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Assessment of the effect of sulfate attack on cement stabilized montmorillonite

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Abstract. In this study, aiming to investigate the effects of sulfate attack on cement stabilized highly plastic clay; an experimental study was carried out considering the effects of cement type, sulfate type and its concentration, cement content and curing period. Unconfined compressive strength and chloride-ion penetration tests were performed to obtain strength and permeability characteristics of specimens cured under different conditions. Test results were evaluated along with microstructural investigations including SEM and EDS analyses. Results revealed that use of sulfate resistance cement instead of normal portland cement is more plausible for soils under the threat of sulfate attack. Besides, it was verified that sulfate concentration is responsible for strength loss and permeability increase in cement stabilized montmorillonite. Finally, empirical equations were proposed to estimate the unconfined compressive strength of cement stabilized montmorillonite, which was exposed to sulfate attack for 28 days.

Keywords: montmorillonite; sulfate attack; cement stabilization; unconfined compressive strength; chloride-ion penetration

1. Introduction

As the population is still increasing in a very high rate, urbanization expands through unsuitable zones over compressible and weak soils. Over the last decades, stabilization methods have been widely used in these areas to improve engineering properties of soil. Cement is often used as a chemical additive to improve static and dynamic strength properties of soils (AlZubaidi *et al*. 2013, Voottipruex and Jamsawang 2014, Shooshpasha and Shirvani 2015, Verástegui-Flores and Di Emidio 2014). Cement stabilization also leads to a reduction in permeability and increase in volumetric stability (Lee and Yong 1991, Kamon 1992, Tatsuoka *et al*. 1997, O'Rourke *et al*. 1998, Wong and Poh 2000). The improvement in engineering properties of cement stabilized soils is related to the primary and secondary cementitious materials in the soil cement matrix, which were produced by soil cement reactions (Kezdi 1979, Schaefer *et al*. 1997, Çokca 2001). Post hydration products, namely, hydrated calcium silicates (C-S-H), calcium aluminate hydrates (C-A-H) and hydrated lime (CH) are formed. The formation of further C-S-Hs and C-A-Hs are induced by the secondary pozzolanic reaction between the CH, silica and alumina from the clay minerals

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(Kamruzzamman 2002). These reactions among soil and cement clearly explain strength improvement in cement stabilized soils (Chew *et al*. 2004). On the other hand, chemical reactions occurring in cement stabilized soil which may include sulfate salt under sulfate attack causes reduction in strength and loss in volumetric stability. Petry and Little (1992) reported that sulfates in groundwater caused reactions among the calcium-pozzolans and they are responsible for formation of ettringite and monosulfate hydrate. For cement-stabilized soils, the formation mechanism of ettringite is similar to that of concrete. However, there are two possible mechanisms for sulfate attack. The Portland cement hydration products lead calcium and alumina to react with sulfates to form ettringite and this mechanism is the conventional type of sulfate attack. Second mechanism is clay-based sulfate attack. In this mechanism, ettringite is formed by calcium and the clay minerals in the soil that provide alumina to react with sulfates. Sulfate-resistant cements are low in C_3A and may protect against the first mechanism of sulfate attack. However, soil stabilized with sulfate-resistant cements can be exposed to second type of mechanism sulfate attack (Wang 2002). Determination of the resistance of soil-cement mixtures to sulfate salts is not an easy task since many factors control this phenomenon. pH, clay content and presence of chloride are several factors that affect sulfate resistance (Murdock *et al*. 1991, Havlica and Sahu 1992, Huntington 1995). Scientists investigated these effects on stabilized soils by various experimental methods and demonstrated the effects of sulfates parametrically (Mehra *et al*. 1955, Lambe *et al*. 1960, Ladd *et al*. 1960, Sherwoood 1962). One of the first studies on this subject was conducted by Sherwood (1958). Cement and lime stabilized clay specimens were cured in calcium, magnesium and sodium sulfate solutions to address the influence of sulfate ions on stabilized soils. Degradation of specimens was observed in samples within a few days, while cement stabilized sand specimens were unaffected even after exposed to sulfate attack for 365 days. As a result of this study, it was indicated that sulfate ions were more effective for reactions between clay minerals and cement. Hunter (1988) presented a mechanism clarifying the ettringite formation process in sulfate rich montmorillonite. Later, experimental research by Puppala *et al*. (2005) documented the effects of sulfate attack on cement/lime stabilized soils. The authors emphasized that ettringite formation as a result of ionic reactions caused heaving in clayey soils, and the expansions were higher in clays in comparison with those in sand, under similar environmental conditions. It was also stated that, the ratio of sulfate weight over dry weight of soil ranged between 320 mg/kg and 43,500 mg/kg. Needless to say, this is a very broad range. On the other hand, it was underlined that sulfate heave was evident after a wide period starting from a few days up to 18 months, which adds another uncertainty to the problem in hand. Klein and Simon (2006) discussed the effects of sulfate attack on engineering properties of cemented paste backfills. Evidences obtained from recent studies reveal similar results: sulfate attack adversely influences engineering properties of cement-stabilized soils. Ramon and Alonso (2013) analyzed heave in cement-stabilized railway bases and figured out an expansion rate of 0.9-1.3 mm/month, due to ettringite and thaumasite formation. Chrysochoou *et al*. (2012) different combinations of lime, cement kiln dust, fly ash, Portland cement and the slag cement in stabilization of a dredged material. Lowest ettringite potential was observed in mixtures of highest sulfate salt inclusion, where this outcome was ensued with low pH level, buffering, limited aluminum presence in solution. Emidio and Flores (2012) carried out experiments to assess the effect of sulfate attack on cement-clay mixtures. It was noticed that sulfate attack causes an increase in permeability and reduction in small-strain shear modulus of cement-clay mixture. In the recent past, a number of researchers conducted studies considering sulfate attack phenomenon within an environmental framework (Chittoori *et al*. 2013, Du *et al*. 2014). Recent studies concerning sulfate attack in cement stabilized soil is focused on environmental considerations: several effects including sulfate attack on solidified-stabilized soils were investigated by several researchers (Chittoori and Puppala 2011, Du *et al*. 2012, Chittoori *et al*. 2013, Du *et al*. 2014).

Although the subject was investigated by extensive studies in the literature, several shortcomings are encountered. First of all, it was observed that effect of sodium and magnesium sulfate on properties of cement stabilized soils were not individually investigated. In this manner, selection of the cement type to be used in clay stabilization in contact with structural elements is of great importance since minimization of the expansion of mixture is a need for minimization of damage in superstructure due to sulfate existence. Investigations on concrete elements and/or cement stabilized soils addressed the adverse effects of sulfate attack on engineering properties of concrete or stabilized soil.

It is considered that this study is a necessity for a comprehensive evaluation of the effects of cement type and its content, curing condition, sulfate concentration as well as its effect on strength and chloride-ion penetration values. Effects of sulfate attack on strength and permeability of cement stabilized specimens prepared with different materials and cured in different conditions will reveal additional knowledge about the cement stabilization mechanism in fine grained soils. Nevertheless, every stabilization decision is an engineering problem, and results of this study can be useful for discussion of the advantages and drawbacks of cement stabilization of high liquid limit clay under the threat of sulfate attack.

2. Experimental study

Tests were conducted on a montmorillonite type of clay. Atterberg limits, optimum moisture content and specific gravity of montmorillonite were determined in accordance with ASTM D698, ASTM D4318, ASTM D854 standards, respectively. Physical properties of montmorillonite clay were presented in Table 1. The liquid limit of montmorillonite clay was obtained as 191% and the plasticity index of montmorillonite was determined as 114%.

