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Mechanical Property of Cement-stabilized Soil with Nano-CaO and Reinforcement Mechanism Analysis

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Nanometer minerals as new additives can improve the property of the cement-stabilized soil through some previous researches. Nano-CaO, which has rarely been attempted in admixtures of cemented soft clays for now, was mixed into Tianjin soft clay combined with cement. The unconfined compression tests were carried out to find out the mechanical property of the cemented soil after cured for appropriate days. Additionally the test results were compared with the cemented soil containing other nanometer minerals to clarify the reinforcement effect furthermore. The results show that the strength and the brittleness of cemented soil increases first and then decreases, and the deformation modulus has opposite variation trend with the content of nano-CaO. Compared with other nanometer minerals, the reinforcing effect is similar to nanometer aluminium powder. It can be concluded that if the minerals could improve the strength originally in chemistry, the nanometer treatment can upgrade the chemical reactivity, and improve the strength of cemented soil.

1. Introduction

Cement as an additive of stabilizing soil, which can improve the mechanics and deformation properties of soil, is widely used in foundation treatment projects in China, Japan and Europe (Han and Gabr, 2014). Recently a large number of new additives were mixed into cemented soil to study the reinforcement effect, such as polypropylene fiber (Cristelo et al., 2015), waste plastic fibres (Subramaniaprasad et al., 2014), recycled glass (Arulrajah et al., 2015), metakaolin (Zhang et al., 2014), and so on.
Nanometer mineral materials with fine particles, large specific surface and high reaction activity have been used in cement-based materials. In Zhu et al.'s study (Zhu et al., 2003; Wang and Zhu, 2004; Wang et al., 2006), the strong contribution of nanometer silica was demonstrated, and its reinforcement mechanism was analyzed. In Li Gang's study (2003), the nano-Al_2O_3 and nano-TiO_2 were mixed into the cement-stabilized soil to study the strengthening effect. Nanometer minerals, as a new type of soil-cement additive, haven't been concerned until recently.
Calcium silicate hydrate (C-S-H) is produced as the chief cementing and hardening agent in hydrates of Portland cement. The amount of C-S-H relates to the concentration of calcium hydroxide in the liquid phase. Suzuki (1985) concluded the thermodynamic equations as follows,

$$6Ca^{2+}(aq.)+5HSiO_3^-(aq.)+7OH^-(aq.) \leftrightarrow 6CaO\cdot5SiO_2\cdot6H_2O(C\text{-}S\text{-}H) \quad (1)$$

With rising initial Ca/Si mole ratio, the amount of C-S-H increases, and the strength increases meanwhile. Huang and Zhou (1994) also pointed out that in cement-stabilized soil, the amount of CSH would be influenced by the soil absorption of Ca^+ and OH^- until calcium hydroxide (CH) reaches the saturated state. It can be concluded that the mix of a certain amount of lime can increase the Ca/Si, OH^-/Si mole ratio. And in that condition CSH could exist steadily, and the strength of cement-stabilized soil increases meanwhile. Tong (2000) mixed soil with cement and lime, and found that the additive of lime can improve the strength of cemented soil to some extend.
In this study, nano-CaO was chosen as a new additive of cement-stabilized soil to investigate the mechanical property of the reinforced cemented soil. To achieve the above objectives, ordinary Portland cement, nano-CaO and Tianjin marine clay (a type of marine clay typically located in North China) were mixed to obtain the cemented soil samples. The samples were then cured for 7 days, 28 days and 60 days individually at standard

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conditions in water. Unconfined compression tests were performed to clarify the evolution. At last the results were compared with that containing other nanometer minerals to analyze the reinforcement mechanism.

2. Materials and testing methods

2.1 Materials

Tianjin soft clay, a type of Quaternary Holocene marine sedimentation, is of the high water content (50 %), high plasticity, liquid-plastic state, and high compressibility. The basic properties of the selected soil samples are listed in Table 1. The mineral component of the Tianjin soft clay was obtained through X-ray diffraction test (XRD), which is listed in Table 2. Note that the clay minerals are the main component and the content of illite is up to 39 %. Table 3 presents the oxides of the Tianjin soft clay, which was obtained through the chemical quantitative analysis test. Note that the total content of SiO_2 is over 50 %, followed by Al_2O_3, CaO, Fe_2O_3. The content of the active oxide like SiO_2 and Al_2O_3, et al. plays an important role in the pozzolanic reaction in cemented soil.

