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Experimental Feasibility Research on a High-efficiency Cement-based Clay Stabilizer

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Abstract

In many civil engineering constructions, soft clayey soils are often stabilized with Ordinary Portland Cement (OPC) whose production process is energy intensive and emits a large quantity of CO_2. In this paper, an OPC-based clay stabilizer (CSCN) which contains some eco-friendly materials is studied to compare with OPC by investigating the mechanical properties of the stabilized clays. Microstructural and mineralogical studies using Scanning Electron Microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) are performed to reveal the mechanisms controlling the development of the strength and modulus. The test results indicate that the compressive strength and secant modulus increase with increasing the content of CSCN and curing age. To achieve the equivalent improvement of the strength and modulus, much less CSCN is needed relative to OPC, which illustrates that CSCN can be a more effective and relatively eco-friendly clay stabilizer. The analysis on pH values and moisture consumption indicates that the hydration and pozzolanic reactions in CSCN-stabilized clays may be quicker than those in OPC-stabilized clays. The microstructural analyses confirm the formation of C-S-H gels in stabilized clays and the types of C-S-H gels are dependent upon the Ca/Si molar ratio according to EDX results. The types and amounts of new minerals in stabilized clays are the possible mechanisms controlling the enhancement of mechanical properties.

Keywords: *clay stabilizer, mechanical properties, pH values, microstructural changes*

1. Introduction

In the field of geotechnical engineering, soft clayey soils lack sufficient strength to support the loading, which may generate severe damage to overlying structures (Gao, 1996; Zhang and Tao, 2008). One of the extensively used techniques for the improvement of problematic soils in relatively wet states is in situ deep mixing (Horpibulsuk *et al.*, 2004; Kasama *et al.*, 2012). There are a number of additives, which may be utilized for ground modification (Jie *et al.*, 2012). The most commonly used additives for soil modification are Ordinary Portland Cement (OPC) and lime (Niazi and Jalili, 2009, Naeini *et al.*, 2012; Yee *et al.*, 2014). In China, especially in South and East China, OPC is more widely used in comparison to quick lime which reacts with water rapidly and increases the difficulty of deep mixing. Nevertheless, a major issue with conventional soil stabilizers (i.e., OPC and lime) is that their production processes are energy intensive and emit a large quantity of CO_2. For instance, approximately one ton of CO_2 is emitted for the production of one ton of cement (Meyer, 2009).

Recently, the replacement of the cement by waste materials, such as fly ash, rich hush ash and phosphogypsum, has been applied in practice (Shen *et al.*, 2007; Horpibulsuk *et al.*, 2009; Zaimoglu, 2015). This technique has several advantages: (i) reduce the construction cost; (ii) transform the waste materials into assets, and (iii) improve the environmental acceptability of soil stabilizers. However, the engineering properties of the waste materials vary greatly with different regions in China, which may result in the unstable performance of the construction.

Application of sodium silicate for geotechnical works has been reported by some researchers (Kazemian *et al.*, 2011a, b). Compared with the waste materials, sodium silicate used as the supplementary cementing materials has distinctly unique advantages: (i) reliable and proven performance, (ii) safety and convenient for construction, and (iii) environmental acceptability and compatibility. In China, liquid sodium silicate with high silica modulus is applied in the improvement of tunnel and subway foundation.

In recent years, some researchers investigated the effects of the silica modulusof sodium silicate and the kinds of promoters on the properties of OPC or non-OPC stabilized soils (Sukmak *et al.*, 2013; Ma *et al.*, 2014). The silica modulus is the molar ratio of SiO_2 and Na_2O and generally between 1.5 and 3.5. When liquid sodium

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silicate is applied in geotechnical engineering, its silica modulus is often high due to its high bonding effect. The previous studies used single sodium hydroxide (NaOH) or calcium chloride ($CaCl_2$) as a promoter, and their results indicated that the application of sodium silicate and single promoter can improve the compressive strength of OPC-stabilized soils by 20% to 50%. For deep soft soil improvement (i.e. chemical grouting) and fly ash based geopolymers, the appropriate silica modulus is about 3.1.

For the precipitation of lime [$Ca(OH)_2$] in soil by successive mixing of $CaCl_2$ and NaOH solutions, it will develop much stronger soil-$Ca(OH)_2$ pozzolanic reactions than those caused by directly adding $Ca(OH)_2$ (Thyagaraj *et al.*, 2012). Therefore, the lime precipitation technique can be used as a novel method which can be compatible with cement to get strong bonding properties in stabilized soils. This paper has used a kind of composite promoter which consists of NaOH and $CaCl_2$. The promoters and sodium silicate can be regarded as the supplementary cementing materials substituting cement to improve the properties of stabilized soils (Papadakis and Tsimas, 2002).

This research studied two clay stabilizers, OPC and CSCN which consists of OPC, sodium silicate and composite promoter. The effects of the clay stabilizers on the mechanical properties were compared by determining the following properties: unconfined compressive strength (q_u), failure strain (ε_f), and secant modulus (E_s). The statistical trend of the development of mechanical properties with stabilizer contents and curing ages was analyzed. The changes of the clay stabilized with OPC and CSCN in minerals and microstructure are examined by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses. On the basis of mechanical property observation and mineralogical characterization, the possible mechanisms controlling the development of mechanical properties are discussed.

2. Experiment Details

2.1 Materials

The soil sample is soft clay collected from the Shanghai Jiao Tong University campus in Shanghai, China, at a depth of 6m. The soil contains high fine particle content, similar to many marine soft clayey soils. Particle size analysis was performed on the soil, and the result is shown in Fig. 1. Its specific gravity is 2.70. The liquid and plastic limits are approximately 42% and 24%, respectively. According to the Unified Soil Classification System (USCS), this soil is a CL. The natural water content and pH value were approximately 41% and 7.14. The chemical composition and morphology of the clay are shown in Table 1 and Fig. 2, respectively.

