

Article

Chemo-Mechanical Interactions in the Ettringite Induced Expansion of Sulfate-Bearing Soils

Zhongmei Wang ¹, Pawan Sigdel ² and Liangbo Hu ^{3,*}¹ College of Resources and Environmental Engineering, Guizhou University, Guizhou 550025, China² CTL Engineering Inc., Indianapolis, IN 46239, USA³ Department of Civil & Environmental Engineering, University of Toledo, Toledo, OH 43606, USA

* Correspondence: Liangbo.Hu@utoledo.edu; Tel.: +1-419-530-8124

Received: 15 July 2019; Accepted: 26 August 2019; Published: 29 August 2019



Abstract: Expansive sulfate-bearing soils are frequently encountered in transportation and construction practices. These soils are often treated with a lime or cement stabilizer to improve the relevant qualities. However, the reaction between sulfate and alumina in soils and calcium of lime or cement can lead to the formation of ettringite, an expansive sulfate mineral resulting in soil swelling or heaving. The underlying mechanisms often involve intricate interactions between chemical processes and mechanical responses. The present study explores a chemo–mechanical approach in an attempt to quantify several mechanisms potentially responsible for the volume expansion, including the geochemical formation of ettringite, crystallization pressure, and osmosis-induced swelling. The geochemical reaction leading to ettringite formation is examined with a specific focus on the circumstances under which it may lead to volume change. The crystallization pressure developed during the ettringite formation may also play a significant role in the soil expansion and is investigated in the present study based on thermodynamic formulations, and the resulting volume expansion is simulated. The osmosis-induced swelling is studied within the context of the chemo–mechanical framework, and its kinetics is also explored. Numerical simulations are performed in the present study to examine different scenarios driven by distinct predominant mechanisms. In particular, the interplay between ettringite formation and osmosis swelling as interpreted from some recently-reported experimental studies shows that these mechanisms can all contribute to the observed expansion processes, and overall, the modeling results are consistent with the experimental findings.

Keywords: expansive soils; sulfate; chemo–mechanical; coupling; ettringite; osmosis; crystallization

1. Introduction

Natural expansive soils are susceptible to volume change when exposed to varying environmental conditions. This process can be also complicated by further alteration or stabilization of natural soils when additional material is mixed with the soil with the aim to improve certain soil qualities. For example, treatment of soil subgrade with the use of lime or cement stabilizer is widespread in transportation and construction practices, as it offers a potential benefit of the reduction of swelling potential by early substitution of the clay cations through the formation of calcium silicate and aluminate hydrates, thus making them less available for later clay–water interaction [1]. However, paradoxically, this potential benefit of swelling mitigation could be compounded by a new possibility of volume expansion in sulfate-bearing soils, arising from well-known ettringite-induced heaving when lime or cement stabilizer may react with sulfates in natural soils and form ettringite, an expansive sulfate mineral that may contribute to expansion by hydration and/or by its own continuous growth [2–4].

While sulfate-induced reaction and the associated ettringite-induced swelling have been widely observed in soils, as well as in other construction materials [5–11], the underlying mechanisms have not been fully understood. The mineralogical reaction between sulfate and cement, which produces ettringite, is by no means the only source of the chemo–mechanical effects involved, and this reaction itself may involve multiple intricate interactions between physical, chemical, and mechanical processes. Indeed, numerous studies have indicated that there are strong possibilities for other mechanisms to become the dominant factors in such expansive soils, which undergo complicated geochemical reactions when they are exposed to complex environmental changes inducing potential hydration/dehydration. Experimental investigations by Abdi and Wild [1] and Wild et al. [12] indicated that the primary mechanism in sulfate-bearing lime-stabilized clays might be the imbibition of water by osmosis, rather than the direct formation of solid reaction products. Little and co-workers [13,14] suggested that the overall swelling and distress associated with sulfate-induced heaving in lime-treated clay was caused by a synergy of multiple mechanisms, including the formation of ettringite, water absorption of formed ettringite, and osmosis-induced swelling of clay minerals.

In engineering practice, traditional assessment of the potential for ettringite-induced expansion is typically related to the sulfate content contained in the soil; nonetheless, the direct correlation between sulfate content and swelling has yet to be firmly established. The present study is inspired partially by field observations of considerable heaving in pavements overlaid on cement-stabilized sulfate-bearing soils in several recent construction projects in Ohio, USA [15]; subsequent experimental studies of these sulfate-containing soils did not reveal a direct correlation between sulfate content and swelling [16–18]. Improved understanding of the development of the soil swelling demands considerations of specific predominant mechanisms to be formulated and assessed in a quantitative manner.

It is of particular interest to note that understanding of expansive soils subjected to hydration/dehydration has been significantly enriched by the development of chemo–mechanical theories since a number of seminal works were published over the last two decades [19–22]. These theories attempt to address the effect of chemical change on the mechanical behavior of expansive clays, and such concepts provide a viable approach to formulate and quantify the processes involved in ettringite-induced swelling theoretically, to which plenty of experimental work has been devoted, while theoretical developments appear somewhat behind. The present study aims to explore the interplay between a number of potential underlying mechanisms including ettringite formation, crystallization pressure (arising from the growth of mineral crystals and exerted on the surrounding solid matrix), and osmosis-induced swelling. The relevant phenomenological background of ettringite formation and various expansion mechanisms is summarized; subsequently, theoretical formulations are presented in an attempt to quantify the relevant mechanisms, and numerical simulations are conducted in the context of an experimental study recently reported [18].

2. Underlying Mechanisms of Ettringite Formation and Induced Expansion

Ettringite, a hydrous calcium aluminum sulfate mineral ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), in treated sulfate-bearing soils is produced by the reaction between the sulfate (typically gypsum) in the soil, calcium oxide provided by the cement or lime stabilizer, aluminum ions from the clay minerals, and water, which can be schematically represented by Equation (1), although the actual series of reactions may involve far more complicated processes. Nonetheless, the volume change after the reaction can be computed based on the stoichiometry of this reaction and the molar volumes of the reactants and product, as demonstrated in Little et al. [13]. Comparing the volumes of all the reactants in the left-handed side of Equation (1) including the consumed water, with the volume of the product (ettringite), this study showed that the volume change is negative, that is transformation of all reactants into ettringite actually does not cause any expansion; on the contrary, it leads to about 5% contraction.



