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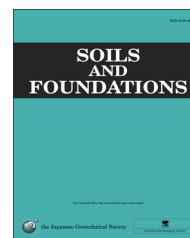


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Effect of cation exchange capacity of soil on stabilized soil strength

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Abstract

While a certain correlation between the cation exchange capacity (CEC) of the soil and the strength of the cement stabilized soil has been reported, the mechanism remains unclear. In this research, a set of soil samples with different CECs were stabilized with different proportions of cement and calcium hydroxide (Ca(OH)₂, CH). The influence of soil CEC on the strength of the stabilized soil was investigated by analyzing the CH saturation in the pore solution and measuring the strength of the stabilized soil specimens. It is revealed that cation exchange in the soil can reduce the CH saturation of the stabilized soil. If the CEC of the soil is too high, the CH in the pore solution of the stabilized soil cannot reach the saturation level, and further cation exchange would then consume the Ca²⁺ ions which should be originally used to generate calcium silicate hydrate, thus result in the poor strength of the stabilized soil.

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Keywords: Stabilized soil; Strength; Cation exchange capacity; Pore solution; CH saturation

1. Introduction

Cement stabilized soil is a kind of treatment technique which has been broadly used in subgrade stabilization (Arman et al., 1990; Kawasaki et al., 1983; Nishimura et al., 2012; Reuben, 2003; Taheri et al., 2012; Zhou and Ye, 2008). It is well known that soil's physical characters, such as water content, porosity, and clay content, have great influence on the strength of cement stabilized soil (Anagnostopoulos and Chatziangelou, 2008; Kawasaki et al., 1978). However, it is noticed that the strength of the stabilized soils made with same cement content, and even the strength of soils with similar

physical properties, differs greatly (Huang, 1997). Therefore, there must be other factors besides the physical properties of the soil which cause the difference in the strength of stabilized soils. Croft and Nettleton (1962) reported that cement could hydrate normally in clay minerals, kaolinite and illite consumed little calcium hydroxide (Ca(OH)₂, CH) and the strength of the stabilized soil made of the soil mainly composed of them was higher, while montmorillonite consumed more CH and the strength of the stabilized soil made of the soil mainly composed of it was lower. Cui et al. (2011) reported that the higher the montmorillonite content in bentonite, the higher was the soil's cation exchange capacity (CEC). Saitoh and Suzuki (1986) reported that cement hydration mainly produced the calcium silicate hydrate (C–S–H) and CH. The soil could absorb CH until it reached saturation point. Then the pozzolanic reaction occurred between the remaining CH and the soil to generate additional C–S–H, which determined the strength difference of the cement stabilized soils made from different soils. However,

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this theory does not satisfactorily explain the phenomenon mentioned above. Nakatsukasa (1986) reported that other cations absorbed by the soil could exchange with Ca^{2+} , and there was certain correlation between CEC and the strength of the cement stabilized soil. This study offered the test phenomenon, but did not explain the mechanism. Kawamura et al. (1971) studied the relationship between soil CEC and the stabilized strength of the cement stabilized soil, and proposed that the C–S–H with different lime–silicate ratios could be formed in the cement stabilized soils which were made from the soil samples with different CECs, and led to the strength difference among the cement stabilized soils. No experimental evidence, however, can prove that the C–S–H with different lime–silicate ratios can lead to a significant strength difference in the cement stabilized soils. Huang and Zhou (1994) proposed that because the CH in stabilized soils might be under-saturated, the further consumption of Ca^{2+} and OH^- ions by the soil decreases the amount of C–S–H generated by the cement. This explains why an equal amount of cement would not produce equal amount of hydrates in the stabilized soils made from soils with different absorption capacities of the ions, but resulted in a strength difference of the stabilized soils. However, the factors which affected the CH saturation were not clarified (the ratio of CH concentration in the pore solution to the saturated concentration is expressed as the CH saturation index (SI) in this study) for the stabilized soils, or how they affected the strength of the stabilized soils.

In this research, a set of soil samples with different CECs were selected. The stabilized soil specimens were made by mixing the soil samples with different amounts of cement and CH. The influence of soil CEC on the CH saturation in the pore solution and in turn on the strength of the stabilized soil specimens was investigated by analyzing the pore solution of the specimens and measuring the strength of the specimens.