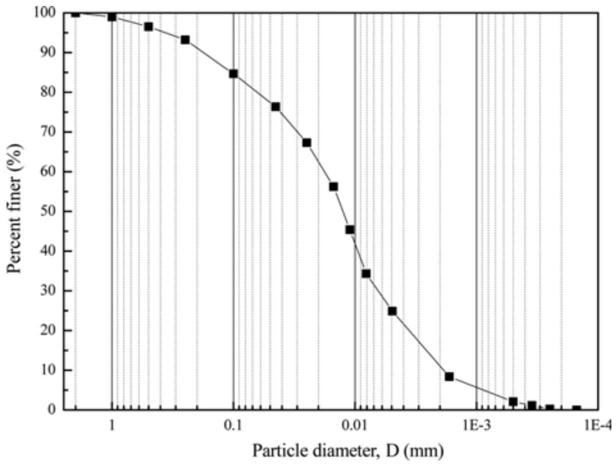


Fig. 1. Grain Size Distribution Curves of the Studied Clay

Table 1. Chemical Composition of Clay and OPC

Oxide	Chemical composition (%)	
	Clay	OPC
Silicon dioxide (SiO_2)	57.02	21.60
Calcium oxide (CaO)	3.63	64.44
Aluminum oxide (Al_2O_3)	16.42	4.13
Ferric oxide (Fe_2O_3)	6.79	4.57
Magnesium oxide (MgO)	3.68	1.06
Sodium oxide (Na_2O)	0.81	0.11
Potassium oxide (K_2O)	3.59	0.56
Sulfur trioxide (SO_3)	0.05	1.74
Loss on ignition (LOI)	6.43	0.76

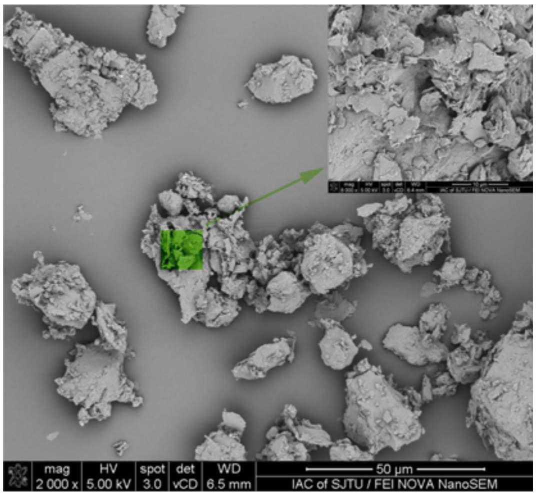


Fig. 2. SEM Photos of the Studied Clay

The binding agents consist of Portland cement and the supplementary cementing materials. ASTM Type I ordinary Portland cement (hereinafter called cement, OPC) was used for all stabilized clay mixtures in this study. The chemical composition of OPC is also shown in Table 1. The supplementary cementing materials are sodium silicate and composite promoter. Liquid sodium silicate consists of SiO_2 (29.48%), Na_2O (9.52%), and the silica modulus (molar ratio of SiO_2 and Na_2O) is 3.2. The density and pH are 1.40×10^4 N/m^3 and 11.98, respectively. Composite promoter consists of sodium hydroxide and calcium chloride at the mass ratio of 1:1 (Ma *et al.*, 2015). Sodium hydroxide (NaOH) and calcium chloride ($CaCl_2$) used in this study are both chemically pure. The selected component proportion

Table 2. Detail of Specimen Mixtures

Specimens	Content of each component (%)			Total content of stabilizer
	OPC	Sodium silicate	Composite promoter	
C-1	10	0	0	10% OPC
C-2	15	0	0	15% OPC
S-1	5	1	2	8% CSCN
S-2	6.25	1.25	2.5	10% CSCN
S-3	7.5	1.5	3	12% CSCN
S-4	8.75	1.75	3.5	14% CSCN
S-5	10	2	4	16% CSCN

of OPC, sodium silicate and composite promoter in CSCN is 5:1:2 (Ma *et al*., 2015).

2.2 Methodology

The specimen mixtures and the corresponding designations are listed in Table 2. It's notable that the content of stabilizer is the mass percentage of the soft clay. For preparing the specimens, the predetermined quantity of water was firstly mixed with the oven-dry clay, and the mass ratio of water and clay was 0.7. Then the rest of the water was blended with the binders at the mass ratio of 0.5, and the binders consisting of the desired amount of promoter, OPC and sodium silicate were added. Initial mixing was carried out in a laboratory mixer for at least 10 min and the mix was subsequently transferred to the PVC molds. For squeezing the air and achieve a homogeneous mixture, the molds were put onto vibrating table to vibrate for at least 2 min. Then, the molds were sealed and stored in the curing room (20±2ºC, 98±2% RH) for 7 days. Afterwards, the stabilized specimens were demolded and put into airtight vinyl bags in the curing room until the testing ages.

The unconfined compressive strength (UCS) test was performed according to ASTM standard D1633-00 on the samples after 7, 28, 60 and 90 days of curing. The rate of vertical displacement was fixed at 0.5 mm/min. At least three replicates of each sample set were prepared and tested under the same conditions to assure reproducibility. In most cases, the results under the same testing condition were reproducible with low mean standard deviations, SD (SD/$\bar{x}$ < 10%, where $\bar{x}$ = the mean strength value). The failure strain (ε_f) of the stabilized specimens was determined in UCS tests. The secant modulus (E_s) is defined as the ratio of one half of the compressive strength to the axial strain corresponding to this stress. The pH value and moisture content were taken on broken specimens after UCS tests at a predicted curing age. The samples were oven drying at 40 ± 2ºC in order to avoid losing crystal water in hydration products. According to ASTM standard D 4972-13, the liquid-to-solid ratio (deionized water/oven-dry samples) was kept at 4:1 for the pH value tests.

To examine the micromorphological change of the stabilized specimens, SEM imaging was performed on selected samples. The EDX spectra were collected within the selected areas of SEM samples in order to verify whether any hydration products were formed. SEM samples were prepared by following a procedure suggested in previous study (Zhang *et al*., 2013). To investigate the mineralogical changes in the stabilized clay, XRD patterns were taken on broken samples after UCS tests. The powder samples were scanned with X-ray powder diffractometer using a Cu K_α radiation. The data were collected from 5° to 65° 2θ at 0.02°/step.

