www.nature.com/scientificreports

scientific reports

OPEN

Effect and microscopic mechanism of nano-oxide modified cement solidified silty soft soil

Xianshi Deng[1], Xiqi Liu[2,3], Zechen Xiao[1]✉, Rong Hu[2,3], Zhiqi Wang[4], Hongtao Fan[1] & Xin Huang[1]

To enhance the engineering properties of cement solidified silty soft soil, nano-oxides such as nano-SiO_2(NS), nano-Al_2O_3(NA), nano-MgO(NM) and nano-Fe_3O_4(NF) were selected for modification. The unconfined compressive strength, one-dimensional consolidation and water stability tests were carried out, and the microstructure was analyzed by X-ray diffraction, scanning electron microscopy and mercury intrusion tests. The test results show that nano-oxides can significantly improve the compressive strength of cement solidified silty soft soil. After curing for 28 days, The unconfined compressive strength of samples modified with 1.5% NS, NA, NF, and NM increased by 187.44%, 171.67%, 122.55%, and 189.37%, respectively, compared to that of pure cement soil. With the increase of nano-oxide content, the void ratio and compression coefficient of the sample gradually decrease, and the strength residual coefficient gradually increases. Microscopic test analysis shows that the addition of nano-oxides causes the difference in the type and quantity of hydration products in cement solidified soil, promotes the formation of an effective whole of soil particles wrapped by gel products, transforms the pores from inter-particle pores into intra-particle pores, and improves the integrity of microstructure. Furthermore, the microscopic mechanism of nano-oxide modified cement solidified silty soft soil is established, which can provide theoretical guidance for related research and engineering.

Keywords Nano-oxide, Silty soft soil, Solidification, Strength, Microstructure

Soft soil foundations are widely distributed in coastal and riverside areas of China, which often have adverse engineering geological characteristics such as high water content, high compressibility, and low strength. If they are not properly disposed, they will cause great harm to the safety and stability of upper buildings (structures). Construction techniques such as shallow/deep mixing pile and cement integral solidification are the most commonly used methods to treat soft soil foundation. Its working principle lies in the filling and cementation of cement hydration products to soil particles, which promotes the soil to form a composite reinforcement with certain strength and stiffness[1,2]. However, when the traditional portland cement is used to solidify the silty soft soil, its rich organic matter inhibits the hydration reaction by lowering the pH value of the soil and adsorbing the surface of cement particles[3,4]. It leads to poor solidification effect and strength deterioration, seriously affecting the quality and safety of the project.

In recent years, the method of nano-materials modified cement solidified soil has been widely concerned by many scholars. Common materials include nano-SiO_2, nano-Al_2O_3 and nano-TiO_2. Due to their large specific surface area, high activity, and strong adsorption capacity, nano-materials have shown excellent performance in enhancing the mechanical and durability properties of cement soil[5–8]. Lang Lei et al.[9] studied the strength characteristics of cement stabilized soft soil modified by nano-SiO_2, nano-Al_2O_3 and nano-MgO. It was found that nano-materials can improve the mechanical properties of cement stabilized soil. It is believed that high surface energy, nano-induction and filling promote the formation of a more dense and homogeneous microstructure of solidified soil. Lu Jianguo[10] studied the effects of nano-SiO_2 and nano-Fe_3O_4 on the strength of cement soil. It is concluded that the strength of cement soil increases with the increase of nano-SiO_2 content, and shows a trend of first increasing and then decreasing with the increase of nano-Fe_3O_4 content. Zhang Xingchen

[1]School of Landscape, Hunan Polytechnic of Environment and Biology, Hengyang 421005, Hunan, China. [2]Institute of Hydraulic Engineering, Pearl River Water Resources Research Institute, Guangzhou 510611, Guangdong, China. [3]Key Laboratory of Water Security Guarantee in Guangdong-Hong Kong-Macao Greater Bay Area of Ministry of Water Resources, Foshan 528244, Guangdong, China. [4]School of New Energy, Hunan Vocational Institute of Technology, Xiangtan 411104, Hunan, China. ✉email: dxs15074777625@126.com

Moisture content %	Clay particle	Silt particle	Sand particle	Proportion	Plastic limit	Liquid limit	Organic matter content/%	Optimal water content/%	Maximum dry density/g cm^{-3}
49.6	42.5	26.7	30.8	2. 688	21.6	48.2	3.16	18.9	1.79

Table 1. Physical properties of soil.