Of course, this consideration of volume contraction implies that the water is supplied within the soil matrix (i.e., a closed system); if the water consumed in ettringite formation comes from outside the matrix (i.e., an open system) and hence is excluded from the original reactant volume considered, then indeed, the reaction produces a volume expansion of 137%, and the increase is almost entirely due to the water supplied externally. Therefore, the source, timing, and availability of the water consumed may have a profound effect on the ettringite formation and induced expansion [13,14]. It is also of interest to note that the percentage of volume change mentioned above is based on the original volume of the involved reactants, which likely occupy only a small to modest fraction of the total volume of the soil; for example, even a sulfate content as high as 10,000 ppm (widely considered as high to unacceptable risk in engineering practice) represents only 1% mass content of soil; even with the 137% volume expansion for ettringite formation as discussed, it is difficult to conceive that such a small amount of sulfate can lead to 10~20% swelling strains as routinely reported.

Experimental studies have also successfully identified other potential mechanisms responsible for the swelling behavior of stabilized sulfate-containing soils. Abdi and Wild [1] identified osmosis-induced water imbibition as the main cause for the volume expansion of a lime-stabilized sulfate-containing clay. Nair and Little [13] found that there was a significant evolution of osmosis suction, which might also induce swelling of clay minerals in lime-treated soils, and proposed that a combination of multiple mechanisms was responsible for the overall swelling. Involvement of osmosis-induced swelling may have a profound impact; because if the water is drawn by osmosis into the clay minerals, some of the water may be available for further ettringite formation; however, the reaction may not produce additional volume expansion as the water is supplied within; the volume expansion would be almost entirely due to the swelling of the clay minerals induced by osmosis. Such scenarios again demonstrate that the precise path of volume expansion is largely dependent on the timing and availability of water, which are susceptible to specific environmental factors.

In addition, the crystallization pressure from the ettringite growth is commonly believed to be the major factor of swelling in constructional materials such as concrete [9,23,24]; its role in swelling sulfate-bearing soils is largely unexplored. Here, the reaction of ettringite formation may indeed involve complicated crystal growth and rearrangement: when the specific structural characteristics of clay clusters does not allow enough room for such changes, the formation of new mineral crystals may generate significant stress or pressure for volume expansion.

Therefore, it is possible to propose a conceptual model to describe multiple sources for volume change $d\epsilon_v$ induced by ettringite formation-related processes in sulfate-bearing soils,

$$d\epsilon_v = d\epsilon_v^{\xi} + d\epsilon_v^s + d\epsilon_v^c \quad (2)$$

where $d\epsilon_v^{\xi}$ represents the absorption of externally-supplied water, which leads to the aforementioned 137% volume expansion, and its kinetic rate is largely dictated by the chemical reaction rate described in Section 3. The second term and third term of the right-hand side represent the osmosis (suction)-induced volumetric strain, $d\epsilon_v^s$, and the crystallization pressure-induced expansion, $d\epsilon_v^c$, respectively. These two processes likely involve more complex mechanisms, and their quantitative descriptions would rely on formulations built within a chemo-mechanical framework. In what follows, the role of crystallization pressure in ettringite formation is examined in Section 4, and the mechanism of osmosis-induced expansion is discussed in Section 5.

3. Geochemical Reactions for Ettringite Formation

The most common sulfate-bearing mineral in soils is gypsum (or anhydrite); gypsum is a calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and is usually the main source of sulfate in a typical sulfate-bearing soil, as considered in the present study. The evolution rate of swelling accompanied with the progression of the mineral reaction is dependent on the kinetic processes. However, these reactive processes usually involve very complicated series of geochemical reactions and are typically very

difficult to quantify precisely. At the risk of a simplistic approach, we adopted the first-order kinetic rate law for gypsum dissolution employed by Oldecop and Alonso ([25]),

$$\dot{m}_{GYP} = k_{GYP}^D A_{GYP} \left(\frac{c}{c_{GYP}^{sat}} - 1 \right), \text{ for } \frac{c}{c_{GYP}^{sat}} < 1 \quad (3)$$

\dot{m}_{GYP} is the rate of the growing gypsum crystals, here positive, indicating precipitation (growth), while negative dissolution. k_{GYP}^D is the dissolution rate constant. A_{GYP} is the surface area available for water-mineral reaction. Equation (3) is invoked as the dissolution occurs if the concentration of sulfate, c (i.e., $[SO_4]$), is lower than its saturated concentration (solubility) c_{GYP}^{sat} . Similarly, in the present study, the kinetic rate for ettringite growth (precipitation) is also formulated in a first-order kinetic law as adopted in Bary ([26]),

$$\dot{m}_{ETT} = k_{ETT}^P A_{ETT} \left(\frac{c}{c_{ETT}^{sat}} - 1 \right), \text{ for } \frac{c}{c_{ETT}^{sat}} > 1 \quad (4)$$

\dot{m}_{ETT} is the rate of the growing ettringite crystals; k_{ETT}^P indicates the precipitation rate constant; and A_{ETT} is the surface area available. Evidently, backward reactions such as precipitation of gypsum and dissolution of ettringite can be also considered if necessary, to offer more complete descriptions of the system of geochemical reactions potentially involved. For the sake of simplicity, in the present study, the kinetics were limited to the gypsum dissolution and ettringite precipitation, which were considered to act as the key geochemical reactions leading to the formation of ettringite.

Now, it can be readily formulated that $d\epsilon_v^{\xi}$ in Equation (2), caused by the absorption of externally-supplied water, is simply linked to the change in the gypsum,

$$d\epsilon_v^{\xi} = 1.37\theta_H^0 d\xi \quad (5)$$

ξ represents the change of gypsum mass (or mol), m_{GYP} , with respect to its original mass (or mol), m_{GYP}^0 . θ_H^0 is the original volume fraction of gypsum in the soil. Clearly, the kinetic time rate, $\dot{\xi} = \dot{m}_{GYP}/m_{GYP}^0$, is related to the geochemical reaction described in Equation (3).

