presented at intermediate magnification in Figure 19. Figure 19A illustrates a fracture surface of the one day-cured sample. Edge-to-face oriented, two to three micrometer diameter plates (P) are present . EDS analyses of these plates yield a Ca/Si ratio of 4.09 and an Al/Si ratio of one. The matrix material (M) consists of roughly spherical crystals, needles and small blades. At this intermediate magnification it is apparent that the fine crystals are more numerous in the matrix after 28 days of curing (Figure 19B) than after one day of curing (Figure 19A). The platey crystals look like calcite. Note fly ash spheres embedded in the matrix (M). There is no space for these grains to move. The pore bridging edge-to-face oriented plates completely surround the fly ash spheres.

Figure 19C illustrates a fractured surface of the 90 day-cured sample. Edge-to-face oriented five micrometer diameter plates (P) are present. They appear to be better developed than the plates observed in the one and the twenty-eight day-cured samples, because their outlines are very sharp. EDS analyses of the area (P) yield a Ca/Si ratio of 3.98 and an Al/Si ratio of 1.18 . EDS analyses of the crystals forming the imprint of a five micrometer diameter fly ash sphere at (P) yield a Ca/Si ratio of 3.39 and an Al/Si ratio of 0.89.

Figure 19D shows a fractured surface of the 180 day-cured sample. The plates appear to be etched longitudinally. EDS analyses on one of the etched plates yield a Ca/Si ratio of 3.99 and an Al/Si ratio of 1.22 which is the same as the plates in Figure 19C. EDS analyses of the matrix (M) formed by C-S-H Type II crystals, yield a Ca/Si ratio of 1.91 and an Al/Si ratio of 0.68. EDS analyses of the plate (P), yield a Ca/Si ratio of 3.03 and an Al/Si ratio of 1.42. The matrix

Figure 18. Scanning electron micrographs of fly ash-lime samples cured at 23^{o}C. A) A matrix of fine crystals (M) fills the pores between the fly ash grains after one day of curing. The outlines of the fly ash grains (S) are distinct. B) A representative fracture surface of the 90 day cured samples at low magnification. The outlines of the fly ash grains are less distinct indicating more extensive cementation of the spheres. C) Matrix material (M) engulfing the fly ash grains and hexagonal plates (P) bridging the pores after 28 days of curing. D) A fly ash sphere (S) covered with reaction products after 28 days of curing.

Figure 19. Scanning electron micrographs of the cementitious reaction products in fly ash-lime samples cured at 23^{O}C. A) The initial stages of plates (P) after one day of curing. B) The matrix material (M) engulfs the fly ash grains after 28 days of curing. C) A representative fracture surface of the 90 day cured sample with edge-to-face oriented hexagonal plates (P) bridging the pores. D) After 180 days of curing some of the plates appear to be etched longitudinally (1).

material which is composed of sub-spherical crystals and rods, fills the pores between fly ash grains and plates are present between them. This figure illustrates the interaction between the fly ash spheres and cementitious matrix and helps to explain qualitatively why this material behaves rigidly. The displacement of the fly ash spheres is restricted by the matrix and the plates which fill the pores between the fly ash grains.

Figure 20A shows the imprint of a 22 micrometer diameter fly ash sphere at high magnification in the one day-cured sample. A network of roughly spherical crystals (SC), blades (B) and needles (N) is present. The needles and blades are edge-to-face oriented with roughly spherical crystals and rods lying between them. EDS analyses at the center of the mat yield a Ca/Si ratio of 2.72 and an Al/Si ratio of 0.73 . The sub-spherical crystal morphology of the 90 day-cured sample is presented in Figure 20B at high magnification. These aggregates are composed of one to three micrometer diameter roughly spherical crystals (SC) and one to 1.5 micrometers long, 0.2 micrometer diameter fibrous crystals (FC). The fibrous crystals are better developed and fewer in number than in the pure fly ash. Figure 20C presents a fractured surface of the 90 day-cured sample at intermediate magnification. All the pores are filled with plates. An aggregate of fine equant crystals (E) less than 0.5 micrometers in diameter is seen. This appears to be C-S-H Type III. Figure 20D illustrates a 40 micrometer long, 30 micrometer wide pull out feature in the 180 day-cured sample. The grain was surrounded by hexagonal plates (P) at the bottom and was surrounded by a dense mat of roughly spherical crystals (M) on the sides.

The X-Ray diffractograms for the fly ash-lime mixtures (80% fly ash and 20% lime) at different curing periods are presented in Figure 21. The major mineral is portlandite (R). The intensities of the portlandite peaks decrease after 28 days of curing but show an increase after 90 days. A decrease in peak intensities is observed after 180 days. This fluctuation may be due to varying orientation of the powder sample or other sample heterogenities. The second major mineral is quartz (Q) and its peak intensities remain unchanged. One of the major constituents of fly ash powder, anhydrite, is not seen even after one day of curing which suggests that it is totally consumed. The tricalcium aluminate peak (T) is present at all times and appears to be unchanged. Periclase peaks (P) are present at all times.

The new cementitious minerals are tetracalcium aluminate thirteen hydrate (C_4AH_{13}) and tricalcium aluminate six hydrate (C_3AH_6). The hexagonal plates that are seen in the scanning electron micrographs and d-spacings of 8.14A, 4.08A, and 2.87A confirm the presence of the former. The intensities of the 4.08A and 2.87A peaks increase after 28 days of curing. The 2.76A and 2.02A peaks are tentatively identified as C_3AH_6. These are cubic crystals. The unidentified peaks are listed below (Table 5).

Figure 20. Scanning electron micrographs of the cementitious products in fly ash-lime samples at 23^{o}C. A) An imprint of a fly ash sphere at high magnification after one day of curing. A network of roughly spherical crystals (SC), blades (B) and needles (N) is present. B) The roughly spherical crystals in the 90 day-cured sample are seen at high majnification. Fibrous crystals (FC) connect the roughly spherical crystals (SC) forming a mat. C) A representative fracture surface after 90 days of curing at intermediate magnification. An aggregation of fine equant crystals (E) is present engulfing the fly ash grains. D) A pull-out feature is seen after 180 days of curing. The grain was surrounded by hexagonal plates (P) at the bottom and was surrounded by a dense mat (M) of roughly spherical crystals on the sides.

TABLE 5

UNIDENTIFIED PEAKS IN FLY ASH-LIME CURED AT 23°C.

D-spacing	Remarks
3.80 (1)	Appears after 28 days and its intensity increases slightly.
2.96 (2)	Appears after 28 days.
2.39 (3)	Intensity increases after 28 days.
2.33 (4)	Is present after one day and its intensity increases sharply after 90 days and decreases after 180 days.
2.28 (5)	Unchanged.
1.66 (6)	Appears after 90 days.
1.43 (7)	Appears after 28 days with high intensity, and its intensity decreases after 180 days.

A significant observation is the presence of the portlandite peaks even after 180 days of curing. Apparently the sample was not completely reacted even at the end of the 180 day curing period. The increase in the intensities of C_4AH_{13} (G) and C_3AH_6 (J) after 28 days corresponds to a major strength increase which suggests that these new cementitious minerals are responsible for the strength increase. The 2.33A (4) and 1.43A (7) peaks seem to be important because of their high intensities at certain curing periods but no specific cementitious minerals having these d-spacings could be identified.

Fly Ash - Lime (Cured at 50°C)

The changes in the unconfined compressive strength of the 50°C cured fly ash-lime mixture are illustrated in Figure 22. The unconfined compressive strength of the one day-cured sample is 7372 kPa (1067 psi) which is approximately the same as the strength of the sample cured at 23°C sample. A major strength increase occurs between one and twenty-eight days. The strength increase continues at 90 days to 39472 kPa (5716 psi) and then levels off.

The cementitious compounds observed in the higher temperature samples were morphologically similar to those in the 23°C cured samples so only some highlights will be presented in this section. The one day-cured sample has two dominant features; the matrix (M), which is composed of sub-spherical grains, and edge-to-face oriented hexagonal plates (P) (Figure 23A). EDS analyses of the plates yield a Ca/Si ratio of 5.31 and an Al/Si ratio of 1.41. The matrix is more abundant after 90 days of curing (Figure 23B) and the outlines of the fly ash particles are not as distinct. The morphology of the sub-spherical crystals is better defined at this curing period. The crystals (M) are 0.5 to one micrometer long and they occur as aggregates. EDS analyses of these crystals gave a Ca/Si ratio of 1.03 and an Al/Si ratio of 0.44.

Figure 23C illustrates the hexagonal plates at higher magnification after 90 days of curing. The plates are five to six micrometers across and roughly 0.3 to 0.4 micrometers thick with fibrous crystals on their edges. This may be the beginning of a transformation to a different phase. EDS analyses of the hexagonal plate at P yield a Ca/Si ratio of 2.21 and an Al/Si ratio of 1.00. They have less Ca than the plates seen in the one day-cured sample.