2. Materials and methods

2.1. Materials

Ordinary 32.5 Portland cement (PC, based on the standard *Common Portland Cement*, GB175-1999), the analytic reagent CH, and distilled water were used in this test. The soil samples T₁, T₂, T₃, T₄, and T₅ had significant differences in their CEC content, and were made by mixing kaoline (GT), Na texture montmorillonite (NT) and the silt soil (FT) with particle sizes between 0.1 mm and 0.074 mm. Table 1 provides details of the mixing proportions as well as the physical properties and CEC content of the soil samples. The physical properties of the soil samples T₁, T₂, T₃, T₄, and T₅ were measured based on *Standard for Soil Test Method* (GB/T50123-1999). The determination of soil samples' CEC was conducted by the Chemical Testing Center of China University of Geosciences (Beijing, China) based on the standard *Cation exchange capacity of soils (sodium acetate)* (US EPA Method 9081). The main procedures were as follows: (1) 4 g air-dried soil sample was put into a centrifuge tube; (2) 33 mL of 1 mol/L sodium acetate solution was added to the centrifuge tube, then

Table 1
Mixing proportion and characteristics of testing soil samples.

| Soil samples | Mixing proportion (%) | | | Physical characteristics | | | | | CEC (mol/kg) |
|----------------|-----------------------|------|-------|------------------------------|--------------|---------|----------------|----------------|--------------|
| | GT | NT | FT | ρ (g cm ⁻³) | ω (%) | n (%) | ω_L (%) | ω_P (%) | |
| T ₁ | 0 | 87.5 | 12.51 | 1.53 | 92.50 | 52.15 | 101.34 | 40.23 | 86 |
| T ₂ | 30 | 60.0 | 0.0 | 1.54 | 81.00 | 52.38 | 92.32 | 38.64 | 65 |
| T ₃ | 50 | 42.5 | 7.5 | 1.55 | 72.50 | 53.05 | 85.51 | 35.36 | 48 |
| T ₄ | 70 | 24.5 | 5.5 | 1.57 | 60.00 | 53.49 | 79.24 | 32.48 | 32 |
| T ₅ | 100 | 0 | 0 | 1.52 | 52.50 | 50.50 | 60.29 | 27.23 | 4 |

GT: kaoline; NT: Na texture montmorillonite; FT: silt soil whose particle size was between 0.1 mm and 0.074 mm. ρ : wet density; ω : water content; n : porosity; ω_L : liquid limit; ω_P : plastic limit.

the tube was vibrated for 5 min, and then the centrifuge was operated for 5 min at a speed of 4000 r/min; (3) the excess sodium acetate solution in the centrifuge tube was removed; (4) procedures (2) and (3) were repeated more than 3 times; (5) 25 mL of isopropyl alcohol with purity of 99% was put to the centrifuge tube, which was then vibrated for 5 min, followed by 5 min in the centrifuge at a speed of 4000 r/min; (6) the excess of isopropyl alcohol in the centrifuge tube was removed; (7) procedures (5) and (6) were repeated more than 3 times; (8) 25 mL of 1 mol/L ammonium acetate solution was put into a centrifuge tube, which was then vibrated for 5 min, followed by 5 min in the centrifuge at a speed of 4000 r/min; (9) the excess solution was transferred into a 100 mL volumetric flask; (10) procedures (8) and (9) were repeated more than 2 times; (11) 1 mol/L ammonium acetate solution was added to the volumetric flask until the volume of solution reach 100 mL, and then the concentration of Na^+ in the solution in the volumetric flask was measured by means of atomic absorption spectrometry.

The value of the CEC was calculated by the following formula:

$$\text{CEC} = \frac{cV}{23mK \times 10} \quad (1)$$

where c is the concentration of Na^+ in the solution in the volumetric flask, V is the volume of the volumetric flask, m is the mass of the soil sample, and K = the coefficient of the soil sample transformed from air-dried to oven-dried, K is 0.87 in this study.