Clay was stabilized with cement, afterwards, unconfined compression and chloride ion penetration tests were carried out to determine the unconfined compression test and permeability of different soil/cement mixtures. In this regard, the effects of curing period, cement content and its type, sulfate type as well as the concentration of the sulfate solution was assessed based on the test results. Two types of cements (normal and sulfate resistance) were used to question the advantage of use of sulfate-resistant cement in soil stabilization. Besides, two types sulfate salts (sodium and magnesium sulfate) and two different sulfate concentrations (0.5 and 1%) were used to evaluate the effects of sulfate environment on permeability and strength of these specimens.

Table 1 Index properties of montmorillonite clay

Properties	Value
Liquid limit	191
Plastic limit	76
Plasticity index	114
Optimum moisture content (%)	45
Maximum dry unit weight (t/m^3)	1.04

Table 2 Chemical and physical properties of clay and cement

Component	Montmorillonite clay	Normal Cement CEM I 42.5 R	Sulfate resistance cement CEM I 42.5 R- SR
SiO_2 (%)	71	20.69	19.66
Al_2O_3 (%)	14	6.24	4.03
Fe_2O_3 (%)	0.7	2.48	4.53
CaO (%)	1.1	61.78	63.05
MgO (%)	3.2	1.90	2.10
SO_3 (%)	-	2.99	2.76
TiO_2 (%)	0.05	-	-
Na_2O (%)	0.25	0.25	0.12
K_2O (%)	1	0.98	0.54
Cl- (%)	-	0.0084	0.0071
Insoluble residue (%)	-	1.89	0.30
Loss of ignition (%)	6	2.19	3.22
Specific gravity	2.35	-	3.13
Specific surface – Blaine (cm^2/g)	N/A	3339	3481
Volumetric expansion (mm)	N/A	1.0	2.0

Lastly, three curing periods (1, 7 and 28 days) were selected to investigate the effect of curing period on the above mentioned properties. The effect of cement on the compaction characteristics of montmorillonite clay was determined by Standard Proctor Tests according to ASTM D698-12e1 standard with different inclusion level of cement. In specimen labels, C indicates the cement inclusion level, N and SR indicate the cement type (normal and sulfate resistance), Na and Mg indicate the solution type (sodium and magnesium sulfate), respectively. For instance, C5Na0.5SR1 label represents specimen including 5% of cement by weight and later cured in a sodium sulfate solution of 0.5% concentration for 1 days. Clay was stabilized by addition of 0, 5, 10 and 15% of cement in clay mixture by dry weight of clay. Normal Portland and sulfate resistance cements were preferred to stabilise the clay soil. Several properties of the cements and clay were given in Table 2.

All specimens for the unconfined strength tests and chloride-ion penetration tests were prepared at their optimum moisture contents. To prepare the specimens for testing, necessary amount of cement was initially mixed with water (corresponding to the optimum water content of soil) and this cement-water suspension was immediately mixed with clay until a uniform color was observed. Each specimen was compacted to 100% relative compaction by use of a standard proctor hammer and specimens were prepared within less than an hour to avoid setting. A dimension of 50×100 mm was selected for unconfined compression tests and permeability tests were conducted on specimens of 100 mm. diameter and 50 mm thickness. The specimens were covered with plastic wrap and kept in in a curing room before immersing in sulfate solutions. The important point here is the duration before immersing in sulfate solution. In this scope, a trial and error approach was adopted. Initially, it was decided to keep the specimens in a curing room for 7 days since this is a key period for strength gain of cementitious materials. Unconfined compressive strength tests were conducted to determine the strength of specimens after 7 and 21 days, and 21 day curing period was selected as the rational period, before immersing these specimens in sulfate solutions. Unconfined compression tests were conducted in accordance with ASTM D 2166 test standard. Additionally, in order to determine the permeability of the specimens, chloride ion penetration tests were conducted in accordance with ASTM C1202. As stated in the standard, solutions of 0.3% NaOH and 3% NaCl were prepared. The specimens were then placed between caps and silicone was used to isolate the specimen.

The current passing through the specimen is in terms of Coulomb, which is an indicator of the permeability level of the specimen. Nevertheless, chloride ion penetration tests were designed to test concrete specimens, therefore, the relatively high permeable specimens (in comparison with concrete) caused overheating problems in testing device. As the current passes through the specimen, when device temperature surpasses 70 ℃, it automatically terminates the procedure, therefore, a fixed period of 30 minutes is selected and the amount of current was measured after this period.

3. Results and discussion

After carrying out unconfined compressive strength and chloride ion penetration tests, the results were evaluated in terms of sulfate salt type, cement content, cement type, sulfate concentration and curing period. Afterwards, selected specimens were subjected to microstructural analysis for assessment of reasons of probable strength losses and permeability increases in soil specimens.

3.1 Compaction properties of cement-stabilized montmorillonite

The compaction curves of montmorillonite clay with different cement contents were shown in Fig. 1. The compaction curves were generated by plotting the dry unit weight and corresponding water contents of the compacted specimens. From Fig. 1, it is well understood that optimum moisture contents of the mixtures were determined as 45, 47, 45 and 47% for cement inclusion levels of 0, 5, 10 and 15%, respectively. The results revealed that, increase in cement inclusion level does not cause a significant change in optimum moisture content of mixtures. On the other hand, cement content caused a slight increase in maximum dry unit weight of the specimens. Maximum dry unit of specimens including 0, 5, 10 and 15% cement (by dry unit weight of clay) were determined as 1.04, 1.045, 1.05 and 1.09 t/m^3, respectively.

3.2 Strength properties of cement-stabilized montmorillonite

In order to investigate the alteration of the strength properties of montmorillonite under different conditions, a series of unconfined compression tests were conducted. Effects of cement content, cement type, curing time and sulfate solution on strength and stress-strain behavior were analyzed. Unconfined compression tests were performed on samples at an axial deformation rate of 1 mm/min. The load was applied until a strict decrease in axial stress was observed along with increasing axial strain, constrained with an upper limit of 15% for axial strain. Obviously, maximum value of axial stress is the unconfined compressive strength. At least three specimens were prepared and tested for repeatability considerations.

3.2.1 Effect of cement content

Fig. 2 shows the variation of unconfined compressive strength of specimens including 5, 10 and 15% sulfate resistance cement exposed to sulfate attack for 1 and 28 days. Fig. 2 also demonstrates

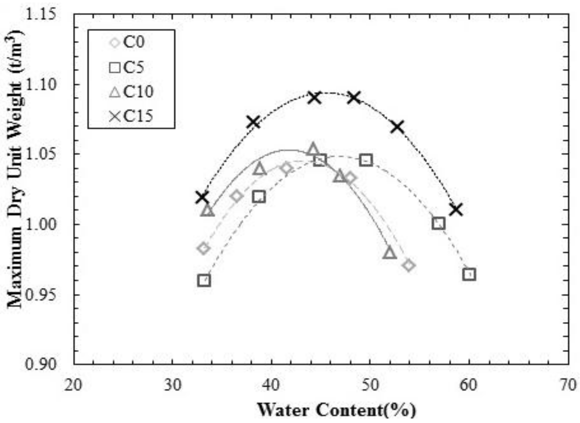


Fig. 1 Results of compaction tests on cement stabilized montmorillonite

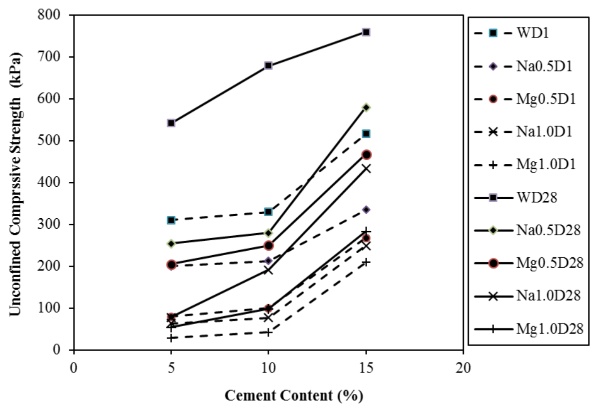


Fig. 2 Unconfined compressive strength - cement inclusion level plot of specimens incorporating sulfate resistance cement cured under different conditions

increases in unconfined compressive strength of specimens immersed in different sulfate solutions by means of increases in cement content. Inclusion of 15% cement by weight caused considerable increases in 1 and 28-day unconfined compressive strength of specimens cured in different sulfate solutions, in comparison with lower cement contents. As stated previously, increase in strength is related to hydration and pozzolanic reactions that lead to pozzolanic products. These products create stronger bonding in soil. Moreover, unconfined compression strength of specimens of different cement inclusion levels immersed in two different types of sulfate solutions decreased, as the sulfate concentration was increased. As expected, greatest strength values were obtained by testing specimens cured in water. It is evident that, hydration reaction is dominating the early age strength of cement stabilized clay exposed to sulfate attack. The strength gain at early ages is faster. Later, towards 28 days, pozzolanic reactions dominate the strength gain mechanism. It can be revealed that, sulfate attack suppresses 28-day strength gain, which is dominated by pozzolanic reactions.

