

# Ettringite formation and behaviour in clayey soils

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## Abstract

Failures in soil stabilization have been reported previously as being due to the formation of ettringite, an expansive mineral which develops in the presence of sulfate, calcium, and aluminum compounds of clay fraction in high pH levels between 10.36 and 14. By comparing the pattern of formation of ettringite, formed from different possible sources and specifically in stabilized soil, it is expected that a clearer picture of the kinetics of ettringite formation from different sources will be obtained. In this paper, a set of physico-chemical experiments and XRD tests were performed to investigate the process of ettringite formation and to explore its possible performance in clayey soils. The growth of the ettringite XRD peaks was used as a measure of the rate and its formation pattern. It is shown that the rate of ettringite formation in soil stabilization is much slower than that of artificial ettringite. Furthermore, it is shown that ettringite swells to the order of 50% and its fluid retention is significantly higher (by as much as 400%) than that of the soil sample studied in this research.

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**Keywords:** Soil stabilization; Lime; Ettringite; Swelling; XRD; Clay mineral

## 1. Introduction

Soil stabilization is usually accomplished by mechanical or chemical means. Among soil stabilization methods, the use of lime (CaO or Ca(OH)<sub>2</sub>) and cement are the most common. Soil stabilization should not be considered just in terms of strength; in fact, to do so could cause serious structural failures. On the other hand, the production of low cost roads using calcium compounds or cement stabilized soil, while offering an apparently simple remedy for good and cheap transportation infrastructure, has created several problems because of seemingly “peculiar” swelling and resultant instability in post-stabilization periods (Yong and Ouhadi, 1997; Ouhadi and Yong, 2003a). The destructive effects of high sulfate concentration on cement and lime (CaO or Ca(OH)<sub>2</sub>) stabilized soils have been reported by Mehra et al. (1955) and Sherwood (1958, 1962). Mitchell (1986) reported surface cracking in a roadway system in Las Vegas, U.S., which

occurred within a period of two years following CaO stabilization. This failure happened in spite of acceptable preliminary geotechnical investigations and excellent initial performance. Heaves often amounted to several centimetres. In some cases, heaves as high as 30 cm above the adjacent pavement were observed. These normally ranged anywhere from 30–60 cm in width (Hunter, 1988). Representative samples of damaged subbase analyzed by XRD indicated the presence of ettringite minerals {Ca<sub>6</sub>A<sub>12</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O} (Mitchell and Dermatas, 1992). Other problem areas have included Southern California, and Texas, U.S., in highway construction (California Department of Transportation, 1974) and even in foundations and slabs in Paris, France (Hunter, 1989). Other major occurrences of calcium compound-induced heave have been documented, as well (Yong and Ouhadi, 2007).

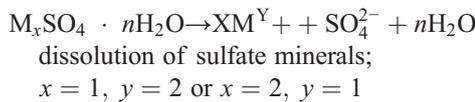
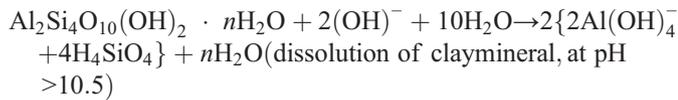
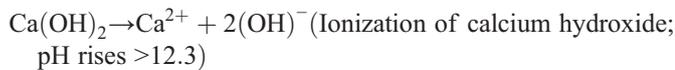
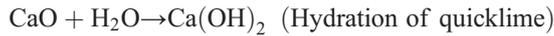
The induced heave has been attributed to the growth of ettringite. However, the exact mechanism of these failures is still not well known (Mitchell, 1986; Yong and Ouhadi, 1997). Generally, limited information is available on ettringite formation in sulfate enriched clays (Rajasekaran et al., 1997; Rajasekaran, 2005; Yong and Ouhadi, 2007). Ettringite is known as one of the

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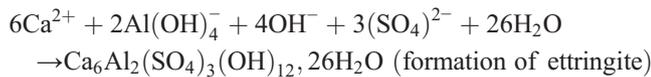
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main substances responsible for severe cracking of cement paste and resultant deterioration of concrete (Mehta and Klein, 1966; Mehta, 1973; Neville, 1983; Ma et al., in press; Lee et al., 2005).

Chemical interactions involved in ettringite formation during lime (CaO or Ca(OH)<sub>2</sub>) stabilization of soil are given in summary, using information from Hunter (1988) and Ouhadi (1997) as follows:



Sulfate (from soil or groundwater)  
 + Aluminum compounds (released from the clay)  
 + Calcium (from hydrate lime or quicklime)  
 → calcium–aluminum sulfate (ettringite)



Many investigators have derived equations for the rate of ettringite formation (Jander, 1927; Ginstling and Brounshtein, 1950; Mori and Minegishi, 1968; Plowman and Cabrera, 1984; Gruszczinski et al., 1993). However, there exist few experimental studies for validation of these derivations. Prior research has revolved around the stabilization of soil from a mechanical viewpoint and has generally neglected ettringite development, which is intrinsic to the cement hydration process. For this reason, there is less attention in the literature to the kinetics of ettringite formation. As such, the purpose of this study is to develop a better knowledge of the theoretical and experimental aspects of ettringite formation and its possible behaviour in clayey soil. This would allow for a better comprehension of the failure mechanism and contribute to strategies aimed at the prevention of these failures. For this purpose, a series of experiments are performed. These experiments include: XRD to investigate the kinetics of ettringite formation in laboratory prepared ettringite; digestion testing to look into the maximum available aluminum compounds of different clay minerals; fluid retention to examine the ability of samples to take in more water from lower strata; and swelling measurement to investigate the role of ettringite on the volume change behaviour of soils.