4. Expansion Resulting from Crystal Growth

4.1. General Concepts and Mathematical Formulations

The crystallization pressure arising from the growth of the ettringite crystals is known to play a crucial role in macroscopic swelling in constructional materials such as concrete or cement subjected to sulfate attacks [6,9,23,24], and its role in sulfate-bearing soils has not been extensively investigated and is the main focus of this section. The crystallization pressure can be represented in the following form, known as Correns' equation [6,9,27], based on thermodynamic considerations,

$$p_c = \frac{RT}{v_m} \ln \left(\frac{Q_{\text{reac}}}{K_{\text{reac}}} \right) \quad (6)$$

R and T are the gas constant and absolute temperature, respectively. The activity product Q_{reac} is defined as $Q_{\text{reac}} = \prod_i a_i^{v_i}$, where a_i and v_i are the activity and the stoichiometric coefficient of species i in the solution. K_{reac} is the equilibrium product constant, and v_m is the molar volume of the crystal. It is worth noting that the complicated interplay between multiple processes potentially across different scales may be behind the generation of crystallization pressure that arises from the growing crystals, as detailed in Scherer [9,24], including the evolution of surface energy and configuration, the solubility and saturation of crystals, as well as pore-scale surface forces. Meanwhile, the consequences of the crystallization pressure manifested on the macroscopic scale must be also

addressed in a multi-scale manner as discussed in Bary ([26]); based on a micro-mechanical approach, the macroscopic constitutive relation can be described in a tensor form as:

$$\sigma = K\epsilon - \alpha p_c I \quad (7)$$

σ and ϵ are the stress and strain tensor, respectively. K is the stiffness tensor, and I is the second-order identity tensor. α is a macroscopic scalar interaction coefficient, which typically can be formulated as a function of volume fraction and elastic constants of different material constituents, as employed in Bary [26], where the Mori–Tanaka scheme was used. In addition, as the present study focuses on the volume change only, the relationship between the mean stress and the volumetric strain can be expressed as:

$$\sigma = K_b \epsilon_v^c - \alpha p_c \quad (8)$$

where σ and ϵ_v^c are the mean stress and (crystallization pressure-induced) volumetric strain, respectively. K_b is the bulk modulus.

Now, the key chemical reaction of ettringite formation [26] is considered to derive the crystallization pressure expressed in Equation (6); the activity product can be substituted by the product of the concentrations of calcium and sulfate,

$$p_c = \frac{RT}{V_{ETT}} \ln \left(\frac{[Ca]^2 [SO_4]^2}{[Ca]_0^2 [SO_4]_0^2} \right) \quad (9)$$

where $[Ca]_0$ and $[SO_4]_0$ are the calcium and sulfate concentrations at chemical equilibrium, respectively. A simplification can be made by considering only the change of sulfate concentration, c ($= [SO_4]$), when the present study assumes that calcium concentration remains constant, as it can be supplied continuously by the lime or cement stabilizer. As such, the sulfate evolution can be readily computed based on the kinetics presented in Section 3, and the resulting crystallization pressure can be numerically simulated from Equation (9).

The evolution of the crystallization pressure-induced swelling strain, ϵ_v^c , can be readily computed from Equation (8) when applied to a stress-free swelling case ($\sigma = 0$). As the volume fraction of ettringite is typically very small, the interaction coefficient α can be simply replaced by the volume fraction of the ettringite crystals θ_{ETT} .

4.2. Numerical Simulations

The process of ettringite formation and crystallization pressure is examined in numerical simulations of a freely-swelling scenario mentioned above. The relevant parameters used in this simulation are summarized in Table 1. The temperature considered was 20 °C for the simulations presented in Figures 1 and 2, later varied to examine its effect.

Table 1. Parameters involved in geochemical reactions and crystalline expansion.

Parameter	Symbol	Value
Saturated concentration (gypsum)	c_{GYP}^{sat}	15.5 mol/m ³
Saturated concentration (ettringite)	c_{ETT}^{sat}	1.56 mol/m ³
Rate constant (gypsum)	k_{GYP}^D	9.48×10^{-9} mol/m ³
Rate constant (ettringite)	k_{ETT}^D	9.48×10^{-10} mol/m ³
Molar volume (ettringite)	v_m	7.25×10^{-4} m ³ /mol
Initial volume fraction of gypsum	θ_{GYP0}	0.1
Initial volume fraction of ettringite	θ_{ETT0}	0

Figure 1 shows the simulation results of the evolution of ettringite formation, as well as the sulfate solute concentration plotted together with the prescribed constant gypsum solubility (saturated concentration) and ettringite solubility (saturated concentration). Evidently, two geochemical reactions progress simultaneously: the dissolution of gypsum and the precipitation of ettringite as indicated by Equations (3) and (4), respectively; they are driven by the imbalance/difference between the saturated concentration and evolving concentration of the sulfate solute. Sulfate concentration accumulated rapidly in an initially very dilute solution, but then, its accumulation slowed down as some of the dissolved sulfate participated in the precipitation of ettringite. After about 40 days, the sulfate concentration continued to rise very little and reached almost a constant threshold eventually. This late period coincided with a nearly constant rate of ettringite growth, as shown in Figure 1. Clearly, a dynamic equilibrium was approached when the newly-dissolved sulfate from gypsum dissolution was entirely consumed by the precipitation of ettringite; both reactions progressed with equal kinetic rates.

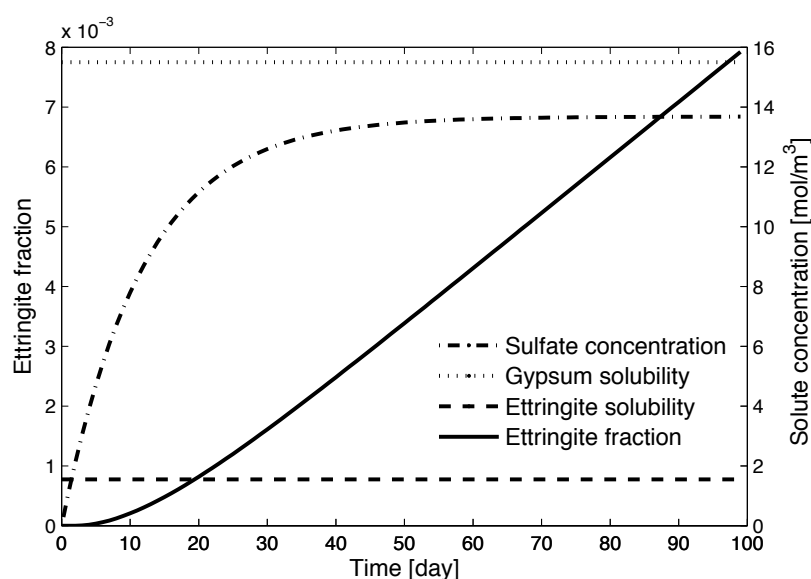


Figure 1. Simulation results of the evolution of the volume fraction of ettringite crystals formed and the sulfate concentration at $T = 20\text{ }^{\circ}\text{C}$.