3.2.2 Effect of sulfate type

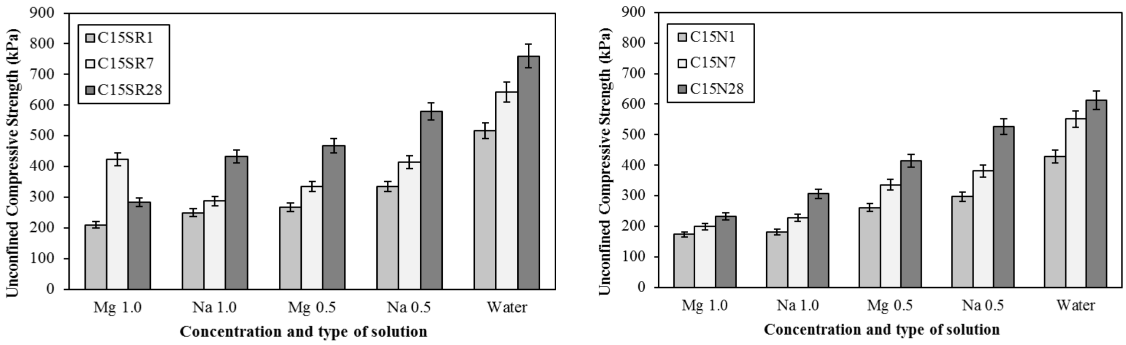
The effects of sulfate concentration and its type as well were also investigated within this study.

The unconfined compressive strengths of specimens incorporating 15% sulfate resistance cement and immersed in different solutions are given in Fig. 3. Analyzing Figs. 3(a) and (b), it is apparent that unconfined compressive strength of specimens decrease as the salt concentration of the solution is increased, regardless of the cement and sulfate type. The 28-day strength gain by increasing curing period ranges between 37.5-50% and 23-40% for specimens including sulfate resistance and normal portland cements, respectively.

It was understood that the maximum unconfined compressive strength value is obtained from the specimen immersed in water. On the other hand, minimum unconfined compressive strength value was obtained by testing the specimen incorporating normal portland cement immersed in 1% magnesium sulfate solution for 1 day. It was also observed that at the same concentration level, loss in strength of specimens immersed in magnesium sulfate solutions were higher than those immersed in sodium sulfate solution, regardless of the cement type. Furthermore, it is clear that magnesium sulfate salt is more aggressive than sodium sulfate, which caused more damage in specimens. This effect was due to expansion and crack formation by sulfate attack in magnesium sulfate solution and evanishing of binding property of calcium silicate hydrate and the cement as well. On the other hand, specimens immersed in water showed greater strength in comparison with the specimens cured in sulfate solutions. Unconfined compressive strength of specimens immersed in water was at least 2 times greater than those exposed to sulfate attack for 1 day. As expected, the increase in salt concentration increased the level of sulfate borne damage.

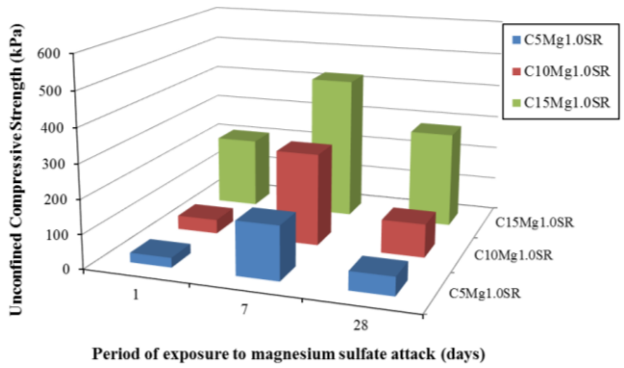
3.2.3 Effect of curing period

The unconfined compressive strengths of specimens incorporating sulfate resistance and normal portland cements of different inclusion levels immersed in 1% magnesium sulfate solutions were presented in Figs. 4(a) and (b). Considering specimens including sulfate resistance cement, the highest unconfined compressive strength was observed in the specimens that were exposed to sulfate attack for 7 days. However, after 7-day exposure period, strength of the specimens tends to decrease. In this regard, two reverse mechanisms are evident. Firstly, it is apparent that rapid development of cement hydration causes formation of calcium silicate hydrate gel, resulting an increase in the strength of specimens. On the other hand, the second mechanism here is the sulfate attack, which causes expansion and crack formation, and subsequently, decrease in strength of specimens. Test results also revealed that, in the first 7 days due to hydration of cement, and this

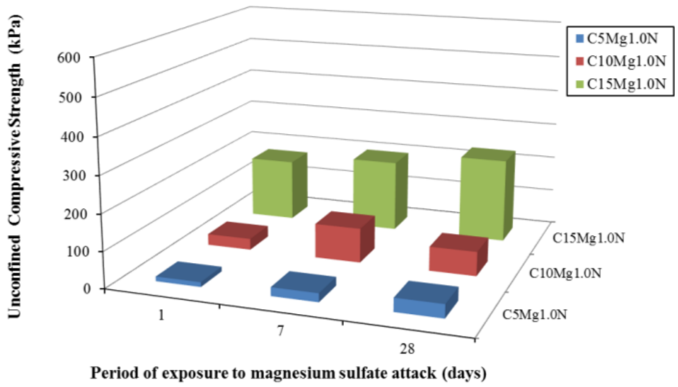


(a) (b)

Fig. 3 Variation of unconfined compressive strength of specimens cured under different conditions prepared using: (a) sulfate resistance cement; (b) normal portland cement



(a)

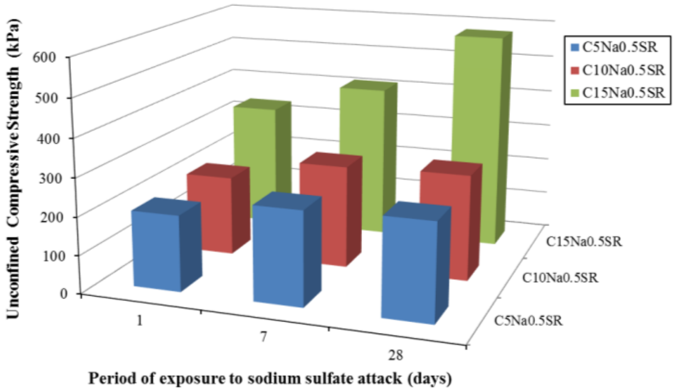


(b)

