Geotechnical Engineering Journal of the SEAGS & AGSSEA Vol. 46 No.4 December 2015 ISSN 0046-5828

Geochemistry in Geotechnical Engineering Problems: Ettringite as Case Study

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ABSTRACT: Chemical and environmental changes in soils can affect their geotechnical properties, a fact that is increasingly acknowledged in recent years. Geochemistry offers a wide variety of modelling and experimental tools that can be used to study related problems. An increased number of researchers utilize geochemical modelling and spectroscopy to study changes in soil chemistry in the geotechnical field. This study illustrates the application of this methodology to a significant geotechnical problem, ettringite-induced heave in stabilized clays. Geochemical modelling was used to estimate the ranges of dissolved constituents that are needed to make ettringite, i.e. Ca, Al and SO_4, as well of silica, which is known to influence indirectly ettringite stability. The study illustrates that systematic testing of ion activities in stabilized soils to generate data for modelling is needed, as well as understanding of the relationship of these activities to soil mineralogy, the type of stabilizer and time. Spectroscopy, such as X-ray Diffraction, can aid in this regard by providing an understanding of soil mineralogy, both qualitative and quantitative.

KEYWORDS: Geochemistry, Geochemical modelling, Mineralogy, Ettringite

1. INTRODUCTION

Geochemistry may be broadly defined as the study of geological problems that involve chemical changes (Clarke, 1924). More specifically, geochemistry focuses on the distribution and reactions of elements in minerals, soils and rocks, as a function of environmental conditions. Temperature, pressure, the presence and composition of liquids and gases in the subsurface are some of the variables that influence chemical reactions in rocks and soils and are included in the study of geochemistry.

In the past, geochemistry typically focused on problems involving the deeper parts of the earth's crust (sedimentary geochemistry), mining (exploration geochemistry) and the biosphere (organic geochemistry). In recent years, environmental geochemistry has emerged as a new field that utilizes the same principles and tools to study problems such as water quality and movement of chemicals in soil, water and even human tissues.

Geotechnical engineering, on the other hand, is also a study of soil and rock, however primarily from the mechanical point of view, as it relates to human activities. A fundamental difference between most geotechnical and traditional geochemistry problems is the time scale; geochemistry may study changes that occur over geologic time (tens of thousands of years), while the time scale of geotechnical engineering problems typically extends to the service life of human construction, i.e. 100 (roads, foundations) to maximum 200 (dams, levees) years. In addition, the geotechnical engineer often assumes that soil properties will remain constant over time, while geochemists and soil scientists will investigate how they will change as a function of environmental conditions (DeJong et al., 2015).

Because of these two fundamental differences (focus on mechanics vs. chemistry and time scale), there has been little overlap between geochemists and geotechnical engineers. A classic example of such overlap is the pioneering work of J.K. Mitchell at Stewart Ave. (Mitchell, 1986), which introduced the effects of short-term chemical and mineralogical changes on engineering properties of soils. Since then a substantial body of literature emerged in order to further investigate ettringite-induced heave in lime-stabilized soils (Little et al., 2010). More recently, interest in soil treatment using enhanced microbial activity has also re-ignited engagement of geotechnical engineers in soil chemistry research (e.g. van Paassen et al., 2010, Al Qabany et al., 2012).

Fields closely related to geotechnical engineering, such as cement and concrete technology, have benefited enormously from the adoption of analytical and modelling methods traditionally employed in geochemistry (Scrivener and Nonat, 2011). Geoenvironmental engineering is already moving in this direction, as it overlaps with certain aspects of environmental geochemistry. Ultimately, greater integration into more traditional geotechnical engineering (where applicable) can provide greater flexibility in research and practice. Ettringite-induced swelling is perhaps the most prominent example of geochemistry application in geotechnical engineering; both microstructural techniques and thermodynamic models have been employed to date to study this problem. Accordingly, this paper will review the ettringite problem as a case study that illustrates the application of geochemistry tool in geotechnical engineering.