3. Results and Discussion

3.1 Mechanical Properties

The unconfined compressive strength of stabilized clay specimens is shown in Fig. 3. For all curing ages, as the CSCN content increases, the strengths of the CSCN-stabilized clay specimens increase. It also can be seen that the strengths of specimens S-3 and S-4 are much higher than those of specimens C-1 and C-2 in spite of the higher stabilizer content in specimens C-2. Compared with specimens C-1, the strengths of specimens S-2 with 10% CSCN consisting of only 6.25% OPC at 7 and 60 days are 124 and 327 kPa, which are almost equivalent to the strengths of specimens C-2. When the content of CSCN is 16%, the strengths at 7, 28 and 60 days are 489, 739, and 907 kPa, which are almost three times higher than those of specimens C-2. This implies that the addition of the supplementary cementing materials can replace a considerable amount of OPC for the equivalent enhancement of the unconfined compressive strength. The possible reason may be that the hydration products generated by the pozzolanic reactions improve the degree of bonding of soil particles. This can be demonstrated by the SEM imaging of untreated, OPC-stabilized, CSCN-stabilized clay specimens in the following sections.

Figure 4 shows the failure strain of stabilized clay specimens at different curing times. As shown in Fig. 4, the failure strains of specimens stabilized with CSCN are mostly lower than that of specimens stabilized with OPC. This means that CSCN-stabilized clay specimens are more brittle compared to the two

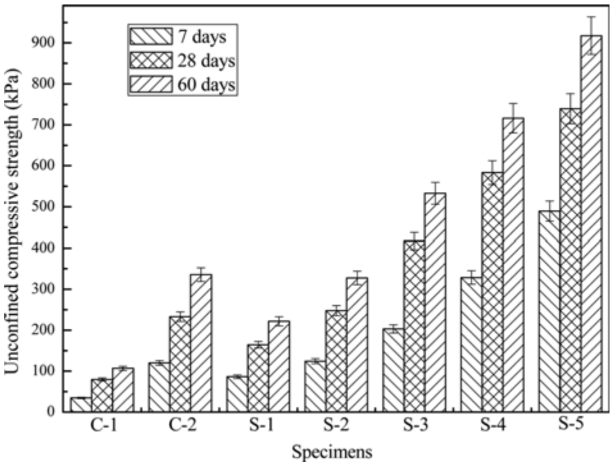


Fig. 3. The Compressive Strength of OPC- and CSCN-stabilized Clays at Different Curing Ages

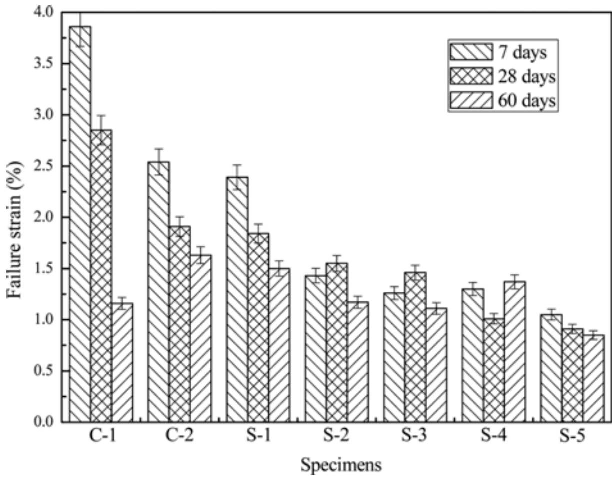


Fig. 4. The Failure Strain of OPC- and CSCN-stabilized Clays at Different Curing Ages

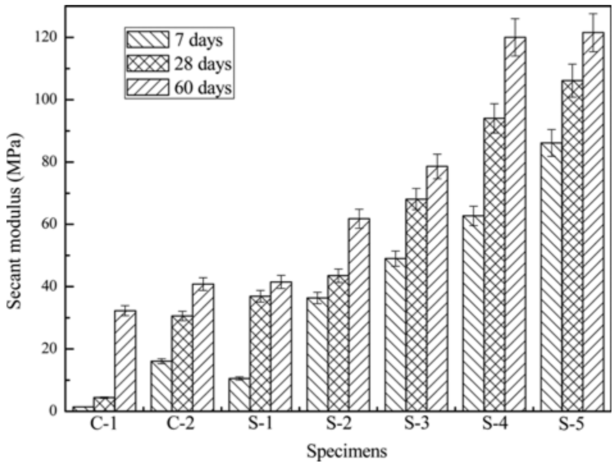


Fig. 5. The Secant Modulus of OPC- and CSCN-stabilized Clays at Different Curing Ages

control specimens. Although the failure strains of specimens C-1 and C-2 decrease with curing ages, those of specimens S-2, S-3 and S-4 have not experienced a decrease with curing ages. The possible reason may be that the values of failure strains in CSCN-stabilized clay specimens change in a small range and present obvious discreteness.

Figure 5 shows the secant modulus of stabilized clay specimens at different curing times. As shown in Fig. 5, the secant modulus increases with curing age and the content of CSCN, this is approximately consistent with the tendency of strength development. On account of the decrease of failure strain, the secant moduli of specimens S-1 at different curing ages are almost equal to those of specimens C-2. The possible reason may be that there are some different hydration products dispersed within the CSCN-stabilized clay specimens. Nevertheless, when the content of CSCN is larger than 14%, the secant moduli after 60 days of curing tend to be almost constant.

Figure 6 shows the stress-strain relationship of stabilized clay specimens at 28 days of curing. As shown in Fig. 6, a similar stress-strain behavior of specimens stabilized with OPC and CSCN is figured out. The difference is that CSCN-stabilized clay specimens are more brittle than OPC-stabilized specimens with similar compressive strength. For instance, the remaining strength of specimens C-2 is about 80% of the maximal stress, and that of specimens S-2 only accounts for only about 50% of the maximal stress.