This scenario also explains the development of the swelling strain and crystallization pressure as presented in Figure 2. The crystallization pressure developed rapidly, despite that in the beginning, it dropped from the initial value of zero because the initial concentration of sulfate solute was set up very low in the simulation, and it took a very short period of time (1~2 days) for enough gypsum dissolution to participate in ettringite formation. Once the precipitated ettringite started to grow, the crystallization pressure developed in a similar manner as the sulfate solute concentration, as its rate dropped sharply and reached almost a constant rate after 40 days. During this late stage, the swelling strain grew almost linearly with time, similarly to the evolution of the volume fraction of precipitated ettringite, as shown in Figure 1; since the crystallization pressure no longer evolved much, the evolution of further swelling was dictated by the ettringite growth, which proceeded at an almost constant kinetic rate mentioned earlier.

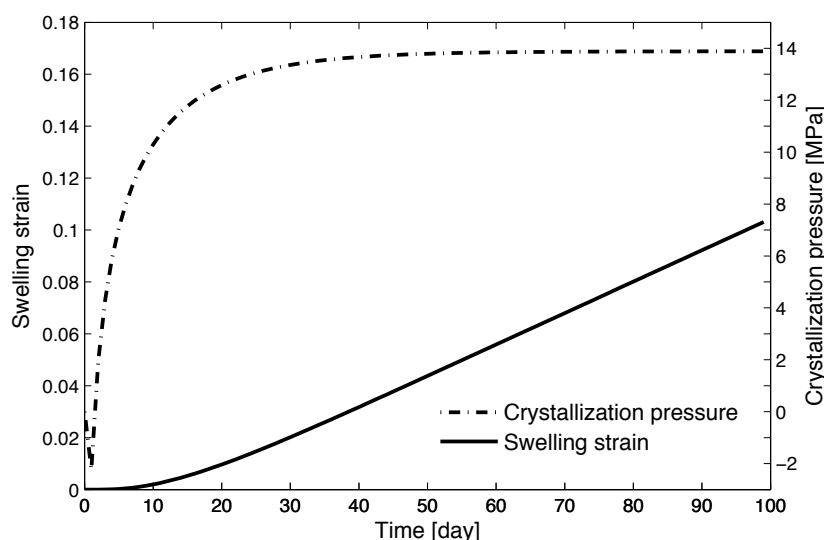


Figure 2. Simulation results of the evolution of crystallization pressure and swelling strain at $T = 20\text{ }^{\circ}\text{C}$.

Evolution of the swelling strain caused by crystallization pressure at different temperatures is presented in Figure 3. While the temperature evidently had some significant influence on the swelling due to higher crystallization pressure at a higher temperature, the accumulation of volume expansion took a certain time to become appreciable. The effect caused by temperature was more significant at the later stage, but could result in approximately a 20% difference in swelling strains. It should be noted that the geochemical kinetic rates of mineral reactions may be also enhanced or affected by temperature, but they were not considered in the present study.

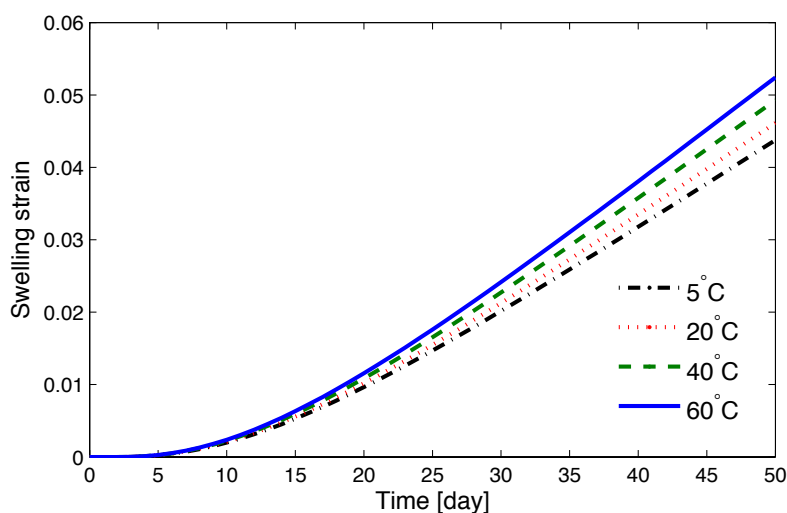


Figure 3. Evolution of swelling strain resulting from crystallization pressure at different temperatures.

5. Osmosis-Induced Expansion

5.1. Phenomenological Concepts and Mathematical Formulations

Expansive behavior of clays induced by osmosis has been intensively examined over the last two decades from the constitutive modeling perspective, which extended the plasticity theory to address the effects of chemo–mechanical couplings [20,21,28–30]. In addition, some recent developments in the theory of chemo–mechanics offered an excellent opportunity to assess some available experimental results summarized in this section more conveniently; these theoretical developments implemented

the use of osmotic suction (or potential) as a governing variable, which was clearly tailored for encompassing the ability to address the behavior of partially-saturated soils (e.g., [31,32]).

Since certain choices in the mathematical modeling in the present study were motivated in part by the aim to assess a recently-reported experimental study of sulfate-bearing soils that experienced significant expansion in engineering practices [18], it may be beneficial to first offer some background and details of the experimental observations of interest to us. In this experimental study, Weir et al. [18] investigated the remolded sulfate-bearing soil samples collected from the heaving locations at the pavement construction sites in northeast Ohio, USA [15], where approximately 15~100 mm of heaving occurred at numerous locations along the newly-paved interstate highway. The pavement was asphalt concrete overlaid on 150 mm of aggregate base over 300 mm of cement-stabilized soil subgrade. The soil was originally stabilized with a cement content of 6% by the Ohio Department of Transportation for this construction project. The sulfate contents of these soils from the sites were determined with various testing methods. Subsequently, reconstituted soil samples were subjected to swelling tests using two different soaking liquids: distilled water and 7000-ppm sodium sulfate solution. A more detailed description of the experimental results can be found in Weir et al. [18]. Only some relevant results and observations are summarized here to provide the context within which the theoretical and numerical effort of the present study was made.

