HOSTED BY

The Japanese Geotechnical Society

Soils and Foundations

www.sciencedirect.com

journal homepage: www.elsevier.com/locate/sandf

SOILS AND FOUNDATIONS
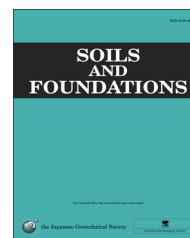
Influence of sodium silicate and promoters on unconfined compressive strength of Portland cement-stabilized clay

Cong Ma[a], Zhaohui Qin[a], Yingchun Zhuang[b], Longzhu Chen[a,*], Bing Chen[a]

[a]Department of Civil Engineering, Shanghai Jiaotong University, Shanghai 200240, People's Republic of China
[b]Hydrochina Huadong Engineering Corporation Ltd., Hangzhou 310014, People's Republic of China

Abstract

Eco-friendly sodium silicate and promoters, which are compatible with cement and are used to obtain super properties, have been developed into a variety of soil stabilizers. This paper investigates the possibility of using cement and sodium silicate admixed with composite promoters to improve the strength of soft clay in Shanghai, China. The influential factors involved in this study are the type of promoters, the proportion of each binding agent, the binder content, and the curing time. The unconfined compressive strength of stabilized clay at different ages is tested. Based on an orthogonal experiment, the selected clay stabilizer (CSCN) is determined. More importantly, it is found that much less CSCN is needed to achieve the equivalent improvement in strength compared with cement, which illustrates that CSCN can be a more effective and eco-friendly clay stabilizer. Mineralogical and microstructural tests are performed to reveal the possible mechanisms controlling the strength development. The effect of CSCN on cement hydration and pozzolanic reactions is discussed. Microstructural analyses confirm the formation of hydration and pozzolanic products, and show that the clay tends to form more compact microstructures after being stabilized with CSCN.
© 2015 The Japanese Geotechnical Society. Production and hosting by Elsevier B.V. All rights reserved.

Keywords: Soft clay; Soil stabilization; Unconfined compressive strength; Sodium silicate; Composite promoters

1. Introduction

Clayey soils are found in most regions of South and East China (Gao, 1996). The lower strength of soft clays causes severe damage to pavements, runways, and building foundations, which are founded on these soils (e.g., Horpibulsuk et al., 2006; Kempfert and Gebreselassie, 2006). To improve the strength and stiffness of those less competent soils, soil stabilization with cementitious materials has been widely practiced.

Soil stabilization is a technique that was introduced many years ago for the main purpose of rendering the soils capable of meeting the requirements of specific engineering projects (e.g., Rogers et al., 1997; Gao and Wang, 2014). One of the effective soft ground-improvement techniques is in situ deep mixing. This method was developed primarily to effect columnar inclusions into the soft ground to transform such a whole soft ground into a composite ground (Bell, 1988). Quicklime and ordinary Portland cement slurry (OPC) have been used as binding agents (e.g., Prusinski and Bhattacharja, 1999; Horpibulsuk et al., 2004, 2005; Niazi and Jalili, 2009). However, quicklime reacts with water rapidly, which increases the difficulty of deep mixing. In China, OPC is the most common binder since it is readily available at a reasonable cost

*Corresponding author.
  E-mail address: lzchen@sjtu.edu.cn (L. Chen).
Peer review under responsibility of The Japanese Geotechnical Society.

(e.g., Duan et al., 1994; Yu et al., 1997; Huang et al., 2005). However, the energy-intensive production process of OPC is the driving force in studies on alternative cementitious additives (e.g., Gartner, 2004; Meyer, 2009).

Used for soil stabilization, sodium silicate has unique advantages: (i) its reliable and proven performance, (ii) its safety and convenience for construction, and (iii) its environmental acceptability and compatibility (e.g., Rowles and O'Connor, 2003; Ma et al., 2014). Sodium silicates have been developed into a variety of different clay-stabilizer systems. These systems consist of sodium silicate and a reactor or accelerator (e.g., calcium chloride and kaolinite), which can be compatible with cement to achieve high mechanical properties. However, when used as reactors, calcium chloride or Kaolinite can only improve the strength of OPC-sodium silicate-stabilized soils by 20–50% (Kazemian et al., 2011a, 2011b). Montmorillonite-rich clay soil stabilization with powdered sodium silicate and lime was reported, but the low solubility and migration of the lime in the pore liquid inhibited the application of this technique for in situ construction (Rafalko et al., 2007; Sukmak et al., 2013a; Phetchuay et al., 2014). Indeed, sodium silicate was widely used to prepare clay-fly ash geopolymer in previous studies, and the influence of its curing conditions and binder contents has been studied (Sukmak et al., 2013b, 2014; Pangdaeng et al., 2014; Phoo-ngerkham et al., 2013).

The aim of this paper is to achieve an OPC-based clay stabilizer which has the equivalent enhancement of the mechanical properties as a higher content of OPC. The effect of a single promoter and composite promoters on the strength development of samples stabilized with OPC and sodium silicate was investigated. The unconfined compressive strength was used as a practical indicator to investigate the strength development. The binders consisting of OPC, sodium silicate, and composite promoters were studied through an orthogonal experiment which can ascertain the optimal proportion of each component. The changes in minerals and the microstructure are examined by X-ray Diffraction (XRD) and a scanning electron microscope (SEM). On the basis of strength observations and a mineralogical characterization, the possible mechanisms controlling the strength development are discussed.

2. Materials and methodology

2.1. Soil sample

The soil sample used here is soft clay collected from the Shanghai Jiao Tong University campus in Shanghai, China, at a depth of 6 m. The soil contains highly fine particle contents, similar to many marine soft clayey soils. A particle size analysis was performed on the soil by following the standard method. About 100% and 80% of the soil are finer than 2 mm and 0.075 mm, respectively, so that clay and fine sand are the major components of this soil. 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 soil based on two aspects: the liquid limit is smaller than 50% and the plasticity index is

higher than 17%. The natural water content and pH value were approximately 41% and 7.14%, respectively. The chemical composition and morphology of the clay are shown in Table 1 and Fig. 1, respectively.

2.2. Binding agents

ASTM Type I ordinary Portland cement (hereinafter called OPC) was used for all stabilized clay mixtures in this study. The chemical composition of OPC is also shown in Table 1. The density and specific surface area of OPC are 3.13 g/cm^3 and 3630 cm^2/g, respectively.

Sodium silicate (SS), a syrupy liquid, is used as the second binding agent. It consists of SiO_2 (29.48%) and Na_2O (9.52%), and the silica modulus (molar ratio of SiO_2 and Na_2O) is 3.2. The density and pH are 1.43 g/cm^3 and 11.98, respectively.

Sodium hydroxide (NaOH, SH), a flaked solid at room temperature, was used to improve the pH value of the stabilized clay. Calcium hydroxide ($Ca(OH)_2$, CH), a powdered material, can react with pozzolanic material and produce

Table 1
Chemical composition of clay and OPC.