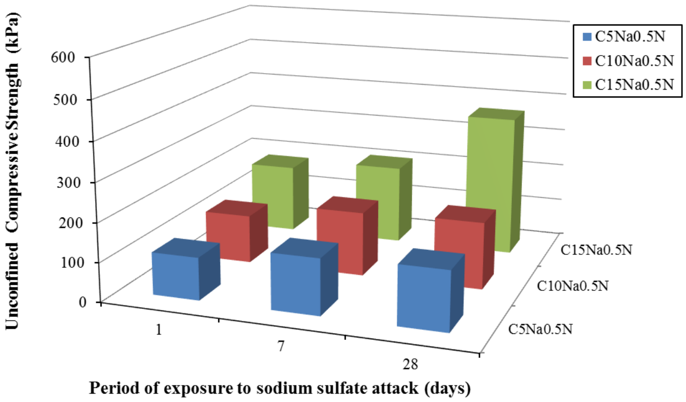
Fig. 4 Effects of exposure period and cement content on unconfined compressive strength of specimens immersed in magnesium sulfate solution. (a) Specimens containing sulfate resistance cement; (b) Specimens containing normal portland cement

dominated the process. Analyzing the specimens exposed to 28-day sulfate attack, a strength loss was apparent in comparison to those exposed to 7-day sulfate attack. Arguably, this proved that sulfate attack dominated the strength gain mechanism. Specimens incorporating normal Portland cements behaved differently. For specimens of 10% cement content, unconfined compressive strength of specimens cured for 7 days were higher than those cured for 28 days. Unlike other cement contents, after 7 days of curing, strength gain suppresses sulfate attack of specimens including 10% cement. When cement content is 15%, magnesium sulfate solution is incapable of damaging the cementitious bonding in stabilized medium. In this way, strength loss seems to be due to ettringite formation due to sulfate attack. 5% cement content is incapable of creating a sufficient amount of bonding expected from a cement stabilized clay exposed to sulfate attack.

The results of unconfined compression strength tests conducted on specimens including sulfate resistance and normal cements immersed in 0.5% sodium sulfate solution were shown in Fig. 5. Unconfined compression strength of specimens including both types of cements immersed in 0.5% sodium sulfate solution was increased after 28 days, in contrast with the specimens immersed in 1% magnesium sulfate solution. From this point, it can be revealed that the hydration process in specimens incorporating 15% cement immersed in 0.5% sodium sulfate solution dominated effects



(a)



(b)

Fig. 5 Effects of exposure period and cement content on unconfined compressive strength of specimens immersed in sodium sulfate solution. (a) Specimens containing sulfate resistance cement; (b) Specimens containing normal portland cement

of sulfate attack. However, the strength of specimens including 5 and 10% cement by weight showed no significant change between 7 and 28 exposure day. Thus, rate of the strength gains due to hydration and strength loss depending on sulfate attack were equivalent with each other.

3.2.4 Effect of cement type

In this study, two different types of cement were used to investigate the effect of ettringite formation due to sulfate attack. Fig. 6 shows the unconfined compressive strength of sulfate resistance and normal portland cement contained specimens immersed in different sulfate solutions. From the figure, it is apparent that, sulfate resistance cement showed better performance in comparison with normal portland cement, since the C_3A content of sulfate resistance cement was lower. This effect provides a decrease in risk of ettringite formation, which is responsible for expansion and microcrack formation in specimens.

3.2.5 Stress-strain behavior

The stress-strain relationship of cement stabilized clay of various cement contents were also

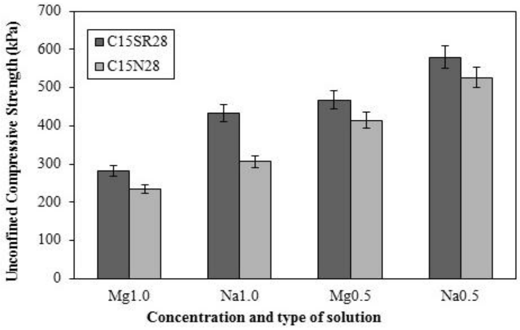


Fig. 6 The effect of cement type and solution concentration on strength of specimens including 15% cement by weight

investigated. As stated before, cement content and concentration of sulfate solutions affect the stress-strain behavior of specimens as well as the maximum axial stresses and the axial strains. In Fig. 7, the stress- strain curves of specimens with different cement inclusion levels immersed in varying magnesium sulfate solutions for 1 day are shown. Pure montmorillonite clay specimen immersed in different solutions showed a ductile behavior. However, with the addition of cement, the unconfined compressive strength of specimens increased due to formation of C-S-H gel. Besides, C-S-H gels also affect the stiffness characteristics of specimens. At higher cement inclusion level, the specimens become much brittle. On the other hand, the sulfate solutions lead to sulfate attack that contributes reduction in binding property of C-S-H gels. Furthermore, attenuation in binding properties of C-S-H gel causes a more ductile behavior. In this case, it is evident that, two factors affect the stress-strain behavior and also stiffness characteristics of the specimens. Analyzing Fig. 7, it is understood that specimens immersed in 0.5% magnesium sulfate solution behaved more brittle in comparison with those immersed in 1% magnesium sulfate solution.

The secant modulus (E_{50}), which reflects the resistance capacity to elastic and plastic deformation, is an important parameter in soil behavior that includes valuable information about

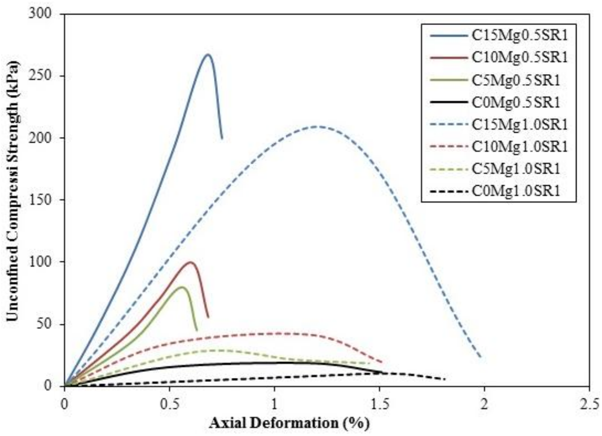


Fig. 7 Behavior of specimens exposed to solutions of different concentrations during unconfined compressive testing

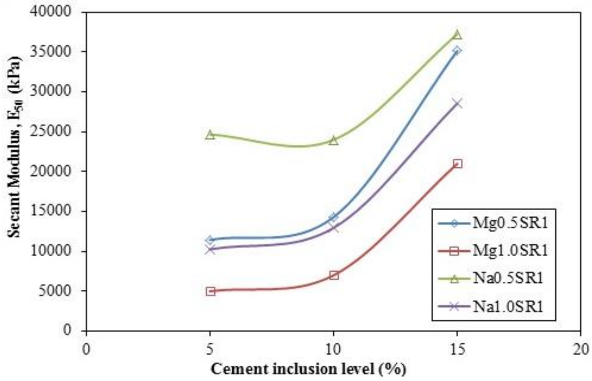


Fig. 8 Secant modulus of specimens exposed to solutions of different concentrations

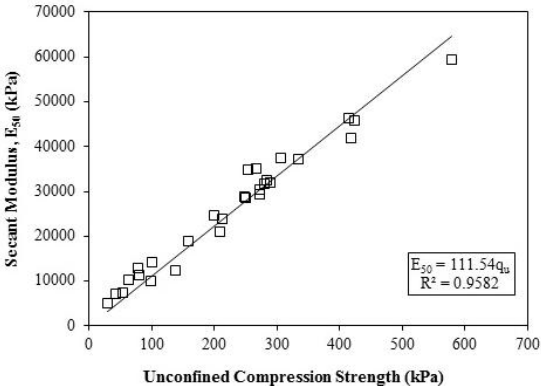


Fig. 9 The relationship between deformation modulus and unconfined compression strength of specimens exposed to sulfate attack