## 2. Materials and methods

This study was performed using: (1) Aluminum sulfate and calcium hydroxide to produce artificial ettringite. (2) Natural unweathered marly soil, representing the marly soils of the southern area of Iran and the northern sector of the

Persian Gulf in different states of weathering. This region is highly prone to both natural and artificial slope instability problems. (3) A pure palygorskite  $\{\text{(Mg, Al)}_5(\text{Si, Al})_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O}\}$  sample that was extracted from the natural marl. (4) Illite (Domtar sealbond) obtained from Domtar Construction Materials of Canada (Ltd.).

Various experiments were performed following procedures and methods given by different investigators. Duplicate samples were made for all of the experiments. These procedures and/or methods are as follows.

XRD analysis was performed based on the method suggested in the study reported by Moore and Reynolds (1989), and Ouhadi and Yong (2003b). A Phillips apparatus “PW1710-System, 1984” with Cu-K $\alpha$  radiation was used to obtain the X-ray diffraction patterns of samples. The X-ray diffraction mineral patterns were identified by comparison with file standard X-ray powder diffraction patterns (International Centre for Diffraction Data (ICDD), Mineral Powder diffraction file Search Manual, 1988) of the most commonly found minerals. In addition, pore fluid chemistry analysis was performed in order to focus attention on the chemical aspects of soil samples (Ouhadi and Goodarzi, 2007). Atomic Absorption Spectrophotometer (AAS-GBC 932, AB Plus) was used to analyze soil pore fluid of samples.

To investigate the kinetics of artificial ettringite formation when aluminum sulfate and calcium hydroxide are used as the source of mineral formation, a series of XRD tests were performed on mixtures of these two elements with distilled-water at different time intervals. Artificial ettringite was prepared using the method suggested by Older and Abdul-Maula (1984). According to this method, a suspension containing 0.02 mol of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and 0.12 mol Ca(OH)<sub>2</sub> in 1:1 H<sub>2</sub>O was prepared at room temperature. For complete mineral formation, 48 h of agitation of the prepared mixtures was required. To monitor and establish the rate of ettringite formation at different time periods, a sample was taken from the prepared mixture at the specified time intervals, dried and analyzed by XRD. It was observed, after 48 h that agitation does not cause any increase of the intensity of ettringite peaks, confirming that 48 h agitation period is enough for completion of ettringite formation where the major sources for ettringite are  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and Ca(OH)<sub>2</sub> as it is also previously addressed by other authors (Older and Abdul-Maula, 1984).

The ratio of major reflection line of ettringite peak in any time interval to the major reflection line of ettringite after 48 h of agitation gives the reaction ratios in different time intervals. For calculation of reaction ratios, two mixtures for artificial ettringite formation were prepared. The agitation of one sample was continued for 48 h. The other sample also was agitated for 48 h, but there were time intervals in which the agitation was stopped for almost 5 s, 0.2 g of sample was taken for XRD evaluation, and then the agitation was continued. After 48 h of agitation, XRD analysis was performed on both samples to make sure that the break of sample agitation did not affect the extent of ettringite formation. It was observed that the difference of the quantity of XRD peaks of both samples at the end of agitation period was less than the standard deviation of sample preparation as was previously indicated (Ouhadi, 1997).

Scanning Electron Microscope (SEM) techniques were used to achieve information on the morphology of ettringite and its crystal size. Samples of natural marl and lime stabilized marl were analyzed by using a SEM Jeol-Jsm 840A. Stabilized marl was cured at constant water content in sealed containers, in a 20 °C, and 100% relative humidity environment.

Maximum dry density and optimum water content of marl, palygorskite and ettringite were measured using the Harvard Miniature apparatus with the application of a 15 lb (6.81 kg) hammer and 30 taps per layer (ASTM D 4609-86). These maximum dry density and optimum water content measurements were used to compact samples in specific molds for swelling measurement and fluid retention experiments.