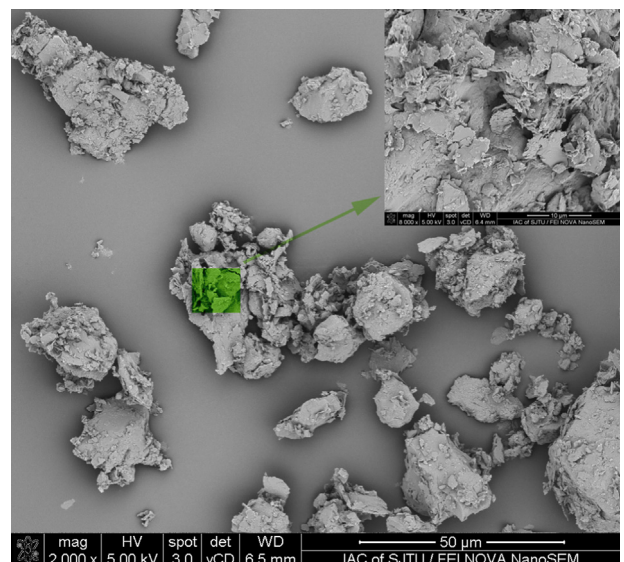| Oxide	Chemical composition (%)	
	Clay	OPC
Silicon dioxide (SiO_2)	57.02	21.60
Calcium oxide (CaO)	3.63	64.44
Aluminum oxide (Al_2O_3)	16.42	4.13
Ferric oxide (Fe_2O_3)	6.79	4.57
Magnesium oxide (MgO)	3.68	1.06
Sodium oxide (Na_2O)	0.81	0.11
Potassium oxide (K_2O)	3.59	0.56
Sulfur trioxide (SO_3)	0.05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

Fig. 1. SEM photos of the soft clay.

cementitious material. The sodium aluminate ($Na_2Al_2O_4$, SA) solution can react with sodium silicate and produce a mineral gel. Calcium chloride ($CaCl_2$, CC), an anhydrous powder, was used as an accelerator. It can serve as a source of calcium ions in the solution, unlike many other calcium compounds, as calcium chloride is soluble. These powdered promoters are all chemically pure and are obtained from Sinopharm Chemical Reagent Co., Ltd. In this study, they can be used as a single component or as part of a compound.

2.3. Sample preparation

In order to investigate the influence of OPC and sodium silicate binders on soft clay, different promoters were admixed with specific amounts of oven-dried clay. For preparing the samples, the water was added through a two-step process. Firstly, the predetermined quantity of water was initially mixed with the oven-dried clay, and the mass ratio of water to clay was 0.7. Then, the rest of the water was blended with the binders at a mass ratio of 0.5, and the binders consisting of the desired amount of promoters, OPC, and sodium silicate were added by the weight of the dry clay. Soluble promoters (such as NaOH and $CaCl_2$) were added into the mixtures in the form of a solution, and sequential mixing with the $CaCl_2$ solution, followed by the NaOH solution, was selected. The initial mixing was carried out in a laboratory mixer for at least 10 min. Subsequently, the mix was transferred to a PVC cylindrical mold. To squeeze the air and to achieve a homogeneous mixture, the mold was put onto a vibrating table to vibrate it for at least 2 min. Then, the mold was sealed and stored in the curing room (20 ± 2 °C, $98 \pm 2\%$ RH) for 7 days. Afterwards, the stabilized samples were demoulded and put into airtight vinyl bags in the curing room until the testing ages had been reached. Unconfined compression tests were performed 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 were reproducible under the same testing conditions with low mean standard deviations, SD ($SD/\bar{x} < 10\%$, where $\bar{x} =$ the mean strength value). The pH values were taken on broken samples after unconfined compression tests at a predicted curing age. The broken samples were immersed in absolute ethyl alcohol, in order to terminate the hydration reaction, and then oven dried. The liquid-to-solid ratio (deionized water/oven-dry samples) was kept at 4:1 for the pH value tests. The actual pH values can be calculated by hydroxyl ion concentration achieved from the dilute solution.

2.4. Mineralogical and microstructural characterization

To investigate the mineralogical changes in the stabilized clay, XRD patterns were taken on the broken samples after the unconfined compression tests. A crushed sample was collected in a mortar, and some absolute ethyl alcohol was immediately added to the mortar to terminate the hydration reaction. Then, it was ground with a pestle, and 10 g of ground soil was sieved through a 45-µm sieve. The minus 45 µm portion was immersed in absolute ethyl alcohol and kept in a desiccator at room temperature until XRD testing. The prepared powder sample was side-loaded on the sample holder. The purpose of the XRD tests was to determine whether any reaction occurs between the binder and the clay, which can be identified by observing the changes in diffraction peaks. The powder samples were scanned with an X-ray powder diffractometer using Cu $K\alpha$ radiation. The data were collected from 5° to 65° 2θ at 0.02°/step.

To examine the micromorphological changes in the stabilized clay and shed some light on the stabilization mechanisms, SEM imaging was performed on the selected samples. SEM samples were prepared by following the procedure suggested in a previous study (Zhang et al., 2013). A $1 \times 1 \times 1$ cm^3 cubic specimen was trimmed off and immersed in absolute ethyl alcohol, and then air dried in a desiccator at an ambient temperature. The dried specimen was broken into two parts and the debris on the surface was removed with adhesive tape. The specimen was mounted on an alumina stud with conductive tapes, and then sputter-coated with a gold–palladium alloy.

3. Test results

3.1. Single promoter

The effect of the single promoter on the OPC- and the sodium silicate-stabilized clay was investigated by preparing different samples with 10% OPC, 1% sodium silicate, and different dosages of the single promoter. The results are presented in Figs. 2–5.

As shown in Fig. 2, the unconfined compressive strength significantly increased with the increase in the contents of NaOH. In comparison to the strength (143 kPa) of the
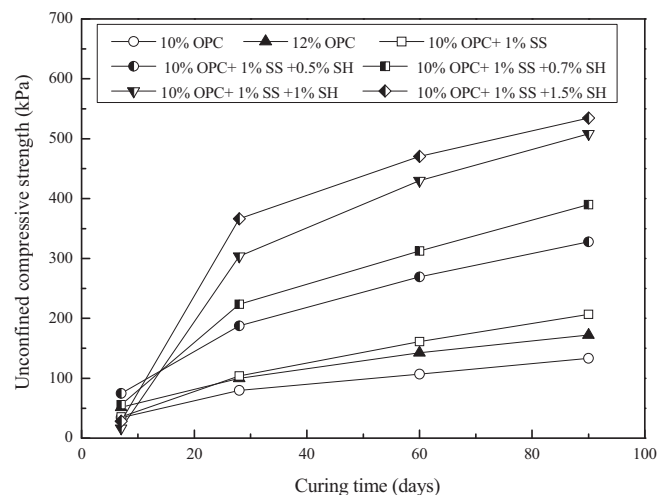

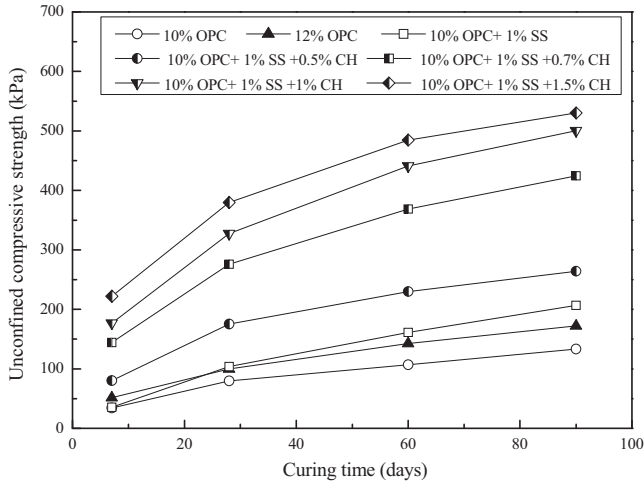Fig. 2. Strength development in OPC–SS stabilized clay admixed with single NaOH.