The swelling tests on the specimens reconstituted from these soils offered some quite interesting results. Specimens of three different sulfate contents, 4307, 5329, and 6027 ppm, each of which was the sulfate content of the soil collected from a specific location, were the main subjects under discussion. All specimens were placed under soaking in distilled water or in 7000-ppm sodium sulfate solution. When soaked in the distilled water, in somewhat of a surprise, the specimen of 5329-ppm sulfate content experienced the largest swelling, approximately 7%, followed by 3% in the specimen of 4307-ppm sulfate content, and finally, 1% in the specimen of 6027 ppm. It was speculated that mechanisms besides the water absorption (as described by Equation (5)) may have played a role. When soaked in the 7000-ppm sodium sulfate solution, the specimen swelled slightly more, approximately 1% more than in the distilled water, and this was consistent with all soils of different sulfate contents. Later, in a new set of tests, some specimens were air-dried for three days before they were subjected to swelling; this procedure did not result in much appreciable difference between the initially air-dried specimens and regular wet ones after being remolded with water; perhaps it may suggest that the matric suction or capillary mechanism had not produced a significant effect.

In the present study, it was possible to establish some relevant mathematical formulations, specifically focusing on the osmosis-induced swelling ϵ_v^s as introduced in Equation (2), when a certain sulfate-containing soil was subjected to swelling under the different soaking fluids described above. The following modeling was aimed to examine this scenario of osmosis-induced swelling, and it attempted to keep the mathematical formulations as simple as possible. It should be noted that more complete mathematical framework addressing both volumetric and deviatoric strain induced by chemical changes may be established based on the constitutive models mentioned earlier [20,21,29,30]. In addition, although it was possible to include the crystalline pressure-induced expansion as part of the simulation if the involved processes could be modeled simultaneously with the introduction of more presumptions, the specific scenario in the experimental study discussed above seemed to indicate that the predominate mechanisms in these swelling tests were related to the osmosis and possibly adsorption of externally-supplied water during the ettringite formation; thus, the crystalline pressure-induced expansion was not considered here for this reason and also for the sake of simplicity.

The osmotically-induced volumetric strain $d\epsilon_v^s$ can be expressed as:

$$d\epsilon_v^s = \frac{d\psi}{K_m} \quad (10)$$

It describes the volume change due to the incremental effective stress, $d\psi$, which could be potentially associated with matric suction, osmosis, or other physico-chemical phenomena, as proposed

by Guimaraes et al. ([31]). For the specific scenario of our interest as summarized in the experimental study above, the effect of matric suction was neglected in the present study; of course, no change in the mechanical load was considered (net mean stress, $d\sigma = 0$) for a free-swelling scenario. Consequently, the incremental effective stress $d\psi$ can be replaced by the incremental osmotic suction $d\Pi$ in Equation (10). The stiffness parameter K_m is described by a hardening/softening function [31]:

$$K_m = K_0 \exp(\beta\Pi) \quad (11)$$

K_0 and β are model parameters. The osmotic suction, Π , can be represented by the well-known van't Hoff equation,

$$\Pi = \frac{RT}{\nu_w} \ln a_w \quad (12)$$

where R is the gas constant, T is the absolute temperature, ν_w is the molar volume of water, and a_w is the activity of the water. For an ideal dilute solution, the activity of the water as the solvent a_w can be replaced by the its molar fraction x_1 , which is related to the molar fraction of the solute x_2 , by $x_1 = 1 - x_2$. It can be established that for a dilute solution, when x_2 is very small, $\ln(1 - x_2) \approx -x_2$, and thus:

$$\Pi = \frac{RT}{\nu_w} \ln x_1 = \frac{RT}{\nu_w} \ln(1 - x_2) = -\frac{RT}{\nu_w} x_2 \quad (13)$$

Equations (10)–(13) provide the calculation of osmosis-induced volumetric (swelling) strain in a closed system if $d\Pi$ is specified.

5.2. Numerical Simulations

In this section, a simple simulation was conducted based on the theoretical framework presented in Section 5.1. The main focus was to evaluate the volumetric strain if the “loading” path was dictated by the specified change of the osmosis suction through the salinity difference imposed between the pore fluid and soaking fluid, $d\Pi$, which was the driving force behind the osmosis swelling; as such a scenario may have produced significant swelling strain in various sulfate-bearing soil samples under different soaking fluids in the experimental study [30] discussed earlier.

The presented simulations attempted to emulate the scenarios examined in this experimental study where soils with various sulfate contents swelled under distilled water or under a 7000-ppm sodium sulfate solution. Two sulfate contents discussed in the aforementioned experimental study, 4307-ppm sulfate (lower sulfate content) and 5329-ppm soluble sulfate (higher sulfate content), were under consideration as the original sulfate contents for soil specimens to be soaked in a swelling scenario. Figure 4 shows the simulation results of the eventual swelling strain in these two different sulfate-bearing soils in response to soaking fluid with varying concentrations of sulfate solution (in the range of [0, 10,000] ppm). It is noted that in the absence of information about the actual sulfate concentration in the pore fluid of each soil specimen, a higher concentration $c_p = 5000$ as assumed for the specimen with the higher sulfate content; while a lower one $c_p = 3000$ ppm was assumed for the specimen with the lower sulfate content, in order for the simulation to proceed as an osmosis difference was imposed between the externally-controlled sulfate concentration in the soaking fluid and sulfate salt concentration in the pore fluid. Swelling ($\epsilon_v^s > 0$) occurred when soaked in a fluid with a lower ion concentration, and contraction occurred ($\epsilon_v^s < 0$) when in a fluid with a higher concentration. The simulation was a very basic mathematical implementation of Equations (10)–(13). Meanwhile, as discussed in Section 5.1, the experimental study revealed that the soil actually swelled slightly more under the 7000-ppm sodium sulfate solution than distilled water, and this strongly indicated the possibility of other mechanisms including ettringite-induced strain (ϵ_v^{ξ}), as presented in Equation (5). Thus, this mechanism was provoked here and progressed based on the geochemical kinetics outlined in Equations (3) and (4). The simulated swelling strain was a combination of these two volumetric strains, ϵ_v^{ξ} and ϵ_v^s .