Material	Average particle size (nm)	Specific surface area (m²/g)	Main surface functional groups
Nano-SiO_2 (NS)	15	200	Silanol (Si–OH)
γ-nano-Al_2O_3 (NA)	20	130	Aluminol (Al–OH)
Nano-Fe_3O_4 (NF)	25	70	Hydroxyl (–OH)
Nano-MgO (NM)	40	50	Hydroxyl (–OH)

Table 2. Physical parameters of the nano-oxides.

et al.[11] analyzed the influence of nano-SiO_2 on the microstructure and chemical composition of cement soil by means of SEM and EDX micro test methods, and found that nano-SiO_2 significantly reduced the porosity of the sample and changed the type and quantity of hydration products. Yao Kai et al.[12] solidified silty clay by nano-MgO modified cement, and found that 1% nano-MgO content can effectively improve the shear performance of cement solidified soil. Lang et al.[13] used nano-SiO_2 modified cement to solidify humic acid-containing sludge and found that the strength of the sample with 1% nano-SiO_2 content after curing for 60 days was more than twice that of the unadded sample. The above research shows that the mechanical properties of nano-materials modified cement solidified soil are excellent, but there is a lack of research on the properties of different nano-materials on silty soft soil. The micro-mechanism among nano-materials, cement, soil particles and organic matter is not clear, and the relevant theories and mechanisms are rarely reported publicly.

In this paper, four kinds of nano-oxide modified cements, namely, nano-SiO_2, nano-Al_2O_3, nano-Fe_3O_4 and nano-MgO, were used to solidify silty soft soil. The effects of oxide type, content and curing age on the properties of solidified silty soft soil were investigated by laboratory tests such as unconfined compressive strength, one-dimensional consolidation and water stability. Combined with X-ray diffraction, mercury intrusion and scanning electron microscopy, the micro-morphology and pore analysis of nano-oxide modified cement solidified silty soft soil were carried out, and the micro-mechanism between soil particles and hydration products was deeply analyzed and established to promote the development of silty soft soil foundation treatment technology.

Test materials and methods
Test materials
The test soil is taken from the silty soft soil layer of a construction site in Guangzhou. In natural state, the water content is 49.6%. The clay particles, silt particles, and sand particles account for 42.5%, 26.7% and 30.8%, respectively. The organic matter content is 3.16%. The basic physical properties are shown in Table 1. According to Engineering Classification Standard of Soil GB/T50145-2007 (Ministry of Construction of People's Republic of China (PRC), 2007), this soil belongs to low liquid limit silty clay[14].

The curing materials used in the experiment are all commercially available. The cement is P.O.42.5 ordinary portland cement, and the main components are CaO, SiO_2, Al_2O_3, MgO, etc. The nano-oxides are nano-SiO_2, γ-phase nano-Al_2O_3, nano-Fe_3O_4 and nano-MgO, and the main components are all over 98%. The key physical parameters of the nano-oxides are summarized in Table 2.

Test scheme
According to the Specification for mix proportion design of cement soil JGJ/T233-2011[15], the mix proportion was calculated. This specification, oriented toward in-situ construction practice, employs the mass of the natural wet soil as the calculation benchmark, which directly reflects field conditions for additive proportioning. Considering this, the initial water content of the silty soft soil was taken as 50% for mix design. The cement content was therefore defined as 15% by mass of the initial wet soil. Five nano-oxide contents were selected: 0.5%, 1%, 1.5%, 2%, and 2.5%, also by mass of the initial wet soil. During specimen preparation, the total water content of the soil-additive mixture was adjusted to the optimal moisture content (18.9%, see Table 1) prior to compaction to ensure consistent density. C represents cement, NS represents nano-SiO_2, NA represents γ-phase nano-Al_2O_3, NF represents nano-Fe_3O_4, and NM represents nano-MgO. The specific test scheme is shown in Table 3.

Test procedure
The test materials were uniformly stirred after being weighed according to the mixture proportion, and then uniformly filled into a three-lobe mold (Φ = 39.1 mm, h = 80.0 mm). The filling was divided into three layers and the filling quality was strictly controlled. The samples were cured in standard environment (20 ± 2℃, 95% humidity) for 3 days, and then demoulded. The samples were wrapped with plastic wrap and then cured to a predetermined age for unconfined compressive strength test, which was conducted at a constant displacement

Experimental group	Content/%		Initial water content/%	Curing age/d
	C	Nano-oxide		
C15	15	0	50	3, 7, 14, 28
C15NS	15	0.5, 1, 1.5, 2, 2.5	50	3, 7, 14, 28
C15NA	15	0.5, 1, 1.5, 2, 2.5	50	3, 7, 14, 28
C15NF	15	0.5, 1, 1.5, 2, 2.5	50	3, 7, 14, 28
C15NM	15	0.5, 1, 1.5, 2, 2.5	50	3, 7, 14, 28

Table 3. Test scheme of solidified soil.