Fluid retention of samples was performed in conformance to the test procedures detailed in the laboratory manual of the Geotechnical Research Centre of McGill University. A pressure plate apparatus was employed to investigate the fluid retention/suction behaviour of ettringite and marl samples. Soil–water potential/suction measurement is made for two purposes. First, it is made to define the equilibrium relationship between potential and water content for a soil sample. Second, it is intended to measure soil suction for evaluation of water movement, and water availability in soil stabilization/post-stabilization processes. For preparation purposes, the sample was compacted in a lucite ring of 38.1 mm diameter and 15 mm height until achieving the desired dry density. Following preparation, the samples were placed in pressure plate extractors,

(a closed chamber device) for suction measurement. In this apparatus a water-saturated ceramic plate was placed at the bottom of the samples and the bottom of this plate was retained in connection with atmospheric pressure. After increasing the air pressure in the enclosed chamber, water was caused to move out of the samples and through the ceramic plate. This process was endured in order to reach equilibrium between the applied air pressure and the energy at which pore fluid was retained in the sample (i.e. soil–water potential). This process was carried out by applying different pressures in each case. Following equilibrium the moisture content was measured. The suction range was adopted between pF 0.0 and pF 3.8. If the water content of a soil sample is more than another sample at any given suction, it means it has the tendency to take in more water in soil structure.

Free-swelling, pH measurement and solubility of clay soils were determined according to ASTM standards [ASTM, 1992].

### 3. Kinetics of ettringite formation

Several investigators have tried to derive and establish equations for the rate of ettringite formation (Ouhadi, 1997). The equation suggested by Jander (1927) is the most frequently used. This equation is as follows:

$$\left[1 - (1 - \alpha)^{1/3}\right]^N = Pt \quad (1)$$

where  $\alpha$  is the reaction ratio (fraction which has reacted),  $t$  is time of hydration, and  $P$  is a rate constant. This equation is based on the assumption that ettringite forms when substance  $A$  reacts with substance  $B$  to form product  $AB$ . While Jander reported that the  $N$  value was equal to 2, Mori and Minegishi (1968) observed that kinetics of ettringite formation, and consequently the value of  $N$ , is dependent on the variation of temperature. Ginstling and Brounshtein (1950) defined a more precise derivation. Their equation is as follows:

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = Pt \quad (2)$$

where  $\alpha$ ,  $t$  and  $P$  are the same as in the Jander expression. This equation has the ability to consider the size of particles that participate in the interaction process. Plowman and Cabrera (1984) investigated the kinetics of ettringite formation using tri-calcium aluminate that was extracted from cement. In this instance the rate of ettringite formation, presumably at room temperature, followed the following form:

$$\left[1 - (1 - \alpha)^{1/3}\right] = (Pt - c)^{1/2} \quad (3)$$

Where  $\alpha$ ,  $t$  and  $P$  are similar parameters as were used in the Jander expression. In addition, the parameter  $c$  is an empirical constant obtained by statistical analysis. In a recent study by Brown and LaCroix (1989), the kinetics of ettringite formation was evaluated by the use of tri-calcium aluminate as a source of ettringite formation. They used a rearranged form of the equation suggested by Jander (1927) and Mori and Minegishi (1968) as follows:

$$\left[1 - (1 - \alpha)^{1/3}\right] = Pt^N \quad (4)$$

in which  $N=0.5$  implies diffusion control, while  $N=1$  implies surface area control. According to a widely accepted theory

Table 1

Reaction ratio variations for laboratory prepared ettringite by the use of the intensity of the major reflection line of ettringite (9.7 Å) in different time intervals

Time (min)	XRD intensity	Reaction ratio
0.0167	206	0.48
0.1	249	0.58
4	258	0.60
1520	357	0.83
2880	430	1.00
3000	430	1.00
6000	430	1.00

(Schwiete et al., 1966), layers of ettringite develop on the  $Al_2(SO_4)_3 \cdot 18H_2O$  or  $C_3A$  (tri-calcium aluminate) particles causing the transport of water and various ionic species to these compound surfaces to become controlled by diffusion. Among the above-suggested equations, the latter seems to be more practical because it takes into consideration both the diffusion and the surface area of the chemicals involved in the interaction. In other words, from the beginning, Eqs. (1) and (3) assume that the process of interaction is governed by the diffusion role of the elements present in the chemical interaction.

In the current research, by application of XRD analysis, the kinetics of ettringite formation is monitored for two different cases. First, the rate of artificial ettringite formation is evaluated using aluminum sulfate and calcium hydroxide at the different time intervals. Second, the kinetics of ettringite formation on stabilized soil is evaluated.

### 4. Kinetics of artificial ettringite

As previously mentioned, the theoretical basis of kinetics of artificial ettringite has already been addressed by several researchers. Most of the previous experimental studies were performed by application of tri-calcium aluminate (Mehta, 1976, Plowman and Cabrera, 1984, Older and Abdul-Maula, 1984, Gruszczinski et al., 1993). However, the two major sources of artificial ettringite formation are known to be by use of tri-calcium aluminate and aluminum sulfate.

Generally, the evaluation of a reaction ratio is an applicable way to investigate the impact of equilibrium time on the extent of ettringite formation. This is due to the fact that a reaction ratio is highly dependent on the equilibrium time (Older and Abdul-Maula, 1984, Brown and LaCroix, 1989).

In this research, the kinetics of ettringite formation is experimentally evaluated by the use of aluminum sulfate and calcium hydroxide. Table 1 shows the variations of reaction ratio for these experiments in different time intervals. The monitoring of intensity of major reflection line of ettringite is extended over 48 h to ensure that the equilibrium is attained.