2.2. Test methods

The mixing apparatus was a SJ-160 mortar mixer (based on the standard *Mortar mixers for testing*, JG/T 3033-1996). The specimen was prepared as follows (based on the standard *Test Methods of Materials Stabilized with Inorganic Binders for Highway Engineering* (JTG E51-2009):

(1) The cement, CH, and distilled water was weighed according to the component proportion of the stabilizer, and all

- were added to the mixer pot, and mixed for 30 s at a mixing speed of 60 r/min,
- (2) The soil was added to the mixer pot, and mixed for 1 min at a mixing speed of 60 r/min.
 - (3) The soil adhering to blade and pot wall was removed and placed in the pot center, and finally mixed for 2 min at a mixing speed of 120 r/min.
 - (4) The mixtures were placed in a cubic steel mold with dimensions $50 \times 50 \times 50\text{mm}^3$ in 3 equal layers, and the mold was vibrated for 60 s after each layer was filled on the ZT-1 \times 1 jolting table (based on the standard *Jolting table for compacting mortars specimen*, JC/T 682–2005). The mold was then shaped and the surface was covered with plastic film.
 - (5) The specimens were removed from the mold after 24 h and cured for 30d in standard curing chamber kept at a constant temperature of $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and humidity $\geq 95\%$. The unconfined compressive strength (UCS) was then carried out, and the pore solution was analyzed.

The UCS test was conducted based on the standard JTG E51-2009. The extraction of the pore solution was conducted based on Xue's (Xue et al., 1983) design as follows: the specimens wrapped in ninon were compressed by the expression device, and the pressure was increased at a rate of 0.2 kN/s until 300 kN until the pore solution was squeezed out completely.

In order to determine the affect of the other ions on the CH saturation in the pore solution of the stabilized soil specimens, the concentration of some main ions in the pore solution was measured based on *Standard for Soil Test Method* (GB/T50123-1999). The main analysis methods were as follows: $[\text{Ca}^{2+}]$ and $[\text{Al}^{3+}]$ were determined with atomic absorption spectrometry, $[\text{OH}^-]$ was determined with hydrochloric acid titration solution through a methyl red indicator, $[\text{K}^+]$ and $[\text{Na}^+]$ were determined with flame photometry, $[\text{SiO}_4^{4-}]$ was determined with silicon–molybdenum blue colorimetry, and $[\text{SO}_4^{2-}]$ was determined with barium sulfate gravimetry.

3. Results

The stabilized soil specimens were made by mixing the samples (T₁, T₂, T₃, T₄ and T₅) with different PC and CH contents. The water-stabilizer ratio was 0.5. The relationship between the UCS of the stabilized soil specimens which were stabilized only by PC and the cement–wet soil ratio by mass (a_w) are shown in Fig. 1. The relationship between the UCS of the stabilized soil specimens and CH–wet soil ratio by mass (D_w) when $a_w = 15\%$ are shown in Fig. 2. The concentration of the main ions in the pore solutions of some typical stabilized soil specimens when $D_w = 0$ are given in Table 2. In Figs. 1, 2 and Table 2, S₁ represents the stabilized soil specimens made by mixing T₁ only with PC, and S₁₋₁₅ represents the S₁ with a_w of 15%, CS₁ represents the specimens made by mixing T₁ with CH in addition to 15% PC. The D_w are 0%, 1%, 2%, 3%,

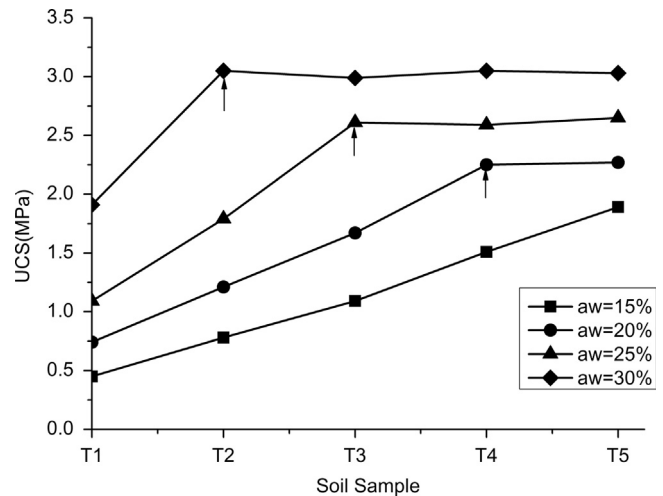


Fig. 1. UCS of specimens stabilized only by PC. Note: The arrows indicate the threshold that UCS does not increase and remain stable.