2. BACKGROUND ON ETTRINGITE

Certain cement or lime-stabilized clays still undergo swelling primarily due to the formation of the mineral ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$). This heave is known as ettringite-induced heave and has caused damage to civil infrastructure in various states, including Texas, Iowa, California, Nevada, Oklahoma and Louisiana (Mitchell 1986; Little and Graves 1993; LTRC 2003; Lee et al. 2004; Chen et al. 2005; Puppala and Cerato 2009), all of which are areas with naturally occurring sulfate-bearing clays. While ettringite had been known for years to cause cement cracking (Taylor et al., 2001), it was not demonstrated that it was an active expansion mechanism in lime- and cement-stabilized clayey subgrades until 1984, when pavement heave distress was noted on Stewart Ave., Las Vegas, Nevada. In a classic keynote paper, Mitchell (1986) demonstrated using qualitative X-ray Diffraction (XRD) analyses that ettringite and the isostructural mineral thaumasite ($Ca_3Si(CO_3)(SO_4)(OH)_6\bullet 12(H_2O)$) were associated with surface heaving. Mitchell and Dermatas (1992) and Dermatas (1995) followed up with studies that showed that the rates of ettringite formation and thus the rate of heave manifestation were different in kaolinite and montmorillonite clays.

Since then, the role of ettringite formation in swell of stabilized clays has been widely studied both in forensic investigations and in laboratory-controlled swell tests (Little and Graves 1993; LTRC 2003; Lee et al. 2004; Puppala et al. 2004, 2005; Chen et al. 2005, Yoon et al., 2007). The mechanism of ettringite formation in stabilized clays is chemically well known: alumina dissolves from clay minerals at high pH and reacts with the Ca source of lime/cement and ground sulfates to form the ettringite mineral. It has been hypothesized that ettringite expands in the presence of water, so that hydration instead of mineral formation contributes to the induced pressures (Mehta and Wang 1982). Little et al. (2010) concluded that both mechanisms are likely responsible for ettringite-induced expansion and that external water intrusion into the matrix is a necessary precondition for the manifestation of heave. There are several factors that affect swell or cracking phenomena as a result of ettringite formation: the amount of sulfates and sulfate type; crystal size (affected by temperature); the rate of ettringite formation; soil moisture content and dry unit weight; confining pressure; and others. Given the complexity of the problem, it is difficult to develop defensible guidelines when designing the stabilization of sulfate-rich subgrades. Several studies have been published to this end, and despite a convergence towards a lower threshold of 2,000-3,000 mg/kg sulfate as the highest acceptable concentration (Little et al. 2010), most authors conclude that the soil susceptibility to ettringite formation should be evaluated on a case-by-case basis, as reaction rates could not be captured. Furthermore, the influence of all other aforementioned factors has not been considered in a systematic way.

Hunter (1989) suggested a sulfate threshold of 5,000 mg/Kg based on the forensic investigation at Stewart Ave. Mitchell and Dermatas (1992) reported swell down to 3,000 mg/Kg SO_4. Puppala et al. (2005) reported swell in kaolinite clay that was compacted with soluble sulfates at 2,500 mg/Kg but noted that the reason for swelling was due to swell reactions dominating pozzolanic reactions that were occurring simultaneously. National Lime Association guidelines (2000) acknowledged the role of early solubilization and recommended that soils are blended and compacted at a moisture content 5% wet of optimum, to achieve early formation of ettringite during the compaction stage and thus avoid heave at a later stage. Phillips et al. (2003) divided soils into three categories according to their sulfate level: <1500 mg/Kg, 1500-5000 mg/Kg and >5000 mg/kg, but noted that low-sulfate soils may still cause heave problems upon lime treatment. The Texas Department of Transportation currently recommends a 2,000 mg/Kg threshold for acceptable risk (Little and Nair, 2009).

These recommended sulfate levels apply to soils stabilized with lime only, while other pozzolanic products may lead to different swell behavior. For example, Wang et al. (2003) suggested the use of ground granulated blast furnace slag (GGBFS), class C fly ash, silica fume and amorphous silica in high-sulfate soils, while Harris et al. (2006) found that the addition of GGBFS to lime could eliminate ettringite-induced swell in soils with sulfates exceeding 10,000 mg/kg. Chrysochoou et al. (2012) observed no swell in dredged sediments stabilized with Cement Kiln Dust with sulfate levels exceeding 70,000 mg/kg. Even though the mechanism of swell suppression has been hypothesized to be the change in the Al/Si ratio that reduced the stability field of ettringite (Little et al., 2005), Harris et al. (2006) could not definitively delineate it and stressed that more research was needed in this area.

This review, with additional analyses, will focus on the geochemistry of the ettringite problem, i.e. the factors influencing its formation and stability in stabilized soils.