Figure 23D illustrates a fractured surface of the 28 day-cured sample at intermediate magnification. A major increase in strength occured between one and twenty eight days and this figure demonstrates that when this takes place the pores are spanned with hexagonal crystals (P) and the outlines of the fly ash grains are less distinct. The most significant observations that can be used to relate the strength increase to the changes in the morphology are the densification of the matrix and the presence of hexagonal crystals in the pores (C_4AH_{13}). Their relative importance is hard to judge but the densification of the matrix appears to be the more dominant factor in the strength improvement of this mixture. When the 180 day-cured samples are compared no difference is seen between the morphology of the cementitous materials in the elevated temperature sample and the room temperature cured sample.

Figure 23. Scanning electron micrographs of the fly ash-lime samples cured at 50°C. A) There are two dominate features in the one day cured samples: The matrix (M) of roughly spherical grains and edge-to-face oriented hexagonal plates (P). B) A representative fracture surface of the 90-day cured sample at intermediate magnification. The outlines of the most of the fly ash grains are not distinct indicating more thorough participation in the reactions. C) Hexagonal plates (P) are seen at high magnification after 90 days of curing. There are fibrous crystals on their edges which may phase. D) A fracture surface of the 28 day-cured sample at intermediate magnification. The outlines of the fly ash grains are less distinct and the pores are spanned with hexagonal crystals (P).

Figure 24. Powder X-Ray Diffraction Patterns of the 50°C Cured Fly Ash-Lime Mixture. R=portlandite, Q=quartz, P=periclase, T=tricalcium aluminate, H=hematite, J=C_3AH_6, G=C_4AH_{13}. For d-spacings represented by numbers refer to the text.

The powder X-Ray diffractograms of the 50°C cured fly ash-lime mixtures are presented in Figure 24. The major differences from the 23°C cured sample are summarized below. The intensities of the portlandite peaks (R) are lower in the 50°C cured sample. The 4.08A and 2.87A peak (G) intensities assigned to C_4AH_{13} increase after 28 days. C_3AH_6 is tentatively identified from 2.76A and 2.03A peaks (J). The intensity of the 2.76A peak increases after 28 days. The 3.07 C-S-H Type I peak (C) appears as a shoulder on the 3.10 A portlandite peak (R) after 28 days of curing and its intensity increases after 90 days of curing. The unidentified peaks are summarized below (Table 6).

TABLE 6

UNIDENTIFIED PEAKS IN FLY ASH-LIME CURED AT 50°C.

D-spacing	Remarks
5.34 (1)	Appears after 90 days.
2.53 (2)	Unchanged.
2.33 (3)	Intensity is high only at 90 days.
2.28 (4)	Unchanged.
2.24 (5)	Unchanged.
1.99 (6)	Appears after 28 days of curing.
1.66 (7)	Appears after one day and its intensity increases after 28 days.
1.43 (8)	Intensity is high after one day of curing and same at other curing times except its intensity is low after 90 days.

At 50^{o}C, C_3AH_6 peaks (J) appeared after one day whereas the same peaks appeared only after 28 days of curing at 23^{o}C· The intensities of the 4.08A (G), 2.76A (J), 1.99A (6) and 1.66A (7) increased considerably after 28 days of curing at 50^{o}C and correlated with the time when a major increase in compressive strength was observed.

Bentonite-Fly Ash (Cured at 23^{o}C)

The stress-strain diagrams with zero confining pressure and with 100 kPa confining pressure are presented in Figure 25. The major strength increase occurs between one and 28 days. The strengths fluctuate slightly following this period. The one day average strength is 906 kPa (131 psi) and it increases to 1414 kPa (205 psi) after 28 days. The average strain at failure for the one day cured sample is 0.016 and decreases to approximately 0.007 for the 28,90, and 180 day-cured samples. The confining pressure affects the strain at failure for the one day-cured sample by increasing it to 0.0353 but at longer curing periods after cementitious products have formed its effect on strain at failure becomes smaller. The average strain at failure for the 28,90 and 180 day samples is 0.0078. Despite some variation the 28,90 and 180 day stress strain curves plot in a narrow region. When an average curve is used in that region to compute the elastic modulus value, 240,000 kPa (34752 psi) is obtained.

This is a three fold increase compared to that of the one day-cured sample (80000 kPa). In stabilized soils the initial portion of the stress-strain curve up to approximately seventy percent of the maximum strength is practically linear, so the values at 0.70 times the maximum strength were used to compute the elastic modulus.

Figure 26A shows a fractured surface of the one day-cured sample at low magnification. The outlines of fly ash grains are very smooth and distinct which suggest that these grains have not reacted. Figure 26B shows a fractured surface of the 28 day-cured sample at low magnification. The outlines of some of the fly ash grains are becoming irregular because of dissolution.

The comparison of the fly ash spheres is better illustrated in Figures 26C and 26D at intermediate magnification. Figure 26C shows a fracture surface of the one-day cured sample. A 40 micrometer diameter fly ash particle (S) is supported by montmorillonite aggregates (MA). Note that there are no reaction products on the fly ash sphere. Fly ash spheres (S) with irregular outlines are present in the 28 day-cured sample (Figure 26D) and the spheres show evidence of dissolution and cementation (R).

Figure 26. Scanning electron micrographs of the bentonite-fly ash samples cured at 23°C. A) A representative fracture surface of the one day-cured sample at low magnification. The outlines of fly ash grains are very smooth and distinct which suggest that these grains have not reacted. B) After 28 days of curing the outlines of the fly ash grains are becoming irregular because of dissolution. C) A fracture surface of the one day-cured sample is seen at intermediate magnification. A fly ash grain (S) is supported by montmorillonite aggregates (MA). D) Fly ash spheres (S) with irregular outlines are present in the 28 day-cured sample. The spheres show evidence of dissolution and cementation (R).

Some individual grains affected by hydration reactions are presented in Figure 27. In Figure 27A, a broken 32 micrometer diameter fly ash particle (S) is seen after 28 days of curing to be filled with fly ash particles and montmorillonite aggregates. The fly ash sphere (S) of Figure 26D is presented in Figure 27B at a higher magnification. After 28 days of curing, hexagonal crystals (H) with varying dimensions are readily apparent. The larger ones are 3.5 micrometers wide and four micrometers long and the smaller ones are 1.5 micrometers wide and two micrometers long. They are randomly oriented and they are only seen on some grains.

After 90 days of curing, other reaction products are seen on the fly ash grains (Figure 27C). A fly ash sphere is covered with two types of reaction products, needles (N) and hexagonal crystals (H). The randomly oriented needles are approximately one micrometer long, 0.2 to 0.4 micrometers in diameter, and have a hexagonal cross section. At H, hexagonal crystals are present which are two micrometers long. Figure 27D presents a unique material (M) where spherical particles were either pulled out during fracture or were dissolved after 180 days of curing. This feature represents a very localized occurrence of incompletely combusted coal.

Figure 27. Scanning electron micrographs of some reacted grains in bentonite-fly ash samples cured at 23^{o}C. A) A broken fly ash sphere filled with montmorillonite and fly ash grains is seen after 28 days of curing. B) Hexagonal crystals (H) are readily apparent on some fly ash grains after 28 days of curing. C) A reacted fly ash grain with needles (N) and hexagonal crystals (H) are seen after 90 days of curing. D) Supporting matrix left after either dissolution of fly ash grains or after the fly ash grains were pulled out during fracture through a piece of unburned coal.

Some of the fly ash particles have reaction products on their surfaces after 28 days of reaction, but dissolution of the fly ash spheres is not observed. Apparently the cementitious products are forming from the finely divided soluble materials, such as anhydrite, in the unreacted fly ash. After 28 days of curing hexagonal crystals appear on some of the fly ash spheres and after 90 days, needles and hexagonal crystals cover some of the particles. The reactions differ on an individual grain level.

The powder X-Ray diffractograms for the bentonite-fly ash mixture are presented in Figure 28. The major constituents are montmorillonite (M) and quartz (Q). Calcite (K), tricalcium aluminate (T), periclase (P) and hematite (H) are the minor constituents. The peaks corresponding to these minerals (except hematite) do not change with increasing curing time. The intensity of the hematite peak decreases after 180 days of curing. The 9.84A and 5.61A d-spacings (E) after one day of curing are tentatively assigned to ettringite. The 9.84A peak is present at all curing times but the 5.61A peak dissappears after one day of curing. The strongest peak for C-S-H Type I , 3.07A (C), appears after 90 days of curing and its intensity increases after 180 days of curing. The unidentified peaks are listed in Table 7.