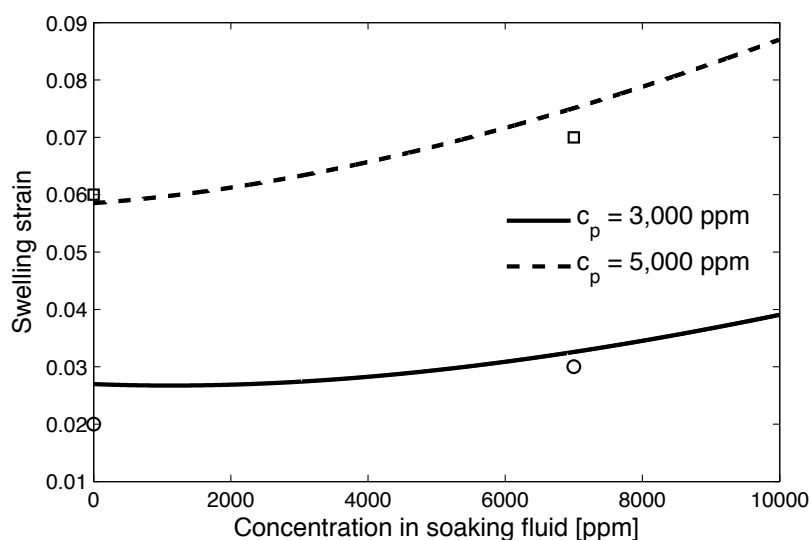


Figure 4. Swelling induced by osmosis and ettringite formation in soils permeated with two different sulfate salt concentrations subjected to soaking fluids of varying salt concentrations. Isolated square and circle markers indicate the experimental data points interpreted from [18].

The experimental study provided two swelling strains for each of the two soil specimens, one under distilled water (zero sulfate concentration) and the other under a 7000-ppm sulfate solution; these two measurements are marked in Figure 4. The circle markers indicate the experimental results of the lower sulfate-containing soil, while the square markers the higher one. Of course, such interpretations should be treated with caution in the absence of relevant information about the pore fluid and detailed mineralogy of the tested specimens in the experimental study. These are more of an attempt to calibrate for the data points by using the following parameters for the simulations (conducted at room temperature $T = 25\text{ }^{\circ}\text{C}$): $\beta = 5\text{ MPa}^{-1}$ and $K_0 = 5\text{ MPa}$. These results demonstrated an intriguing scenario related to a combination of osmosis-induced volume change driven by osmosis potential difference and ettringite formation-induced swelling by adsorbing water. The soaking fluid provided both an osmosis potential difference and potentially more sulfate for ettringite formation; the latter may partly explain the apparent small increase in the overall swelling when soaked in a highly-concentrated sulfate solution. In addition, it is worth noting that apart from sulfate, lime or cement stabilizer is also needed for the formation of ettringite. Its availability may also have a considerable impact on the growth of ettringite and subsequent swelling. In the present study, it was assumed that the amount of cement in the studied specimens was sufficient. The geochemical kinetics presented in Section 3 would need to be expanded for a quantitative analysis in order to better evaluate the effect of the stabilizer.

5.3. Assessing the Kinetics of Osmosis

It is of interest to assess the kinetic rate of the development of swelling strain, following the previous section where the focus was on the eventual swelling strain at the end of the osmosis hydration or consolidation. Its kinetics was most likely related to the time rate of osmosis-induced water movement from the soaking fluid. However, not much attention has been paid to the kinetics of osmosis in the literature. A recent study adopted the theoretical formulation proposed in an early work of Northrop [33], who studied the osmosis in the context of biological processes, with some modifications introduced for consideration of clayey soils. It assumed that the rate of pore fluid flow is proportional to the pressure gradient related to both osmotic pressure and hydrostatic pressure. The principal equation about the rate of pore fluid volume change is:

$$\frac{dV}{dt} = \frac{1}{R_e} \left(\frac{P_{\Pi}}{V} - [P_0 + K_e(v - v_0)] \right) \quad (14)$$

V is the volume of the pore fluid; P_{II} is the parameter associated with the osmotic potential (see Equation (13)) and can be expressed as $P_{II} = RTn/\gamma_w$, where n is the mol of the solute in the pore fluid and γ_w is the unit weight of water; P_0 is the initial pressure head; V_0 is the initial volume of the pore fluid. The two key material constants K_e and R_e need some elaborations. K_e represents the increase in pressure per increase in volume; in clayey soils, it may reflect the stiffness or compressibility of the soil matrix. The resistance parameter R_e depends on the mechanisms for the passage of water through the membrane. Northrop [33] offered two possibilities: if the dominant mechanism is the water diffusion in the membrane, then $1/R_e$ is the diffusion coefficient of the solvent in the membrane; if the water flows through capillaries in the membrane, $1/R_e$ is related to permeability or Poiseuille's coefficient. In analogy to clayey soils, it may be possible to assume that $1/R_e$ should be related to the diffusion properties and/or pore size characteristics of the adsorbed water around clay clusters. Incidentally, Coussy's formulation [34] based on a poro-mechanics approach leads to similar results to Equation (14).

Figure 5 shows the time evolution of the osmosis-induced swelling strain of the two soils with different sulfate contents as discussed in Section 5.1. The two key material constants R_e and K_e were calibrated against the reported experimental data for the soil with the higher sulfate content (with assumed $c_p = 5000$ ppm) soaked in distilled water, as presented in the preceding Section 5.2. The calibrated values of parameters ($R_e = 1.25 \times 10^{12} \text{ m}^{-2}\text{s}$ and $K = 1.55 \times 10^5 \text{ m}^{-2}$) were then used to calculate the swelling of the soil with the lower sulfate content (with $c_p = 3000$ ppm). The model predicted a swelling of about 3%, while the experiment showed a 2% eventual swelling for soils of the lower sulfate content. A significant decrease in the swelling rate occurred after approximately 10~13 days for each of the two soils. The general kinetic characteristics of simulated swelling strain development for both soils were consistent with the experimental measurements.