Table 1: Mechanical properties of soft clay

Wet density (g/cm^3)	Natural water content (%)	Void ratio *e*	Particle size distribution(%)			Liquid limits Wl (%)	Plastic limits Wp (%)
			Sand	Silt	Clay		
1.73	50	1.373	3	61.9	35.1	49.4	30.7

Table 2: Mineral composition of soft clay(%)

Quartz	Feldspar	Plagioclase	Amphibole	Calcite	Kaolinite	Illite	Chlorite
27	6	9	1	3	6	39	9

Table 3: Chemical component of soft clay(%)

SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	LoI
54.27	14.02	3.48	2.13	6.47	3.04	2.73	2.22	0.65	0.16	0.12	10.54

The ordinary Portland cement (OPC 42.5 R/N) used in this study complys to Chinese standard GB 175-2007 (similar to cement prepared by co-grinding type I Portland cement clinker and supplementary materials), of which the specific surface area is 357 kg/m^2. Its oxide composition is listed in Table 4. The nano-CaO used in this study is white powder, the purity reaches up to 99.9 %, the fineness is 20±5 nm.

Table 4: Oxide composition of ordinary Portland cement(%)

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	MaO	Na_2O	K_2O	LOI	Total
19.5	6.5	63.5	3.3	0.85	2.1	0.9	0.6	0.3	2.2	97.55

2.2 Sample preparation

To prepare the testing samples, the selected soft clay was first dried naturally, then the soil was filtered through the screen with the hole diameter of 2 mm. The OPC (mass content of cement to wet soil at 8 %, 12 %, 15 % and 20 %), the nano-CaO (mass content to wet soil at 0 ‰, 5 ‰, 10 ‰, 15 ‰, 20 ‰), and water (content of which consists of 2 parts: part 1, which was added to make dried clay arrive at natural moisture content 50 %; part 2, which was added to meet the water cement ration 0.5) were mixed uniformity into the grouting machine. Then the mixture was transferred into a cube mould, with 70.7 mm on each side. The mixture was artificially compacted by vibration. After the first 24 hours of curing, the cemented soil samples were removed from the moulds, and were cured in water at 20 ± 3 °C for 7 days, 28 days and 60 days.

2.3 Unconfined compression test (UCS)

Unconfined compression test was carried out through the electronic universal testing machine (DNS-100), of which effective loading is 0.4-100 kN. In compression process the surfaces of samples should be contacted smoothly to avoid stress concentration. The compression rate was defined at 1.2 mm/min in this study. The DNS-100 was connected with the computer to record the stress-strain data during the test.

3 Experimental results

3.1 Unconfined compression strength (UCS)

The typical relationship between the unconfined compression strength and nano-CaO content is shown in Figure 1 (all samples containing 15 % cement). Note that the strength had no significant increase with the content of nano-CaO after 7 days of curing. When cured for 28 days, the strength increased at first then decreased with the content of nano-CaO. The strength (2623.0 kPa) of the optimal nano-CaO content (10 ‰) increased 22.28 % than that without nano-CaO (2093.8 kPa). When the content was above 10 ‰, the strength decreased to some extent. The strength behaviors of samples after 60 days of curing were similar with that cured for 28 days, the strength (3825.02 kPa) with 10 ‰ nano-CaO increased 19.22 % than that without nano-CaO (3208.4 kPa). It can be concluded that nano-CaO presents its advantages with curing time, and the optimal content is all about 10 ‰.

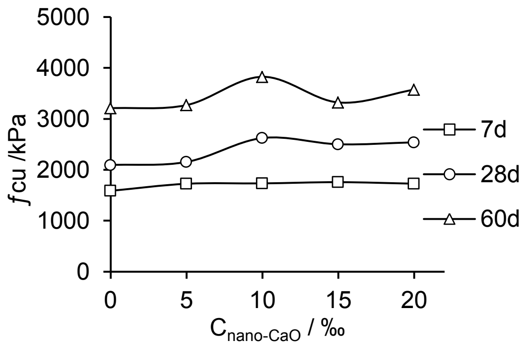

Figure 1: Relationship between f_{cu} (kPa) and nano-CaO content (‰)

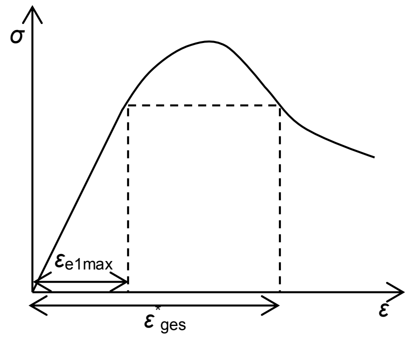

Figure 2: Sketch of brittleness modulus

3.2 Stress-strain relationship

Wu (1983) proposed a kind of definition of brittleness modulus just according to the stress-strain relation, of which the formula is shown in Eq.(2). The sketch of brittleness modulus is shown in Figure 2.

$$S = \frac{\varepsilon_{e1max}}{\varepsilon^{*}_{ges}} \qquad (2)$$

Where ε_{e1max} is the maximum elastic strain; ε^{*}_{ges} is total strain of critical state, the stress of which corresponds to the maximum elastic stress. For ideal elastic brittle materials, ε_{e1max} is equal to ε^{*}_{ges}, where the brittleness modulus is 1; for ideal elastic plastic materials, ε^{*}_{ges} goes to infinity, where the brittleness modulus is 0; for normal authentic materials, range of the brittleness modulus is from 0 to 1, and the closer its value is to 1, the more brittle the materials are. Since the brittleness modulus could be obtained just according to the stress-strain relationship, it was used to describe the brittleness characteristic in this study.