3. GEOCHEMICAL MODELING

Ettringite (Ett) forms according to the reaction

$$6Ca^{2+} + 2Al(OH)_4^{-} + 3SO_4^{2-} + 4OH^{-} + 26(H_2O) \rightarrow Ett \tag{1}$$

whereby the soluble components are derived from the stabilizer (Ca for lime, Ca and Al for other cementitious stabilizers), the clay mineral (Al) and gypsum or another sulfate-bearing mineral (SO_4). Using lime, kaolinite and gypsum as examples, we may write:

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+} + 2OH^{-} \tag{2}$$

$$Al_2Si_2O_5(OH)_{2(s)} + 4H^{+} + H_2O \rightarrow 2Al(OH)_4^{-} + 2H_4SiO_4^{0} \tag{3}$$

$$CaSO_4 \cdot 2H_2O_{(s)} \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{4}$$

In a multicomponent system (i.e. with four components Ca, Al, Si and SO_4), there are several additional possible phases that can precipitate from solution, for example monosulfate ($Ca_4Al_2SO_4(OH)_{12} \cdot 6H_2O$) and gibbsite ($Al(OH)_3$). In addition, dissolved silica forms calcium silicate hydrates (CSH), consuming partially the available calcium. Given the aforementioned suppression of ettringite stability due to silica, its reactions should be included in the model. Ions such as sodium (Na^+) also influence the stability field of ettringite (Damidot and Glasser, 1993), so that ideally, a geochemical model should consider all major ions in order to determine the stability of ettringite under field conditions. In this regard, choosing a comprehensive and internally consistent thermodynamic database is important for proper interpretation of results (Little et al., 2010). A thermodynamic database is essentially a compilation of chemical reactions and the associated thermodynamic data, i.e. solubility products, Gibbs free energies and enthalpies. There are two major available thermodynamic databases in the cement literature, as reviewed by Damidot et al. (2011), which are also suitable to model cementitious systems such as stabilized clays. In this study, thermodynamic data by Blanc et al. (2010a and 2010b) was used to modify the Visual Minteq 3.0 database (Gustafsson, 2010). All reactions and stability constants use are shown in Table 1. It should be noted that log Ks are consistent with species used in the Minteq geochemical code and the shown reactions.

Table 1 Thermodynamic reactions considered
(source: Blanc et al. (2010a, 2010b)

Phase	**Reactions**	**Log K**
CSH1.6	$Ca_{1.6}SiO_{3.6}(OH)_{1.54} \cdot 1.81H_2O + 3.2H^+ \rightarrow 1.6Ca^{2+} + 2.18H_2O + H_4SiO_4$	28.00
CSH1.2	$Ca_{1.2}SiO_{3.2}(OH)_{1.08} \cdot 1.52H_2O + 2.4H^+ \rightarrow 1.2Ca^{2+} + 1.26H_2O + H_4SiO_4$	19.30
CSH0.8	$Ca_{0.8}SiO_{2.8}(OH)_{0.6} \cdot 1.24H_2O + 1.6H^+ \rightarrow 0.8Ca^{2+} + 0.34H_2O + H_4SiO_4$	11.05
Portlandite	$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O$	22.81
Gibbsite	$Al(OH)_3 + 3\,H^+ \rightarrow Al^{3+} + 3H_2O$	7.74
Diaspore*	$Al(OH)_3 + 3\,H^+ \rightarrow Al^{3+} + 3H_2O$	6.87
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O + 12H^+ \rightarrow 2Al^{3+} + 6Ca^{2+} + 38H_2O + 3SO_4^{2-}$	56.97
Monosulfate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O + 12H^+ \rightarrow 2Al^{3+} + 4Ca^{2+} + 18H_2O + SO_4^{2}$	73.07
Gypsum	$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.61
Hydrogrossular	$Ca_3Al_2(OH)_{12} + 12H^+ \rightarrow 2Al^{3+} + 3Ca^{2+} + 12H_2O$	80.32
C4AH13	$Ca_4Al_2(OH)_{14} \cdot 6H_2O + 14H^+ \rightarrow 2Al^{3+} + 4Ca^{2+} + 20H_2O$	103.65
Straetlingite	$Ca_2Al_2SiO_2(OH)_{10} \cdot 2.5H_2O + 10H^+ \rightarrow 2Al^{3+} + 2Ca^{2+} + 10.5H_2O + H_4SiO_4$	49.66

* only included in one model, as described in text

Data of ion activities in clays stabilized with cementitious materials are generally scarce and limit the application of thermodynamic models to assess the evolution of the stable phase assemblage over time. Little et al. (2005) utilized two approaches to this end: directly measuring ion activities in solution at two pH values, 7 and 12. The extraction methodology, analyses methods and time frame are not given in the paper, but clearly represent a point in time, likely early in the stabilization process. Taking this approach to the next level, it would be necessary to monitor ion activities in solution over time, and to construct a kinetic model for mineral dissolution and precipitation. In the absence of such a comprehensive dataset, we will consider here some broad analyses of the problem.