In these experiments, Fig. 1 indicates the variation of reaction ratio of ettringite formation versus time. It can be observed that ettringite forms at the beginning of the mixing process and reaches equilibrium after 48 h. Analyses of the relation between reaction ratio versus time are performed by application of non-linear least square regression applied by *TableCurve Software* (Jandel Scientific TableCurve, Version 3.01, 1991). The four

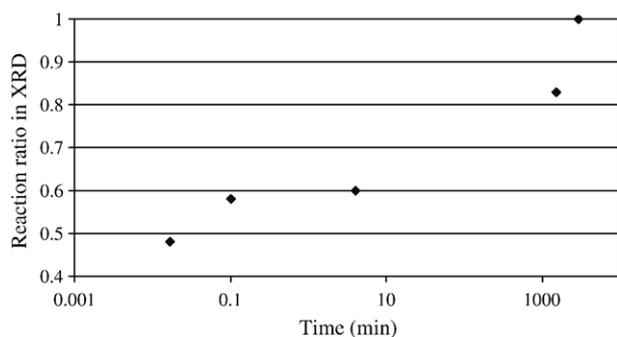


Fig. 1. Variation of reaction ratio and time (min) to establish the kinetics of artificial ettringite.

different equations suggested by Jander (1927), Ginstling and Brounshtein (1950), Plowman and Cabrera (1984), and Brown and LaCroix (1989), as was addressed, are applied to the received data. The coefficients introduced in Eqs. (1), (2), (3), and (4) are presented in Table 2. The results of XRD analysis indicate that ettringite forms right after the mixing of different compounds. Brown and LaCroix (1989) report, in the study of the kinetics of ettringite formation using tri-calcium aluminate, the appearance of ettringite peaks after 10 min. The value of  $N$  obtained in the current research (Table 2) is consistent with the value obtained by both Plowman and Cabrera (1984) and Brown and LaCroix (1989). However, the values of  $P$  indicated in Table 2 are much smaller than values reported by the above-mentioned authors.

A comparison of the results, indicated in Table 2 and previous works, shows that as the time required for ettringite formation increases the value of  $P$  decreases. It should be noted that by rearranging Eq. (4) to fit the form of Eq. (1), the coefficient of  $N$  will be  $1/0.63$  or  $1.59$  and coefficient of  $P$  will be  $0.00033$ , which are in the same order of magnitude as those of the other equation coefficients presented in Table 2. The range of values of  $N$  obtained in this study predict that, in the mixture of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ , the rate of ettringite growth will be diffusionally controlled. Other researches have used tri-calcium aluminate as a source for production of ettringite. The general mechanism of mineral transformation in both cases is similar. The faster formation of ettringite in the current research may be attributed to the faster availability of aluminum compounds and sulfate ions (when aluminum sulfate is used as a source of ettringite formation). It is also due to the higher solubility of aluminum sulfate in comparison with that of

tri-calcium aluminate (Ouhadi, 1997). In addition, the pH of prepared ettringite in a 1:10 solution was 12.3.

## 5. Kinetics of ettringite on the stabilized soil

It is reported that in marl stabilization, ettringite may form after 7 days of curing (Yong and Ouhadi, 1997). Mitchell and Dermatas (1992) report the continuation of ettringite formation for more than 20 months. In the failure reported in the lime ( $\text{CaO}$ )-treated subbase of roadways in the U.S., damage due to the ettringite formation was visible within six months following construction, and had increased severely by the end of two years (Hunter, 1988, Mitchell, 1986). As the results of both the current research and previous studies have indicated, the rate of ettringite formation in stabilized soil is much slower than that of artificial ettringite. This can be attributed to the fact that the availability and flow of pore water are necessary conditions for ettringite formation in soil stabilization (Hunter, 1988). Water movement in stabilized/compacted soil requires a substantial amount of time. In addition, water via downwards percolating or migration upwards would introduce a significant amount of sulfates, which provide a favoured condition for ettringite formation. This process also needs a substantial amount of time, which, consequently, causes a delay in ettringite formation/growth in stabilized soil.

Data presented by Mitchell and Dermatas (1992) were used for a quantitative comparison of the kinetics of ettringite formation in soil stabilization with the data presented in this paper. It was previously pointed out that the coefficients of Eqs. (1)–(4) express the features of kinetics of ettringite. Table 3 gives the coefficients for the previously addressed equations dealing with the kinetics of ettringite formation in soil stabilization. For calculation of the coefficients presented in Table 3, the data plotted in Fig. 2 were used. In this evaluation, reaction ratios are calculated with the assumption that the ettringite formed after 20 months of curing represents the equilibrium condition, with respect to the maximum quantity of ettringite which may form under these specific conditions. These data were used because of the longer period of monitoring ettringite mineral in soil stabilization.