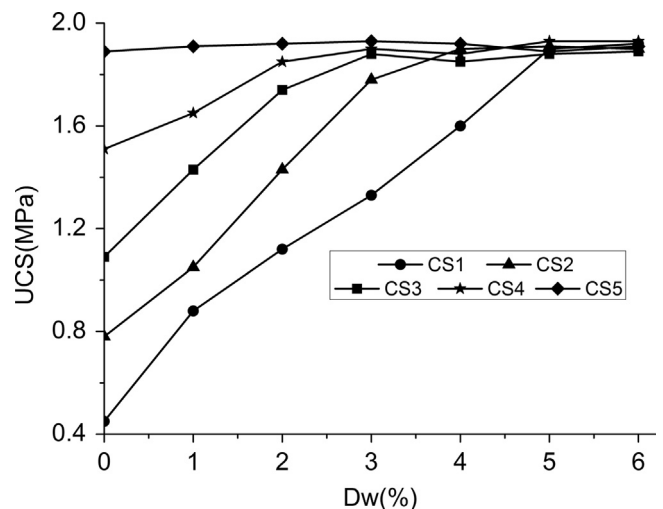


Fig. 2. Relationship between UCS and CH content of stabilized specimens.

Table 2
Concentration of main ions in pore solutions and SI of specimens.

| Specimen | a_w (%) | Concentration (mmol L ⁻¹) | | | | | | | SI |
|-------------------|-----------|---------------------------------------|----------------|------------------|-----------------|------------------|-------------------------------|------------------|--------|
| | | Na ⁺ | K ⁺ | Ca ²⁺ | OH ⁻ | Al ³⁺ | SO ₄ ²⁻ | Si ⁴⁺ | |
| S ₁₋₃₀ | 30 | 59.912 | 26.660 | 1.442 | 119.460 | 2.076 | 0.387 | 0.631 | -0.042 |
| S ₂₋₃₀ | | 60.229 | 29.300 | 2.911 | 140.060 | 2.432 | 0.674 | 0.538 | 0.050 |
| S ₂₋₂₅ | 25 | 45.455 | 12.975 | 1.081 | 127.680 | 2.753 | 0.975 | 0.675 | -0.039 |
| S ₃₋₂₅ | | 49.329 | 10.321 | 2.018 | 151.540 | 1.987 | 0.823 | 0.491 | 0.041 |
| S ₃₋₂₀ | 20 | 28.101 | 7.322 | 0.999 | 130.360 | 1.785 | 0.754 | 0.632 | -0.037 |
| S ₄₋₂₀ | | 30.416 | 8.909 | 1.766 | 167.010 | 2.078 | 0.832 | 0.631 | 0.042 |
| S ₅₋₁₅ | 15 | 10.276 | 2.589 | 2.214 | 187.840 | 2.432 | 0.643 | 0.432 | 0.050 |
| S ₄₋₁₅ | | 9.257 | 2.012 | 1.534 | 158.350 | 2.341 | 0.643 | 0.411 | -0.079 |
| S ₃₋₁₅ | | 9.125 | 1.921 | 0.741 | 120.340 | 2.076 | 0.614 | 0.421 | -0.175 |
| S ₂₋₁₅ | | 9.997 | 2.011 | 0.435 | 100.210 | 1.987 | 0.514 | 0.462 | -0.235 |
| S ₁₋₁₅ | | 9.045 | 2.432 | 0.213 | 90.470 | 2.331 | 0.622 | 0.436 | -0.427 |

4%, 5%, and 6%. When $D_w = 0$, CS₁ is the same as S₁₋₁₅. The denominations of the other stabilized soil specimens follow the same code rule described above.

In Table 2, SI was calculated according to the method introduced in the references (Rothstein et al., 2002; Thomas, et al., 2003) as follows.

The activity of the Ca^{2+} and OH^- ions under the effect of other ions were calculated based on the data in Table 2 and then the ion activity product IAP ($\text{IAP} = [\text{Ca}^{2+}][\text{OH}^-]^2$) were calculated according to the ion equation $\text{Ca}(\text{OH})_2 = \text{Ca}^{2+} + 2\text{OH}^-$. The SI of the solution was calculated by Eq. (2), in which K_{sp} is the thermodynamic solubility product constant of CH at 25 °C. The value used in this paper is 6.3096×10^{-6} .

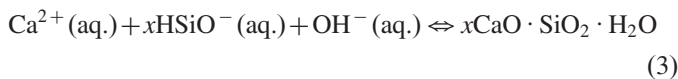
$$\text{SI} = \log \frac{\text{IAP}}{K_{\text{sp}}} \quad (2)$$

The results of SI are shown in Table 2. $\text{SI} = 0$ means that the CH is just saturated in the pore solution; $\text{SI} > 0$ means that CH is supersaturated; $\text{SI} < 0$ means that CH is under-saturated.