The first and most important parameter to consider is the sulfate concentration. This is a problematic issue in the pertinent literature, as pointed out by Little et al. (2010), because of the measurement method for sulfate. This is based on a water extraction method using a liquid-to-solid ratio of 10:1 or 20:1, and the measured amount (which depends on the amount of water used) is then translated to mg/Kg of solid. For example, Little et al. (2005) used sulfate activities in solution that ranged between 13 and 61 mmol/L, corresponding to 3,000 mg/Kg and 10,000 mg/Kg sulfate in soil. However, the maximum sulfate aqueous solubility in the Ca-Al-SO_4-H_2O system is controlled by gypsum (Damidot and Glasser, 1993). Figure 1 shows the SO_4^{2-} concentrations in equilibrium with gypsum as a function of pH.

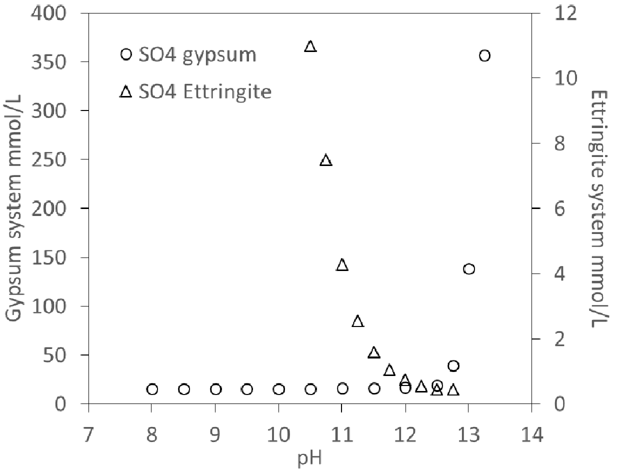

Figure 1 Modeled SO_4^{2-} concentrations in equilibrium with a solution containing only gypsum and only ettringite

In the pH range 8 to 12.5, the two ions are equal in order to maintain charge balance, and their concentration ranges from 15.9 mmol/L at pH 8 to 19.4 mmol/L at pH 12.5. Above that value, portlandite becomes saturated and precipitates, at which point the sulfate concentration increases to counter-balance the Ca consumption by portlandite. However, charge balance is not maintained in this scenario, which indicates that the model prediction on the basis of mass balance is inaccurate. In any case, the upper limit for dissolved sulfate at the saturated lime pH of 12.4, which is the criterion for optimum lime dosage, is 18.7 mmol/L if it is in equilibrium with gypsum. When other sulfate-bearing phases such as ettringite precipitate, the value is even lower, ranging from 11 mmol/L at pH 10.5 to 0.45 mmol/L at pH 12.5. Thus, it is not realistic to model an aqueous system in equilibrium with total, solid-based sulfate concentrations, but rather with the upper gypsum solubility for a worst-case scenario.

The next crucial parameter for the stability of ettringite is the alumina concentration, for which there is even less available data in the literature. Little et al. (2005) provide a range of ion activities for alumina between 0.7 and 14 mg/L in a pH 12 extract. Kunagalli (2004) reported a large dataset for Al in pH 12 extracts that reached up to 1,400 mg/Kg; however, the liquid-to-solid ratio and the extraction method were not specified, so that conclusions are difficult to draw. Andersson et al. (1989) reported pore solution composition data for a variety of cements, including standard Portland cement, high alumina and sulfate-resistant cement, slag and fly ash cement; most were in the range 5-30 mg/L, except high alumina cement, which had a pore solution concentration of 2,800 mg/L Al. In order to frame the range of possible Al concentrations in solution, three modeling scenarios were considered, as shown in Table 2. These three models represent the three most relevant scenarios for kaolinitic soils, i.e. kaolinite present as an infinite source of Al (model 1), kaolinite dissolving in small increments and reacting with lime (model 2) and kaolinite dissolving in small increments and reacting with lime and gypsum. The results for the dissolved Al^{3+} (sum of all Al species in solution) are shown in Figure 2.