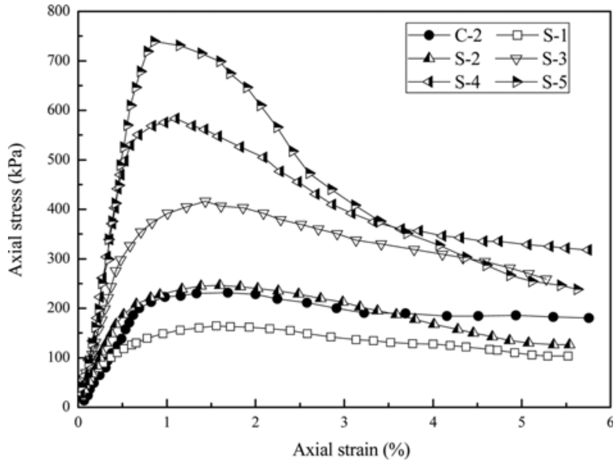


Fig. 6. Stress-strain Relationship of OPC- and CSCN-stabilized Clays at 28 days of Curing

3.2 Analysis of the Development of Mechanical Properties

As shown in Figs. 3-5, there are some statistical regulars among mechanical properties, the content of CSCN and curing ages. Consoli *et al.* (2010) reported that the relationship of unconfined compressive strength to the content of soil stabilizer can be expressed as the following equation:

$$q_u = A \cdot e^{C_i/B} - C \tag{1}$$

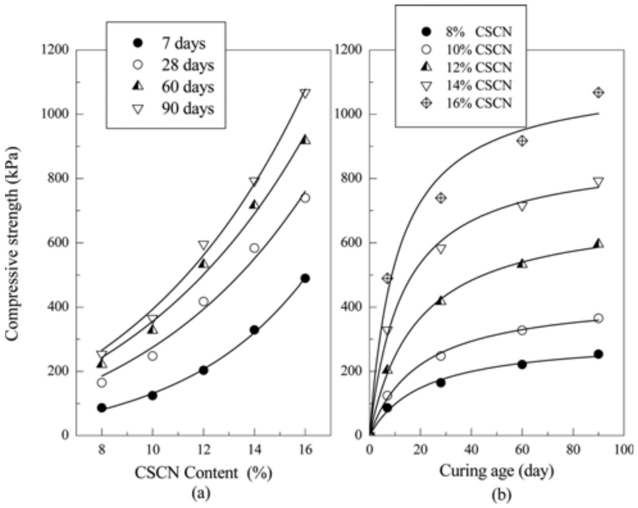
where q_u is the compressive strength of CSCN-stabilized clay at a given curing age, C_i is the content of CSCN, A, B and C are empirical constants. In this study, q_u is 0 when C_i is 0%, which results in the values of A and C identical.

The relationship of unconfined compressive strength to curing ages introduced by Kaniraj and Havanagi (1999) is expressed as follows:

$$q_u = q_0 + \frac{1}{Mt+N} \tag{2}$$

where q_0 is the measured initial compressive strength ($t = 0$), t is the curing age, M and N are empirical constants. In this study, q_u is 0 when t is 0, that is to say, the value of q_0 is 0.

Figure 7 shows the relationship of compressive strength to the content of CSCN and curing age, and the empirical constants are listed in Table 3. As shown in Table 3, the constants A and B, M and N that govern the strength development depend upon curing age and the content of CSCN, respectively. The values of A and B increase with curing age, and the coefficient of determination (R-square) is greater than 0.95. This implies that the compressive

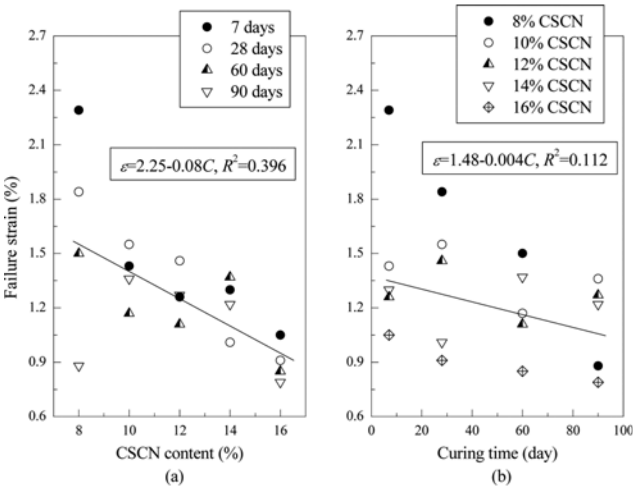


(a) (b)

Fig. 7. The Relationship of Compressive Strength to the Content of CSCN and Curing Age

strength increases exponentially with increasing the content of CSCN. The values of *M* and *N* decrease with increasing the content of CSCN and the smaller the values of *M* and *N*, the larger is the gain in strength with curing age.

A linear relationship of failure strain to the content of soil stabilizer was proposed by Zhang *et al.* (2013), but its coefficient of determination is low ($R^2 < 0.8$). Fig. 8 shows the trend and fitted curves of failure strain with the content of CSCN and curing age. The failure strain itself is small, varying from 0.7 to 2.3%. As shown in Fig. 8(a), the failure strain mostly tends to decrease with increasing the content of CSCN. The coefficient of determination of the fitted curve is only about 0.396, which implies that the values of failure strain at different curing ages are widely dispersed. As shown in Fig. 8(b), the failure strain of specimens S-1 and S-5 tends to decrease with curing age, and the failure strain of the other specimens exhibited a “wave” variation. The coefficient of determination of the fitted curve is only 0.112. Hence, it is difficult to discover a precisely statistical trend of failure strain for stabilized soil for the reason of the distractiveness of failure strain of specimens stabilized with different contents of soil stabilizer.



(a) (b)

Fig. 8. The Trend and Fitted Curves of Failure Strain with the Content of CSCN and Curing Age

Similar with the statistical trend of the development of compressive strength, the relationship of secant modulus to the content of CSCN and curing age can be expressed as the following equations:

$$E_s = H \cdot e^{C_i/I} - Q \tag{3}$$

$$E_s = E_0 + \frac{1}{Jt+K} \tag{4}$$

where E_s is the secant modulu of CSCN-stabilized clay at a given curing age, C_i is the content of CSCN, *H*, *I*, *J*, *Q* and *K* are empirical constants. In this study, E_0 is 0. E_s is 0 when C_i is 0%, so *H* and *Q* are equal.