It should be noted that by rearranging Eq. (4) to fit the form of Eq. (1), the coefficient of  $N$  will be  $1/0.904$  or  $1.1$  and coefficient of  $P$  will be  $1.2 \times 10^{-6}$ . As previously mentioned, Eq. (4) has the advantage that it takes into consideration both

Table 2  
Application of experimental results on the theoretical equations for kinetics of ettringite, based on the four proposed equations by different authors

Coefficients	Applied equations for kinetics of ettringite formation			
	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)
$P$	0.00033	0.00012	0.00034	0.0065
$N$	2	–	–	0.63
$c$	–	–	0.02	–
$r^a$	0.92	0.94	0.92	0.93

<sup>a</sup> $r$  = Coefficient of correlation.

Table 3  
Application of experimental results on the theoretical equations for kinetics of ettringite in soil stabilization, based on the four proposed equations by different authors

Coefficients	Applied equations for kinetics of ettringite formation in stabilized soil			
	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)
$P$	1.13	3.78	1.26	$4.3 \times 10^{-6}$
$N$	2	–	–	0.904
$C$	–	–	0.1	–
$r^a$	0.97	0.99	0.98	0.99

<sup>a</sup> $r$  = Coefficient of correlation.

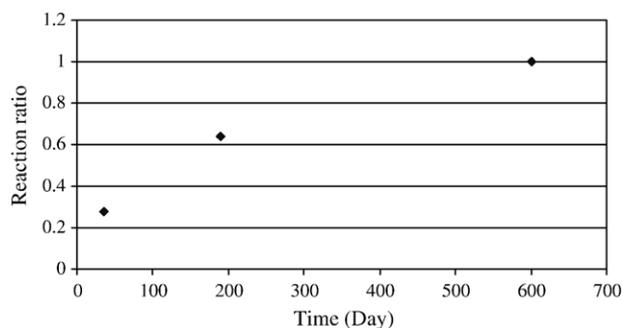


Fig. 2. Variation of reaction ratio and time calculated based on experimental data of Mitchell and Dermatas (1992).

the surface area and diffusion roles in the ettringite formation process. The range of values of  $N$  obtained by application of Eq. (4) indicates that in spite of artificial ettringite, the ettringite formation in soil stabilization is accomplished with surface area control. It may be concluded that, in soil stabilization, due to the lower solubility of aluminum compounds of clay fraction as a major source of ettringite formation, the formation of ettringite is governed by the exposed surface area of clay fraction to the high pH impact of lime. In other words, adsorption or chemisorption of ionic components present in the pore fluid phase, such as calcium and sulfate, on the surface area of the hydrated clay particles, provides proper conditions for their interaction with the aluminum compounds released in high pH reaction from clay fraction, leading to the ettringite formation.

## 6. The role of different ions on ettringite formation

To investigate the role of different ions, including aluminum compounds, sulfate and calcium, on ettringite formation and to evaluate the extent of ettringite formation in the system of aluminum compounds–sulfate/calcium compounds/distilled-water, tests were carried out on samples by varying the following constituents: aluminum sulfate, slaked lime, and distilled-water. The variation of these elements takes into account the role of change on the main elements present in the ettringite structure. For this purpose, eight different mixtures of aluminum sulfate, hydrated lime and distilled-water were prepared, equi-

librated, and monitored for the quantity of ettringite minerals by application of XRD analysis. The process of sample preparation followed the method suggested by Older and Abdul-Maula (1984).

Fig. 3 shows the variation of XRD intensity of ettringite peak versus variation of concentration of sulfate for a series of samples having 0.12 mol calcium in the mixtures. The first three major reflection lines of ettringite are plotted in this figure. As can be seen, by increasing the sulfate concentration, the intensity of ettringite peak formation increases by amounts up to 0.06 mol of added sulfate, where a maximum peak intensity is achieved. Thus, it follows that the intensity of ettringite peaks would decrease when the sulfate concentration is increased. Furthermore, when the concentration of aluminum and sulfate were fixed at 0.04 and 0.06 mol respectively, varying the concentration of calcium follows the above-described pattern for ettringite peak intensity. On the other hand, in all prepared samples it was observed that the applied concentration of Ca(OH)<sub>2</sub> was enough to increase the pH to more than 12.3, as is also addressed by previous researchers (Warren and Reardon 1994). Therefore, it can be concluded that the pH variation is not responsible for those differences in the intensity variation of ettringite peaks. Those observed patterns can be attributed to the “stoichiometric” relations of elements required for ettringite formation. In fact, it was noted that, in all these points where the maximum quantity of ettringite’s XRD peak are achieved, the concentrations of different elements, including sulfate, aluminum and calcium, corresponded exactly with the “stoichiometric” relations of the elements required for ettringite formation. Moreover, in this series of experiments, the formation of ettringite seems to be more sensitive to the variation of available sulfate and aluminum compounds, rather than that of calcium concentrations. This can be concluded by comparing the slope of the graphs and the variation range of horizontal axis’s values in Figs. 3, and 4.

