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Internal And External Sulfate Attack on Expansive Soil Stabilized With Calcium Based Stabilizers: A Review

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Abstract. Expansive clays by nature are not suitable for construction of road, rail embankments or lightly loaded structures as the major clay constituent montmorillonite causes the swell-shrink movements with the variation in available moisture. Decades of research has resulted in making these soils usable for construction through numerous stabilization techniques. Based on past research, it can be argued that among the technique available for stabilization, the chemical stabilization with calcium-based stabilizers has proved as an effective and reliable method of stabilization. However, the problem with the addition of calcium-based stabilizers to sulfate bearing expansive clays is the formation of ettringite and thaumasite. The formed deleterious minerals deteriorate the engineering properties of the stabilized clay. Several studies were performed to mitigate the effect of sulfate present in the natural expansive clays. Based on the studies, the use of non-calcium based stabilizers or low-calcium based stabilizers are recommended for stabilization of sulfate bearing expansive clays. Moreover, in recent years, the external sulfate attacks on stabilized expansive clays from external sources such as acid rains, oxidation of iron sulfide (pyrite), industrial and agricultural effluents are also linked to the deterioration of stabilized clays. However, the external sulfate contamination on stabilized expansive clays will not only result in the formation of the ettringite but also results in pH reduction of the cemented soil matrix. This results in leaching of the Ca ions from the cemented matrix. Even though the experimental data on sulfate attack based on past researches is enormous, the data is not cohesive to elucidate the two modes of contamination. Thus, this review paper aims at providing a clear understanding of both the internal and external sulfate attack on stabilized expansive clay through a detailed review of literature in the past few decades.

Keywords: Expansive soil, Internal sulfate attack, Ettringite, Soil stabilization, and External sulfate attack.

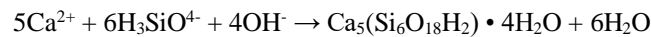
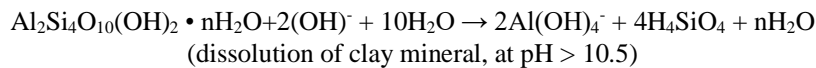
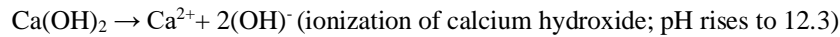
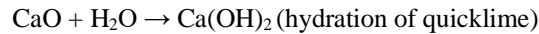
1 Introduction

The most widely used method of stabilizing the expansive soils is with the use of chemical admixtures such as lime and cement. The use of lime as a soil stabilizer is documented even during the ancient period of Roman Empire for the construction of Roman roads. Such mixers have retained their strength and volume stability for thousands of years [1]. The addition of such stabilizers improves the strength and durability of soils

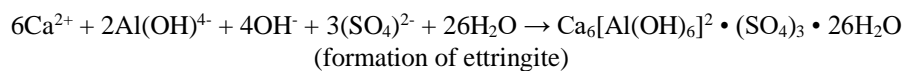
by ion exchange and pozzolanic reactions, so as to make the soils usable for engineering purposes such as construction of lightly loaded structures, pavements and runways.

The first ever problem of sulfate attack on lime stabilized soil was reported by Sherwood in the year 1962 [2]. However, the problem due to sulfate attack was not given due importance until 1986 [3]. In the late 1980's and early 1990's number of cases were documented in which the lime-stabilized pavements, while being effective during the initial period after construction, have subsequently started undergoing large amount of volumetric deformation and strength reduction, resulting in the destruction and damage of the pavements [4,5,6]. These volume deformation and failure of the pavements were then related to the sulfate reactions, that causes the formation of new expansive minerals like ettringite and thaumasite over a period of time. The new minerals formed are highly expansive in nature, swelling and softening of these minerals takes place when in contact with water [1].