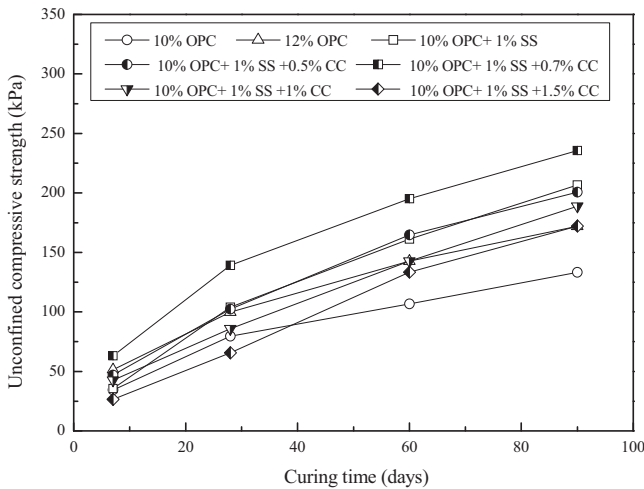Fig. 3. Strength development in OPC–SS stabilized clay admixed with single Ca(OH)$_2$.

Fig. 4. Strength development in OPC–SS stabilized clay admixed with single CaCl$_2$.
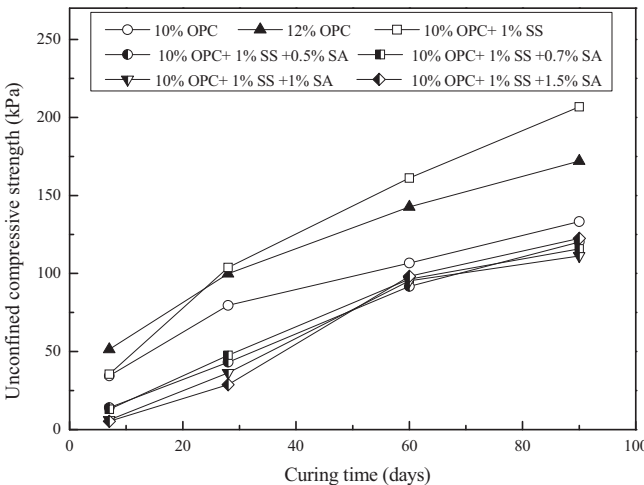

Fig. 5. Strength development in OPC–SS stabilized clay admixed with single Na$_2$Al$_2$O$_4$.

stabilized clay with 12% OPC at the age of 60 days, the strength increased to 450 kPa when NaOH was used with sodium silicate at the mass ratio of 1:1. As the mass ratio of Ca(OH)$_2$ and sodium silicate increased (Fig. 3), the strength of the samples at different curing ages increased markedly. The strength of the samples with 1% Ca(OH)$_2$ at 7 and 60 days was 177 and 441 kPa, respectively, which was 240% and 208% higher, respectively, than those of samples stabilized with 12% OPC. Nevertheless, the strength development of the samples stabilized with 10% OPC and 1% sodium silicate was seen to be able to improve the strength at 60 days to merely 161 kPa. This really shows that the synergistic effect occurs when sodium silicate is used with NaOH or Ca(OH)$_2$.

As shown in Fig. 4, the strength increased gradually with the initial increase in the content of CaCl$_2$ and decreased sharply as the promoter content went beyond 0.7%. Consequently, the samples with the SS:CC ratio of 1:0.7 exhibited the highest strengths for all the curing ages, and the strength at 60 days was only 21% higher than that of the samples stabilized with 10% OPC and 1% sodium silicate. Unlike the other three promoters, the samples with different contents of Na$_2$Al$_2$O$_4$ (Fig. 5) had lower strengths than those of samples with 10% OPC. The strength of the samples with 1% Na$_2$Al$_2$O$_4$ at 7 days was only 6 kPa, which was 82% lower than that of the samples stabilized with 10% OPC.

According to the above results, the single promoters used as the component of clay stabilizers have several disadvantages: (i) there is a decrease in strength at 7 days when NaOH is used as a promoter, and (ii) the high content of Ca(OH)$_2$ significantly increases the difficulty of in situ construction.

3.2. Composite promoters

Fig. 6 shows the typical strength development in the specimens with different composite promoters and component ratios. The contents of OPC, sodium silicate, and composite promoters were 10%, 1%, and 1%, respectively. For Ca(OH)$_2$/NaOH composite promoters, the change in component ratios had little impact on the strengths at 28 and 60 days. For CaCl$_2$/Ca(OH)$_2$ composite promoters, the strength increased with the increasing proportion of Ca(OH)$_2$. The strength development of samples with Ca(OH)$_2$/NaOH or CaCl$_2$/Ca(OH)$_2$ composite promoters shows that the strength at 60 days was generally lower than that of the samples with single 1% Ca(OH)$_2$. This indicates that Ca(OH)$_2$ plays a major role in the composite promoters. From Fig. 6(c), it is observed that the strengths at different ages increased firstly and then decreased with the increase in the CaCl$_2$/NaOH ratio. The optimal proportion of CaCl$_2$/NaOH in the composite promoters is 1:1. When specimens were mixed with 0.5% CaCl$_2$ and 0.5% NaOH, the strength at 7 days was 193 kPa, which was over 10 times higher than that of the specimens with 1% NaOH. Moreover, the strength at 28 and 60 days was 349 and 517 kPa, respectively, 6–17% higher than those of specimens with 1% Ca(OH)$_2$. Therefore, the selected composite promoter consists of CaCl$_2$ and NaOH at the mass ratio of
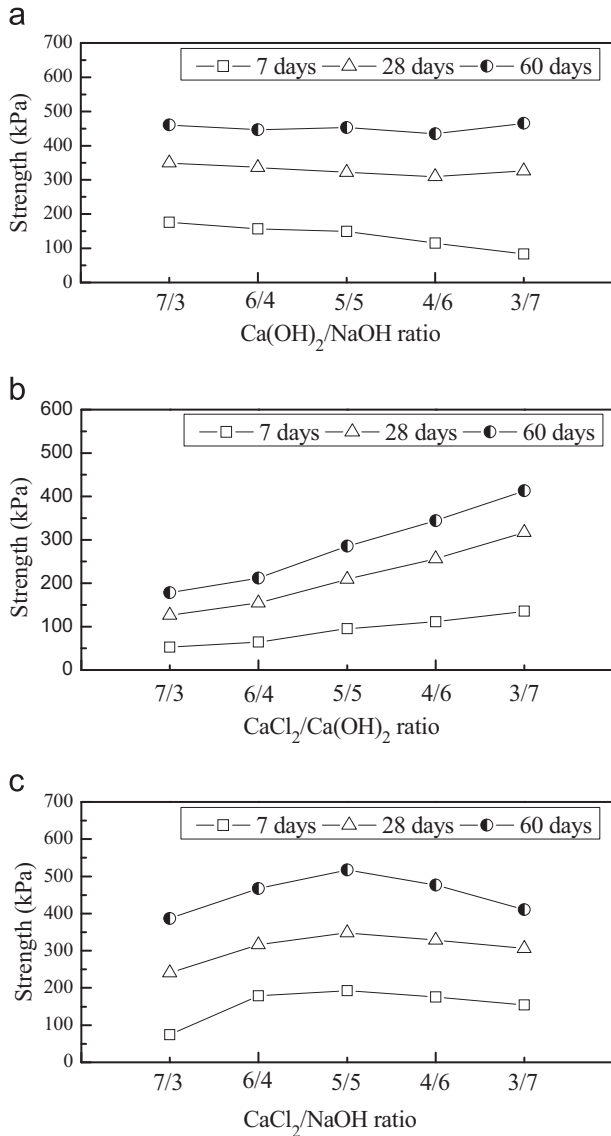
a

b

c

Fig. 6. Strength development in OPC–SS stabilized clay with different composite promoters.

1:1 and it should be added into the clay–water mixture by the sequential mixing of $CaCl_2$ and NaOH solutions.

Compared with single NaOH and $Ca(OH)_2$, the selected composite promoters have unique advantages: (i) the sample have higher strengths with the same content of promoters at different curing ages, (ii) the mixing of composite promoters will not increase the consistency of the specimens, and (iii) the very soluble $CaCl_2$ and NaOH are conducive to in situ construction.