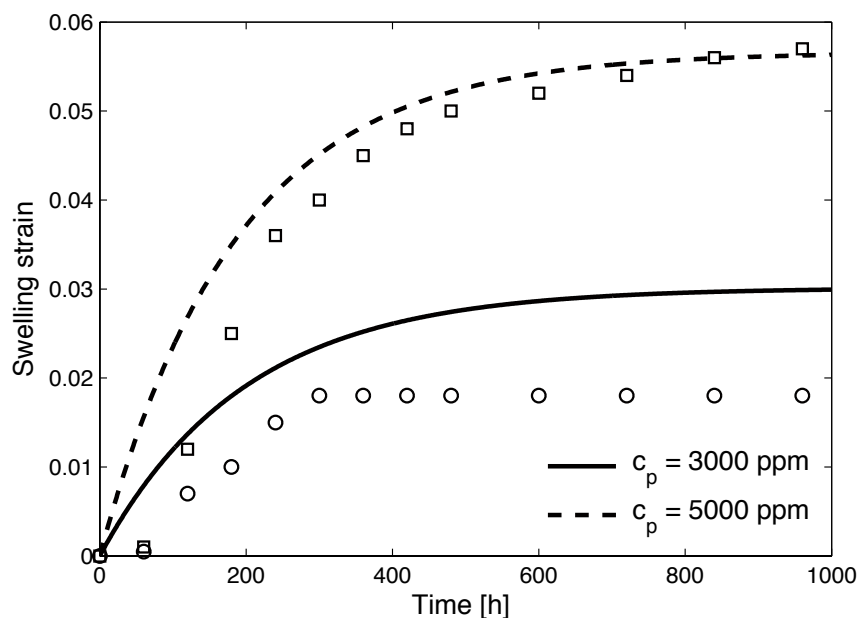


Figure 5. Simulated evolution of swelling strain; square and circle markers indicate the experimental data points for two different soils [18].

6. Conclusions

Numerous experimental studies have gradually revealed that sulfate-induced expansion could be caused by a combination of multiple mechanisms, which may include ettringite formation, osmosis swelling, and crystallization pressure. The present study aimed to explore a chemo-mechanical approach to model the relevant mechanisms responsible for the expansive behavior of sulfate-bearing

soils in a quantitative manner. The volume change affected by the water supplied externally during ettringite formation was characterized as an expansive strain, and its kinetics was mainly dictated by the kinetics of the geochemical reactions involved such as gypsum or ettringite dissolution and precipitation. The osmosis-induced strain was investigated in a chemo–mechanical constitutive framework that adopted the gradient of osmotic suction or mass concentration as the driving force for the induced volumetric strain. The kinetics of osmosis was also explored and led to intriguing possibilities for further investigations on clay properties related to osmosis kinetics. Numerical simulations following the mathematical formulations were attempted to assess some recently-reported experimental results on soil swelling. The experimental results were interpreted based on the proposed theoretical framework. The rate of swelling strain gradually declined after 10~13 days, and the characteristics of the simulated osmosis-induced swelling strain rate were consistent with the experimental observations. Numerical simulations of soil specimens with a higher sulfate content led to greater swelling strains, when both the osmosis-induced volume change and ettringite formation-induced swelling by adsorbing water were considered. Exposure to higher sulfate salt concentrated solution caused a slight increase in the swelling compared to the distilled water for the examined scenarios. However, it should be pointed out this numerical exercise was not intended as a precise replication of field problems, which can only be attempted in terms of properly formulated boundary value problems; rather, it was an effort aiming to use a chemo–mechanical approach to address the relevant mechanisms in a quantitative manner.

The crystallization pressure during ettringite formation in the swelling of sulfate-bearing stabilized soils can be also part of the potentially very complex processes involved. The crystallization pressure developed rapidly in the beginning as gypsum dissolution continued to progress and participate in ettringite formation. Subsequently, the rate of crystallization pressure dropped sharply and reached almost constant after 40 days, while the swelling strain grew almost linearly with time. The effect of temperature on the swelling strain was also examined, and the results showed that a higher temperature typically resulted in higher crystallization pressure and greater swelling strain, which, however, took a certain time to become appreciable. The relevant mathematical formulations were established based on a brief survey of the key physical, chemical, and mechanical concepts. The subsequent simulation was restricted to the evolution of a closed system, taking into account the relevant geochemical kinetics formulated. Here, an improved understanding of this mechanism would demand enhanced experimental effort to offer more insights regarding various key phenomena, particularly those across the scales, such as crystal growth/rearrangement and pore structure evolution. In addition, it remains a significant challenge to distinguish the effects of different mechanisms in the field where the triggering or influencing environmental factors are often of an episodic, seasonal/cyclic nature. The presented numerical approach can definitely benefit from future experimental studies that are capable of separating the effects of diverse mechanisms in the laboratories.

Author Contributions: All authors collectively developed the aims, methodologies, and results of the research and drafted the manuscript collaboratively.

Funding: Z. Wang would like to acknowledge the financial support from the Science and Technology Plan Joint Foundation of Guizhou Province (Grant No. LH[2017]7284) and the Science and Technology Platform and Talent Team Planning Project of Guizhou Province (Grant No. [2017]5402); the funding from the China Scholarship Council (Grant No. 201406675006) that supported the visit at the University of Toledo for this collaborative research is also acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abdi, M.R.; Wild, S. Sulphate expansion of lime-stabilized kaolinite: I. Physical characteristics. *Clay Miner.* **1993**, *28*, 569–584. [[CrossRef](#)]
2. Mitchell, J.K. Practical problems from surprising soil behavior. *J. Geotech. Eng.* **1986**, *112*, 255–289. [[CrossRef](#)]
3. Hunter, D. Lime-induced heave in sulfate-bearing clay soils. *J. Geotech. Eng.* **1988**, *114*, 50–167. [[CrossRef](#)]