Figure 28. Powder X-Ray Diffraction Patterns of Bentonite-Fly Ash Mixture Cured at 23°C. Q=quartz, M=montmorillonite, P=periclase, T=tricalcium aluminate, K=calcite, E=ettringite, H=hematite, C-CSH I. For d-spacings represented by numbers refer to the text.

TABLE 7

UNIDENTIFIED PEAKS IN BENTONITE-FLY ASH CURED AT 23°C.

D-spacing	Remarks
3.28 (1)	Appears after 28 days of curing, is not seen after 90 days,has a very low intensity after 180 days.
3.21 (2)	Appears after 90 days and its intensity decreases in the 180 day cured sample, probably afwillite.
3.17 (3)	Is present at all times.
3.11 (4)	Is present at all times.
2.75 (5)	Appears after 180 days of curing.
2.63 (6)	Appears after 90 days of curing and is present in the 180 day-cured sample.
2.33 (7)	Intensity increases with time.
2.02 (8)	Is present at all times.

Bentonite-Fly Ash (Cured at 50°C)

The stress-strain curves for the 50°C cured bentonite-fly ash mixture are presented in Figure 29. The bentonite-fly ash mixture developed an unconfined compressive strength of 1234 kPa (179 psi) after one day of curing. It increased to 1327 kPa (192 psi) after 28 days. The unconfined compressive strength increased further to 1915 kPa (277 psi) after 180 days of curing. These results indicate that at 50°C the bentonite-fly ash mixtures develop most of their strength within the first 24 hours of the curing period. The strain at failure for the one day-cured sample is 0.015 (unconfined) and it decreased to 0.011 after 180 days. Five out of six stress-strain curves for samples cured longer than 28 days plot in a narrow range. Although some increase in unconfined compressive strength was observed, no distinctive change of elastic modulus was obtained after 28 days of curing. With 100 kPa confining pressure the strain at failure after one day was 0.022 . With increased curing time the soil becomes less sensitive to the (100 kPa) confining pressure.

One of the significant observations is that the mineralogical features found in the 50°C cured samples are similar to those in the 23°C cured samples, thus indicating that samples cured at 50°C for 24 hours produce results similar to those cured for 28 days at 23°C. Figure 30A illustrates a fracture surface of the 90 day-cured sample at low magnification. The outlines of some of the fly ash grains (S) are irregular suggesting that they have reacted. At intermediate magnification (Figure 30B) the fly ash particles (S) are supported by montmorillonite aggregates (MA). Strength increases were observed between 90 and 180 days of curing and more reacted fly ash spheres were frequently seen in these samples. Figure 30C illustrates a fractured surface of the 180 day-cured sample at an intermediate magnification. A reacted, six micrometer diameter fly ash particle (R) is seen with the imprints of crystals on its surface. EDS analyses of this sphere yield a Ca/Si ratio of 0.11 and an Al/Si ratio of 0.87. Note that the Ca content is very low relative to silicon. A nine micrometer diameter reacted fly ash particle after 180 days of curing is presented in Figure 30D at high magnification. The features at this curing period are similar to the ones present in the 23°C cured sample. Hexagonal crystals (H) of varying sizes are well developed. Their lengths vary between one and four micrometers. An aggregate of small needles (N) is present. EDS analyses of these needles showed a Ca/Si ratio of 1.90 and an Al/Si ratio of 1.09. EDS analyses of the prisms indicated higher Ca/Si ratio of 3.05 and an Al/Si ratio of 1.19.

The powder X-Ray diffractograms of the 50°C cured bentonite-fly ash mixture are presented in Figure 31. Ettringite (E) is present after one day of curing (9.83A, 5.58A). After 28 days of curing the 9.83A peak shifts to 9.94A. A 3.07A C-S-H I (C) peak is present after one day of curing and its intensity increases after 180 days of curing. The unidentified peaks are listed in Table 8.

Figure 30. Scanning electron micrographs of bentonite-fly ash samples cured at 50°C. A) A representative fracture surface of the 90 day-cured sample at low magnification. The outlines of some of the fly ash grains (S) are irregular suggesting that they have reacted. B) The fly ash grains (S) are supported by montmorillonite aggregates (MA) (90 day-fly ash grains (R) present. The reacted fly ash sphere at location (1) has imprints of crystals on its surface.
D) Hexagonal crystals (H) and needles (N) are seen on a reacted fly ash grain at high magnification after 180 days of curing.

Figure 31. Powder X-Ray Diffraction Patterns of the 50^{O}C Cured Bentonite-Fly Ash. Q=quartz, M=montmorillonite, E=ettringite, K=calcite, H=hematite, P=periclase, C=CSH I. For d-spacings represented by numbers, refer to the text.

TABLE 8

UNIDENTIFIED PEAKS IN BENTONITE-FLY ASH CURED AT 50^{o}C.

D-spacing	Remarks
3.24 (1)	Is present at all times.
3.21 (2)	Appears after one day and its intensity increases after 28 and 90 days and decreases after 180 days of curing, probably afwillite.
3.17 (3)	Intensity decreases after 180 days of curing.
3.12 (4)	Is present at all times.
2.95 (5)	Appears after 28 days of curing.
2.79 (6)	Is present at all times.
2.63 (7)	Appears after one day of curing and dissappears after 180 days.
2.33 (8)	Unchanged.
2.02 (9)	Unchanged.
1.99 (10)	Appears after 180 days with a high intensity peak.
1.79 (11)	Is present after one day of curing and dissappears after 28 days.
1.65 (12)	Appears after 180 days.

At 50^{o}C more C-S-H formation is suggested because of the higher intensity of the 3.07A peak when compared to the lower temperature samples. The strength increase continues up to 180 days of curing. The 3.21A may be the strongest peak of afwillite.

Bentonite-Lime (Cured at 23°C)

The stress-strain curves for the bentonite and lime mixture cured at 23°C are presented in Figure 32. The major increase in strength occurred after 28 days of curing and after this curing period all stress-strain curves plot in a narrow range indicating that significant changes in the physical characteristics of the mixtures are taking place during the first 28 days of curing. The unconfined compressive strength increased from 610 kPa (88 psi) after one day to approximately 1300 kPa (188 psi) for 90 and 180 day-cured samples. The elastic modulus for the one day-cured sample is 52300 kPa (7573 psi) and it increased to an average of 219697 kPa (31812 psi) for the remaining test samples. The axial strain at failure decreased from 0.0144 for one day to an average value of 0.007 for the 28,90 and 180 day-cured samples. A similar trend is observed with 100 kPa confining pressure. The strength (with confining pressure) increases from 746 kPa (108 psi) after one day to approximately 1375 kPa (199 psi) for the 90 and 180 day-cured samples. The elastic modulus value after one day is 55850 kPa (8087 psi), 116000 kPa (16797 psi) after 28 days, and it increased to approximately 253150 kPa (36656 psi) for the 90 and 180 day-cured samples. The reactions that are causing the strength increase are happening between 1 and 90 days.

Figure 33 represents the fracture surfaces of one to 180 day-cured samples at low magnification. In the one day-cured sample, the grain boundaries are hard to find which is typical for plastic, clay-rich material (Figure 33A). The boundaries of the clay aggregates are better defined after 28 days of curing and the overall morphology is more typical of brittle material (Figure 33B). Clay behaves as a coarser grained aggregate after 28 days. This aggregation is more apparent in Figure 33C after 90 days and in Figure 33D after 180 days of curing. The brittle behavior is better illustrated at intermediate magnifications when Figures 34A and 34B are compared . In Figure 34A the aggregates are formed of face-to-face oriented bundles of montmorillonite flakes (one day-cured). Some of the montmorillonite flakes (MO) are curled as a result of water loss during drying. Figure 34B shows a reacted montmorillonite aggregate where the reacted montmorillonite flakes (RM) are seen as laths and blades.

The reaction products of bentonite and lime are clearly shown in Figure 35. Montmorillonite flakes after 28 days of curing are illustrated in Figure 35A at high magnification. There are laths (L) and blades up to two micrometers long and approximately 0.2 micrometers wide. It appears from this picture that the montmorillonite flakes are attacked by lime and are etched longitudinally every 0.1 to 0.2 micrometers and then separated along these lines. EDS analyses (L) reveal a high Ca/Si ratio of 1.05 and an Al/Si ratio of 0.54

for these CSH Type I crystals. The lath and blade-like features are more common after 90 days of reaction at 23^{o}C. Figure 35B shows an excellent example of the final stages of localized lath (L) and blade formation. After 90 days of curing aggregations of approximately 0.8 micrometer wide equant crystals (E) are present (Figure 35C). EDS analyses produce a high Al, low Si and no Ca X-Ray peak for these features. Figure 35D illustrates a similar feature after 180 days of curing. EDS analyses (E) at high magnification yield a Ca/Si ratio of 0.36 and an Al/Si ratio of 1.83 , which shows that Al is the dominant component of this feature.