3.3. Orthogonal experiment

The orthogonal experimental design is a mathematical method used for planning multifactor tests. It is characterized as a balanced arrangement of pairs or groups and applied broadly in many fields to optimize test designs. In the present case, the orthogonal experiment was used to optimize the experimental results and to estimate the significance of the

Table 2
Contents of orthogonal factors and levels.

Factor level	Factors	
	Content of sodium silicate (%) [A]	Content of composite promoter (%) [B]
1	1	1
2	2	2
3	3	4
4	4	6

effect of sodium silicate and composite promoters ($CaCl_2$/NaOH), ultimately achieving the optimal proportion of OPC, sodium silicate, and composite promoters in the binders. Each of the two factors could be changed at four levels and the interaction of the two factors was explored. The $L_{16}(4^4)$ orthogonal array was used to design the tests. Details of the four levels for the two factors are shown in Table 2. The content of OPC for each experiment was 10%.

Sixteen experiments were performed in accordance with the $L_{16}(4^4)$ orthogonal array. The values for the strengths at 7 and 28 days, which will be taken as the objective index for evaluating the significance of the impact of the factors, are presented in Table 3. As can be seen, Ki and Ti represent the sum of the 7-day and the 28-day strengths of row "i", respectively, if the level is i. The calculation results are based on the experimental results via employing the method of variance analysis and are depicted in Tables 4 and 5. Here, S_S is the sum of the squares of deviations, df is the degree of freedom, M_S is the mean value of the squares of deviations, which is equal to S_S divided by the corresponding df, and F is the f-distribution in the Mathematic Statistic, which is used to estimate the significance of the effect of the impact factor on the strengths.

From Tables 4 and 5, it is noted that the strengths at 7 and 28 days are extremely sensitive to the contents of the sodium silicate and the composite promoters. However, the interaction between the sodium silicate and the composite promoters has little effect on the strengths and it can be ignored in comparison to the two factors. The optimal levels for the two factors are A2 and B3, respectively. That is to say, when the content of the OPC is 10%, the specimens admixed with 2% sodium silicate and 4% composite promoters have their maximum strengths at 7 and 28 days. Hence, the elected clay stabilizer (CSCN) consists of OPC, sodium silicate, and composite promoters at the mass ratio of 5:1:2.

3.4. Comparison between CSCN and OPC

Figs. 7–9 show the strength development in the CSCN-stabilized clay compared to that in the OPC-stabilized clay (no sodium silicate or composite promoters), for the same stabilizer content at different curing times (7, 28, and 60 days). The strengths of 15%, 20%, and 30% for the OPC-stabilized clay are used as references and are presented in these figures.

Table 3
Experimental program of orthogonal analysis.

Test no.		A	B	A × B	Error	Error	Unconfined compressive strength	
							7 days	28 days
1		A1	B1	1	1	1	192.55	348.73
2		A1	B2	2	2	2	213.81	436.61
3		A1	B3	3	3	3	312.69	566.34
4		A1	B4	4	4	4	299.09	627.85
5		A2	B1	2	3	4	277.28	426.93
6		A2	B2	1	4	3	312.29	546.71
7		A2	B3	4	1	2	489.15	739.42
8		A2	B4	3	2	1	347.51	717.25
9		A3	B1	3	4	2	217.27	301.74
10		A3	B2	4	3	1	359.31	456.35
11		A3	B3	1	2	4	325.7	441.52
12		A3	B4	2	1	3	345.1	474.45
13		A4	B1	4	2	3	5.27	40.66
14		A4	B2	3	1	4	25.56	105.33
15		A4	B3	2	4	1	162.66	301.41
16		A4	B4	1	3	2	138.75	266.86
7-day strength	K1	1018.14	692.37	969.29	1052.36	1062.03		
	K2	1426.23	910.97	998.85	892.29	1058.98		
	K3	1247.38	1290.2	903.03	1088.03	975.35		
	K4	332.24	1130.45	1152.82	991.31	927.63		
28-day strength	T1	1979.53	1118.06	1603.82	1667.93	1823.74		
	T2	2430.31	1545	1639.4	1636.04	1744.63		
	T3	1674.06	2048.69	1690.66	1716.48	1628.16		
	T4	714.26	2086.41	1864.28	1777.71	1601.63		

Table 4
ANOVA (analysis of variance) table of 7-day strength.

Source	S_S	df	M_S	F	F_C	Significance
A	172239.37	3	57413.12	39.31	$F_{0.01}(3,6)=9.78$	**
B	50912.98	3	16970.99	11.62	$F_{0.05}(3,6)=4.76$	**
A*B	8389.42	3	2796.47	1.91	$F_{0.1}(3,6)=3.29$	
Error	8762.86	6	1460.48		$F_{0.2}(3,6)=2.1$	
Total	240304.6	15				

**is the symbol which presents the great significance.

Table 5
ANOVA (analysis of variance) table of 28-day strength.

Source	S_S	df	M_S	F	F_C	Significance
A	395961.3	3	131987.1	72.70	$F_{0.01}(3,6)=9.78$	**
B	158393.9	3	52797.98	29.08	$F_{0.05}(3,6)=4.76$	**
A*B	9999.32	3	3333.11	1.84	$F_{0.1}(3,6)=3.29$	
Error	10892.29	6	1815.38		$F_{0.2}(3,6)=2.1$	
Total	575246.8	15				

**is the symbol which presents the great significance.

Fig. 7. Strength development in OPC stabilized samples and CSCN stabilized samples at different binder contents for 7 days of curing.

For all curing times, as the CSCN content increases, the strengths of the CSCN-stabilized samples also increase. The strengths of the CSCN-stabilized samples are much higher than those of the samples stabilized with the same content of OPC. Compared with the 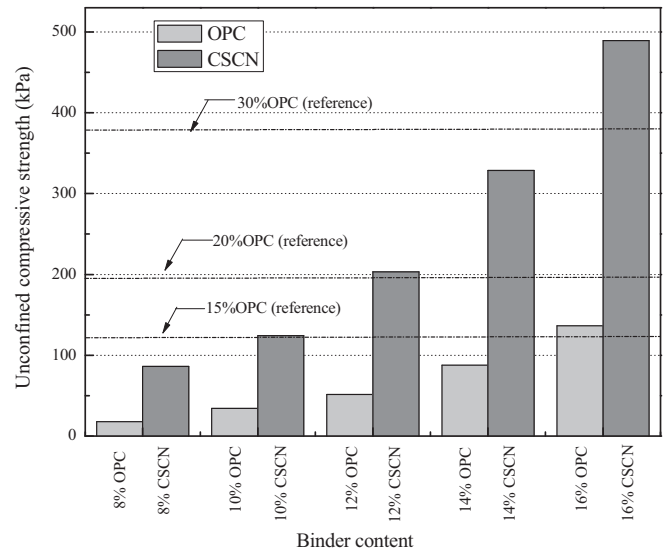samples stabilized with 8% OPC, the strengths of the samples with 8% CSCN, consisting of only 5% OPC at 7 and 60 days, are 86 and 221 kPa, respectively. These amounts are almost equivalent to the strengths of the samples with 12% OPC. In addition, the strengths of the samples stabilized with 10% and 12% CSCN are nearly equivalent to those stabilized with 15% and 20% OPC. When the content of CSCN is 16%, the strengths at 7, 28, and
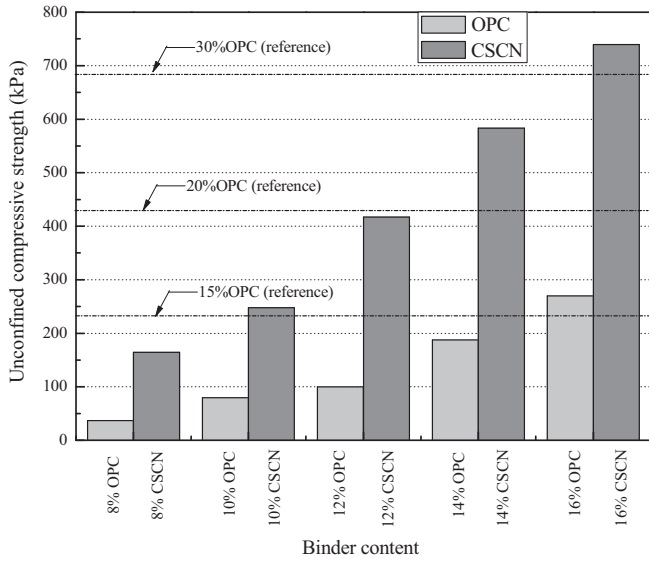
Fig. 8. Strength development in OPC stabilized samples and CSCN stabilized samples at different binder contents for 28 days of curing.
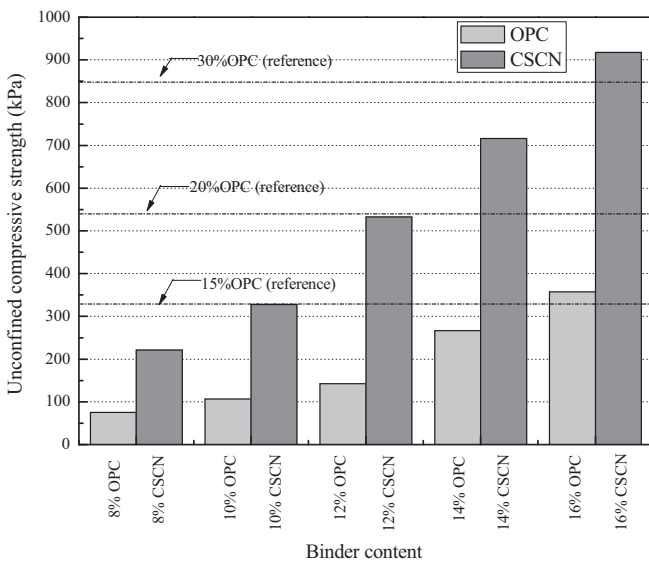