The stress-strain curves of cemented soil with nano-CaO content, cured for 28 days, are shown in Figure 3. Table 5 shows the value of brittleness modulus.

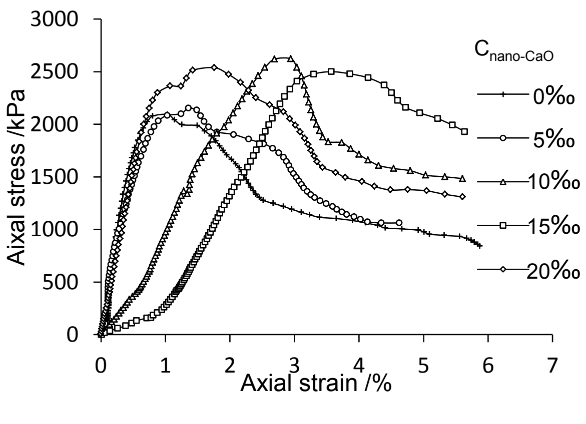

Figure 3: Stress-strain curves after 28 d of curing

Table 5: Brittleness modulus with different content of nano-CaO

	$C_{nano\text{-}CaO}$ (‰)				
	0	5	10	15	20
ε_e (%)	0.513	0.589	2.348	2.930	0.750
ε_g (%)	1.507	2.425	3.152	4.505	2.830
S	0.340	0.243	0.745	0.650	0.265

Note that the brittleness modulus increased at first then decreased with content of nano-CaO. Compared with the strength behaviors, it can be concluded that as the strength increased, the cemented soil became more brittle.
The stress-strain curves of cemented soils with curing time, containing 10 ‰ nano-CaO are shown in Figure 4, and Table 6 shows the brittleness modulus results.

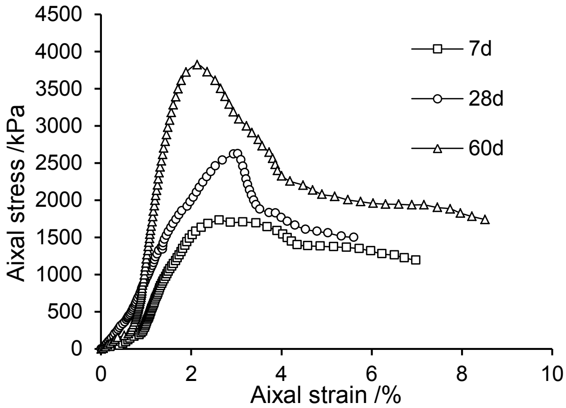

Figure 4: Stress-strain curves after 7d, 28d, 60d of curing

Table 6: Brittleness modulus after 7 d, 28 d, 60 d curing

	7 d	28 d	60 d
ε_e (%)	2.026	2.348	1.782
ε_g (%)	4.137	3.152	2.532
S	0.490	0.745	0.704

Note that at early stage stress increased slowly with strain, and the brittleness modulus was smaller which means the plasticity was larger; the brittleness modulus of 28 days and 60 days were similar to each other. We may draw the conclusion that the brittleness grew not any more after 28 days of curing.