The first ever case study on the problem relating to sulfate attack in lime stabilized expansive soil was reported by Hunter in the distress caused in Stewart Avenue in Las Vegas in 1987 [5]. Following this, several case studies and laboratory studies were reported by number of researchers with regard to the problems pertaining to the sulfate containing soils or sulfate-bearing soils or gypsiferous soils [1,3,4,5,7,8,9,10,11,12]. An experimental study performed at the University of California at Berkley on the Stewart Avenue to find the soil-lime-sulfate reaction responsible for the deterioration of the stabilized sub base. Based on the study by Hunter 1988 [5], the following geochemical mechanism was proposed for the formation of ettringite that resulted in the deterioration of the stabilized soil.

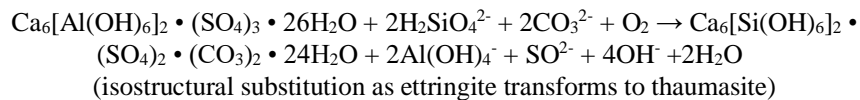


(dissolution of sulfate minerals; x = 1, y = 2 or x = 2, y = 1; M represents Ca, Na, Mg, etc.)



Once ettringite is formed, the crystals continue to grow by imbibing extra water molecules as a pure end member until the temperature of the system drops below 15°C.

Once the temperature falls below 15°C, the ettringite crystals transform into thaumasite through a process of continuous phase transformation. The transformation occurs through the iso-structural substitution of silica for alumina and carbonate for sulfate. The chemical equation of the iso-structural substitution is as follows [5].



The above geochemical reactions for the formation of ettringite and the subsequent transformation into thaumasite was further studied and proved by a number of researchers, namely, Lehman 1874, Michaelis 1896, Lerch et al 1929, Kollman 1978 [13,14,15,16]. They prepared ettringite from aqueous solutions and analysed the stable phases of ettringite, and concluded that the monosulfate hydrate, trisulfate hydrate (ettringite) are the only stable phases. Based on this, the ettringite formation was concluded to be the basic problem relating to soils that contain natural soluble sulfates in them.

In accordance to the above mentioned literature, there has been almost a century of research performed on the sulfate bearing soils, with each study supported the formation of ettringite/thaumasite as the lead reason for the failure of the stabilized soils. Hence many researchers have come forward to explain the mechanism of heave formation [17,18,19,20] and a number of researchers have worked on alternative methods to circumvent the problem of sulfate presence in the expansive soils. However, the impact of external sulfate intrusion on stabilized subgrades through various external means such as acid rains, industrial effluents, mine wastes and excessive use of fertilizers has not been explained in detail in the geotechnical point of view. Hence this paper focuses on the vital differences between the internal and external sulfate attack by reviewing through the existing literature.

2 Internal Sulfate Attack

The internal sulfate attack is manifested only when the soil inherently possesses the soluble sulfate prior to stabilization. Even though the existence of this type of soil is universal, most of the studies related to the sulfate containing soils are from USA [5,6,9,21,22]. In USA, the repair and reconstruction cost of structures damaged by sulfate induced heave has been estimated to be about several million dollars annually [6,9]. It can be noted here that the repair of such projects has exceeded the cost for stabilization of the soils. Hence, over the years a huge amount of research has been focused on sulfate bearing soils.

2.1 Heave formation

The internal sulfate attack is one of the most common problems related to sulfate induced heaving in stabilized soils. The mechanism of heave formation can be explained in two ways, first is the crystal growth theory proposed by Ogawa and Roy 1982 [19] and the second is water absorption or hydration theory proposed by Mehta and Wang 1982 [17].

Crystal growth theory

As per the crystal growth theory, the ettringite forms topochemically surrounding the calcium aluminum sulfate particles during the early stages of hydration as small needles. This formation of ettringite forms an active reactive zone surrounding the calcium aluminum sulfate particles. These ettringite crystals formed grow into large needle like crystals when water is introduced into the system. The heaving of soil occurs only when two reactive zones intersect; mutual pressure is applied on both the adjacent needles resulting in heaving of the system. This mechanism is favored under high pH conditions along with an unrestricted availability of the reaction compounds [19].