The relationship of secant modulus to the content of CSCN

Table 3. The empirical Constants of the Relationship of Compressive Strength to the Content of CSCN and Curing Age

Relationship of q_u to C_i				Relationship of q_u to t			
Curing age (day)	A	B	*R*-square	CSCN content (%)	$M \times 10^{-3}$	$N \times 10^{-2}$	*R*-square
7	19.76	4.92	0.998	8	3.28	6.93	0.992
28	88.18	7.07	0.981	10	2.28	4.50	0.997
60	131.39	7.63	0.986	12	1.41	2.63	0.998
90	129.38	7.16	0.993	14	1.13	1.46	0.996
				16	0.89	0.97	0.976

Table 4. The empirical Constants of the Relationship of Secant Modulus to the Content of CSCN and Curing Age

Relationship of E_s to C_i				Relationship of E_s to t			
Curing age (day)	H	I	*R*-square	CSCN content (%)	$J \times 10^{-3}$	$K \times 10^{-2}$	*R*-square
7	9.61	6.92	0.935	8	13.34	47.5	0.965
28	34.56	11.17	0.957	10	13.17	14.86	0.908
60	58.74	13.72	0.905	12	9.47	10.16	0.910
90	135.74	21.54	0.954	14	7.1	7.29	0.983
				16	7.25	3.56	0.962

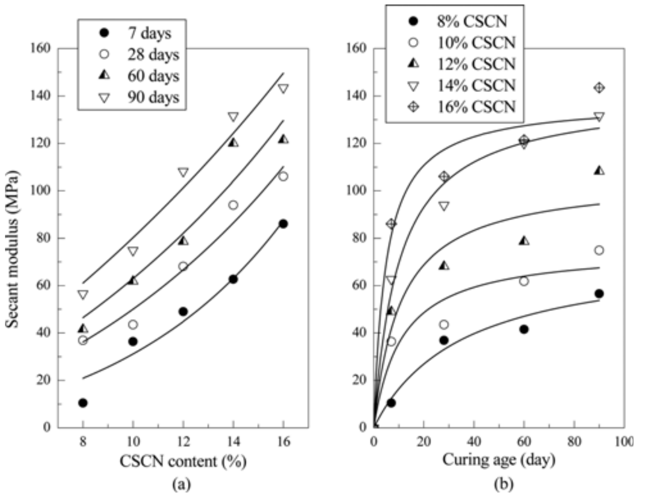


Fig. 9. The Relationship of Secant Modulus to the Content of CSCN and Curing Age

and curing age is shown in Fig. 9, and the empirical constants are listed in Table 4. The constants governing the development of secant modulus vary with the content of CSCN and curing age. The tendency of the constants (i.e. *H*, *I*, *J* and *K*) is similar with that presented in the development of compressive strength. This observation is also consistent with the result reported by Kaniraj and Havanagi (1999).

3.3 pH Values

The pH value is an important index to estimate the chemical reactions occurred in stabilized clay specimens. Fig. 10 shows the relationship between pH values and curing age for stabilized clay specimens. For all specimens stabilized with CSCN, the pH values increased with increasing amounts of CSCN added at the initial setting period. For example, the pH is 12.58 for the specimens S-3, greater than that of specimens S-1 by 0.71. However, the pH value of specimens S-5 shows very limited increase. It is notable that the pH value of specimens S-1 is higher than that of specimens S-2, mainly because CSCN consists of small amount of NaOH. Almost each specimen has the maximal pH value at 1 day of curing. The possible reason may be that the hydration of cement creates $Ca(OH)_2$ which governs the pH value of stabilized clays. And then, the pH values at 3 days of curing decrease sharply for the transformation of $Ca(OH)_2$ to hydrated calcium silicate (C-S-H). It's known that the nuclei of $Ca(OH)_2$ will disappear when the pH value of the pore liquid is below 12.4. Hence, $Ca(OH)_2$ in the stabilized clay after 3 days of curing exists in the form of Ca^{2+} and OH^- in the pore liquid. Ca^{2+} and OH^- perform pozzolanic reactions with the active clay minerals, which results in the quick decrease of the pH values. After 28 days of curing, the pH values decrease slightly, which indicates that the pozzolanic effect is weakened and the growth rate of compressive strength is reduced.

3.4 Moisture Consumption

The free water in the pore liquid of the stabilized soil can be transformed to crystal water in hydration products by hydration and pozzolanic reactions. Hence, the decrease of moisture content reflects the hydration degree of soil stabilizer. In this study, the increase of oven-dry weight of specimens is used instead of the decrease of moisture content, and it can be calculated according to the following equation:

$$R = \frac{w_0 - w_1}{(1+w_0)\cdot(1+w_1)} \times 100\% \tag{5}$$

where *R* is the value of increase of oven-dry weight of stabilized clays, w_0 is the initial moisture content, w_1 is the moisture content at a predicted curing age.

The values of *R* for stabilized clay specimens at different curing ages are shown in Fig. 11. It is observed that the *R*-values increase with curing age for all specimens. For OPC-stabilized clay specimens, the biggest increase in *R*-values occurs from 28 to 60 days of curing. However, for CSCN-stabilized clay specimens, that occurs from 7 to 28 days of curing. And the *R*-values of CSCN-stabilized clay specimens show a very small

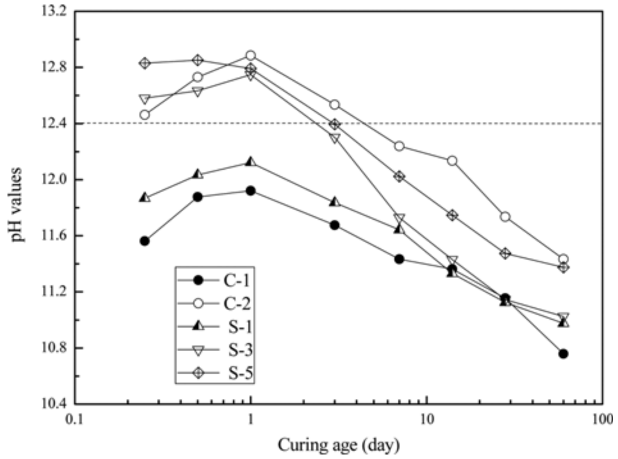


Fig. 10. The Relationship between pH Values and Curing Age for Stabilized Clay Specimens