Fig. 9. Strength development in OPC stabilized samples and CSCN stabilized samples at different binder contents for 60 days of curing.

Table 6
Formulas for mineralogical and microstructural characterization.

No.	Stabilizer content (%)	Characterization	No.	Stabilizer content (%)	Characterization
1	10OPC	XRD/SEM	2	15OPC	XRD/SEM
3	10OPC 1SS 1CH	XRD	4	10OPC 1SS 1CN	XRD
5	10CSCN	XRD/SEM	6	15CSCN	XRD/SEM

OPC: cement, SS: sodium silicate, CH: calcium hydroxide, CN: the selected composite promoter; CSCN: the optimal stabilizer at the mass ratio of OPC:SS:CN=5:1:2.
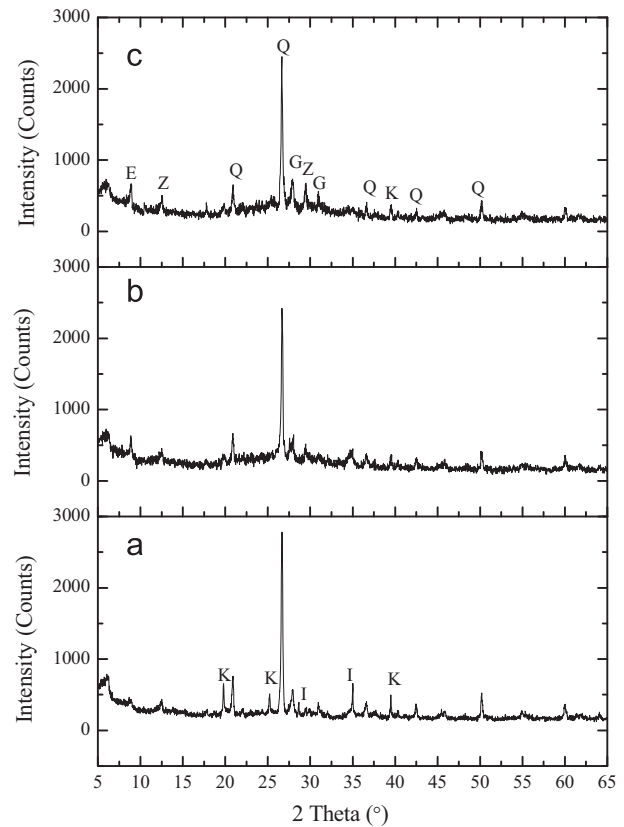

Fig. 10. XRD patterns of (a) the untreated clay, (b) No. 2 and (c) No. 3 specimens for 60 days (Q: SiO_2 quartz, K: kaolinite, I: illite, G: gismondine, Z: zeolites, E: ettringite).

90 days are 489, 739, and 907 kPa, respectively, which are 27%, 8%, and 7% higher than those of the samples stabilized with 30% OPC. This implies that the addition of sodium silicate and composite promoters can replace a considerable amount of OPC for the equivalent enhancement of the unconfined compressive strength.

4. Analysis and discussion

The mechanisms of the clay stabilization of binders were investigated by preparing different samples based on Table 6. As shown in this table, the soft clay was stabilized with different types and contents of stabilizers. For example, sample No. 3 is the treated clay consisting of 10% OPC, 1% sodium silicate, and 1% calcium hydroxide. Fig. 10 shows a comparison of the XRD patterns of the untreated clay and specimen Nos. 2 and 3 after 60 days of curing. Peaks of Quartz, Kaolinite and Illite of the crystalline components in the clay are clearly seen, particularly in the region of 19–35° 2θ (Fig. 10(a)). For stabilized clay, the relatively broad and amorphous humps between 22 and 32° 2θ, which indicate the C–S–H and C–A–H gels, are observed. In comparison with the untreated clay, the diffraction intensity of Kaolinite and Illite significantly decreases, and the intensity of the Gismondine, Zeolites, and Ettringite accordingly increases. In addition, the intensity of Quartz also decreases to some extent. These results indicate the growth of gel products and the consumption of
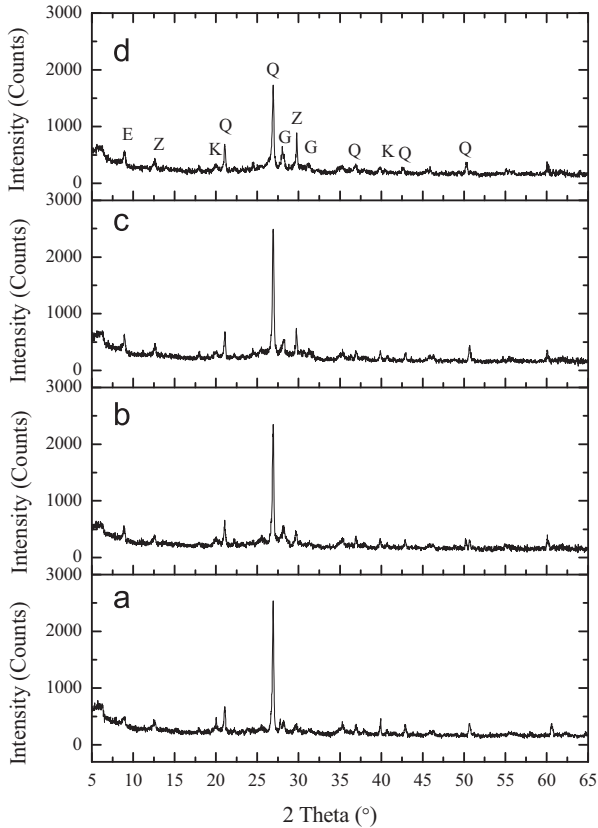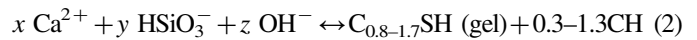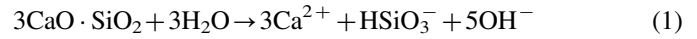
Fig. 11. XRD patterns of (a) No. 1, (b) No. 4, (c) No. 5 and (d) No. 6 specimens for 28 days (Q: SiO_2 quartz, K: kaolinite, I: illite, G: gismondine, Z: Zeolites, E: ettringite).

active minerals existing in the clay, hence, the strength development.