The final conclusion (achieved from Figs. 3 and 4) is achievement of a higher intensity of the first basal spacing of ettringite (i.e.  $d=0.973$  nm), in comparison with other basal spacings presented in these graphs. The major basal spacing of minerals shows the highest possible intensity, and this is a characteristic of crystalline minerals (Cullity, 1976). The general

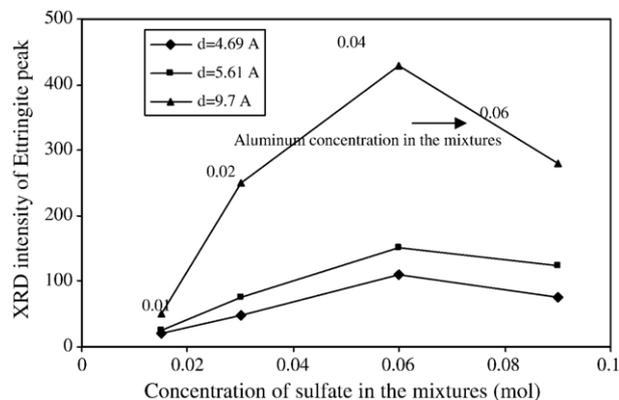


Fig. 3. Role of sulfate concentration on the quantity of ettringite formation, having 0.12 mol calcium in the mixtures.

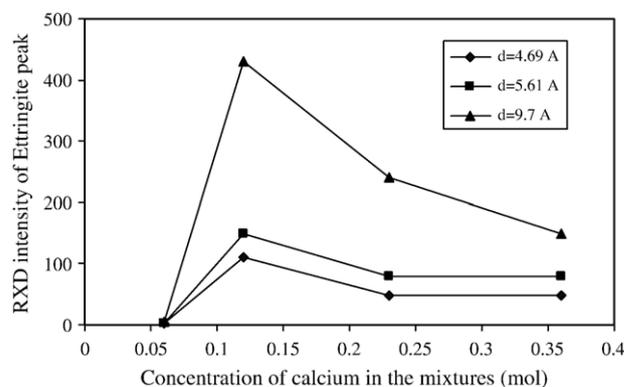


Fig. 4. Role of hydrate lime concentration on the quantity of ettringite formation, having 0.04 mol aluminum and 0.06 mol sulfate in the mixtures.

pattern achieved, in which basal spacing of  $d=0.973$  nm has the highest intensity, can be an indicator of a relatively complete crystal formation of an ettringite mineral. Therefore, the XRD diffraction follows the general pattern of a completely formed ettringite crystal.

## 7. Clay minerals contribution to ettringite formation

As previously discussed, released aluminum compounds in the clay fractions constitute the main elements for ettringite formation. To investigate the possible contribution of different clay minerals on ettringite formation, two series of experiments were performed. These experiments were performed as follows: 1) The maximum amount of releasable aluminum compounds of different clay minerals was measured through a series of digestion tests (EPS, 1979). Achieving pH less than 0.5 in this experiment made it possible to dissolve all releasable aluminum compounds from the clay fraction. It is already indicated that the releasable aluminum compounds of clay minerals is similar in low pH (less than 4) and in very high pH level (Keller, 1964). Attaining pH of 0.5 provides the conditions in which, along with solubility of clay fraction, the concentration measurement of different ionic compounds is made possible. 2) Since the quantity and the rate of releasable aluminum compounds of clay minerals is a function of pH (Keller, 1964), a set of experiments was conducted to investigate the amount of releasable aluminum compounds of clay minerals by variation of pH. In this series of tests, by application of  $1\text{ N NaOH}$  and  $1\text{ N HCl}$ , the different clay–water mixtures were adjusted to different pH levels. Following equilibrium, the solubility of aluminum ions was measured by the use of atomic absorption spectrophotometry (AAS).

Table 4 compares the results of digestion tests, given in terms of measured amounts of total released aluminum compounds of different clay minerals. The results of these experiments indicate that palygorskite has the highest ability to release aluminum compounds, in comparison with the different clay minerals studied in the current research. This confirms that the extent of ettringite formation might be highest when palygorskite is present in the clay fraction of soil, assuming all necessary conditions for ettringite formation are met.

Fig. 5 shows the SEM pictures of stabilized marl (rich in palygorskite); marl+4% lime after 7 days curing (Fig. 5a); and ettringite formation in marl+4% lime after 5 months curing (Figures b and c). The formation of the needle shaped ettringite crystals can be observed in Fig. 5b and c. Different authors showed similar ettringite structures in stabilized soil or in new