Hydration or Water absorption theory

Ettringite expansion through water absorption is widely accepted theory of heave formation in stabilized soils. According to this theory, the presence of calcium hydroxide results in inhibiting the hydration of aluminum significantly. This reduction in hydration of aluminum causes the gel-like and colloidal formation of ettringite. The gel-like crystal formation absorbs large quantities of water owing to its higher surface area and unbalanced negative surface charges. The expansion and growth of the ettringite is aided by the availability of external water under high hydroxyl concentrations. However, under low hydroxyl concentrations, the long needle like ettringite crystals are formed. The expansion due to these crystals is low, owing to their low surface area and low water absorption potential.

A study by Mehta and Wang 1982 [17] inferred that the heave associated with the growth of longer (or) coarser ettringite are less when compared to the heave associated with smaller (or) finer ettringite. Both the above theories are accepted as the principles associated with the heave formation. The heave formation in a stabilized expansive soil due to sulfate contamination will take place following either the crystal growth theory or the water absorption theory or in some cases the heave formation maybe the resultant of both the theories together. It should be noted here that the heave formation due to crystal growth occurs over a longer period of time, as it incorporates the formation of crystalline ettringite.

2.2 Factors contributing to the heave formation

There are a number of factors that affect the formation and growth of ettringite crystals. Table 1 provides an insight into a few of the most important factors that influence the ettringite formation.

Table 1. Factors influencing the ettringite formation

Factor	Description	Reference
pH	High alkaline pH is favorable for ettringite formation (pH> 10.5). The high pH helps in the dissolution of alumina from the clay fraction, which aids in ettringite formation.	Loughnan (1969), Hunter (1988), Dermatas (1995), Boardman et al. (2001), Bensted et al. (2007) [1,5,23,24,25]
Clay mineral	Clay minerals having more alumina content will result in the formation of monosulfates (CaO•Al ₂ O ₃ •CaSO ₄ •12H ₂ O) (e.g. kaolinite), this later gets converted to ettringite with time. Minerals that have less alumina content will directly form ettringite (e.g. montmorillonite). Even with several studies and decades of research, there has not been a definite sulfate concentration value for concluding the risk of ettringite formation in a soil.	Mitchell and Dermatus (1992), Wang et al. (2004) [7,26]
Sulfate concentration	The reason for variable levels of threshold sulfate concentration is due to the variability in soil type, source of sulfate and site conditions. But from experience it can be concluded that the lowest level of sulfate concentration that can cause distress to stabilized soil is 2000 ppm.	Hunter (1988), Kota et al. (1996), Mitchell and Dermatas (1992), Petry and Little (1992), Puppala et al. (1999), Harris et al. (2004), Puppala et al. (2014) [3,5,7,22,27,28]
Moisture content	The availability moisture content is essential for the formation and growth of ettringite crystals. Optimum temperature for the rapid formation of ettringite is 20-40°C.	Hunter (1998), Mitchell and Dermatas (1992) [5,7]
Temperature	The increase in temperature will speed up the ettringite formation. Ettringite is stable above 4°C and below 90°C. Ettringite below 4°C will transform into thaumasite by isostructural substitution of silica for alumina.	Hunter (1988), Taylor (1997), Brown and Badger (2000), Brown et al. (2003), Wang et al. (2004) [5,26,29,30,31]

3 External Sulfate Attack

The term external sulfate attack refers to the contamination of a stabilized soil matrix through an external sulfate source post stabilization of the soil. The major difference between the internal sulfate attack (soil bearing sulfates) and external sulfate attack (sulfate intrusion post stabilization) is presented in Table 2. External sulfate attack on a stabilized expansive soil can occur through acid rains, mine wastes, salt water intrusion, and industrial effluents from tanning factories, and excessive use of potash in agricultural fields [32]. In general, the sulfate concentrations in industrial wastes range from 12,500 to 35,000 mg/L [33]. Moreover the concentration of sulfate in seawater and municipal wastewater can also reach levels that are detrimental to the stabilized soil matrix [34, 35]. The most possible and convenient way of secondary external sulfate contamination on stabilized soils can occur through oxidative weathering of sulfide bearing rocks [36].