No reaction products are observed after one day curing time, but major changes in the microstructure and strength occur at 28 days by the formation of blade and lath like crystals. Clay behaves as lumps after 28 days and the aggregate boundaries are more distinct. C-S-H Type I-lath and blade-like acicular crystals develop with increased curing time. After 90 days of curing, a blocky crystal morphology is present which has Al as its dominant component.

The X-Ray diffractograms of bentonite-lime mixtures are presented in Figure 36. The major mineral is montmorillonite and its peaks (M) are labeled on the one day-cured sample pattern. The montmorillonite peaks remain unchanged at all curing periods. The second major mineral is quartz (Q) and it does not show any change. Calcite (K) is present in bentonite and the intensity of its peaks appears to be the

Figure 33. Low magnification scanning electron micrographs of bentonite-lime samples cured at 23°C. A) In the one day-cured sample the grain boundaries are hard to find which is typical for plastic, clay-rich material. B) The boundaries of the clay aggregates are better defined after 28 days of curing and the overall morphology is more typical of brittle material. Clay behaves as coarser grained aggregates. C) The aggregates can be seen in this 90 day-cured sample. D) A representative fracture surface after 180 day of curing demonstrates the brittle appearance of the material.

Figure 34. Scanning electron micrographs of representative fracture surfaces of bentonite-lime samples at intermediate magnification. A) The aggregates are formed of face-to-face oriented bundles of montmorillonite flakes (one day-cured). Some of the montmorillonite flakes (MO) are curled as a result of water loss during drying. B) Montmorillonite flakes (RM) react with the fly ash and lime to form laths and blades after 28 days of curing. The boundaries of the clay aggregates are better defined.

Figure 35. Scanning electron micrographs of the reaction products in bentonite-lime samples cured at 23°C. A) Laths and blades (L) have formed on the edges of the montmorillonite flakes after 28 days of curing. B) An example of the final stages of lath and blade (L) formation after 90 days of curing. C) An aggregate of equant crystals (E) is seen after 90 days of curing. D) After 180 days of curing similar aggregates of equant crystals (E) are present.

same at all curing times. The major cementitious mineral is C-S-H Type I as identified from 3.07A and 1.79A peaks (C). The 1.79A peak is present after one day with a low intensity. Its intensity increases after 28 days of curing. The 3.07A peak appears as a shoulder on the calcite peak after 28 days and its intensity increases with longer curing. The presence of C-S-H Type I is supported by the needles seen in the scanning electron micrographs. The unidentified peaks are presented in Table 9.

TABLE 9

UNIDENTIFIED PEAKS IN BENTONITE-LIME CURED AT 23^oC.

D-spacing	Remarks
3.45 (1)	Appears after 1 day and its intensity increases after 90 days.
3.27 (2)	Is present in bentonite and its intensity increases till 90 days and decreases.
3.21 (3)	Is not present in bentonite, appears after one day and its intensity increases, probably afwillite.
3.12 (4)	Appears after 180 days.
2.79 (5)	Intensity increases after 28 days and decreases with increasing curing time.
2.33 (6)	Unchanged.
2.02 (7)	Intensity increases slightly after 90 days.
1.90 (8)	Intensity decreases with time.
1.87 (9)	Intensity is higher after one and 180 days and low at 28 and 90 days of curing.
1.60 (10)	Intensity decreases with time.
1.56 (11)	Is present after 90 days of curing.
1.43 (12)	Intensity slightly increases after 180 days.

The major change is the formation of C-S-H Type I crystals and the increase in strength appears to be due to the formation of this mineral.

Bentonite-Lime (Cured at 50°C)

The stress-strain curves for the bentonite-lime mixture cured at 50°C are shown in Figure 37. The unconfined compressive strength of the one day-cured sample at 50°C is 1084 kPa (157 psi) which is similar to the unconfined compressive strength of the 28 day, 23°C cured sample, thus samples cured at 50°C for one day developed unconfined compressive strenghts similar to those cured for 28 days at 23°C (Figure 32). The stress-strain curves for the remaining time periods plot in a narrow range with an average unconfined compressive strength of 1316 kPa (191 psi). The elastic modulus for the one day-cured sample is 100000 kPa (14480 psi) and it increases to an average of 207292 kPa (30016 psi) for the 28, 90, and 180 day-cured samples. With 100 kPa confining pressure, the stress strain curve of the one day-cured sample is steeper (Figure 37B). The elastic modulus for the one-day cured sample is 157407 kPa (22793 psi). The stress-strain curves for the 28, 90, and 180 day-cured samples plot in a region where the elastic modulus changes from 157407 kPa (22793 psi) to 243902 kPa (35317 psi). The strain at failure for the one day-cured sample with no confining pressure is 0.0142 and the strain decreases to approximately 0.0075 for the 28, 90 and 180 day-cured samples.

Overall the morphology of the samples cured at 50°C is similar to those cured at 23°C, however needle like crystals were not observed. Figure 38A shows a fractured surface of the one day-cured sample at low magnification. The aggregate boundaries (B) are well defined which is typical for brittle material. The dominant reaction products at this elevated temperature are the equant crystals (E) illustrated in Figure 38B after 90 days of curing time. From morphological criteria this feature (E) appears to be C-S-H Type III. Figure 38C shows that these reaction products are local. Other C-S-H Type III crystals are illustrated in Figure 38D after 180 days of curing. EDS analyses of these crystals give a Ca/Si ratio of 0.04 and an Al/Si ratio of 0.19.

The X-Ray patterns of samples cured at 50°C (Figure 39) are similar to the X-Ray patterns of those cured at 23°C (Figure 36). The 3.07A C-S-H Type I peak (C) appears after one day of curing instead of after 28 days as in the lower temperature samples, and its intensity increases with time. The second peak assigned to C-S-H Type I is the 1.79A (C) peak which is present at all times. Higher curing temperature increased the rate of formation of C-S-H Type I which also increased the rate of strength gain during this period. The unidentified peaks are listed in Table 10.

Figure 38. Scanning electron micrographs of bentonite-lime samples cured at 50°C. A) The aggregate boundaries are well defined after one day of curing which is typical for brittle material. B) Equant crystals are seen at intermediate magnification after 90 days of curing. C) The reaction products are localized (180 day-cured). D) Equant crystals at high magnification after 180 days of curing.

TABLE 10

UNIDENTIFIED PEAKS IN BENTONITE-LIME CURED AT 50°C.

D-spacing	Remarks
9.86 (E)	Appears after one day,shifts to 9.92 after 28 days and to 9.83 after 180 days (possibly ettringite).
5.60 (E)	Is present after one day, then it dissappears.
3.74 (1)	Is present after one day and its intensity increases slightly after 28 days.
3.45 (2)	Appears after 28 days.
3.24 (3)	Appears after 90 days of curing .
3.21 (4)	Is present at all times, its intensity decreases after 180 days of curing, possibly afwillite.
2.89 (5)	Is present after 90 days.
2.79 (6)	Is present at all times.
2.33 (7)	Is present at all times, its intensity increases sharply after 180 days.
2.04 (8)	Its intensity increases sharply after 180 days of curing.
2.02 (9)	Is present at all times.
1.67 (10) after	Is present at all times. Its intensity increases after 28 days, it is highest 180 days of curing.
1.37 (11)	Appears after 180 days.

Figure 39. Powder X-Ray Diffraction Patterns of Bentonite-Lime Cured at 50^{o}C. Q=quartz, M=montmorillonite, K=calcite, E=ettringite, H=hematite C=CSH I. For d-spacings represented by numbers refer to the text.

Bentonite-Fly Ash-Lime (Cured at 23^{o}C)

The stress-strain curves of the bentonite-fly ash-lime mixture are presented in Figures 40A and 40B. The unconfined compressive strength of the one day-cured sample is 1061 kPa (154 psi). The stress-strain curves of the 28, 90 and 180 day-cured samples again plot in a narrow region with the 28 day-cured sample having a lower unconfined compressive strength (1800 kPa-261 psi) than the 90 and 180 day-cured samples (2300 kPa-333 psi). The elastic modulus value for the one day-cured sample is 137931 kPa (19972 psi) and it increases to 346667 kPa (50197 psi) after 28 days and to 426667 kPa (61781 psi) for the 90 and 180 day-cured samples. The strain at failure decreases from 0.012 for the one day to 0.006 for the 180 day-cured sample.

The 100 kPa confining pressure causes an increase in strain at failure, thus a decrease in the elastic modulus in the initial stages. The elastic modulus for the one day-cured sample is 116667 kPa (16893 psi), after 28 days it increases to 201493 kPa (29176 psi) and for 90 days it is 345238 kPa (49990 psi). A higher elastic modulus of 500000 kPa (72400 psi) is obtained with 100 kPa confining pressure for the 180 day-cured sample. Strain at failure after one day is 0.0275 and it decreases to 0.006 after 180 days.