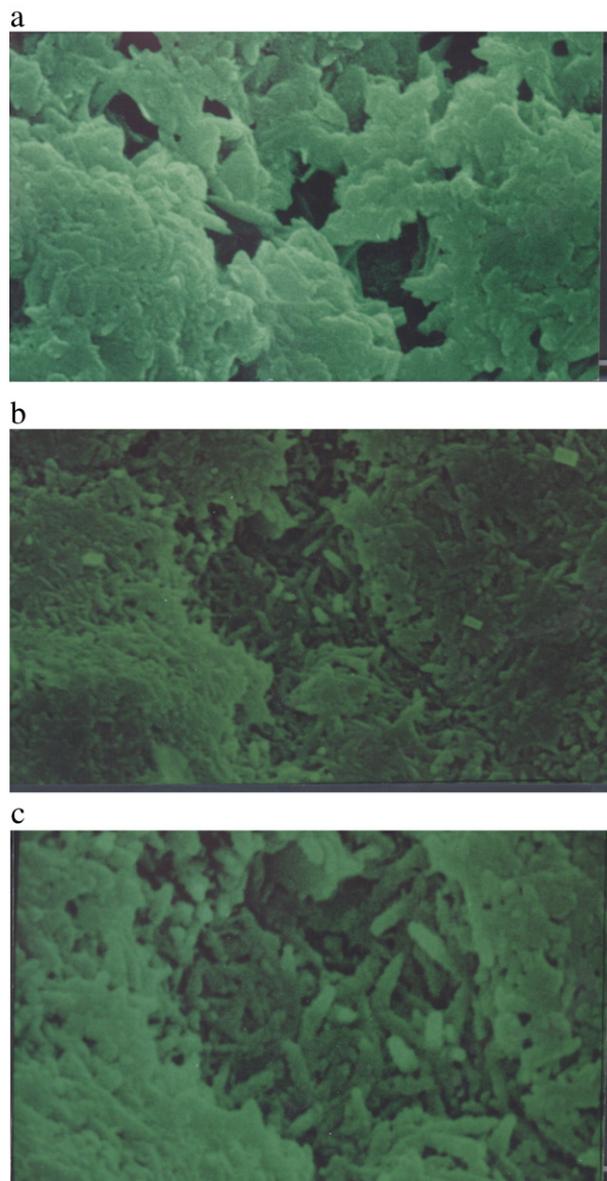


Fig. 5. SEM pictures; (a) marl+4% lime, after 7 days of curing, EHT=15.3 kV, Magnification=10,000; (b) marl+4% lime, after 5 months of curing, EHT=15.3 kV, Magnification=10,000; (c) marl+4% lime, after 5 months of curing, EHT=15.3 kV, Magnification=20,000.

cement like stabilizer (Kamon and Nontananandh, 1991; Mitchell and Dermatas, 1992; Rajasekaran, 2005). As the figure shows, the ettringite crystals are not very large, ranging from  $0.5\ \mu\text{m}$  to  $1\ \mu\text{m}$  in length and  $0.1\ \mu\text{m}$  to  $0.2\ \mu\text{m}$  in width.

## 8. Fluid retention during ettringite formation

The availability and flow of pore water is the single most important factor controlling lime-induced heave. It is shown that without an abundance of water, ettringite cannot form. In other words, ions must migrate through the soil in pore water solutions to generate the observed heave magnitudes (Hunter, 1988). Therefore, the precise evaluation of the long-term behaviour of stabilized soil with regard to ettringite formation will be

Table 4

The results of digestion testing on different clay minerals

Clay minerals	Cations monitored in digestion experiments (meq/100 g soil)					
	Na	K	Mg	Ca	Si	Al
Palygorskite	$80\pm7$	$51\pm5$	$321\pm21$	$9\pm0.8$	$14\pm1$	$578\pm54$
Sepiolite	$2\pm0.2$	$10\pm1$	$1012\pm90$	$1\pm0.1$	$80\pm7$	$9\pm1$
Marl	$305\pm20$	$12\pm1$	$260\pm20$	$370\pm25$	$23\pm2$	$270\pm20$
Illite	$8\pm0.8$	$16\pm1$	$139\pm10$	$62\pm6$	$18\pm1$	$288\pm20$
Kaolinite	$5\pm0.8$	0	$0.3\pm0.1$	0	$16\pm1$	$88\pm7$

accomplished by evaluating the soil's fluid retention, and by assessing the minerals' transformation effects on this retention potential. In fact, these properties of soil can provide access to the sulfate and water from the environment to extend mineral transformation. It is worth mentioning that, in the failure reported in soil stabilization in the U.S., the high concentration of sulfate due to the water migrating upwards is known as one of the important mechanisms for availability of sulfate to stabilized soil (Mitchell and Dermatas, 1992). Therefore, the evaluation of fluid retention/suction is a helpful way to study the availability of water and sulfate to stabilized soil. On the other hand, as was discussed before, the growth of ettringite, as a mineral which forms after soil stabilization, occurs slowly. Therefore, the effect of mineral transformation on the retention potential of soil is also of interest.

To investigate the role of ettringite formation on soil solute retention, artificial ettringite was compacted in a suction mold for measurement of fluid retention potential. To provide similar initial conditions to other suction experiments, the compaction characteristics of ettringite were measured, using a Harvard Miniature apparatus. Performing compaction testing by use of a Harvard Miniature apparatus revealed the optimum water content of ettringite to be 78% and its maximum dry density to be  $0.83 \text{ Mg/m}^3$ . The optimum water content and maximum dry density for marl sample was 14% and  $1.97 \text{ Mg/m}^3$ , respectively. These compaction characteristics were used to compact samples in a suction mold by application of a static loading, as previously addressed in the Materials and methods section. For these experiments, Fig. 6 compares the fluid retention characteristics of pure artificial ettringite with that of a marly sample.