Similarly, the XRD traces of specimens stabilized with different binders after 28 days of curing are shown in Fig. 11. Comparing Fig. 11(b), (c), and (a), the diffraction intensity of Quartz and Kaolinite became weaker due to the existence of sodium silicate and promoters. Comparing Fig. 11(d) with the other figures, the diffraction intensity of Quartz showed a remarkable reduction and the intensity of Zeolite and Gismondine largely increased. Indeed, the increase in Zeolite is more remarkable than the increase in Gismondine. In addition, more broad and amorphous humps are clearly observed between $22°$ and $32°$ 2θ; this is similar to the specimens stabilized with 15% cement after 60 days of curing (Fig. 10(b)). Therefore, the enhancement of the compressive strength is largely due to the increase in Gismondine crystallization and the binding effect of C–S–H and C–A–H gels.

It is known that the strength improvement is associated with the content and the variety of binding agents because the strength is governed by the growth of cementitious products which are controlled by the hydration of cement and the pozzolanic reactions (Horpibulsuk et al., 2011).

The hydration reaction of C_3S occurs in the samples immediately after the mixing of OPC with the water as the following two equations:

$$3CaO \cdot SiO_2 + 3H_2O \rightarrow 3Ca^{2+} + HSiO_3^- + 5OH^- \tag{1}$$

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

For the OPC-clay system, the H^+ and K^+ existing in the diffused double layer of the clay colloids perform the ion exchange and neutralization reaction with Ca^{2+} and OH^- created by Eq. (1), decreasing the production of C–S–H and CH. For the OPC-clay admixed with the NaOH or $Ca(OH)_2$ system, more OH^- in the pore liquid of the stabilized clay can meet the consumption of H^+, which is conducive to forming more C–S–H and CH, generating higher strengths.
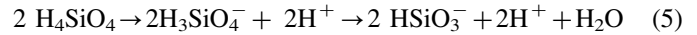
After being added into the mixture of clay, water, and OPC, the high-modulus sodium silicate dissolves and ionizes in the liquid phase. In the presence of Ca^{2+} created by Eq. (1), sodium silicate can form soluble calcium silicate, with difficulty, which polymerizes further to form gels that bind clay or sediment particles together and fills the voids as seen in the following equation (Brykov et al., 2002):

$$Ca^{2+} + Na_2O \cdot 3SiO_2 + mH_2O \rightarrow CaO \cdot 3SiO_2 \cdot mH_2O + 2Na^+ \tag{3}$$
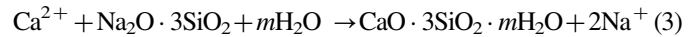
Pozzolanic reactions occur when the pH value of the pore liquid is higher than 10.5, and the active clay minerals (such as Kaolinite) will dissolve in the pore liquid, as follows (Hunter, 1988):

$$Al_4Si_4O_{10}(OH)_8 + 4(OH)^- + 10H_2O \rightarrow 4\, Al(OH)_4^- + 4H_4SiO_4 \tag{4}$$
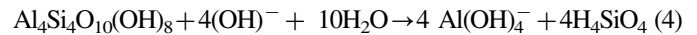
Then, the silicic acid dissociates as the following equation:

$$2\, H_4SiO_4 \rightarrow 2H_3SiO_4^- + 2H^+ \rightarrow 2\, HSiO_3^- + 2H^+ + H_2O \tag{5}$$

As shown in Fig. 12, the pH values for each formula are greater than 10.5; this indicates that the Kaolinite and Illite perform the chemical reactions as Eq. (4). This is the real reason why the peaks of Kaolinite and Illite almost disappear in the stabilized clay samples (Figs. 10 and 11). What is more, the active SiO_2 in the clay will react with OH^- to form $HSiO_3^-$ in the alkaline pore liquid according to the following reaction:
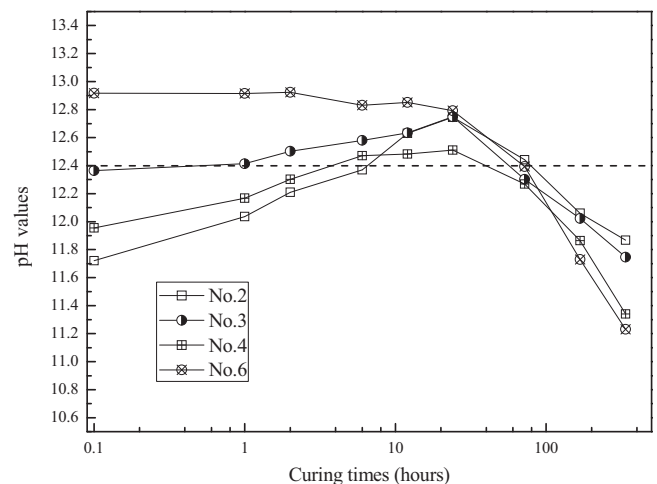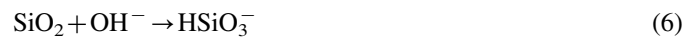
$$SiO_2 + OH^- \rightarrow HSiO_3^- \tag{6}$$

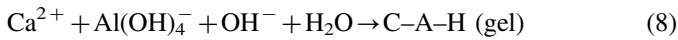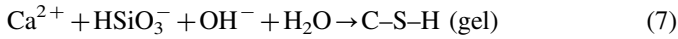

Fig. 12. The pH value development of stabilized clay.

It is known that the nuclei of $Ca(OH)_2$ will not appear until the pH value of the pore liquid reaches 12.4. Hence, the CH in the stabilized clay after 7 days of curing exists in the form of Ca^{2+} and OH^- in the pore liquid. In the presence of abundant $HSiO_3^-$ and $Al(OH)_4^-$, more C–S–H and C–A–H gels, which coat the soil particles and subsequently polymerize to bond them, can be formed as the following equations:

$$Ca^{2+} + HSiO_3^- + OH^- + H_2O \rightarrow \text{C–S–H (gel)} \tag{7}$$

$$Ca^{2+} + Al(OH)_4^- + OH^- + H_2O \rightarrow \text{C–A–H (gel)} \tag{8}$$

In addition, some geopolymerization products produced by the chemical reaction of Na_2SiO_3, NaOH, active SiO_2, and Al_2O_3 in the clay might contribute to the strength of the stabilized material. Based on the above analysis, the reaction can be summarized as follows:

$$n \ Na^+ + (z \times n) \ HSiO_3^- + n \ Al(OH)_4^- + OH^- + H_2O \rightarrow Na_n \{-(SiO_2)_z\text{-}AlO_2\}_n \cdot wH_2O \tag{9}$$
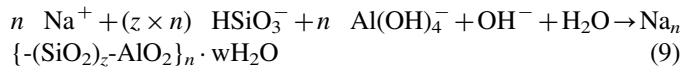
where n is the degree of polycondensation and z is 1, 2, or 3.