The major change in strength and elastic modulus occurs between one and 28 days. The rate of strength increase is lower between 28 and 90 days of curing, but the strength remains essentially constant between 90 and 180 days. With no confining pressure an elastic modulus value of 427,000 kPa (61830 psi) is reached after 90 days of curing which reflects a 3.1 fold increase relative to the elastic modulus of the one-day cured sample.

A fractured surface of the one day-cured sample is presented in Figure 41A at an intermediate magnification. This fracture surface contains mostly clay particles which suggests that the fractured surface is passing through the clay matrix. Some of the fly ash spheres have irregular outlines indicating that they are beginning to react chemically. As seen earlier, the boundaries of clay aggregates are not distinct which is a feature typical for plastic materials such as montmorillonite-rich clays.

Figure 41B presents a fractured surface of the 180 day-cured sample at low magnification. Abundant reaction products are typical of this long curing period. Pull out features (PO) and needles (N) along the pores are the dominant features. The major reaction products are acicular crystals with varying crystal forms and dimensions. The development stages of the acicular crystals are presented in Figure 42. Figure 42A represents (high magnification) the initial stages of formation of ettringite needles (ET) (one day). The reaction

Figure 41. Scanning electron micrographs of bentonite-fly ash-lime samples cured at 23^{O}C. A) A representative fracture surface of the one day-cured sample is seen at intermediate magnification. The fracture surface contains mostly clay particles which suggests that the fracture surface is occurring within the clay matrix. B) A representative fracture surface of the 180 day-cured sample at low magnification. Reaction products are abundant. Pull out features (PO) and needles (N) are dominant.

products are so small that they are only visible at high magnifications. They are generally seen on montmorillonite aggregate surfaces and are composed of acicular crystals which are two to three micrometers long with diameters ranging from 0.3 to 0.4 micrometers. Four to six of these crystals form bundles oriented parallel to the montmorillonite aggregate surface and randomly oriented relative to each other. They protrude into the pores. It is apparent that the montmorillonite flakes are participating in the reactions because needles are seen at the edges of the montmorillonite flakes. The newly formed needles become wider and flatter towards the origination point suggesting that the portlandite-rich solutions are attacking the edges of the clay causing calcium silicate hydrate gel to form as needles. The reaction products are more numerous at certain areas associated with microporosity between the aggregates of clay.

After 28 days of curing, a network of needles dominates the microstructure of the fracture surface as presented in Figures 42B and 42C at intermediate magnification. The radiating needles (N) are more numerous in or near the pores (Figure 42B) and their sizes vary. The types of needles present at this time may be grouped in two morphological categories. (1-) Three to six micrometer long, 0.2 to 0.4 micrometer diameter needles (N) with pointed ends forming radiating bundles (Figure 42B). They are identified as C-S-H Type I by comparision to the morphologies described by

Diamond (23) in cured cement pastes. In this case longer needles have formed. The presence of C-S-H gel is confirmed by the X-Ray powder patterns (Figure 44). (2-) Five to six micrometer long , 0.5 to 0.6 micrometer diameter rods with parallel sides and better defined crystal form (ET) relative to the first type (Figure 42C) they are randomly oriented and span the pores. The morphology of these rods resembles ettringite.

The ettringite and C-S-H Type I crystals co-exist. The formation and increased abundance of the acicular crystals (rods and needles) are accompanied by a major strength increase and decrease in the strain at failure. The more rigid behavior of these samples is attributed to the three dimensional network of rods and needles that supports the montmorillonite aggregates and the fly ash spheres and restricts their relative displacement.

Figure 42D presents a fractured surface of the 90 day-cured sample at intermediate magnification. The acicular crystals are less abundant at this curing period and they are being transformed into other reaction products. The outlines of most of the fly ash grains are irregular indicating that they are reacting. A two micrometer diameter fly ash sphere is seen with a crust of small crystals completely encasing it. Square imprints of crystals which were pulled out when the sample was fractured, are readily apparent.

Figure 42. Scanning electron micrographs showing the development stages of the acicular crystals found in bentonite-fly ash-lime samples cured at 23°C. A) The initial stages of formation of ettringite (E) needles (one day-cured) at high magnification. B) After 28 days of curing a network of needles (N) dominates the microstructure of the fracture surface. C) Another representative fracture surface of the 28 day-cured sample reveals acicular crystals with parallel sides (ET). Their morphology resembles ettringite. D) The acicular crystals are less abundant after 90 days of curing.

Figures 43A and 43B illustrate representative fracture surfaces of the 180 day-cured sample at an intermediate magnification. The acicular crystals (C-S-H Type I and ettringite) are still present although they are less abundant relative to the 28 day-cured sample. EDS analyses of the acicular crystals yield a Ca/Si ratio of 1.25 and an Al/Si ratio of 0.66 typical of C-S-H Type I.

Figure 43A illustrates reacted fly ash particles. Needles (N) form a crust on a 7.5 micrometer diameter fly ash sphere. During fracture one part of this reacted crust was pulled out suggesting that this coating acted as a binder to the neighboring features. A broken, reacted (R) five micrometer fly ash sphere is eaten away and replaced by a three dimensional network of needles. A pull out feature (PO) (20 micrometers long and 10 micrometers wide) reveals that tiny needles less than one micrometer long are present on the edges of the montmorillonite flakes. In Figure 43B the remnant of a 45 micrometer fly ash sphere (S) is filled with reacted fly ash spheres and other reaction products. One of the flyash spheres (R) exhibits a reacted crust displaying the typical morphology of C-S-H Type IV "inner product" . EDS analyses of this product give a Ca/Si ratio of 0.12 and an Al/Si ratio of one. Different aggregates (E) of less than 0.4 micrometer equant crystals are apparent. EDS analyses yield a Ca/Si ratio of 0.58 and an Al/Si ratio of 0.54. These are C-S-H Type III crystals.

XRD powder patterns for the cured samples are presented in Figure 44. The major mineral is montmorillonite and no change is observed in the relative intensities of its peaks (M). Quartz (Q) and calcite (K) are present. The relative intensity of the major calcite peak changes with time and it is lowest after 180 days of curing. The intensity of the tricalcium aluminate peak (T) which is one of the abundant minerals in fly ash is drastically reduced because of the small quantity of fly ash in the mixture. Portlandite peaks are not present. The intensity of the periclase peak (P) does not change with increasing curing time. The intensity of the hematite peak (H) increases after 28 days and then does not change. The strongest peak of C-S-H Type I (C) appears after 28 days of curing (3.07A) which corresponds to a major strength increase. The intensity of the 3.07A C-S-H peak is highest after 180 days of curing. The other peaks that can be assigned to C-S-H Type I are at 1.79A or 1.83A (C). Another d-spacing for C-S-H Type I varies between 2.76A and 2.81A (C), and is overlapped by the 2.79A montmorillonite peak. The presence of C-S-H Type I needles is confirmed by the scanning electron micrographs. Even though crystals of ettringite are readily identifiable in the scanning electron micrographs, its presence is not always obvious in XRD results. The major ettringite peak (E) at 10A appears to shift with time from 9.91A to 9.89A and 10.09A and the relative intensities of these peaks decrease with time.

Afwillite (3.21A peak) appears after 28 days of curing and its major peak (W) increases with time. The other strong peaks reported for afwillite are at 2.84A and 2.74A. The first appears after 90 days of curing and the latter is seen after 180 days of curing. The other peaks, which represent minerals that could not be readily identified because of low peak intensities, or severe overlaps by other minerals are listed in Table 11.

Afwillite, C-S-H Type I and ettringite are identified as newly forming cementitious minerals. Their appearance in the X-Ray pattern or changes in their peak intensities correspond to an increase in the compressive strength of the bentonite-fly ash-lime mixture. The scanning electron microscopy study confirms the formation of C-S-H Type I and ettringite. The X-Ray diffraction patterns show that the newly forming minerals are not very abundant and are poorly crystallized. The crystal structure of montmorillonite is not noticebly altered by reaction with fly ash and lime dissolution products.

Figure 43. Scanning electron micrographs of representative fracture surfaces of the 180 day-cured bentonite-fly ash-lime samples cured at 23^{O}C. A) A fly ash grain is seen with a coating of needles (N). A pullout feature (P) has tiny needles on the edges of the montmorillonite flakes illustrating that montmorillonite is participating in the reaction. A broken fly ash sphere (R) is eaten away and replaced by a three dimensional network of needles. B) The remnant of a reacted fly ash sphere (S) is filled with other fly ash spheres and reaction products. Aggregates of equant crystals (E) engulf a fly ash spheres.

Figure 44. Powder X-Ray Diffraction Patterns of Bentonite-Fly Ash-Lime Cured at 23°C. Q=quartz, M=montmorillonite, K=calcite, T=tricalcium aluminate, P=periclase, H=hematite, C=CSH I, W=afwillite, E=ettringite. For d-spacings represented by numbers refer to the text.