Table 2 Input of geochemical models for Al solubility evaluation

Model 1	Model 2	Model 3
Kaolinite infinite	Kaolinite 0.05 mol/L	Kaolinite 0.05 mol/L
Ca^{2+} 20 mM	Lime 0.1 mol/L	Lime 0.1 mol/L
Al^{3+} 0.1 mM		Gypsum 0.058 mol/L
Initial H_4SiO_4 0.1 mM	Initial Al, Si, Ca, SO_4 0.1 mM	Initial Al, Si, Ca, SO_4 0.1 mM
No mineral precipitation	Precipitation allowed	Precipitation allowed

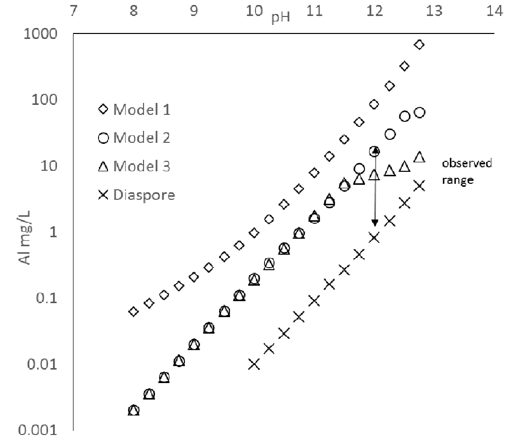

Figure 2 Total dissolved Al^{3+} in three modeling scenarios and in equilibrium with diaspore

In the first model, kaolinite is an infinite phase, i.e. a solid that is in equilibrium with the solution under all conditions. Thus, kaolinite the phase that controls Al solubility and produces the highest concentrations at the entire pH range considered, reaching 322 mg/L at pH 12.5. In the second model, a finite amount of kaolinite and lime dissolve in solution, and a new solid phase assemblage is allowed to form under equilibrium conditions. In this case, Al solubility is controlled by gibbsite, which is stable throughout the entire pH range considered. Straetlingite is also predicted to be stable in the pH range 10.75-12.75, but does not seem to affect Al solubility. In the pH range 12-12.5 Al solubility increases rapidly from 16 to 57 mg/L, which agrees with some of the observed values for Portland cement and the upper range of activities reported by Little et al. (2005) for pH 12. In model 3, gypsum is added on top of the model 2 input and thus sulfate-bearing phases are allowed to precipitate. In this case, ettringite further reduces Al solubility when it becomes stable at pH 10 in the model considered. At pH 12, Al solubility is predicted at 8.5 mg/L. The lower values of reported Al solubilities are not captured by the kaolinite model, except when considering the Al-polymorph diaspore. While is this predicted to be thermodynamically more stable (Peryea and Kittrick, 1988), it is rarely found in alkaline environments and was thus omitted from all other models. Models that include other clay minerals, such as montmorillonite, and a larger suite of ions are needed to capture the full behavior of Al in stabilized clays.

Next, Ca solubility is considered. Given that lime is highly soluble, Ca solubility is either controlled by portlandite at pH 12.4 and higher, or by CSH/CAH phases. Figure 3 shows the predicted Ca solubilities in models 2 and 3, along with solubility of a portlandite-only solution. It should be noted that no carbonate (i.e. calcite precipitation) was considered in any of the models and this is an additional parameter to include for more comprehensive model development.

When only portlandite is present in the system, Ca is predicted to be entirely soluble until pH 12 and when portlandite precipitates its solubility is reduced to 580 mg/L. These values are too high compared to the observed values in the literature. The consideration of CSH/CAH precipitation in models 2 and 3 yields much improved agreement with reported values in lime stabilized soils. Lower solubilities are controlled by CSH0.8 and straetlingite precipitation, which is predicted to be dominant in the absence of sulfate, while ettringite precipitation increases Ca solubility above pH 11 in model 3. In the pH range 10-11, there is overlap between models 2 and 3, likely because in this range the system is most dynamic, with several phases changing stability.

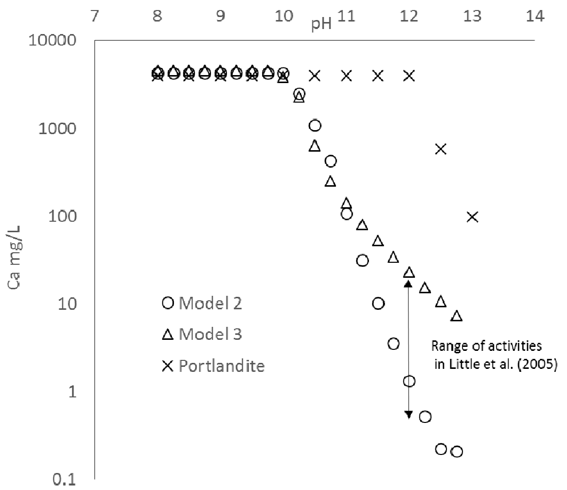

Figure 3 Total dissolved Ca^{2+} in two modeling scenarios and in equilibrium with portlandite