4. Discussions

Fig. 2 and Table 2 show that when $a_w = 15\%$ and $D_w = 0$, the strength of specimen CS_5 (i.e. $\text{S}_5\text{-15}$) was the highest, and the strength of specimens CS_4 , CS_3 , CS_2 , CS_1 (i.e. $\text{S}_4\text{-15}$, $\text{S}_3\text{-15}$, $\text{S}_2\text{-15}$, and $\text{S}_1\text{-15}$) decreased in turn. The pore solution of $\text{S}_5\text{-15}$ was CH saturated while the CH in the pore solution of the other specimens $\text{S}_4\text{-15}$, $\text{S}_3\text{-15}$, $\text{S}_2\text{-15}$, and $\text{S}_1\text{-15}$ was under-saturated, and the SI decreased in turn. Fig. 2 also shows that the strength of CS_5 remained almost the same with the increase of D_w ; however, the strength of the other specimens ($\text{CS}_1\text{-CS}_4$) increased with the increase of D_w until D_w reached a certain upper limit, at which point the strength remained almost the same with the increase of D_w .

Cement hydration mainly produces C–S–H and CH. C–S–H forms according to the following thermodynamic equation (Taylor, 1997):



Huang et al. (2009) reported that according to Eq. (3), the production of C–S–H in cement stabilized soil was determined by the concentration of Ca^{2+} and OH^- ions in the pore solution when the CH concentration was under-saturated. C–S–H is the main contributor to strength, while CH has no direct contribution to the strength of stabilized soil specimens. As such, the CH saturation in the pore solution of the cement stabilized soil determines the production of C–S–H which determines the strength of the specimen. Based on above research, the results shown in Fig. 2 and Table 2 can be explained as follows. When the CH in the pore solution of the stabilized soil specimen is under-saturated, the C–S–H cannot be produced fully because there is not enough Ca^{2+} and OH^- ions, and the lower the SI (i.e. the less the amount of Ca^{2+} and OH^- ions), the less the production of C–S–H, in turn the poorer the strength of the stabilized soil specimens. As D_w increases, the concentration of the Ca^{2+} and OH^- ions in the pore solution increases, which results in increased C–S–H production and enhances the strength of the stabilized soil specimens. When the CH in the pore solution is saturated, the

C–S–H can be fully produced in stabilized soil specimens and the strength reaches the maximum. Then, C–S–H production is not increased by further increases of D_w , therefore, the strength cannot increase any more.

Fig. 2 indicates that with the increase of D_w , after the pore solution is CH saturated, the final strength of the stabilized soil specimens $\text{CS}_1\text{-CS}_5$, which are made from the samples $\text{T}_1\text{-T}_5$ is almost the same, although the original strength of $\text{CS}_1\text{-CS}_5$ is different. The strength of the cement stabilized soil is determined only by the amount of C–S–H and the physical characteristics of the soil sample from which the stabilized soil is made. In addition, the amount of C–S–H in the stabilized soil specimens $\text{CS}_1\text{-CS}_5$ is the same, since the same content of cement produces the same amount of C–S–H when the pore solution of $\text{CS}_1\text{-CS}_5$ is CH saturated. Therefore, the results in Fig. 2 imply that, from the point of view of the construction of stabilized specimens' microstructure, the physical properties of soil samples $\text{T}_1\text{-T}_5$ have similar comprehensive performance. Although the physical properties of samples $\text{T}_1\text{-T}_5$ vary (see Fig. 2), the overall influence of these physical properties on the strength of the stabilized soil specimens are almost the same, i.e., the sum effect of the physical properties of each sample is almost the same. Consequently, the samples $\text{T}_1\text{-T}_5$ could be regarded as five samples which have the same overall physical character.