deformation behavior (Wang *et al*. 2013). In the stress-strain relationship obtained from an unconfined compressive strength test, this parameter is simply formulated as the ratio of the stress to strain at 50% of the unconfined compressive strength (Lorenzo and Bergado 2006, Zhang *et al*. 2014). The deformation modulus of the specimens with varying cement inclusion levels immersed in different sulfate solutions for 1 day were shown in Fig. 8. From the results, a significant increase in deformation modulus is experienced with increasing cement inclusion level. Predictably, the maximum value of E_{50} was attained in the specimens that were immersed in sodium sulfate solution with 0.5% concentration. Comparing the results obtained from specimens immersed in different types and concentrations of sulfate solutions, the highest unconfined compressive strength was obtained at the same specimens. However, there seems to be an explicit relationship between unconfined compressive strength and deformation modulus. In the past, Tang *et al*. (2000), Kukko (2000), Qiao (Qiao *et al*. 2007), Zhu *et al*. (2005), Wang (Wang *et al*. 2013) obtained quantitative correlations from their own experimental data. The correlations between qu and E_{50} values obtained by testing cement-stabilized specimens exposed to sulfate attack were shown in Fig. 9. A linear trendline fits the obtained data and obtained expression was E_{50} = 111.54q_u, having a coefficient of determination value (R^2) of 0.9716. This relationship can be a predictor in identification of the E_{50}-q_u relationship belonging to cement stabilized montmorillonite clay exposed to sulfate attack. In the previous studies, several researchers (Tang *et al*. 2000, Kukko 2000, Qiao *et al*. 2007, Wang *et al*. 2013) formulated similar relationships from data obtained by testing cement stabilized soils. The originality of the expression obtained in present study comes from the fact that it is the first known expression derived from data obtained by testing cement stabilized montmorillonite exposed to sulfate attack. Analyzing the formulations proposed in the literature, the coefficient of UCS in our study is in agreement with the coefficients previously proposed obtained from data belonging to cement stabilized soil.

3.3 Permeability properties of soil

After exposing specimens to sulfate attack for 28 days by immersing in sodium and magnesium sulfate solutions of 0.5 and 1% concentrations, chloride ion penetration tests were performed to determine their permeability. Test results were summarized in Figs. 10 and 11, respectively. It should be mentioned that, uncemented specimens and specimens of 5% cement inclusion level prepared using normal and sulfate resistance cements were not subjected cloride ion penetration test. Therefore, Figs. 10 and 11 include information belonging to C10 and C15 specimens. The amount of current transmitted by the specimen decreased as the cement content was increased

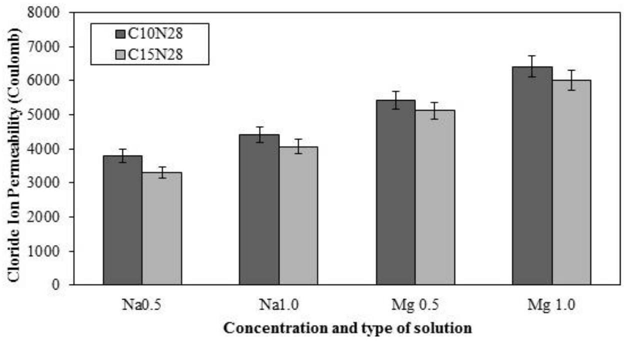


Fig. 10 Chloride ion penetration test results of specimens prepared using normal Portland cement exposed to 28 day sulfate attack

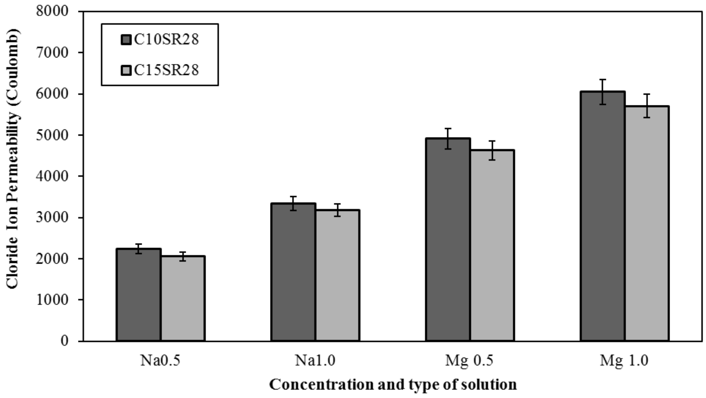


Fig. 11 Chloride ion penetration test results of specimens prepared using sulfate resistance cement exposed to 28 day sulfate attack

from 10 and 15%. Moreover, as stated in the evaluation of unconfined compression tests above, increased strength loss was observed in specimens exposed to magnesium sulfate attack which were approved by chloride ion penetration tests: Coulomb values were considerably higher. The sulfate resistance of normal Portland cement is considered to be based on its C_3A value, which was greater in sulfate resistance cement. Moreover, the Blaine fineness of sulfate resistance cement is higher than that of Normal Portland cement. Superposition of two positive factors is the reason behind the fact that permeability of specimens of sulfate resistance cement were lower than those prepared by normal Portland cement.

3.4 Microstructural investigations

Ettringite formation and its morphology are the most important factors affecting expansion upon sulfate attack (Mardani-Aghabaglou *et al*. 2014, Tosun and Baradan 2010). As it is known, the ball-ettringite formed inside the voids can be transformed into needle-like form after a certain period. Lastly, needle-like ettringite formations are nested together and these two formations would be responsible for the massive ettringite formation (Tosun 2007). The massive ettringite formation is an indicator of the severe sulfate attack accompanying a large expansion (Tosun and Baradan 2010).

In order to support the findings of this study, microstructural investigations were carried out on specimens subjected to sulfate attack. In this regard, in addition to the specimens of 0% cement inclusion level, two additional series of soil specimens including 15% of normal Portland cement and sulfate resistance cement were prepared. After exposing the specimens to sulfate attack in

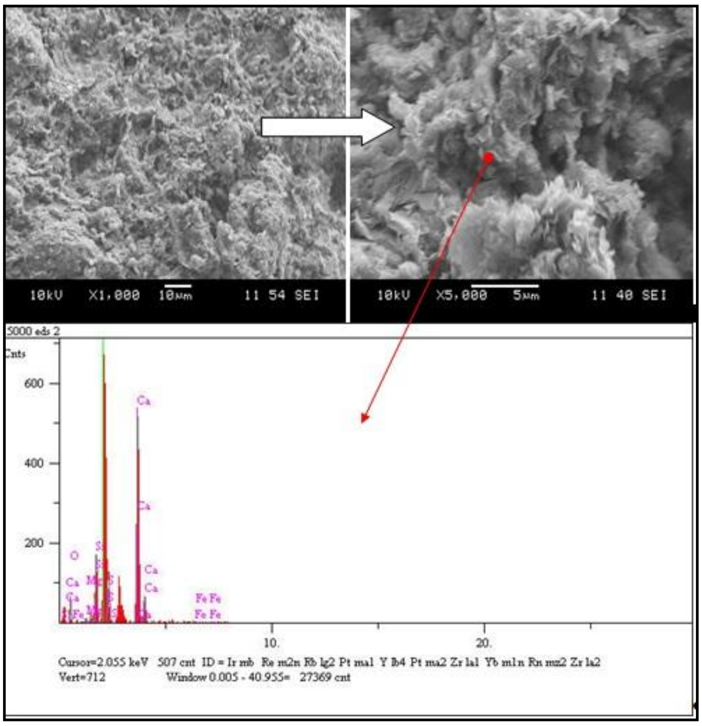


Fig. 12 SEM and EDS analyses of clay specimens (montmorillonite) immersed in water