Finally, the activity of silica in solution is important, since it indirectly influences ettringite stability. The predicted Si solubility on the basis of the three models (Table 2) is shown in Figure 4. In models 2 and 3, Si solubility in alkaline pH follows the Al patterns, which points to straetlingite as a solubility-controlling phase. Two other important observations are that around pH 12, the predicted Si solubilities change very drastically with pH. For example, in model 2 the dissolved Si concentration is predicted to be 100 mg/L at pH 11.75, 200 mg/L at pH 12, 400 mg/L at pH 12.25 and 900 mg/L at pH 12.5. Given the limited accuracy in measuring both pH and dissolved Si, comparison of model and actual data is difficult. The comparison with the data provided by Little et al. (2005) shows that the model is close in some cases, but not at all in others. Blanc et al. (2010a) show that the dissolved Si depends on dissolved Ca in alkaline cements. For the Ca concentrations considered in this study, reported Si concentrations were in the range 10-200 mg/L, which is consistent with the values reported here at pH 12.

Based on this analysis, the stability of ettringite in kaolinitic soils as a function of sulfate concentration and pH may then be considered for some limited scenarios. We will consider the worst-case scenario, with maximum Al and Ca concentration at pH 12.5 in solution, i.e. 57 and 580 mg/L respectively. The stability diagrams were then built for two cases, a Si concentration of 10 and 200 mg/L. The results are shown in Figures 5a and 5b.

The results show that ettringite becomes stable at pH 10.5 above a SO_4 concentration of 6 mM and this result is affected very little by the Si concentration. Below that pH value, there is no sulfate concentration for ettringite stability for the Ca and Al concentrations considered. The threshold sulfate concentration for ettringite stability decreases by one order of magnitude for each pH unit up to pH 12.25, at which a minimum is achieved. At pH 12.5, CSH1.6 becomes stable and scavenges Ca, and hydrogrossular scavenges Al, limiting ettringite stability. Increasing the available Si concentration from 10 to 200 mg/L limits the ettringite stability domain, but only in the pH range 10.5-12.5. The stable phase composition at very low concentrations also changes, limiting gibbsite and favoring CAH phases (Figure 5b). Further increasing the available Si concentration to 500 mg/L only has a small effect in the ettringite stability domain, mostly around pH 12.5. Thus, ettringite is overall stable for a wide range of sulfate concentrations in the worst-case scenario considered. This result is similar to the stability diagrams developed by Little et al. (2005) for specific soils, even though the CAH/CSH phases considered were not the same, i.e. a different database was used.