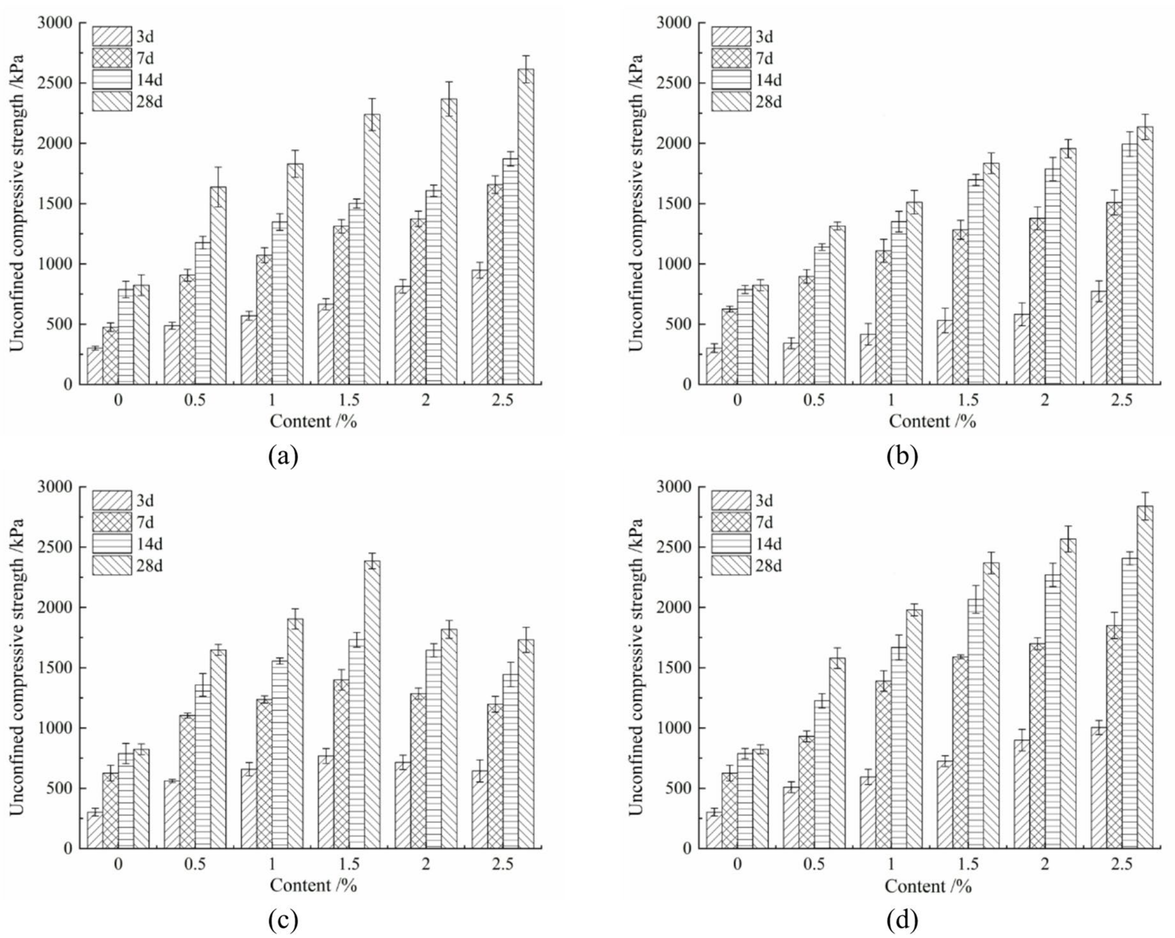


Fig. 1. Compressive strength of nano-oxide modified cement solidified silty soft soil. (**a**) NA, (**b**) NF, (**c**) NM, (**d**) NS.

rate of 1.0 mm/min. In the one-dimensional consolidation test, a ring knife (Φ = 61.8 mm, h = 20 mm) was used to prepare samples. After the strength test of the 28 d curing sample, the central part of the sample was freeze-dried at − 50℃ under a vacuum pressure below 10 Pa for 48 h. A portion of the central section was ground by agate mortar and then X-ray diffraction test was carried out to analyze its mineral characteristics. The fresh section of the rest part was taken for scanning electron microscope and mercury intrusion tests to analyze the microstructure and morphology changes, and the microscopic mechanism was established. The water stability test adopted the samples after standard curing for 28 days, and the strength tests were carried out after the samples were immersed in clear water to a sufficient age.