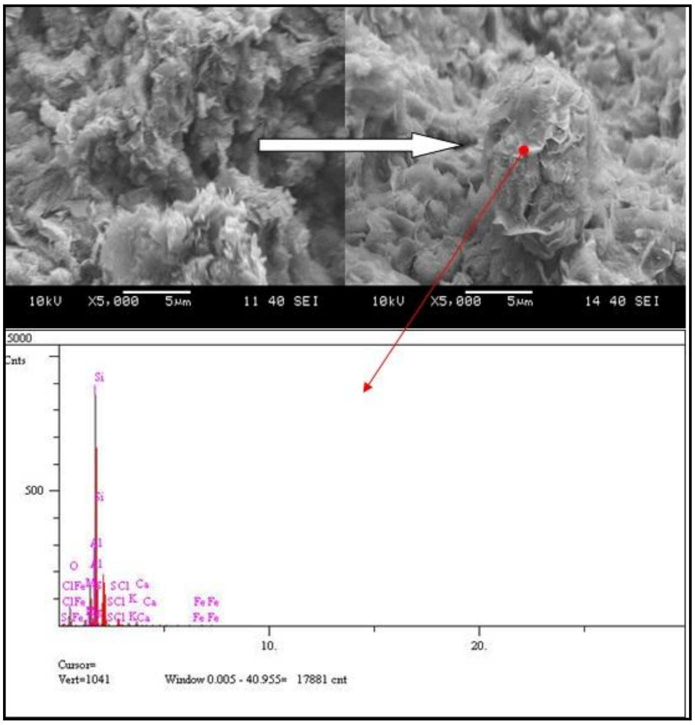


Fig. 13 SEM and EDS analyses of clay specimens (montmorillonite) immersed in magnesium sulfate solution of 1% concentration

$MgSO_4$ solution of 1% concentration for 180 days, they were air dried and gold-coating procedure was applied to small-sized portions of these specimens. Afterwards, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analyses were carried out on fractosurface specimens.

In order to investigate the effect of different types of sulfate solutions on microstructural properties of clay-cement mixtures, specimens prepared under similar conditions were immersed in water and magnesium sulfate solution of 1% concentration for 180 days. SEM and EDS analyses of clay specimens were given in Fig. 12. Outcomes of these analyses revealed typical montmorillonite structure. SEM and EDS analysis on specimens exposed to magnesium sulfate solution of 1% concentration was given in Fig. 13. As can be understood from the results, it is apparent that the morphology of the clay was stable. Additionally, lack of cementitious components (e.g., C_3A) inhibited ettringite formation in both of the specimens.

SEM and EDS analyses of cement stabilized clay specimens incorporating 15% sulfate resistance and normal portland cement were depicted in Figs. 14 and 15, respectively. As can be derived from the results obtained, changes in morphology of cement stabilized soil was observed, when exposed to sulfate attack. Nevertheless, EDS analysis verifies montmorillonite existence. Additionally, as can be derived from the microphotos, ettringite formation was not encountered in 15% sulfate resistance cement specimens. On the contrary, only needle-like ettringite formation was observed in specimens incorporating 15% normal portland cement. Moreover, EDS analyses also provide evidence of ettringite formation in above-mentioned specimens. However, the structure of ettringite formation was not dense, and this effect was attributed to lower cement

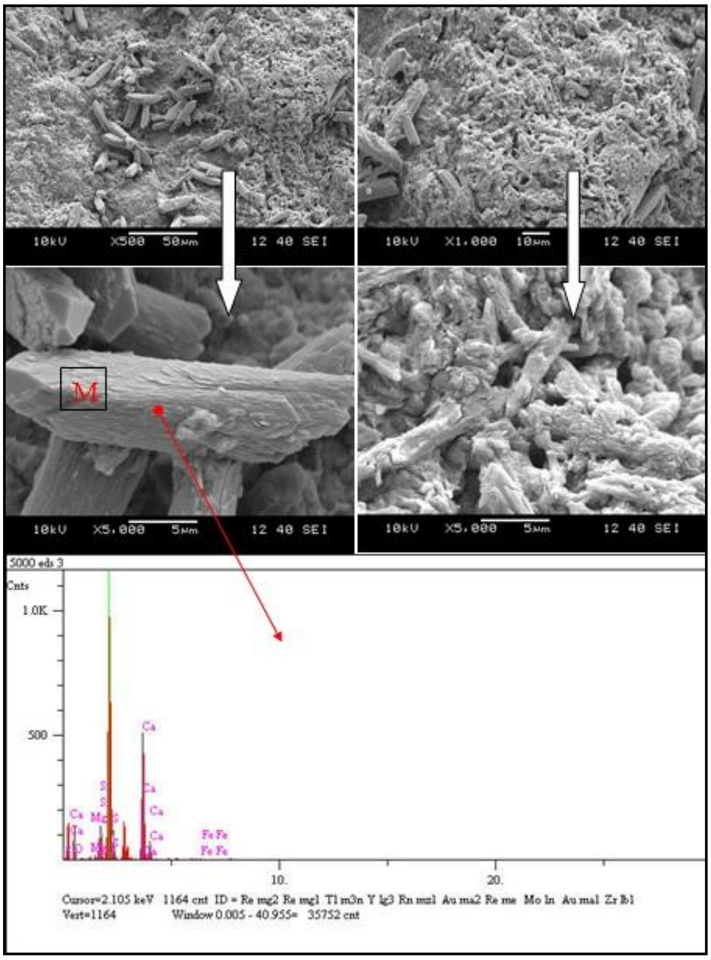


Fig. 14 SEM and EDS analyses of clay specimens incorporating 15% CEMI42.5 R sulfate resistance type cement, M:clay

inclusion level and immersion period. The results of this study underlined that strength increase rovided by cement inclusion masks detrimental effects of ettringitte formation, in cement stabilized clay specimens.

3.5 A simple mathematical approach to analyze obtained data

The last step in the analysis is establishment of simple models for estimation of uncofined compressive strength of specimens after exposure to sulfate attack for 28 days. As explained before, the cement inclusion level less than 5% and increase in sulfate attack duration caused specimens to completely disintegrate. This phenomenon somehow reduced the number of data in hand, in comparison with number of specimens prepared. Analysis of the data led to the result that, it is possible and plausible to study with specimens exposed to 28-day sulfate attack and related dependent parameters including cement incorporation level, salt type, salt concentration, permeability of specimens, unconfined compressive strength of specimens, curing period, etc.

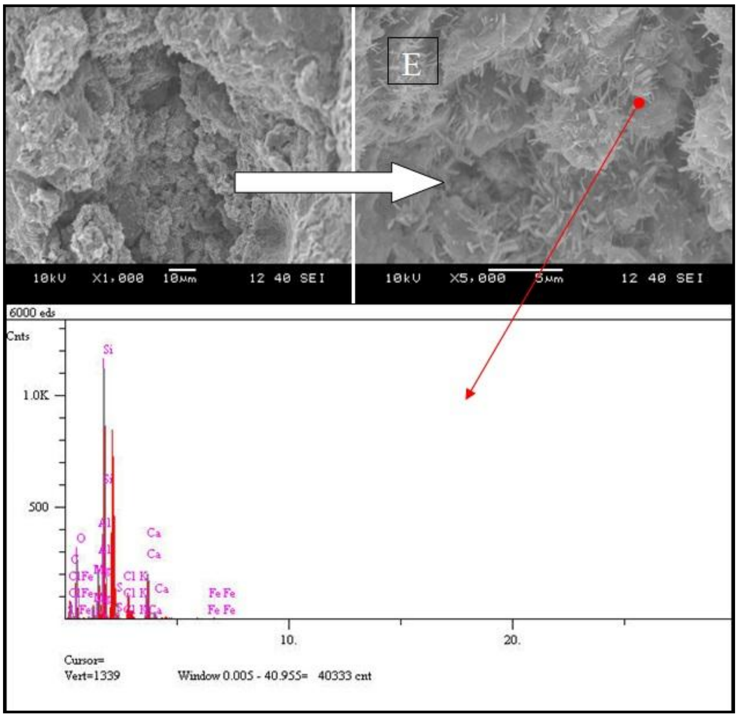


Fig. 15 SEM and EDS analyses of clay specimens incorporating 15% CEMI42.5 R type cement, E:ettringite

In this regard, data in hand was arranged and first step is the application of principal components analysis (PCA). PCA is a useful tool for feature selection and feature extraction (Haykin 2005). The goal of application of PCA, in simplest words, is providing a reduction in the number of variables of interest. After calculating the variances of variables, the variables are reorganized to constitute a new set of components. The new components are independent, and they are arranged in terms of the explained variance in the original components. Further information about the method can be found elsewhere (Haykin 2005). After conducting principal components analysis on the input data, communalities of the permeability (*k*), cement content (CC) and unconfined compressive strength (UCS28) parameters were calculated as 0.892, 0.855 and 0.943, respectively. Actually, the communality parameter is defined as the sum of the square of factor loadings for a specific variable, and is a measure of the multiple R^2 values of regression models predicting the variables of interest. Therefore, communality of a parameter is also the indicator of proportion of variation in that variable explained by predefined number of factors. The results suggest that factor analysis is most useful for explaining variations in permeability, cement content and unconfined compressive strength. Visual inspections gave rise to the same considerations, since there is an apparent relationship between *k*, CC and UCS_{28} parameters in Fig. 16.