As Fig. 6 shows, the fluid retention potential of ettringite is noticeably high. For instance, as can be seen in Fig. 6, in all different pressures applied on samples, the fluid retention of ettringite is significantly higher (as much as 400%) than that of the marl sample. The fluid retention potential indicates that the soil exerts a force to take in water and electrolytes (Yong and Warkentin, 1975). Even though the available sulfate will be utilized to form ettringite, as ettringite grows in stabilized soil, its presence also enhances the water retention of soil. This increasing in water retention potential of soil (due to the ettringite formation) can provide more quantity of sulfate from the

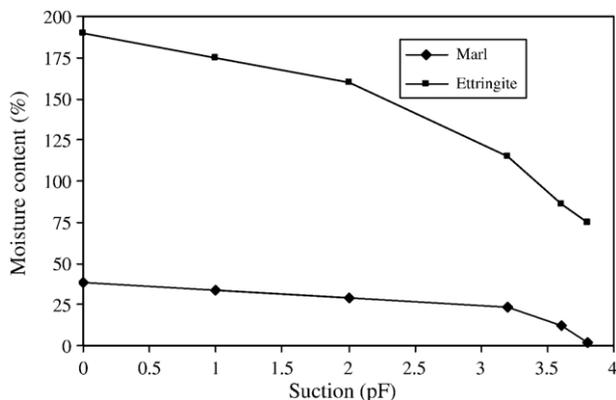


Fig. 6. Fluid retention curve for artificial pure ettringite in comparison to that of marl sample.

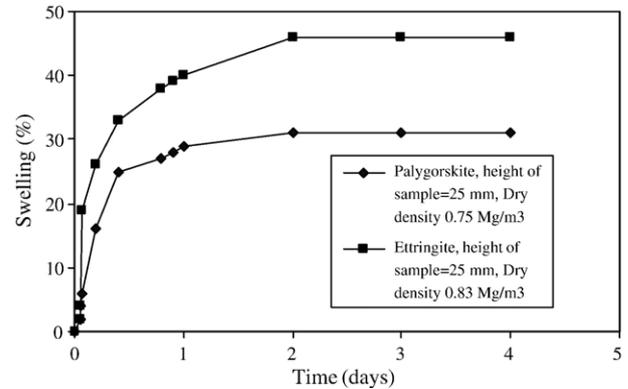


Fig. 7. Free-swelling variation of pure ettringite using Oedometer testing.

available environment for further interaction with the clay fraction of soil. Therefore, in one aspect, formation of ettringite decreases available sulfate while in another aspect, its formation changes the soil–water potential, causing the sample to exert more force to take in water–sulfate solution derived from lower soil strata. Consequently, water migrating upwards would again introduce noticeable amounts of sulfates to the stabilized soil or to the ettringite nuclei.

## 9. Free-swelling measurement of ettringite

For further investigation of the role of ettringite on the stability of soils, the free-swelling measurements of artificial ettringite were evaluated. For this purpose, artificially formed ettringite was compacted to its maximum dry density and optimum water content in an Oedometer testing apparatus. Fig. 7 shows the free-swelling measurement of pure ettringite in comparison with that of a palygorskite sample. By and large, there exist two major schools of thought regarding the expansion associated with ettringite formation. These are the crystal growth theory and the swelling theory (Cohen, 1983). While the first theory relates the expansion caused by ettringite to its crystallization pressure, the second attributes the expansion to the water-adsorption and swelling characteristics of ettringite (Mehta, 1973). The very high swelling of ettringite, which is in the order of 50%, adds strength to the arguments of the latter school of thought, in that expansion produced by ettringite formation is mainly due to its swelling or water-adsorption characteristics. This interpretation is in good accordance with the high fluid retention characteristics of ettringite, as previously addressed. Zeta potential evaluation showed that the artificial ettringite holds a negative charge. This mechanism is associated with the water holding capacity of ettringite, as was shown in Fig. 6. Here, following ettringite formation, the fluid retention of soil increases leading to more water in soil structure. Consequently, due to the high swelling characteristics of ettringite and its high water adsorption, it swells. This leads to the stabilized soil failure.

## 10. Conclusions

The main conclusions derived from this research can be summarized as follows: 1) The kinetics of artificial ettringite

formation using aluminum sulfate follow the pattern of its formation when tri-calcium aluminate is used as a source of ettringite formation. Even though ettringite forms faster in the former case, the rate of ettringite growth is diffusionally controlled in both cases. In soil stabilization, it was observed that the rate of ettringite formation is controlled by the surface area in chemical interaction. 2) Ettringite shows very high water retention potential. Therefore, as ettringite grows in stabilized soil, its presence enhances the water retention of soil, causing the sample to exert more force in order to take in water–sulfate solution from lower soil strata. 3) Laboratory prepared ettringite showed a high swelling, in the order of 50%. This behaviour is in accordance with the noticeable water retention of ettringite, which seems to be a major phenomenon for ettringite-induced failure in stabilized clayey soils.

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