4. Puppala, A.J.; Intharasombat, N.; Vempati, R.K. Experimental studies on ettringite-induced heaving in soils. *J. Geotech. Eng.* **2005**, *131*, 325–337. [[CrossRef](#)]
5. Mehta, P. Mechanism of expansion associated with ettringite formation. *Cem. Concr. Res.* **1973**, *3*, 1–6. [[CrossRef](#)]
6. Xie, P.; Beaudoin, J.J. Mechanism of sulphate expansion. I. Thermodynamic principle of crystallization pressure. *Cem. Concr. Res.* **1992**, *22*, 631–640.
7. Dermatas, D. Ettringite-induced swelling in soils: State-of-the-art. *Appl. Mech. Rev.* **1995**, *48*, 659–673. [[CrossRef](#)]
8. Shimada, Y.; Young, J. Structural changes during thermal dehydration of ettringite. *Adv. Cem. Res.* **2001**, *13*, 77–81. [[CrossRef](#)]
9. Scherer, G.W. Stress from crystallization of salt. *Cem. Concr. Res.* **2004**, *34*, 1613–1624. [[CrossRef](#)]
10. Rajasekaran, G. Sulphate attack and ettringite formation in the lime and cement stabilized marine clays. *Ocean Eng.* **2005**, *32*, 1133–1159. [[CrossRef](#)]
11. Moon, D.H.; Dermatas, D.; Wazne, M.; Sanchez, A.M.; Chrysochoou, M.; Grubb, D.G. Swelling related to ettringite crystal formation in chromite ore processing residue. *Environ. Geochem. Health* **2007**, *29*, 289–294. [[CrossRef](#)] [[PubMed](#)]
12. Wild, S.; Abdi, M.R.; Leng-Ward, G. Sulphate expansion of lime-stabilized kaolinite: II. Reaction products and expansion. *Clay Miner.* **1993**, *28*, 569–584. [[CrossRef](#)]
13. Little, D.N.; Nair, S.; Herbert, B. Addressing sulfate-induced heave in lime treated soils. *J. Geotech. Geoenviron. Eng.* **2011**, *136*, 110–118. [[CrossRef](#)]
14. Nair, S.; Little, D. Mechanisms of distress associated with sulfate-induced heaving in lime-treated soils. *Transp. Res. Rec. J. Transp. Res. Board* **2011**, *2212*, 82–90. [[CrossRef](#)]
15. Narsavage, P.A. Sulfate heaving of cement stabilized soil in Ohio. In Proceedings of the 2011 Ohio Transportation Engineering Conference, Columbus, OH, USA, 25–26 October 2011.
16. Cutright, T.; Wigdahl, J. Assessment of sulfate bearing soils in Ohio. In Proceedings of the 2013 Ohio Transportation Engineering Conference, Columbus, OH, USA, 22–23 October 2013.
17. Freese, K. Assessment of Sulfate in Ohio. Master's Thesis, University of Akron, Akron, OH, USA, 2014.
18. Weir, M.; Mandell, A.; Farver, J. *Role of Sulfates on Highway Heave in Lake County, Ohio*; Report # FHWA/OH-2014/4; Ohio Department of Transportation: Columbus, OH, USA, 2014.
19. Hueckel, T. Water-mineral interaction in hygro-mechanics of clays exposed to environmental loads: A mixture approach. *Can. Geotech. J.* **1992**, *29*, 1071–1086. [[CrossRef](#)]
20. Hueckel, T. Chemo-plasticity of clays subjected to stress and flow of a single contaminant. *Int. J. Numer. Anal. Methods Geomech.* **1997**, *21*, 43–72. [[CrossRef](#)]
21. Loret, B.; Hueckel, T.; Gajo, A. Chemo-mechanical coupling in saturated porous media: Elastic-plastic behaviour of homoionic expansive clays. *Int. J. Solids Struct.* **2002**, *39*, 2773–2806. [[CrossRef](#)]
22. Gajo, A.; Loret, B.; Hueckel, T. Electro-chemo-mechanical couplings in saturated porous media: Elasto-plastic behaviour of heteroionic expansive clays. *Int. J. Solids Struct.* **2002**, *39*, 4327–4362. [[CrossRef](#)]
23. Skoblinskaya, N.; Krasilnikov, K. Changes in crystal structure of ettringite on dehydration. 1. *Cem. Concr. Res.* **1975**, *5*, 381–393. [[CrossRef](#)]
24. Scherer, G.W. Crystallization in pores. *Cem. Concr. Res.* **1999**, *29*, 1347–1358. [[CrossRef](#)]
25. Oldecop, L.; Alonso, E. Modelling the degradation and swelling of clayey rocks bearing calcium-sulphate. *Int. J. Rock Mech. Min. Sci.* **2012**, *54*, 90–102. [[CrossRef](#)]
26. Bary, D. Simplified coupled chemo-mechanical modeling of cement pastes behavior subjected to combined leaching and external sulfate attack. *Int. J. Numer. Anal. Methods Geomech.* **2008**, *32*, 1791–1816. [[CrossRef](#)]
27. Correns, C.W. Growth and dissolution of crystals under linear pressure. *Discuss. Faraday Soc.* **1949**, *5*, 267–271. [[CrossRef](#)]
28. Sigdel, P.; Hu, L.B. Modelling ettringite induced heaving in cement stabilized soils within a chemo-mechanical constitutive framework. In *ASCE Geotechnical Special Publication 256: IFCEE 2015*; Iskander, M., Suleiman, M.T., Anderson, J.B., Laefer D.F., Eds.; ASCE: Reston, VA, USA, 2015; pp. 125–132.
29. Liu, Z.; Boukpeti, N.; Li, X.; Collin, F.; Radu, J.P.; Hueckel, T.; Charlier, R. Modelling chemo-hydro-mechanical behaviour of unsaturated clays: A feasibility study. *Int. J. Numer. Anal. Methods Geomech.* **2005**, *29*, 919–940. [[CrossRef](#)]

30. Wei, C. A theoretical framework for modeling the chemomechanical behavior of unsaturated soils. *Vadose Zone J.* **2014**, *13*. [[CrossRef](#)]
31. Guimaraes, L.D.N.; Gens, A.; Sanchez, M.; Olivella, S. A chemo–mechanical constitutive model accounting for cation exchange in expansive clays. *Geotechnique* **2013**, *63*, 221–234. [[CrossRef](#)]
32. Witteveen, P.; Ferrari, A.; Laloui, L. An experimental and constitutive investigation on the chemo–mechanical behaviour of a clay. *Geotechnique* **2013**, *63*, 244–255. [[CrossRef](#)]
33. Northrop, J.H. The kinetics of osmosis. *J. Gen. Physiol.* **1927**, *10*, 883–892. [[CrossRef](#)]
34. Coussy, O. *Mechanics of Porous Continua*; Wiley: Hoboken, NJ, USA, 1993.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).