TABLE 11

UNIDENTIFIED PEAKS IN BENTONITE-FLY ASH-LIME CURED AT 23°C.

D-spacing	Remarks
4.00-4.03 (1)	Is present after one day of curing, its intensity increases with time; highest after 90 days then decreases.
3.74 (2)	Is present at all times; its intensity is higher after 28 days.
3.25 (3)	Appears after 28 days of curing with high intensity.
3.17 (4)	Is present at all times.
2.91-2.93 (5)	Appears after 28 days of curing, and present after 90 and 180 days.
2.88-2.89 (6)	Is present at all times.
2.79 (7)	Is present at all times, and its intensity increases after 28 days and decreases after 180 days.
2.76 (8)	Is present after one day, dissappears after 28 days.
2.64 (9)	Its intensity decreases with time.
2.33 (10)	Its intensity increases after 28 days and decreases after 90 days.
2.02 (11)	Unchanged.
1.90 (12)	Its intensity is higher after 90 and 180 days of curing.

Bentonite-Fly Ash-Lime (Cured at 50^{o}C)

The stress-strain curves for the 50^{o}C cured bentonite-fly ash-lime mixture are presented in Figure 45. The one day unconfined compressive strength of the bentonite-fly ash-lime mixture is 2100 kPa (304 psi) which is higher than the 28 day unconfined compressive strength (1800 kPa) of the 23^{o}C cured sample (Figure 40). After 28 days of curing the UCS increases to 2639 kPa (382 psi). An average value of 2900 kPa (420 psi) is typical for the 90 and 180 day-cured samples. The elastic modulus value for the one day-cured sample is 246032 kPa (35625 psi), it increases to 370,000 kPa (53576 psi) for the 90 and 180 day-cured samples. The strain at failure is 0.011 for the one day-cured sample and it decreases to 0.009 after 180 days.

One hundred kPa confining pressure increased the elastic modulus to 296296 kPa (42904 psi) for the one day-cured sample. The stress strain curves for the 90 and 180 day-cured samples yield an elastic modulus of 505434 kPa (73187 psi) (confined). The strain at failure decreases from 0.015 for one day to 0.009 after 180 days of curing.

Figure 46A illustrates a representative fracture surface of the one day-cured bentonite-fly ash-lime sample at intermediate magnification. Acicular and lathlike crystals (N) with well developed crystal forms span the pores and support the fly ash spheres and the montmorillonite aggregates. These ettringite crystals support the fly ash particles and montmorillonite aggregates creating a higher strength, more rigid sample after only one day of curing. The fly ash particles have irregular outlines which suggests that they are being corroded. Figure 46B illustrates a fracture surface of the 28 day-cured sample at low magnification with well defined aggregate boundaries typical of brittle material. Figure 46C presents a fracture surface of the 28 day-cured sample at intermediate magnification. There are fewer acicular crystals (N) present at this curing time and they are usually only seen in the pores. There is a 7.5 micrometer diameter completely reacted broken fly ash particle (R) which is filled with a three dimensional network of needles, most probably C-S-H Type I. A "pull out" feature is present with a reacted crust.

After 90 days of curing the acicular crystals are still present in varying developmental stages. Acicular crystals with better developed crystal forms and hexagonal cross sections are seen in Figure 46D. The hexagonal cross section is typical of secondary ettringite. Hexagonal prisms bundle together to form wider rods. C-S-H Type I crystals co-exist with ettringite at this curing period (figure not shown).

Equant crystals (E), often completely engulfing fly ash spheres, are the dominant features (Figure 47A) after 90 days of curing. EDS analyses of these features reveal a Ca/Si ratio of 0.85 and an Al/Si ratio of 0.75 for this CSH Type III material. The compressive strength is highest at this curing period. Figure 47B illustrates the crust of a reacted 25 micrometer diameter fly ash sphere (R) after 180 days of curing. During fracture this hollow sphere was broken exposing the inside of the reacted crust composed of a mat of interlocking one micrometer long, tiny needles. The crust is approximately two micrometers thick which means that at least eight to ten layers of needles are present. EDS analyses yield a Ca/Si ratio of 0.33 and an Al/Si ratio of 0.70.

The reacted crust (RC) of a 13 micrometer fly ash sphere is evident in Figure 47C, after 180 days of curing. The imprint of a 15 micrometer diameter fly ash sphere is seen. Sharp-edged blades (eight micrometers long, one micrometer wide) appear for the first time. Figure 47D illustrates a reacted 14 micrometer fly ash sphere on the surface of the 180 day-cured sample. It has a reacted crust (RC) and an etched interior (EI). A seven micrometer diameter fly ash particle is covered with a film of reaction products.

Figure 46. Scanning electron micrographs of bentonite-fly ash-lime samples cured at 50^{o}C. A) A representative fracture surface of the one day-cured sample at intermediate magnification. Acicular and lathlike (N) crystals span the pores and support the fly ash spheres and the montmorillonite aggregates. B) A fracture surface of the 28 day-cured sample at low magnification. The aggregate boundaries are well defined, typical for brittle material. C) After 28 days of curing the acicular crystals are less abundant and restricted to the pores (N). A reacted crust of a fly ash sphere is seen at (PO). A fly ash grain is replaced by a three-dimensional network of needles (R). D) Acicular crystals with better developed crystal forms and hexagonal cross section are seen after 90 day of curing. The hexagonal cross section is typical for secondary ettringite.

The XRD patterns of the 50°C (Figure 48) and the 23°C (Figure 44) cured bentonite-fly ash-lime mixtures are very similar. The relative intensity of the calcite (K) peak decreases after 90 days of curing similar to the decreases observed in samples cured at 23°C. There are no changes in the montmorillonite (M) and quartz (Q) peak intensities. The intensity of the hematite peak (H) increases after 180 days of curing. C-S-H Type I (C), ettringite (E) and afwillite (W) are identified. The higher curing temperature increased the apparent rate of the reactions because C-S-H Type I needles appear after one day of curing in the 50°C cured sample instead of after 28 days at 23°C. The ettringite 9.905A d-spacing shifts to 9.91A, 9.99A and 10.19A after 28, 90 and 180 days of curing respectively. The relative intensity of the ettringite peaks corresponding to 90 days of reaction is the highest, and it decreases after 180 days of curing. The 3.21A, 2.84A and 2.74A d-spacings assigned to afwillite appear after one day of curing. The relative intensity of the 3.21A afwillite peak increases considerably after 90 days of curing when this mixture attained its highest strength. A decrease in the relative intensity of 3.21A afwillite peak after 180 days of curing is accompanied by a slight decrease in the compressive strength. The unidentified peaks are presented in Table 12.

Figure 47. Scanning electron micrographs of bentonite-fly ash-lime samples cured at 50°C. A) Blocky aggregate of equant crystals (E) engulfs a fly ash grain after 90 days of curing. B) A fracture surface of the 180 day-cured sample at intermediate magnification. A reacted crust (R) of a fly ash grain is present. C) Reacted fly ash grains after 180 days of curing. A reacted crust (RC) of a fly ash grain is present and sharp edged blades (B) are seen in the imprint of a fly ash sphere. D) A fly ash grain with reacted crust (RC) and etched interior (EI) is seen after 180 days of curing.

Figure 48. Powder X-Ray Diffraction Patterns of Bentonite-Fly Ash-Lime Cured at 50°C. Q=quartz, M=montmorillonite, K=calcite, P=periclase, H=hematite, C=CSH I, W=afwillite, E=ettringite. For d-spacings represented by numbers refer to the text.

TABLE 12

UNIDENTIFIED PEAKS IN BENTONITE-FLY ASH-LIME CURED AT 50°C.

D-spacing	Remarks
3.45 (1)	Is present after one and 180 days.
3.26 (2)	Appears after 28 days with a high intensity, is present after 90 and 180 days with very low intensity; similar to the 23°C cured sample.
2.92 (3)	Appears after 28 days of curing and stays unchanged.
2.79 (4)	Its intensity increases after 28 days.
2.33 (5)	Is present at all times, its relative intensity increases sharply after 180 days.
2.27 (6)	Is present at all times, its relative intensity increases after 180 days.
2.08 (7)	Its intensity increases after 28 days and then stays constant.
1.87 (8)	Is present at all times with the highest intensity after 90 days.