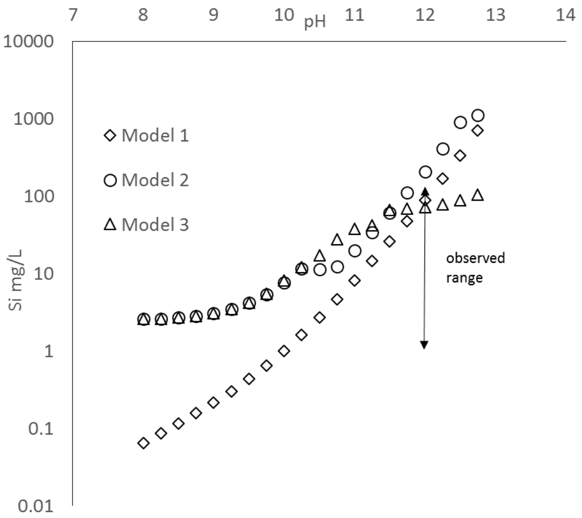

Figure 4 Total dissolved Si in three modeling scenarios

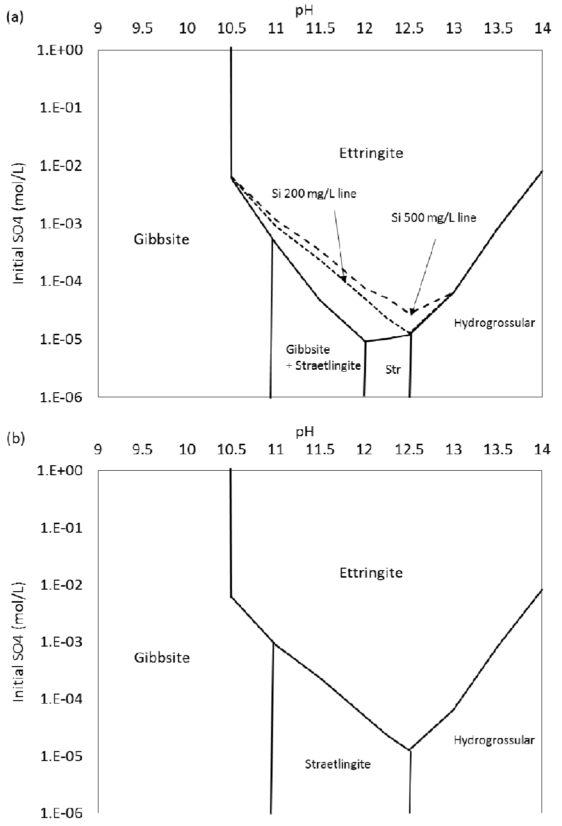

Figure 5 Thermodynamic phase diagrams for worst-case scenario and two Si concentrations (a) 10 mg/L) (b) 200 mg/L

Similarly, a variety of scenarios may be considered on the basis of the observed Al, Ca and Si concentrations that can be measured in soils as a function of time. Ideally, the objective is to understand solubility controls as a function of soil mineralogy. This would involve a mode detailed understanding of the thermodynamics and kinetics of dissolution for more complex clays that are found in real soils, e.g. mixed- layer smectites. The role of adsorption and ion exchange reactions and the activity of water are also geochemical processes to consider in real soils. Ultimately, geochemical modeling in combination with soil characterization can be used to build a robust framework to predict ettringite stability.

4. SPECTROSCOPY

Literature data suggests that ettringite formation in lime-stabilized clays may last from a few days to several months, depending on the solubility of the sulfate source and the type of clay mineral (Little et al., 2010). Swell development is one parameter that may be used to assess reaction kinetics, assuming that continued expansion is due to ongoing ettringite formation. This is not necessarily the case, for example Mitchell and Dermatas (1992) reported that ettringite formation led to expansion in kaolinite-sand mixtures, but not in montmorillonite-sand mixtures, both stabilized with lime. Analysis methods that probe the mineralogy of soil directly are a viable alternative to using macroscopic swell as a proxy for reaction assessment. X-ray Diffraction (XRD) is the most popular method utilized to this end, while Differential Scanning Calorimetry (DSC) has also been employed to specifically detect the quantify the amount of ettringite formed (Little et al., 2005). DSC is suitable to detect very low amounts of ettringite, in the range of 1%, but only quantifies one mineral at a time.

XRD is typically employed in a qualitative fashion, e.g. in Mitchell and Dermatas (1992) and Puppala et al. (2005). To illustrate the comparison of qualitative and quantitative analysis on the ettringite problem, the following test was conducted: A 50-50 wt.% kaolinite-quartz blend was mixed with 5% quicklime, 1% fine corundum (α-Al_2O_3) sand as source of soluble alumina and 3% anhydrite ($CaSO_4$) at 40% water content. The mixture was analysed by XRD at 0, 7, 28 and 90 days of curing time and the resulting patterns are shown in Figure 6. The patterns indicated that gypsum was the only sulfate-bearing phase observed at 0 and 7 days cure. At 28 days, both gypsum and ettringite were present, and at 90 days only ettringite was observed at a higher intensity. Portlandite ($Ca(OH)_2$) was present at all times, which indicates residual potential for further reaction with kaolinite.

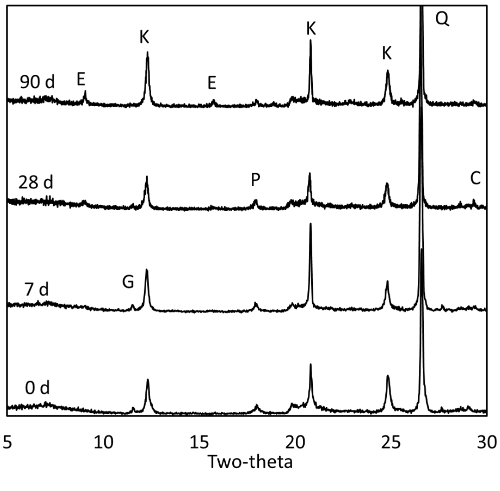

Figure 6 XRD patterns of quartz-kaolinite blend stabilized with 5% lime, 1% corundum and 3% anhydrite at 0, 7, 28 and 90 days curing (Q: Quartz, K: Kaolinite, C: Calcite, P: Portlandite, G: Gypsum, E: Ettringite)

The QXRD analysis (Figure 7a) confirmed that gypsum decreased from 5.5% at 0 days to 2.1% at 28 days and was not detected at 90 days curing. Ettringite was detected at 4.7% at 28 days and 7% at 90 days. This constitutes a relatively fast conversion of gypsum to ettringite, which is due to the presence of the soluble alumina source in the experiment. When the experiment was repeated with kaolinite only, ettringite could only be detected at very high sulfate levels up to 28 days of curing due to the slower dissolution of kaolinite compared to corundum (data not shown). Similar results were obtained by Puppala et al. (2005). The XRD detection limit of about 1 wt.% and the difficulty in the quantification of phases around the detection limit are the most important limitations of QXRD. DSC and infrared spectroscopy alre alternative methods that can be used when ettringite and other phases are very low in content.