Table 2. Differences between internal sulfate attack and external sulfate attack

<u>Internal sulfate attack (Natural sulfate bearing soils prior to stabilization)</u>	<u>External sulfate attack (External sulfate intrusion post stabilization)</u>
Sulfates are present in pockets along the profile of the soil layer	Intrusion of sulfate in solution form is not restrained
Small pockets of sulfates acts as nucleation sites for ettringite formation	There is no restriction in the availability of the sulfate as it enters through all void pores of the soil
Soluble sulfates are present in the soil during the addition of stabilizer	Sulfates enter the soil after the formation of cementation compounds or post stabilization

The early study on sulfate as an external source of contaminant post stabilization of the expansive soil using calcium based stabilizer was studied by Cordon in 1962 [37]. The study was performed on both coarse and fine grained soils obtained from the drainage basin of Blacksmith Fork River in Cache Valley, Utah. Different type of cements like type I, II and V cements were used for the stabilization of the soil. The study was performed to compare the effect of both internal and external sulfate effects on the stabilized soils and to evaluate the performance of the various cement types against sulfate contamination. Based on the study it was concluded that type V and II cement performed better than the other stabilizers. Moreover the stabilized coarse grained soils performed better than the stabilized fine grain soils.

Following the study by Cordon in 1962 there hasn't been any study relating to external sulfate contamination on stabilized soils from a geotechnical point of view. However, the external sulfate attack has been given due importance in the design and durability studies of concrete structures. The authors feel that, as soils stabilized with the help of calcium based stabilizers exhibit comparably the same characteristics of concrete structures. It is of importance to give the external sulfate attack on stabilized soils

the same due importance that is provided to the concrete structures. In view of this, a more recent study by Raja and Thyagaraj (2019) [38] on external sulfate attack on lime stabilized expansive soils reported that the ettringite formation was observed on samples that were cured for 28 days prior to sulfate exposure with 20,000 ppm concentration. Moreover the study also analyzed the changes in physico-chemical and index properties of the stabilized soil before and after sulfate exposure. The pH of the stabilized soil decreased considerably with the increase in the sulfate concentration and the liquid limit of the soil increased due to the formation of ettringite. This formation of ettringite was confirmed through the SEM and XRD analysis. From the study, it can be concluded that the soil stabilized with calcium based stabilizers are under threat even after the completion of the long term soil stabilization reactions, and also the ettringite formation was observed even under a pH of 10.5.

A similar study by Raja and Thyagaraj (2020) [32] on sulfate resistant cement treated expansive soils exposed to external sulfate post stabilization also resulted in the formation of ettringite crystals. The study concluded that the use of sulfate resistant cement was not suitable for soils exposed to sulfate concentrations of above 10,000 ppm. Based on the above studies it can be concluded that the post contamination effect of sulfate is equally or even more dangerous than the internal sulfate attack as presented earlier.

4 Conclusions

The internal sulfate contamination is one of the most widely researched and spoken topic with regard to the sulfate attack on stabilized soils. The internal sulfate attack can be easily negated with the help of proper identification and estimation of sulfate content prior to the stabilization of the soil. But the external sulfate attack is relatively new and unexplored. Almost all the soils that are stabilized using calcium or low calcium based stabilizers are at a risk of external sulfate contamination that cannot be negated. As seen from the above review there has not been many studies that relate to the external sulfate attack on the stabilized soil which needs much exploration and explanations. It can be concluded that the external sulfate attack that has not been given due importance in the geotechnical field and has to be reviewed upon as it has the same potential if not more as that of internal sulfate attack in creating distress and destruction to the stabilized soils.

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