SUMMARY AND DISCUSSION OF RESULTS

In all of the mixtures studied, at both curing temperatures, the unconfined compressive strengths of the treated soils are higher than the unconfined compressive strengths of the untreated bentonite (Tables 13 and 14) as expected. The elastic moduli of the bentonite-fly ash-lime mixtures are higher than the elastic moduli of the bentonite-fly ash or bentonite-lime mixtures. After 180 days of curing at 23^{o}C the elastic modulus of the bentonite-fly ash-lime (S) mixture is approximately fifteen times greater than the elastic modulus of bentonite (the elastic modulus of untreated bentonite is 30500 kPa-4416 psi). The unconfined compressive strength of the bentonite-fly ash-lime (S) mixture increased four times relative to the UCS of bentonite. At 50^{o}C curing temperature the UCS of bentonite-fly ash-lime (S), is 500 kPa (72 psi) higher than the UCS of the 23^{o}C cured sample after 180 days of curing. The maximum values for unconfined compressive strengths and elastic moduli were observed after 90 days of curing and a decrease resulting from the dissolution of some of the fly ash spheres was observed between 90 and 180 days of curing (Figures 49 and 50). Fly ash and fly ash-lime mixtures have an UCS one order of magnitude higher than the UCS of mixtures with bentonite.

TABLE 13

SUMMARY OF COMPRESSIVE STRENGTH TESTS
23°C

	FA	FL	F	L	S
1 Day					
UCS	10237	7189	906	610	1061
CS			1059	746	1107
E(U)			93404	77460	144045
E(C)			155590	70707	118700
28 Days					
UCS	18367	18265	1414	996	1800
CS			1277	1108	1957
E(U)			278289	217945	386882
E(C)			237267	140063	402751
90 Days					
UCS	19745	26492	1467	1252	2444
CS			1299	1323	2144
EU)			210059	218087	647407
E(C)			137893	265269	399049
180 Days					
UCS	26030	32236	1387	1344	2295
CS			1525	1342	2530
E(U)			261050	252500	460823
E(C)			318471	281449	587259

Note: UCS=Unconfined compres ive strength, CS=Confined strength (100 kPa confining pressure), E(U)= Elastic modulus from unconfined test, E(C)= Elastic modulus from confined test. All values presented in the table are in kPa.
UCS of untreated bentonite=590 kPa, CS of untreated bentonite=597 kPa E(U) of untreated bentonite=30500 kPa, E(C) of untreated bentonite=23064 kPa. To convert to psi multiply by 0.1448 . FA=Fly ash, FL=Fly ash-lime, F=Bentonite-Fly ash, L=Bentonite-lime, S=Bentonite-fly ash-lime.

TABLE 14

SUMMARY OF COMPRESSIVE STRENGTH TESTS
50°C

	FA	FL	F	L	S
1 Day					
UCS	10923	7372	1234	1084	2099
CS			1343	1144	2220
E(U)			140950	85861	349250
E(C)			56697	207692	358066
28 Days					
UCS	18877	32398	1327	1309	2639
CS			1775	1341	2691
E(U)			185954	263589	456193
E(C)			291291	251960	494513
90 Days					
UCS	26949	39472	1525	1386	3102
CS			2052	1318	3178
E(U)			116883	243546	614514
E(C)			301117	146857	667697
180 Days					
UCS	22630	39724	1915	1254	2793
CS			1785	1528	3401
E(U)			284450	201538	398135
E(C)			230392	140030	443735

Note: UCS=Unconfined compressive strength (kPa), CS= Confined compressive strength (kPa) (100 kPa confining pressure), E(U)= Elastic modulus (kPa) from unconfined test, E(C)= Elastic modulus from confined test (kPa). To convert to psi multiply by 0.1448 . FA=Fly ash, FL=Fly ash-lime, F=Bentonite-fly ash, L=Bentonite-lime, S=Bentonite-fly ash-lime.

The maximum strength obtained for the bentonite-fly ash-lime mixture is considered satisfactory because most of the material in the mixture is composed of fines without a mechanically stable matrix. The increase in strength is directly related to the formation of cementitous minerals and X-Ray powder diffractograms suggest that these new minerals are poorly crystalline and form in minute quantities.

The minerals identified by X-Ray diffraction techniques are summarized in Tables 15 and 16. Each mixture contained different starting materials and produced different cementitious mineral products. The hydrated calcium aluminates of the fly ash dominated samples were not detected in the montmorillonite dominated samples. The change in bulk composition created favorable conditions for the precipitation of ettringite and afwillite instead. Alternatively, the calcium aluminum hydrates may not be abundant enough to be detected. The most consistent reaction product in the mixtures was C-S-H gel. Its appearance is coincident with the curing times at which considerable compressive strength increases are observed. Ettringite is present in bentonite-fly ash, bentonite-lime and bentonite-fly ash-lime mixtures after one day of curing and ettringite crystals are readily seen in the micrographs. The transformation of ettringite to monosulphoaluminate as expected by comparision with portland cement is not observed in any of the mixtures. The source of the sulphur in ettringite is the anhydrite from the fly ash. Ettringite later reacts and dissolves contributing SO_4 and other elements for the formation of CSH gel and afwillite.

TABLE 15

THE IDENTIFIED MINERALS IN THE X-RAY POWDER PATTERNS

(23°C)

	FA	FL	F	L	S
1 Day	Quartz	Portlan.	Montmo.	Montmo.	Montmo.
	TCA	Quartz	Quartz	Quartz	Quartz
	Periclase	TCA	Calcite	Calcite	Calcite
	Alite	Periclase	TCA	Hemeatite	TCA
	Anhydrite	Hematite	Periclase	Afwil. *	Periclase
	Lime	C_3AH_6 *	Hematite	Ettrin. *	Hematite
	C_4AH_{13} *	C_4AH_{13} *	Ettrin. *		Ettrin. *
	CSH I *		Afwil. *		
28 Days	Same	Same	Same	Same+	Same+
				CSH I *	CSH I *
					Afwil. *
90 Days	Same	Same	Same+	Same	Same
			CSH I *		
180 Days	Same	Same	Same	Same	Same

Note: (*) indicates the newly forming cementitious minerals. (Same) indicates that no change was observed in mineral identifications relative to the previous curing period. Montmo.=Montmorillonite, Afwil.=Afwillite, Ettrin.=Ettringite, Lime=CaO. FA=Fly ash, FL=Fly ash-lime, F=Bentonite-fly ash, L=Bentonite-lime, S=Bentonite-fly ash-lime.

TABLE 16

THE IDENTIFIED MINERALS IN THE X-RAY PATTERNS

50°C

	FA	FL	F	L	S
1 Day	Quartz	Portlan.	Montmo.	Montmo.	Montmo.
	TCA	Quartz	Quartz	Quartz	Quartz
	Periclase	TCA	Calcite	Calcite	Calcite
	Hematite	Periclase	TCA	Hematite	Hematite
	C_4AH_{13} *	C_4AH_{13} *	Periclase	Afwil. *	CSH I *
	CSH I *	C_3AH_6 *	Hematite	CSH I *	Ettrin. *
		Hematite	CSH I *	Ettrin. *	Afwil. *
			Etrin. *		
28 Days	Same	Same	Same	Same	Same
90 Days	Same	Same	Same	Same	Same
180 Days	Same	Same	Same	Same	Same

Note: (*) indicates the newly forming cementitious minerals. (Same) shows that no change was observed in the identified minerals at that curing period. Montmo.= montmorillonite, Afwil.=afwillite, Ettrin.=ettringite, Portlan.= portlandite. FA=Fly ash, FL=Fly ash-lime, F=Bentonite-fly ash, L=Bentonite-lime, S=Bentonite-fly ash-lime.

With the scanning electron microscope the development of needles, hexagonal plates and equant crystals and the participation of montmorillonite flakes and fly ash spheres in the reactions are observed. Needles are apparent in the initial stages of curing (1 day) on the edges of montmorillonite flakes. After 28 days of curing the needles become more abundant and their lengths increase. The needles form in the pores, on the fly ash spheres and on montmorillonite aggregates. Blocky aggregates of 0.5 micrometer equant crystals are observed engulfing the fly ash grains after 90 days of curing. Hexagonal plates spanning the pore are present only in fly ash and fly ash-lime mixtures. Apparently these calcium aluminum hydrates are important reaction products when montmorillonite is not present.

Montmorillonite participates in the strength forming reaction. Even after one day of curing, tiny fibrous crystals form at the edges of the montmorillonite flakes. After longer curing periods, the imprints of the pull out features are full of reacted montmorillonite flakes. The altered montmorillonite flakes are most evident in the simple mixture of bentonite and lime. This observation directly supports Stocker's (30) and Ormsby and Bolz's (27) suggestions about participation of clay flakes in the cementitious reactions.

The participation of the fly ash grains in the reactions occurs in three stages. In the first, the smaller soluble phases (some glass and anhydrite) dissolve immediately and precipitate as acicular crystals (ettringite and C-S-H Type I). In the next stage, acicular crystals (C-S-H Type I) become more numerous and form coatings on fly ash grains. These radiating crystals increase the contact points between grains thus increasing the compressive strength. In the third stage, fly ash particles develop a reacted crust while others are completely replaced by cementitious products. The deterioration of some of the fly ash grains creates weak spots in the matrix and causes a decrease in the elastic modulus. This is particularly evident at the longest curing period, 180 days. All stages of reaction overlap because the reactions are at the individual particle level and the particles have a wide range of chemical composition and density. Some fly ash spheres do not react and behave as inert fillers as reported by Diamond (21), but duplex film morphologies are not as common as in cement and fly ash mixtures.