When the OPC and sodium silicate system are used with single NaOH or $Ca(OH)_2$, the hydration and pozzolanic reactions are both enhanced, resulting in much higher strengths than those of the control samples. When the single $CaCl_2$ is mixed with sodium silicate, the reaction in Eq. (3) can occur. However, the active SiO_2 and Al_2O_3 in the clay cannot be activated effectively; hence, the improvement in compressive strength is smaller than for the samples with single NaOH or $Ca(OH)_2$. It is well known that $Na_2Al_2O_4$ has been widely used as an accelerated agent in concrete and that the appropriate content of $Na_2Al_2O_4$ may be 0.5–3% (by weight of OPC) (Paglia et al., 2001). Nevertheless, the mass ratio of $Na_2Al_2O_4$ and OPC varied between 5% and 15%, which implies that there
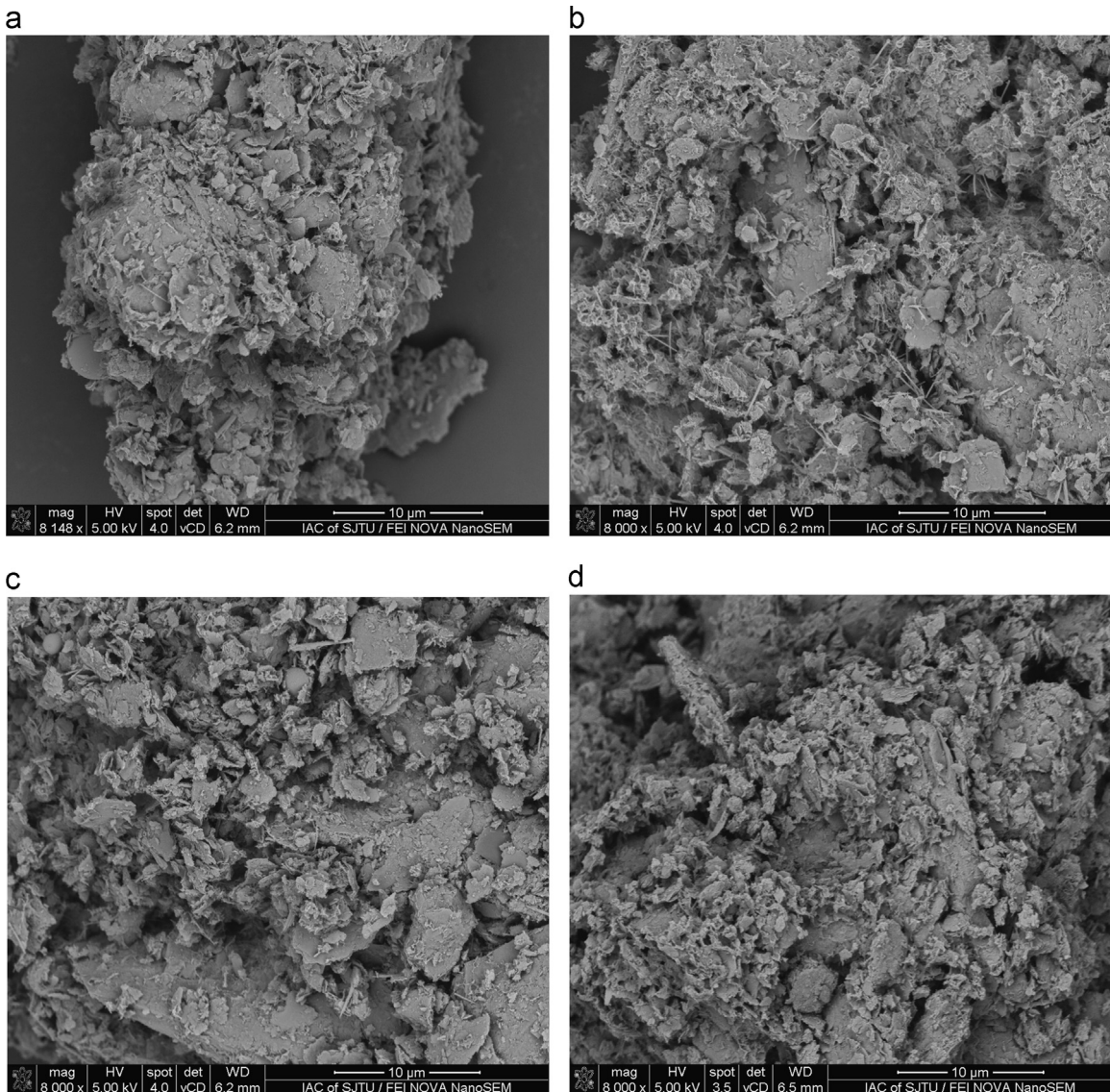

Fig. 13. SEM photos of (a) No. 1, (b) No. 4, (c) No. 5 and (d) No. 6 specimens for 28 days.

was an excess amount of $Na_2Al_2O_4$ in the stabilized samples. Therefore, the addition of $Na_2Al_2O_4$ has a negative effect on the strength development in the OPC-sodium silicate-stabilized samples.

For the OPC and sodium silicate admixed with composite promoters system, the permeation of the $CaCl_2$ and NaOH solutions is expected to facilitate the precipitation of $Ca(OH)_2$ according to the reaction:

$$CaCl_2 + NaOH \rightarrow Ca(OH)_2 + 2NaCl \qquad (10)$$
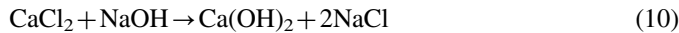
Although only 0.34% $Ca(OH)_2$ can be formed with the remaining 0.14% NaOH, when the binders consist of 0.5% $CaCl_2$ and 0.5% NaOH, the strengths are even higher than those of the specimens with single 1.5% $Ca(OH)_2$. The reason may possibly be the formation of $Ca(OH)_2$ in the soil by the sequential mixing of $CaCl_2$ and NaOH solutions with soil developing much stronger soil-$Ca(OH)_2$ pozzolanic reactions than those caused by directly adding $Ca(OH)_2$ (Thyagaraj et al., 2012). In addition, the remaining NaOH causes the neutralization reaction, which may create a more appropriate environment for the hydration and pozzolanic reactions. Therefore, the selected composite promoter has stronger stabilization effects than the single promoter.

Fig. 13 shows the surface morphology of the soft clay stabilized with 10% and 15% binders at 28 days of curing. Comparing Fig. 13(a) with (b), it can be seen that there are more fibrous C–S–H gels in the 15% OPC-stabilized clay. However, even though the CSCN-stabilized clay may not have many fibrous C–S–H gels, it may develop much more anomalous agglomeration and thin laminated C–S–H gels than the OPC-stabilized clay. Although the microstructure of the sample stabilized with 15% CSCN is still rough, the discrete particles were bonded significantly more closely than the three other samples and the gaps among the particles were more tightly filled. This implies that the samples stabilized with CSCN generate higher amounts of hydration and pozzolanic products, resulting in bonding among the clay particles. The higher degree of bonding and the more compact microstructure are believed to result in the higher strength.

5. Conclusions

This paper has analyzed the strength development in OPC- and sodium silicate-stabilized clay with different promoters, and has achieved the optimal composition of the binders. The possible mechanisms controlling the strength development have been presented by a mineralogical analysis (XRD) and have been confirmed by a microstructural analysis (SEM).