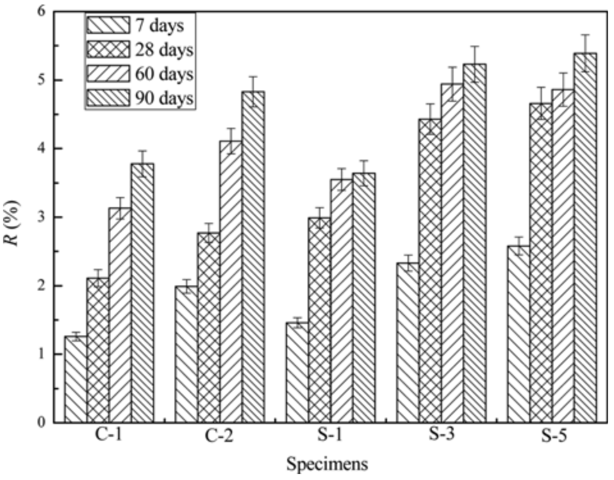
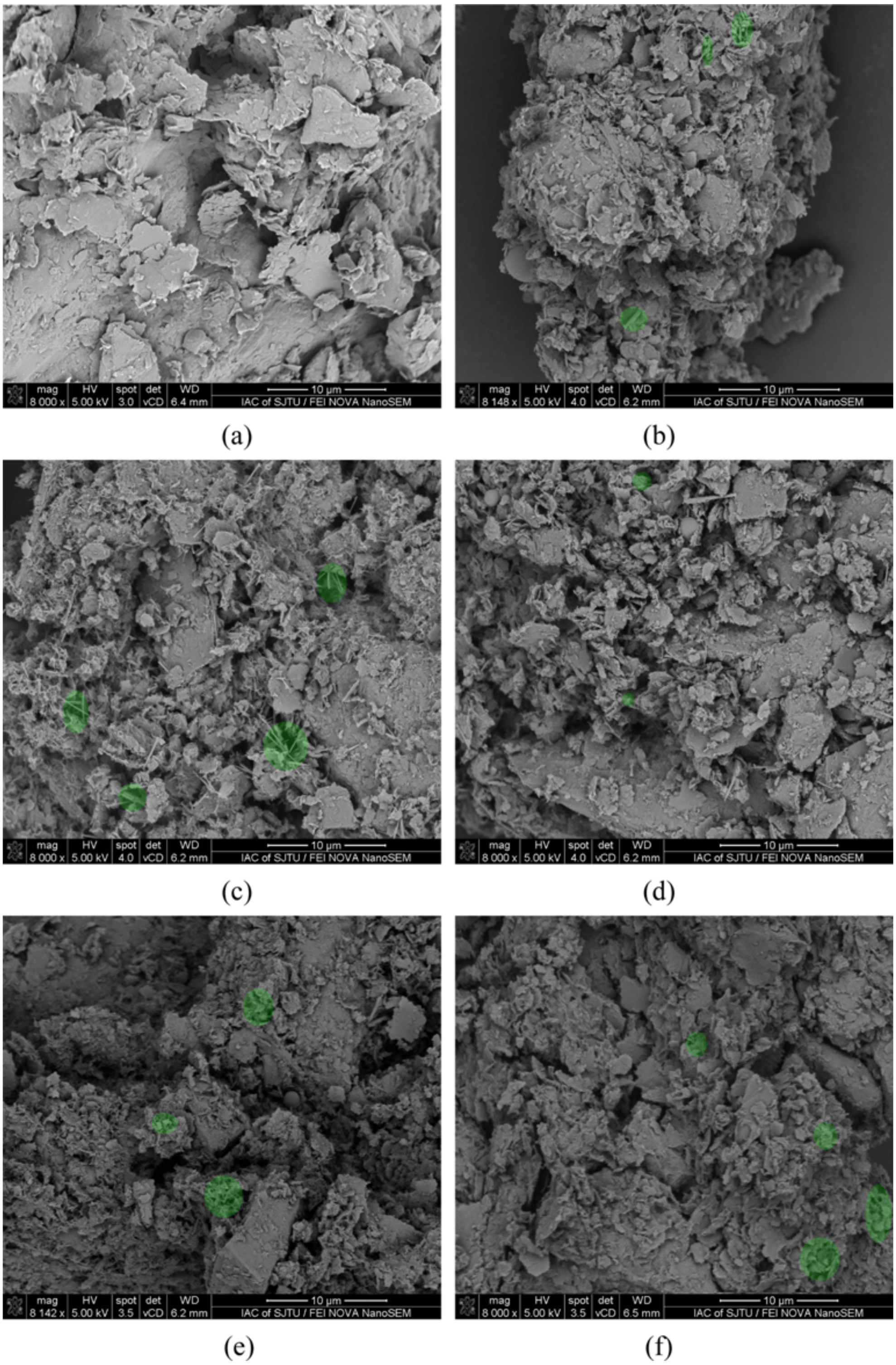


Fig. 11. The Values of *R* for OPC- and CSCN-stabilized Clays at Different Curing Ages

increase from 28 to 90 days of curing. This indicates that only few hydration products are generated beyond 28 days of curing, which confirms the conclusions achieved by analyzing the compressive strength and pH value. Although the compressive strength of specimens S-5 is much more than twice that of specimens C-2, there is only very small difference in *R*-values between the two mixtures. This may be because the hydration products are different in the two mixtures, which can be observed by SEM characterization in the next section.