A general qualitative theory of strength modification can be developed from the SEM, XRD and UCS data. In a plastic clay the failure occurs through the slippage of clay flakes past one another. The addition of fly ash and lime to plastic clay results in the formation of cementitious crystals that bond the aggregates and grains to each other creating larger units. The aggregates and grains are connected to each other with needles and equant crystals. Increased contact points due to the formation of needles increases the compressive strength and decreases the strain at failure. After curing the failure plane passes through the cementitious crystals and failure occurs when the ultimate strength of the cementitious crystals is exceeded. The failure mechanism is similar to that of brittle material. Some of the fly ash grains dissolve and create weak spots in the matrix which appears to be the reason for the decrease in the compressive strength and increase in strain at failure after 180 days of curing. The associated decrease in elastic moduli is expected to level off after longer curing periods and the amount of decrease is most probably limited to the number of deteriorating fly ash grains.

The major effect of the increased curing temperature (50°C) is to increase the rate and degree of the reaction. The same cementitious minerals are present· In bentonite-fly ash-lime samples, C-S-H Type I and ettringite crystals are dominant after one day of curing at 50°C instead of after 28 days at 23°C. The elastic modulus of the higher temperature one day-cured sample is close to the elastic modulus of the lower temperature 28 day cured sample. The major peak of C-S-H Type I appears after one day at 50°C instead of 28 days at 23°C. Fully reacted spheres and spheres with reacted crusts are present after 28 days at 50°C instead of 180 days at the lower temperature. The UCS of the higher temperature samples is typically 500 to 1000 kPa (72 to 144 psi) higher (Figure 50), but the difference decreases with increased curing time.

A decrease in the UCS and elastic modulus is evident after 180 days of curing and if this rate of decrease is maintained it could have important consequences for the use of fly ash in stabilization projects. In field projects the UCS may decrease due to fly ash dissolution. This deterioration results in laboratory test values for the long term cured samples being equal to shorter term sample tests. One day, 50°C curing yields UCS and elastic modulis values comparable to the lower temperature 28 day-cured sample. As a design procedure the UCS and elastic modulus corresponding to either 23°C, 28 day-cured sample or 50°C one day cured sample produce equivalent results.

The fly ash plus lime stabilization of bentonite resulted in an elastic modulus aproximately seventeen times the elastic modulus of untreated bentonite. The ratios of the elastic moduli of bentonite-fly ash-lime to the elastic modulus of bentonite at different curing times were 4.5, 13, 17 and 15 for 1, 28, 90 and 180 day-cured samples, respectively. Theoretical analyses reported in the literature state, "In a layered pavement system, substantial flexural stresses are developed in the layer containing the lime-soil mixture" (100). Thompson (99) indicated that lime-soil mixtures have tensile strength properties capable of resisting the flexural stresses developed. The stabilized layer behaves as a slab on the untreated soil. In the design of pavements the slab action of the stabilized layer should be considered. If the slab action of the stabilized layer is not considered and the flexural stresses in this layer are larger than the flexural strength of the stabilized layer, cracks will form. In all of the mixtures studied in our laboratory experiments the strain at failure was less than one percent and the stabilized soil does not behave as a flexible material. This observation maybe an important design consideration because the deformation capabilities of these mixtures are limited.

The results of this study may be extrapolated to naturally occuring mixed mineral composition soils as follows. The addition of fly ash and lime in the stabilization of fine grained soils increases the elastic modulus considerably due to the formation of cementitious minerals. These minerals form at normal temperatures (field) in laboratory compacted soils. The formation of the cementitious minerals will not be limited by the type of soil because all of the necessary constituents to form cementitious compounds are supplied by fly ash and lime With natural soils higher strengths and larger changes in elastic moduli may be obtained because of the presence of non-clay constituents like quartz which provide a mechanically stable matrix for bonding by the cementitious minerals.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are based on results of our laboratory study. Even though pure bentonite was used the generalizations should be valid for other soils where the dominant mineral is montmorillonite.

1- Addition of fly ash and lime to bentonite results in substantial (17X) increase in the elastic modulus after 90 days of curing. The increase in elastic modulus is related to the formation of cementitious reaction products between fly ash spheres and aggregates of montmorillonite.

2- After 180 days of curing the elastic modulus of lime fly ash bentonite decreases but is still 15X the original. This decrease is the result of the dissolution of some of the fly ash grains creating weak spots in the supporting matrix. A general concept in the stabilization of soils is that the increase in elastic modulus will continue for long time periods, however results of this study show that in the case of fly ash-lime stabilization (of fine grained bentonite) the elastic modulus decreases. The decrease in elastic modulus is expected to level off since it is limited by the number of dissolved fly ash grains.

3- The cementitions reaction products are more abundant when bentonite was stabilized with fly ash and lime than when it was stabilized only with fly ash or only with lime. This resulted in higher elastic moduli and compressive strengths in fly ash-lime stabilized soils. Soils stabilized with lime fly ash rather than only fly ash or only lime will produce higher strengths and higher elastic modului.

4- Strength and elastic modulus increases are associated with the formation of new minerals. Ettringite, C-S-H gel and afwillite form after curing for various lengths of time and the increase in the relative abundances of these minerals corresponds to curing times when major increases in elastic modulus and strength occur. The most consistent reaction product which was observed in the mixtures was C-S-H gel. Calcium aluminum hydrates forming in fly ash containing test specimens were not detected when bentonite was present.

5- Ettringite is a source of early strength increase in fly ash and lime stabilized bentonite. This reaction and strength increase is similar to that observed during portland cement hydration. In the bentonite-fly ash-lime mixture acicular ettringite crystals span the pores providing support to the montmorilonite aggregates and fly ash grains. With increased curing time, ettringite is less abundant and reacts with the soils to form C-S-H minerals.

6- Strength and elastic modulus increases are associated with changes in the microstructure. Acicular crystals on some fly ash grains increase contact points and brace the pore walls thus increasing the compressive strength and decreasing the strain at failure. Equant crystals which appeared after longer curing periods engulfed some of the fly ash grains providing increased support to those grains.

7- Fly ash contributes to increases in the elastic moduli of bentonite-fly ash-lime mixture by affecting it physically and chemically. Physically the fly ash grains provide support in the form of a matrix between montmorillonite aggregates. Chemically, various aluminosilicates, glasses, and other mineral phases found in fly ash react with free lime and bentonite to form cementitious products. After long curing periods the partial dissolution of some fly ash grains creates weak spots in the matrix and decreases the unconfined compressive strength and elastic modulus. The bentonite-fly ash-lime mixtures develop more rigid stabilized products than fly ash-bentonite or lime-bentonite.

8- Montmorillonite participates in the cementitious reactions. Tiny fibrous crystals form at the edges of the montmorillonite flakes providing increased bonding between aggregates and grains. The direct observation of the fibrous crystals forming on montmorillonite flakes supports the findings of

Stocker (92) regarding the attack of lime on the edges of 2:1 clay minerals. The complete deterioration of the crystal structure of montmorillonite as proposed by Eades and Grim (28) is not observed.

9- The 50°C curing temperature increases the rate of reactions. The same cementitious minerals form at, both, 23°C and 50°C curing temperatures. At 50°C, all identified cementitious crystals were present after one day of curing whereas with the 23°C curing temperature the development of the same cementitious minerals was spread over one to 90 days. The unconfined compressive strengths and the elastic moduli of samples cured at 50°C are higher than those cured at 23°C. Results suggest that one day curing at 50°C will produce results compatible with 28 day curing at 23°C thus resulting in considerable time saving in the testing procedure for strength.

10- The increased rigidity of the fly ash-lime stabilized layer should be considered in pavement design. Smaller quantities of lime and fly ash may be desirable to produce more flexible soil layers.

Suggestions for further investigation developed as a result of this study include:

1- Fly ash-lime stabilization of natural soils should be investigated to determine whether the same types of cementitious minerals will form. A comparision of stabilized natural soils with variable contents of kaolinite, illite, chlorite and montmorilonite should produce a more thorough understanding of the cementation in stabilized natural soils.

2- Cores from existing fly ash-lime stabilized fine grained soils should be studied using the same microscopic and X-Ray diffraction techniques to observe the formation of the cementitious minerals under field conditions. The potential development of calcite should be considered in field conditions.

3- Longer term experiments should be conducted to determine the ultimate fate of the fly ash spheres. It would be desirable to establish whether or not the UCS and elastic modulus test values continue to decrease with curing times in excess of 180 days.

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