The following conclusions can be drawn from this study:

1. Single $CaCl_2$ and $Na_2Al_2O_4$ cannot increase the strengths to the anticipated values. Single NaOH or $Ca(OH)_2$ can significantly improve the strengths of OPC- and sodium silicate-stabilized clay. There is a synergic effect between single NaOH or $Ca(OH)_2$ and sodium silicate. However,

several disadvantages restrict the application of single promoters in the OPC and sodium silicate system.
2. The composite promoters, comprised of $CaCl_2$/$Ca(OH)_2$ or $Ca(OH)_2$/NaOH, have no advantage in terms of the strength development in comparison with the same addition of single $Ca(OH)_2$ or NaOH. Moreover, the selected composite promoter (CN) consists of $CaCl_2$ and NaOH at the mass ratio of 1:1, and the strength of the specimens with 1% CN at 60 days is 17% higher than that of the specimens with 1% $Ca(OH)_2$.
3. The content of sodium silicate has a relatively large effect on the strengths at 7 and 28 days compared to the effect of the content of composite promoters. The influence of the interaction between the sodium silicate and the composite promoters can be ignored. In addition, the selected clay stabilizer (CSCN) consists of OPC, sodium silicate, and composite promoters at the mass ratio of 5:1:2.
4. To achieve equivalent strengths, a lower content of CSCN is needed relative to OPC. The strengths of the samples with 16% CSCN at the ages of 7, 28, and 60 days are higher than those of samples with 30% OPC. This implies that CSCN, as an alternative to OPC, is a more environmentally friendly soil stabilizer for in situ construction.
5. The strength development of stabilized clay is controlled by the hydration of cement and the pozzolanic reactions. Mineralogical characterization by XRD indicates that the active clay minerals bring about pozzolanic reactions in the stabilized clay. With the aid of the SEM, the formation of hydration and pozzolanic products in the stabilized clay is qualitatively confirmed.

Acknowledgment

References

Bell, F.G., 1988. Stabilisation and treatment of clay soils with lime. Part 1: basic principles. Ground Eng. 21 (1), 10–15.

Brykov, A.S., Danilov, V.V., Korneev, V.I., Larichkov, A.V., 2002. Effect of hydrated sodium silicates on cement paste hardening. Russ. J. Appl. Chem. 75 (10), 1577–1579.

Duan., J.W., Gong., X.N., Zheng, G.X., 1994. Load transfer behavior of cement treated soil column. Chin. J. Geotech. Eng. 16 (4), 1–8.

Gao, G.R., 1996. The distribution and geotechnical properties of loess soils, lateritic soils and clayey soils in China. Eng. Geol. 42 (1), 95–104.

Gao, Y., Wang, Y.H., 2014. Experimental and DEM examinations of K 0 in sand under different loading conditions. J. Geotechn. Geoenviron. Eng. 140 (5), 95–106.

Gartner, E., 2004. Industrially interesting approaches to "low-CO_2" cements. Cem. Concr. Res. 34 (9), 1489–1498.

Horpibulsuk, S., Miura, N., Bergado, D.T., 2004. Undrained shear behavior of cement admixed clay at high water content. J. Geotechn. Geoenviron. Eng. 130 (10), 1096–1105.

Horpibulsuk, S., Miura, N., Nagaraj, T.S., 2005. Clay–water/cement ratio identity of cement admixed soft clay. J. Geotech. Geoenviron. Eng. 131 (2), 187–192.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., 2011. Soil stabilization by calcium carbide residue and fly ash. J. Mater. Civil Eng. 24 (2), 184–193.

Horpibulsuk, S., Katkan, W., Sirilerdwattana, W., Rachan, R., 2006. Strength development in cement stabilized low plasticity and coarse grained soils: laboratory and field study. Soils Found. 46 (3), 351–366.

Huang, H.S., Yan, T.N., Lan, K., 2005. Laboratory experiment of the anticorrosion of cement stabilized soft soil in deep mixing pile. Geol. Sci. Technol. Inf. 24 (7), 85–88.

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

Kazemian, S., Prasad, A., Huat, B.B., Bazaz, J.B., Abdul Aziz, F.N., Mohammad Ali, T.A., 2011a. Influence of cement–sodium silicate grout admixed with calcium chloride and kaolinite on sapric peat. J. Civil Eng. Manag. 17 (3), 309–318.

Kazemian, S., Prasad, A., Huat, B.B.K., Bazaz, J.B., Mohammed, T.A., Aziz, F.A., 2011b. Effect of aggressive pH media on peat treated by cement and sodium silicate grout. J. Central South Univ. Technol. 18 (3), 840–847.

Kempfert, H.G., Gebreselassie, B., 2006. Excavations and Foundations in Soft Soils. Springer-Verlag, Berlin.

Ma, C., Chen., L.Z., Chen, B., 2014. Analysis of strength development in soft clay stabilized with cement-based stabilizer. Constr. Build. Mater. 71, 354–362.

Meyer, C., 2009. The greening of the concrete industry. Cem. Concr. Compos. 31 (8), 601–605.

Niazi, Y., Jalili, M., 2009. Effect of Portland cement and lime additives on properties of cold in-place recycled mixtures with asphalt emulsion. Constr. Build. Mater. 23 (3), 1338–1343.

Paglia, C., Wombacher, F., Böhni, H., 2001. The influence of alkali-free and alkaline shotcrete accelerators within cement systems: I. Characterization of the setting behavior. Cem. Concr. Res. 31 (6), 913–918.

Pangdaeng, S., Phoo-ngerkham, T., Sata, V., Chindaprasirt, P., 2014. Influence of curing conditions on properties of high calcium fly ash geopolymer containing Portland cement as additive. Mater. Des. 53, 269–274.

Phetchuay, C., Horpibulsuk, S., Suksiripattanpong, C., Chinkulkijniwat, A., Arulrajah, A., Disfani, M.M., 2014. Calcium carbide residue: alkaline activator for clay-fly ash geopolymer. Constr. Build. Mater. 69, 285–294.

Phoo-ngerkham, T., Chindaprasirt, C., Sata, V., Pangdaeng, S., Sinsiri, T., 2013. Properties of high calcium fly ash calcium fly ash geopolymer paste with Portland cement as an additive. Int. J. Miner. Metall. Mater. 53, 269–274.

Prusinski, J.R., Bhattacharja, S., 1999. Effectiveness of Portland cement and lime in stabilizing clay soils. Transp. Res. Rec.: J. Transp. Res. Board 1652 (1), 215–227.

Rafalko, S.D., Filz, G.M., Brandon, T.L., Mitchell, J.K., 2007. Rapid chemical stabilization of soft clay soils. Transp. Res. Rec.: J. Transp. Res. Board 2026 (1), 39–46.

Rogers, C.D.F., Glendinning, S., Roff, T.E.J., 1997. Lime modification of clay soils for construction expediency. Proc. Inst. Civil Eng. – Geotech. Eng. 125 (4), 242–249.

Rowles, M., O'Connor, B., 2003. Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite. J. Mater. Chem. 13 (5), 1161–1165.

Sukmak, P., Horpibulsuk, S., Shen, S.L., 2013a. Strength development in clay-fly ash geopolymer. Constr. Build. Mater. 40, 566–574.

Sukmak, P., Horpibulsuk, S., Shen, S.L., Chindaprasirt, P., Suksiripattanpong, C., 2013b. Factors influencing strength development in clay-fly ash geopolymer. Constr. Build. Mater. 47, 1125–1136.

Sukmak, P., Silva, P.D., Horpibulsuk, S., Chindaprasirt, P., 2014. Sulfate resistance of clay-Portland cement and clay-high calcium fly ash geopolymer. J. Mater. Civil Eng. ASCE 04014158, 1–11.

Thyagaraj, T., Rao, S.M., Sai Suresh, P., Salini, U., 2012. Laboratory studies on stabilization of an expansive soil by lime precipitation technique. J. Mater. Civil Eng. 24 (8), 1067–1075.

Yu, Y., Pu, J., Ugai, K., 1997. Study of mechanical properties of soil-cement mixture for a cutoff wall. Soils Found. 37 (4), 93–103.

Zhang, M., Guo, H., El-Korchi, T., Zhang, G., Tao, M., 2013. Experimental feasibility study of geopolymer as the next-generation soil stabilizer. Constr. Build. Mater. 47, 1468–1478.