As a result of these interpretations, the parameters in charge was reduced to three and nonlinear regression analyses were conducted using these parameters. It was aimed to establish relationships among UCS_{28}, *k* and CC parameters. Among the 242 equations, selected four equations along with related statistics were tabulated in Table 3.

Evaluation of the statistically obtained parameters depicted above, Eq. (1) in Table 3 is statistically the best for explanation of the relationship among *k*, CC and UCS_{28} parameters. However, for

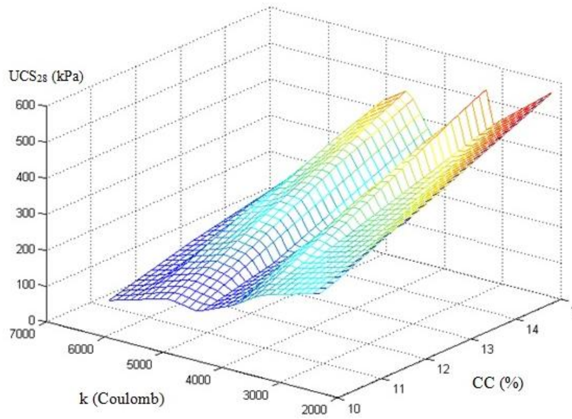
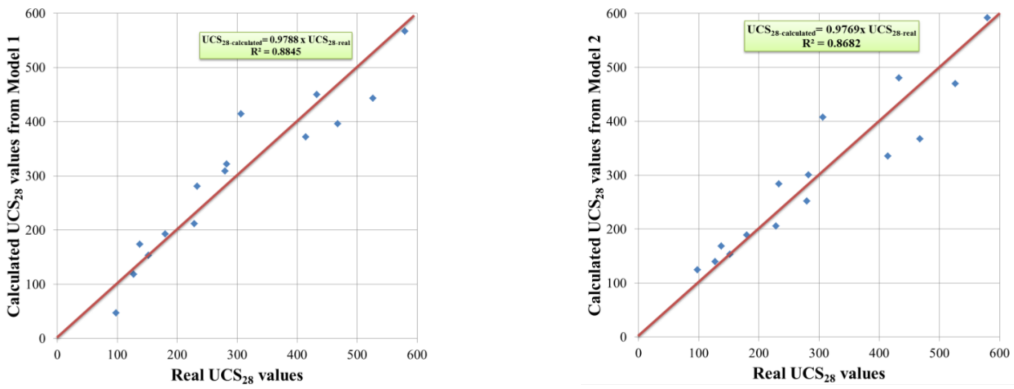


Fig. 16 Relationship among the unconfined compressive strength (UCS_{28}), chloride ion penetration or permeability (k) and cement content by weight (CC)



(a) Model 1 (b) Model 2

Fig. 17 Relationship among the unconfined compressive strength (UCS_{28}), chloride ion penetration or permeability (k) and cement content by weight (CC)

Table 3 Selected regression models for estimation of UCS_{28} parameter

No	Model	Standard error	Residual Sum	Residual sum of squares	R^2
1	$UCS_{28} = 1733.48 - \frac{6903.28}{CC} - 0.567 \times k + 0.00013 \times k^2 - 1.060 \times 10^{-8} \times k^3$	59.13	-1.70×10^{-09}	34967.72	0.894
2	$UCS_{28} = 3.635 \times CC^{2.021} \times 0.999^{k}$	56.38	-1.74×10^{-10}	38140.9	0.885
3	$UCS_{28} = -485.92 + 45.542 \times CC + \frac{792690}{k}$	60.62	-9.66×10^{-13}	44105.45	0.867
4	$UCS_{28} = -1323.64 + 561.6 \times \log(CC) + \frac{792690}{k}$	60.63	-1.88×10^{-12}	44105.45	0.867

simplicity, use of second model is reasonable. Scatter plots of the regression outcomes against real UCS_{28} values were given in Fig. 17. It should be underlined that, these equations are limited to their use for montmorillonite type clay, stabilized with cement a content ranging between 5-15%, and exposed to sulfate attack in a medium having a salt concentration ranging within 0 and 1%.

4. Conclusions

In this study, an experimental study was carried out to evaluate the effect of sulfate attack on cement stabilized montmorillonite. In this scope, the results of unconfined compressive strength and chloride ion penetration tests performed on cement stabilized clay specimens exposed to sulfate attack considering the cement type and its inclusion level, sulfate concentration, salt type and exposure duration were evaluated. Important outcomes of this study are listed below:

(1) Highly active montmorillonite is practically instabilizable material due to its low workability and strength, montmorillonite with a normal activity is used in the experimental study.
(2) Stabilizing a high liquid limit clay with sulfate resistance cement was more efficient: Prepared specimens were more resistant to sulfate attack, in comparison with those prepared by normal Portland cement.
(3) It was observed that, 5% of cement was insufficient for stabilization of montmorillonite exposed to sulfate attack. The specimens were completely disintegrated. Nevertheless, test results revealed that, 10% of cement inclusion level is an acceptable value for the montmorillonite clay under the threat of sulfate attack.
(4) Increase in cement content of specimens led to a considerable increase in unconfined compressive strength and decrease in permeability of the specimens.
(5) Results of strength tests figured out that, magnesium sulfate salt attack caused greater damage on specimens in comparison with specimens exposed to sodium sulfate attack.
(6) The increase in salt concentration adversely affected the strength and permeability properties of cement stabilized clay.
(7) Proposed equations can be used to estimate the unconfined compressive strength of cement stabilized montmorillonite, which was exposed to sulfate attack for 28 days. However, their use is limited to montmorillonite type clay, stabilized with cement a content ranging between 5-15%, and exposed to sulfate attack in a medium having a salt concentration ranging within 0 and 1%.

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References

AlZubaidi, M.R., AlRawi, K.H. and AlFalahi, A.J. (2013), "Using cement dust to reduce swelling of expansive soil", *Geomech. Eng., Int. J.*, **5**(6), 565-574.

Chew, S.H., Kamruzzaman, A.H.M. and Lee, F.H. (2004), "Physicochemical and engineering behavior of cement treated clays", *ASCE J. Geotech. Geoenviron. Eng.*, **130**(7), 696-706.

Chittoori, B.S. and Puppala, A.J. (2011), "Quantitative estimation of clay mineralogy in fine-grained soils", *ASCE J. Geotech. Geoenviron. Eng.*, **137**(11), 997-1008.

Chittoori, B.C.S., Puppala, A.J., Wejrungsikul, T. and Hoyos, L.R. (2013), "Experimental studies on stabilized clays at various leaching cycles", *ASCE J. Geotech. Geoenviron. Eng.*, **139**(10), 1665-1675.

Chrysochoou, M., Grubb, D. and Malasavage, N. (2012), "Assessment of sulfate-induced swell in stabilized dredged material: Is ettringite always a problem?", *J. Geotech. Geoenviron. Eng.*, **138**(3), 407-414.