3.5 SEM-EDX Characterization

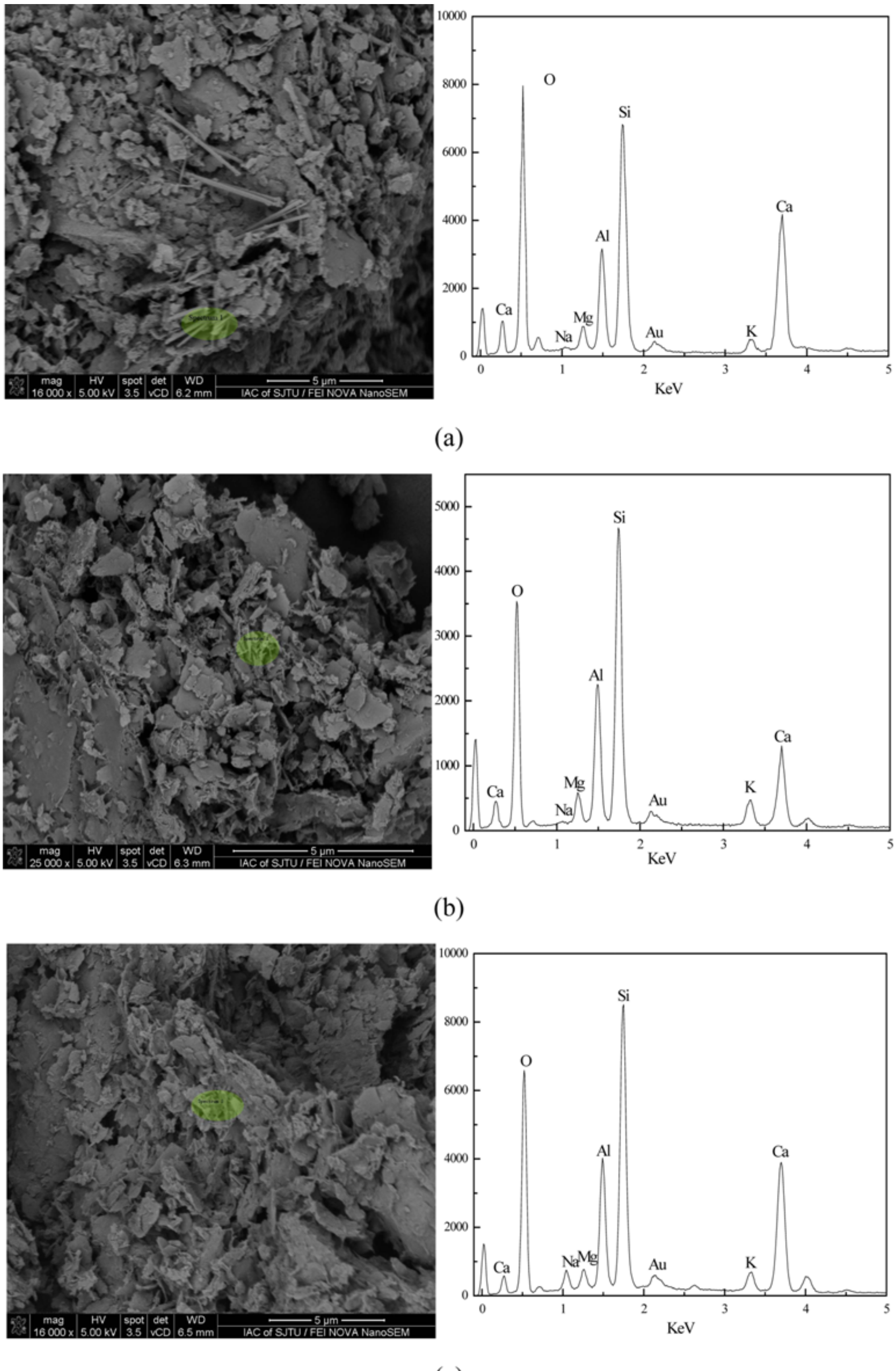
Figure 12 shows the surface morphology of untreated clay, and



(a) (b) (c) (d) (e) (f)

Fig. 12. SEM Photos of: (a) Untreated Clay, (b) C-1, (c) C-2, (d) S-1, (e) S-3, (f) S-5 Specimens after 28 days of Curing

specimens stabilized with different contents of OPC and CSCN at 28 days of curing, respectively. Compared with untreated clay [Fig. 12(a)], there are some fibrous C-S-H gels appeared in specimens C-1 [Fig. 12(b)]. Besides, more fibrous C-S-H gels are formed as the OPC content increasing to 15% [Fig. 12(c)]. However, as shown in Fig. 12(d)-(f), the CSCN-stabilized clay specimens don't have any fibrous C-S-H gels. There exist much anomalously agglomeration and thin laminated C-S-H gels in the CSCN-stabilized clay specimens, which is much higher than that in the OPC-stabilized clay specimens (Gleize *et al*., 2003).



(a)

(b)

(c)

Fig. 13. The EDX of the Selected Specimens of: (a) C-2, (b) S-3, (c) S-5 after 28 days of Curing

Table 5. The Elemental Composition and Ca/Si Molar Ratio of the Selected Areas Studied from EDX Test

EDX specimen	Concentration by weight (%)				Concentration by atom (%)				Ca/Si (molar ratio)
	Na	Al	Ca	Si	Na	Al	Ca	Si	
C-2	0.17	6.57	21.75	12.56	0.16	5.20	11.61	9.56	1.21
S-3	1.46	6.37	15.86	16.73	1.34	4.96	8.34	12.57	0.66
S-5	1.97	8.3	15.31	15.82	1.81	6.49	8.08	11.92	0.68

Although the microstructure of specimens S-3 and S-5 is still rough, the discrete particles were bonded significantly closely and the gaps among the particles were more tightly filled. This implies that the supplementary cementing materials can react with OPC and active clay minerals and generates higher amount of hydration and pozzolanic products which bond among the clay particles. The higher degree of bonding and more compact microstructure are believed to result in higher compressive strength and secant modulus.

The generation of C-S-H gels is mainly from hydration reactions and pozzlanic reactions. After the mixing of cement with water, the C_3S minerals dissolve and perform hydration reactions as the following equations.

$$3CaO{\cdot}SiO_2 + 3H_2O \rightarrow 3Ca^{2+} + HSiO_3^- + 5OH^- \quad (6)$$

$$x\,Ca^{2+} + y\,HSiO_3^- + z\,OH^- \leftrightarrow C_{0.8\text{-}1.7}SH\text{ (gel)} + 0.3\text{-}1.3\text{ CH} \quad (7)$$

In the presence of OH^- created by Eq. (6) and the dissolution of the supplementary materials (pH > 0.5), the active minerals in soft clay could dissolve in the pore liquid as follows (Hunter 1988).

$$Al_4Si_4O_{10}(OH)_8 + 4(OH)^- + 10H_2O \rightarrow 4\,Al(OH)_4^- + 4H_4SiO_4 \quad (8)$$

$$2\,H_4SiO_4 \rightarrow 2H_3SiO_4^- + 2H^+ \rightarrow 2\,HSiO_3^- + 2H^+ + H_2O \quad (9)$$

Moreover, the active SiO_2 could also react with OH^- to form $HSiO_3^-$ in the alkaline pore liquid. In the presence of Ca^{2+}, the more C-S-H and C-A-H gels can be formed as the following equations.

$$Ca^{2+} + HSiO_3^- + OH^- + H_2O \rightarrow \text{C-S-H (gel)} \quad (9)$$

$$Ca^{2+} + Al(OH)_4^- + OH^- + H_2O \rightarrow \text{C-A-H (gel)} \quad (10)$$

The amounts of Ca^{2+}, $HSiO_3^-$ and OH^- in CSCN stabilized clay specimens are different from those in OPC stabilized clay specimens, which is the possible reason for different types of C-S-H gels detected by SEM photos.