4 Reinforcement mechanism

4.1 Comparison with other nanometer minerals

Currently nanometer minerals reinforcing cement-stabilized soil mainly include nanometer silica fume, nano-Al_2O_3 and nano-TiO_2. About nanometer silica fume as additive, through Wang's study (2006), the compression strength reached the maximum with nanometer silica fume content of 15-22 ‰. When the content of nanometer silica fume was less than 15 ‰, the strength of cemented-stabilized soil increased 168 %, 173 %, 270 % after curing of 7 days, 28 days and 60 days with 10 ‰ nanometer silica fume increasing. And when the content was larger than 22 ‰, the strength decreased with the content increased. In his study, the strength of cement-stabilized soil containing nanometer silica fume was greatly improved. About common silica fume as additive, through Zhou's study (2009), when the content of silica fume was 5 %, the strength of cemented-stabilized soil increased 121 % and 124 % after curing of 7 days and 28 days. It can be concluded that the common silica fume is also a kind of effective additive, and the nanometer treatment makes the strength improve further.
About nano-Al_2O_3 as additive, through Li's study (2003), the compression strength reached the maximum with nano-Al_2O_3 content of 5-7.5 ‰. The strength of cemented-stabilized soil increased 16.8 %, 32.5 %, 20.5 %, 25.5 % after 7 days, 28days, 60 days and 90 days of curing. But about nano-TiO_2, its mixture had evident negative effect on strength, and the decrease range was up to 90 %.
Through above analysis, we can see that the reinforcement effect of nanometer silica fume is best, the strength improved up to above 200 % at optimal content; the strength of cemented-stabilized soil containing nano-Al_2O_3 improved 20-30 % at optimal content, of which the reinforcement effect is modest; the mix of nano-TiO_2 has negative effect on cemented-stabilized soil. In this study the strength of cemented-stabilized soil containing 10 ‰ nano-CaO improved about 20 %, the reinforcement effect is similar with nano-Al_2O_3. Above nanometer minerals all have one character in common, the strength increases first then decreases with the content of nanometer minerals.

4.2 Reinforcement mechanism analysis of nano-CaO

The scholars have reached agreement that the strength of cemented-stabilized soil comes mainly from the cementing effect of the cement hydrates, followed by ion exchange aggregation, pozzolanic reaction and carbonation, among which the carbonation effect is very weak actually. In common cemented-stabilized soil, ion exchange aggregation and pozzolanic reaction take place with CH which was produced by the cementing effect of the cement hydrates(Bello et al 2014; Benedetti et al 2015; Gul et al. 2014). After the nano-CaO is mixed into the cemented soil, CH is formed by the reaction of CaO with water, which make aggregation and pozzolanic reaction take place at early stage. The mix of nano-CaO make the ratio of Ca/Si, OH^-/Si increase, result in the amount of CSH increases. Meanwhile CSH could exist stably in the alkaline environment, which was created by the mix of nano-CaO.

In the current cement standards, the content of CaO is limited because that CH, formed by the reaction of CaO with water, could lead to the volume expansion, even damage concrete structure. But there are plenty of pores in soil, which provide enough space for the volume expansion, so the factor of expansion can be ignored. Because CH is produced by cement hydration, when the concentration is high, the cement hydration is impeded. Furthermore the strength of CH crystal is low, so if there is too much CH generating, the strength would decrease to some extent. Therefore the high content of CaO has some negative effect on strength of cemented-stabilized soil.

Nanometer minerals have higher chemical reactivity owe to a large number of fine particles(Teh and Wu 2014; Zamani et al., 2012). And about physical mechanism, nanometer minerals can adsorb water molecules, and fill pores between the soil aggregate. The practical reinforcement effect of nano-CaO is actually modest: when the content of CaO was 10 ‰, the strength increased about 20 %. As for common lime, in Tong's study (2000), the compression strength of cemented-stabilized soil with lime also increased 20 % approximately. The reinforcement effect of common lime and nano-CaO is similar. It can be concluded that because the positive and negative effect both exist simultaneously, the reinforcement effect of nanometer treatment is not good enough for CaO.

Through above analysis, not all nanometer treatment to minerals could improve the strength of cemented-stabilized soil further. We may conclude that if the minerals could improve the strength originally in chemistry, the nanometer treatment can upgrade the chemical reactivity, which can improve reinforcement effect further; but if the minerals have negative effect originally in chemistry, the negative effect would be enhanced after the nanometer treatment.

5. Conclusions

This paper proposed a new nanometer mineral as additive of cemented stabilized soil, nano-CaO, to improve the behavior of cemented soils and analyzed the strength development of cement stabilized Tianjin soft clay by using unconfined compression strength tests, and the results were compared with some other nanometer minerals. The following conclusions can be drawn from this study:

1. The mix of nano-CaO has little effect to the strength of cement-stabilized soil in the early stage, but its advantages presents with curing time gradually. The strength and brittleness increases first then decreases with content of nano-CaO.

2. The positive effects and negative ones exist simultaneously with mix of nano-CaO: one hand, aggregation and pozzolanic reaction could take place with the mix of nano-CaO, and the amount of CSH increases with the ratio of Ca/Si, OH^-/Si increasing, which also contribute the formation of alkaline environment; on the other hand, when the concentration of CH is high, cement hydration is impeded, and too much CH crystal's exist make the strength decrease to some extend. It can be concluded that if the minerals could improve the strength originally in chemistry, the nanometer treatment can upgrade the chemical reactivity.

3. Compared with nanometer silica fume, nano-Al_2O_3 and nano-TiO_2, the reinforcement effect of nanometer silica fume is best, of which nano-CaO similar with nano-Al_2O_3 is modest, and nano-TiO_2 has remarkable negative effect.

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