Çokca, E. (2001), "Use of class C fly ashes for the stabilization of an expansive soil", *ASCE J. Geotech. Geoenviron. Eng.*, **127**(7), 568-573.

Du, Y.J., Jiang, N.J., Shen, S.L. and Jin, F. (2012), "Experimental investigation of influence of acid rain on leaching and hydraulic characteristics of cement based solidified/stabilized lead contaminated clay", *J. Hazard. Mater.*, **225-226**, 195-201.

Du, Y.J., Jiang, N.J., Liu, S.Y., Jin, F., Singh, D.N. and Puppala, A.J. (2014), "Engineering properties and microstructural characteristics of cement-stabilized zinc-contaminated kaolin", *Can. Geotech. J.*, **51**(3), 289-302.

Emidio, G. and Flores, R. (2012), "Monitoring the impact of sulfate attack on a cement-clay mix", *GeoCongress*, Oakland, CA, USA, March.

Havlica, J. and Sahu, S. (1992), "Mechanism of ettringite and monosulfate formation", *Cement Concrete Res.*, **22**(4), 671-677.

Haykin, S. (2005), *Neural Networks, A Comprehensive Foundation*, Prentice Hall, Upper Saddle River, NJ, USA.

Hunter, D. (1988), "Lime-induced heave in sulfate-bearing clay soils", *ASCE J. Geotech. Eng.*, **114**(2), 150-167.

Huntington, G.S. (1995), "Sulfate expansion in cement-treated bases", M.Sc. Thesis, University of Wyoming at Laramie, WY, USA.

Kamon, M. (1992), "Case studies of reinforced ground with micropiling and other improvement techniques", *Proceedings of the Symposium on Prediction versus Performance in Geotechnical Engineering*, Bangkok, Thailand, November-December.

Kamruzzaman, A.H.M. (2002), "Physico–chemical and engineering behavior of cement treated Singapore marine clay", Ph.D. Dissertation; National University of Singapore, Singapore.

Kezdi, A. (1979), *Stabilized Earth Roads*, Elsevier Scientific, Netherlands.

Klein, K. and Simon, D. (2006), "Effect of specimen composition on the strength development in cemented paste backfill", *Can. Geotech. J.*, **43**(3), 310-324.

Kukko, H. (2000), "Stabilization of clay with inorganic by-products", *ASCE J. Mater. Civil Eng.*, **12**(4), 307-309.

Lorenzo, G.A. and Bergado, D.T. (2006), "Fundamental characteristics of cement-admixed clay in deep mixing", *J. Mater. Civil Eng.*, **18**(2), 161-174.

Ladd, C.C., Moh, Z.C. and Lambe, T.W. (1960), "Recent soil-lime research at the Massachusetts Institute of Technology", *Proceedings of the 39th Annual Meeting Highway Research Board 1960*, Washington D.C., USA, January.

Lambe, T.W., Michaels, A.S. and Moh, Z.C. (1960), "Improvement of soil-cement with alkali metal compounds", *Highway Res. Record*, **241**, 67-103.

Lee, S.L. and Yong, K.Y. (1991), "Grouting in substructure construction", *Proceedings of the 9th Asian Regional Conference on Soil Mechanics and Foundation Engineering*, Bangkok, Thailand, December.

Mardani-Aghabaglou, A., İnan Sezer, G. and Ramyar, K. (2014), "Comparison of fly ash, silica fume and metakaolin from mechanical properties, and durability performance of mortar mixtures view point",

Construct. Build. Mater., **70**, 17-25.
Mehra, S.R., Chadda, L.R. and Kapur, R.N. (1955), "Role of detrimental salts in soil stabilization with and without cement. I. The effect of sodium sulphate", *Indian Concrete J.*, **29**(9), 336-337.
Murdock, L.J., Brook, K.M. and Dewar, J.D. (1991), *Concrete Materials and Practice*, (6th Edition), Oxford University Press, Canada.
O'Rourke, T.D., MacGinn, A.J., Dewsnap, J. and Stewart, H.E. (1998), "Case history of an excavation stabilized by deep mixing methods", *ASCE Geotechnical Special Publication*, **83**, 41-63.
Petry, T.M. and Little, D.N. (1992), "Update on sulfate-induced heave in treated clays: Problematic sulfate levels", *J. Transport. Res. Board*, **1362**, 51-55.
Puppala, A.J., Intharasombat, N. and Vempati, R. (2005), "Experimental studies on ettringite-induced heaving in soils", *ASCE J. Geotech. Geoenviron. Eng.*, **31**(3), 325-337.
Qiao, X.C., Poon, C.S. and Cheeseman, C.R. (2007), "Investigation into the stabilization/solidification performance of Portland cement through cement clinker phases", *J. Hazard. Mater.*, **139** (2), 238-243
Ramon, A. and Alonso, E.E. (2013), "Analysis of ettringite attack to stabilized railway bases and embankments", *Proceedings of the 18th International Conference on Soil Mechanics and Geotechnical Engineering*, Paris, France, September.
Schaefer, V.R., Abramson, L.W., Drumheller, J.C. and Sharp, K.D. (1997), "Ground improvement, ground reinforcement and ground treatment: Developments 1987 to 1997", *ASCE Geotechnical Special Publication*.
Sherwood, P.T. (1958), "Effect of sulfates on cement-stabilized clay", *Highway Res. Board Bull.*, **193**, 45-54.
Sherwood, P.T. (1962), "Effect of sulfates on cement and lime-stabilized soils", *Highway Res. Board Bull.*, **353**, 98-107.
Shooshpasha, I. and Shirvani, R.A. (2015), "Effect of cement stabilization on geotechnical properties of sandy soils", *Geomech. Eng., Int. J.*, **8**(1), 17-31.
Tang, Y., Liu, H. and Zhu, W. (2000), "Study on engineering properties of cement-stabilized soil", *Chinese J. Geotech. Eng.*, **22**, 549-554.
Tatsuoka, F., Uchida, K., Imai, K., Ouchi, T. and Kohata, Y. (1997), "Properties of cement treated soil in Trans-Tokyo Bay Highway Project", *Ground Improve.*, **1**(1), 37-57.
Tosun, K. (2007), "The effects of different types of cements on delayed ettringite formation", Ph.D. Dissertation; Dokuz Eylul University, Izmir, Turkey. [In Turkish]
Tosun, K. and Baradan, B. (2010), "Effect of ettringite morphology on DEF-related expansion", *Cement Concrete Compos.*, **32**(4), 271-280.
Verástegui-Flores, R.D. and Di Emidio, G. (2014), "Impact of sulfate attack on mechanical properties and hydraulic conductivity of a cement-admixed clay", *Appl. Clay Sci.*, **101**,490-496.
Voottipruex, P. and Jamsawang, P. (2014), "Characteristics of expansive soils improved with cement and fly ash in Northern Thailand", *Geomech. Eng., Int. J.*, **6**(5), 437-453.
Wang, L. (2002), "Cementitious stabilization of soils in the presence of sulfate", Ph.D. Dissertation; Louisiana State University, Baton Rouge, LA, USA.
Wang, D., Abriak, N. and Zentar, R. (2013), "Strength and deformation properties of Dunkirk marine sediments solidified with cement, lime and fly ash", *Eng. Geol.*, **166**, 90-99.
Wong, I.H. and Poh, T.Y. (2000), "Effects of jet grouting on adjacent ground and structures", *ASCE J. Geotech. Geoviron. Eng.*, **126**(3), 247-256.
Zhang, T.W., Yue, X.B., Deng, Y.F., Zhang, D.W. and Liu, S.Y. (2014), "Mechanical behaviour and micro structure of cement-stabilised marine clay with a metakaolin agent", *Construct. Build. Mater.*, **73**, 51-57.
Zhu, W., Zhang, C., Gao, Y. and Fan, Z. (2005), "Fundamental mechanical properties of solidified dredged marine sediment", *J. Zhejiang Univ.*, **39**(10), 1561-1565.

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