As the overall physical character of the samples $\text{T}_1\text{-T}_5$ are almost the same, if the production of C–S–H produced by the cement in the specimens $\text{CS}_1\text{-CS}_5$ are the same as well, then the strength of the stabilized soil specimens $\text{CS}_1\text{-CS}_5$ should be similar. However, Fig. 2 shows that when $a_w = 15\%$ and $D_w = 0$, the strengths of the stabilized soil specimens $\text{CS}_1\text{-CS}_5$ are different, indicating that the production of C–S–H in the stabilized soil specimens $\text{CS}_1\text{-CS}_5$ differs when the cement content is the same. Fig. 2 and Table 2 indicate that the strength of the stabilized soil specimens $\text{CS}_1\text{-CS}_4$ decreases with the increase of CEC in the sample, which is also the case for SI. As mentioned above, in the cement stabilized soils with the same cement content, the production of C–S–H in the stabilized soils decreases with the decrease of CH saturation, and the strength of the stabilized soil decreases in turn. Therefore, the above results indicate that the cation exchange can decrease the CH saturation in the pore solution of the stabilized soil. If the CEC of the soil samples is too high, the other cation absorbed on the soil particle should exchange the Ca^{2+} produced by cement hydration and result in an under-saturated CH pore solution in the stabilized soil. Under such conditions, further cation exchange consumes the Ca^{2+} ions which otherwise would be used in the production of C–S–H, according to Eq. (2). Therefore, the amount of C–S–H production decreases, which reduces the strength of the stabilized soil.

Fig. 1 and Table 2 show that, when $a_w = 15\%$, only the pore solution of S_5 is CH saturated, while that of the other stabilized soil specimens decreases as the CEC of corresponding samples increases, and the strength of the stabilized soil specimens decreases as the CEC of the soil samples increases. Fig. 1 also shows that when a_w is 20%, 25% and 30%, the strength of the

stabilized soil specimens increases as the CEC of the samples decreases under the same a_w . However, once the amount of CEC in the samples becomes lower than the thresholds indicated by the arrows in Fig. 1, the strength of the stabilized soil specimens does not increase any more with the further decrease of the CEC content. It can be also seen in Fig. 1 that the a_w corresponding to the thresholds increases as the amount of CEC increases in the sample. Table 2 indicates that the thresholds in Fig. 1 exactly correspond to the turning points at which the CH concentration changes from under-saturation to saturation.

Increasing a_w can increase the strength not only by increasing the C–S–H production, but also by increasing the CH saturation. This serves to increase the production of C–S–H as well. The experiment phenomenon explained above indicate that when $a_w = 15\%$, the CH in the pore solution are already saturated. This was the case for the stabilized soil specimens of the S_5 series, which were made from sample T_5 with the lowest CEC level. It implies that when $a_w > 15\%$ (i.e. the cement content is higher than 15%), the CH in the pore solution remains saturated, and ensure the C–S–H can be fully produced fully, while the CH in the pore solution of the other stabilized soil specimens are still under-saturated when $a_w = 15\%$, and the C–S–H could not be fully produced when $a_w = 20\%$, the influence of CEC was compensated by the CH produced by cement in the stabilized soil specimen S_4-20 , which was made from sample T_4 with the second lowest CEC level. Therefore, the amount of C–S–H in the stabilized soil specimen S_4-20 is the same as that in S_5-20 , resulting in stabilized soil specimens, and S_4-20 had almost the same strength as S_5-20 . As a_w increases, the amount of CH generated by the cement increases, and the stabilized soil specimens made from samples T_3 and T_2 (with higher CEC levels) reach CH saturation when a_w is 25% and 30%, respectively. Therefore, the stabilized S_4 and S_5 soil specimens had equal strength with the same a_w . These results further confirm the validity of the assumption that the cation exchange of the soil reduces the CH saturation in the stabilized soil and thus reduces the amount of the C–S–H produced by cement, in turn leading to lower strengths of the stabilized soil.

These results reveal the connection between the phenomenon reported by Kawamura et al. (1971) and Nakatsukasa (1986) and the research reported by Huang and Zhou (1994), and show that soil CEC affects the CH saturation in the pore solution of cement stabilized soil. It also provides an understanding of the mechanism to explain the relevance of soil CEC and the strength of cement stabilized soil. Based on these results, the component and content of the soil stabilizer can be determined according to the amount of CEC in the soil to be stabilized.

5. Conclusions

It was shown that the cation exchange in soil reduces the CH saturation in stabilized soil. If the CEC of soil is high, the CH in the pore solution of the stabilized soil may be unsaturated. Under such condition, any further cation exchange may consume the

Ca^{2+} and OH^- ions which should be used to produce C–S–H, in effect reducing the amount of C–S–H produced by cement, which lowers the strength of the stabilized soil.

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