Figure 13 shows the EDX analysis of the selected areas within specimens C-2, S-3 and S-5 after 28 days of curing. The estimated elemental composition and Ca/Si molar ratio (C/S ratio) of the selected areas are listed in Table 5. The EDX results confirmed the presence of Si and Ca in the selected areas, which provides a qualitative evidence for the formation of C-S-H gels in the specimens. As shown in Table 5, the Na-concentrations of the selected areas in the CSCN-stabilized specimens are higher than that in OPC-stabilized specimens, which indicates that sodium silicate has perform geopolymerization as the following equation.

$$n\,Na^+ + (z \times n)\,HSiO_3^- + n\,Al(OH)_4^- + OH^- + H_2O \rightarrow Na_n\{\text{-}(SiO_2)_z\text{-}AlO_2\}_n{\cdot}wH_2O \quad (11)$$

where n is the degerr of polycondensation and z is 1, 2 or 3.

The C/S ratio of the selected area in the OPC-stabilized specimens is higher than that in CSCN-stabilized specimens. This result verifies that the fibrous minerals in the selected area of OPC-stabilized specimen are C-S-H gels type I which has a higher C/S ratio than C-S-H gels type III generated in the CSCN-stabilized specimens. Therefore, the difference in C/S ratio is primary reason for different types of C-S-H gels in specimens stabilized with the two soil stabilizers.

3.6 XRD Characterization

Figure 14 shows the XRD patterns of untreated clay and stabilized clay specimens after 28 days of curing. For stabilized clay specimens, the diffraction intensity of the peaks associated with Kaolinite and Quartz between 18° to 40° 2θ remarkably decreases, which indicates that some active Quartz could react with OH^- to form $HSiO_3^-$ in the alkaline pore liquid of stabilized specimens. And the intensity of the peaks associated with Gismondine and Zeolites increases. Furthermore, the more broad and amorphous humps between 22° and 32° 2θ are clearly observed in stabilized clay specimens, which confirms the formation of C-S-H and C-A-H gels generated from Eqs. (7), (9) and (10) (Horpibulsuk *et al.*, 2011). As mentioned before, there are no peaks of $Ca(OH)_2$ in any stabilized clay specimen. This observation is consistent with the results

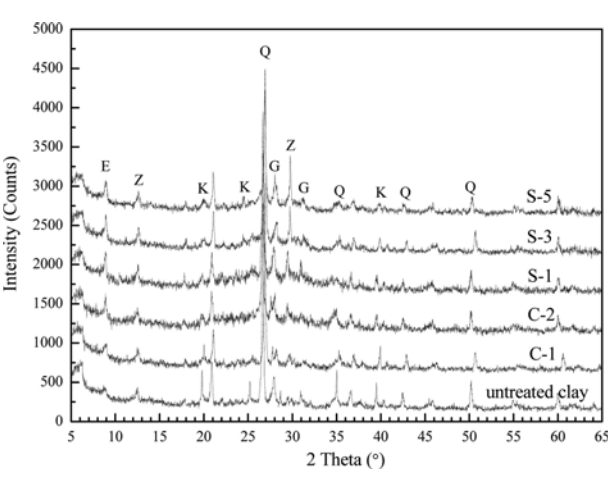


Fig. 14. The XRD Patterns of Untreated Clay and Stabilized Clays after 28 days of Curing (Q: SiO_2 quartz, K: kaolinite, G: gismondine, Z: zeolites, E: ettringite)

presented in the previous studies (Horpibulsuk *et al.*, 2009; Vichan *et al.*, 2013). The changes in the XRD patterns between untreated clay and stabilized clay specimens demonstrate that some new minerals are formed by hydration and pozzolanic reactions. Therefore, the enhancement of mechanical properties is largely due to the increase of Zeolites crystallization and the bonding effects of C-S-H gels.

4. Conclusions

1. The two clay stabilizers, OPC and CSCN, can significantly improve the compressive strength and secant modulus of soft clay. To achieve the equivalent compressive strength and secant modulus, less content of CSCN is needed relative to OPC. This implies that CSCN, which consists of eco-friendly materials, can be used as an eco-friendly clay stabilizer instead of OPC for in situ construction. It is notable that the CSCN-stabilized clays are more brittle than OPC-stabilized clays, and the remaining strengths of CSCN-stabilized clays are also much lower than those of OPC-stabilized clays.
2. The interrelationships of mechanical properties to the content of CSCN and curing age are proposed. The gain in compressive strength and secant modulus is dependent on the content of CSCN and curing age. The strength and modulus increase exponentially with increasing the content of CSCN. And the development of the strength and modulus slow down with increasing curing age. Nevertheless, it is difficult to identify an accurate relationship of failure strain to the content of CSCN and curing age.
3. The pH values of stabilized clays increase within 1 day of curing, and then decrease for the reason of hydration and pozzolanic reactions. The moisture consumption increases with increasing the content of CSCN, which is consistent with the development of the strength and modulus. In spite of the large difference in strengths between OPC- and CSCN-stabilized clays, the difference in moisture consumption is small because the hydration products in the two mixtures are different.
4. With the aid of SEM-EDX, the formation of C-S-H gels in stabilized clay specimens is qualitatively confirmed, and the types of C-S-H gels are dependent upon the Ca/Si molar ratio. Mineralogical characterization by XRD indicates that some new minerals are generated by hydration and pozzolanic reactions in the stabilized clay. The change in mineral and microstructure is the possible mechanism for the improvement in the strength and modulus of the stabilized clays.

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