The accuracy of the QXRD results may be assessed by conducting a mass balance on the sulfate contained in the quantified minerals and the sulfate in the added anhydrite, as shown in Figure 7b. The QXRD method over- underestimated the sulfate content by approximately 25% at different curing times. The larger errors are associated with the higher mineral contents (gypsum at 0 days and ettringite at 90 days), while the intermediate times had 7% and 14% error. This is most likely due to sample variability, rather than the QXRD method itself, and this is also evidenced in the fluctuation of the kaolinite content, which did not show a consistent trend. Chrysochoou (2014) presented a similar study in the absence of sulfate and showed that taking average results from triplicate XRD patterns yielded variations that were lower compared to Unconfined Compressive Strength (UCS) test results for lime-treated kaolinite specimens. Thus, triplicates and mass balances are recommended to increase the confidence in the method results.

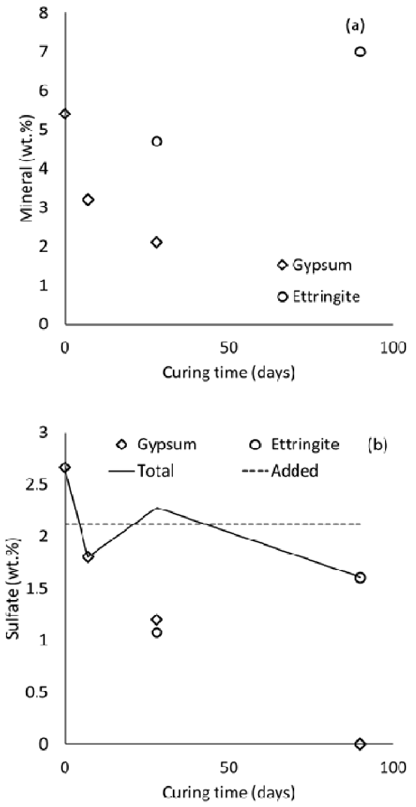

Figure 7 Gypsum and ettringite concentrations quantified in the XRD patterns of Figure 6
(a) and mass balance on sulfate, using the QXRD amounts of ettringite and gypsum compared to the added anhydrite
(b) (total line equals gypsum+ettringite, i.e. diamond + circle)

5. CONCLUSIONS

Chemical and environmental changes in soils can affect their geotechnical properties, a fact that is increasingly acknowledged in recent years. Geochemistry offers a wide variety of modelling and experimental tools that can be used to study related problems. An increased number of researchers utilize geochemical modelling and spectroscopy to study changes in soil chemistry in the geotechnical field. This study illustrates the application of this methodology to a significant geotechnical problem, ettringite-induced heave in stabilized clays. Geochemical modelling was used to estimate the ranges of dissolved constituents that are needed to make ettringite, i.e. Ca, Al and SO_4, as well of silica, which is known to influence indirectly ettringite stability. Modelling of a pure kaolinite soil indicates that gibbsite primarily controls Al availability, CSH/CAH control Ca availability, except in early times when portlandite is the only phase that precipitates rapidly. These concentrations were then used to evaluate a worst-case scenario for ettringite stability. This indicates that ettringite is expected to be stable in a wide range of sulfate concentrations for kaolinitic soils which has higher amounts of available Al. Silica addition restricts to some degree ettringite stability in the pH range 10.5-12.5.

While this study illustrates the applicability of both geochemical modelling and spectroscopy to geotechnical problems and specifically ettringite-induced swell, there are several consideration for its application to real soils. More systematic testing of ion activities in stabilized soils to generate data for modelling is needed, as well as understanding of the relationship of these activities to soil mineralogy, the type of stabilizer and time. Processes such as ion exchange and adsorption have to be considered, along with the presence of carbonate and other ions in solution. The thermodynamics and kinetics of the reactions of clay minerals such as mixed-layer smectites in stabilized soils are poorly known. The activity of water, which is limited in a real soil, has to be modelled more accurately. Spectroscopy, including quantitative X-ray Diffraction can aid in this regard by providing an understanding of soil mineralogy, both qualitative and quantitative.

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