Test results and analysis

Unconfined compressive strength test

Figure 1 shows the change diagram of unconfined compressive strength of nano-oxide modified cement solidified silty soft soil. It can be seen that the addition of nano-oxide promotes the development of compressive strength of cement solidified silty soft soil. Taking the content of 1.5% as an example, the compressive strength of

NM modified cement solidified silty soft soil is 1399.1 kPa and 2385.3 kPa at 7d and 28d, which is 194.05% and 189.37% higher than that of pure cement solidified soil samples (475.8 kPa and 824.3 kPa), respectively. Other nano-oxides also show excellent lifting effect. In addition, the compressive strength of different nano-oxide modified cement solidified silty soft soil is significantly different. After 28d curing age, the compressive strength of NA, NF and NS modified samples with 1.5% content is 2239.4 kPa, 1834.5 kPa and 2369.4 kPa, respectively. The compressive strength of samples with 2.5% content is 2614.5 kPa, 2136.8 kPa and 2839.6 kPa, respectively. It indicates that the strength of solidified soil increases with the increase of nano-oxide content, and NA and NS are more conducive to the strength development of cement solidified soil. In contrast, the compressive strength of NM modified samples shows a trend of increasing first and then decreasing with the increase of content. The compressive strength of NM samples with 1.5% content is 2385.3 kPa, which is 737.4 kPa higher than that of NM samples with 0.5% content, but the strength of NM samples with 2.5% content decreases to 1731.5 kPa. To elucidate this strength reduction from a microstructural perspective, Mercury Intrusion Porosimetry (MIP) data indicate that the 1.5% NM-modified sample possesses a favorable pore structure, with a cumulative intrusion volume of 0.2066 mL/g and a most probable pore size of 0.0905 μm, both superior to those of the pure cement-stabilized soil. In contrast, the sample with 2.5% NM content exhibits an increased cumulative intrusion volume of 0.2268 mL/g and a slightly coarsened most probable pore size. This directly demonstrates that excessive NM leads to an increase in total porosity and a coarsening of the pore structure. We speculate that this deterioration results from the excessive expansion and growth of brucite ($Mg(OH)_2$) crystals formed at high NM content, which may create micro-defects or increase the proportion of harmful pores within the matrix, thereby compromising the structural integrity and leading to the observed strength decrease beyond the optimal content of 1.5%. It fully shows that the addition of NA, NF and NS has a significant promoting effect on the compressive strength of cement solidified silty soft soil. However, NM has the optimum content, and when its content is too high, it is not conducive to strength development.

With the increase of curing age, the compressive strength of nano-oxide modified cement solidified silty soft soil shows an increasing trend, which is basically consistent with the strength development of low water content and high water content solidification tests[9,10]. The strength of solidified soil samples increases rapidly in 3 ~ 7 d, slows down in 7 ~ 14 d, and continues to increase until 28 d. The strength growth rate increases with the increase of the nano-oxide content, due to the increase of high active components and the increase of hydration reaction rate in solidified soil system.

It can be seen that nano-oxides significantly enhance the compressive strength of cement solidified silty soft soil. This is because nano-oxides have the characteristics of high activity and large specific surface area. After adding solidified soil, they can give full play to the role of nucleation and adsorption, and reduce the inhibitory effect of organic matter on the hydration process and products of cement[16]. They can also promote the development of cement hydration rate, and enhance the cementation between gel products such as hydration C-S-H and C-A-H and clay minerals. Under the alkaline environment created by the hydration by-product $Ca(OH)_2$, the potential pozzolanic cementitious materials such as nano-silica and nano-alumina undergo secondary hydration reaction, generating additional C-S-H or C-A-S-H gel[17], which further enhances the function of gel in encapsulating soil particles. In addition, unreacted nano-oxides are deposited inside the sample, and it improves the integrity of microscopic pore structure. This series of complex physical and chemical reactions enhance the macroscopic mechanical properties of solidified soil.

One-dimensional consolidation test

The samples after curing for 7 d and 28 d were selected for consolidation compression test, and the void ratio-pressure (*e-p*) curve of the samples was obtained as shown in Fig. 2. With the increase of curing age, the steepness of the compression curve of the solidified soil sample decreases. It shows that the hydration products in the sample increase in the later stage, and the cementation and filling promote the pore reduction[18], thus increasing the load bearing capacity of the sample. When the nano-oxide content increases, the initial void ratio of the sample decreases correspondingly, and the evolution of compression curves is basically the same, indicating that the internal physical and chemical reaction and microstructure of the sample have little change, and the compression properties remain stable. Comparing the compression curves of NS, NA, NM and NF modified cement solidified soil under the same content and age, it is found that there are obvious differences in the change of void ratio under the same vertical load. For example, after curing for 28 d, the void ratio of 1.5% NS modified samples decreases from 0.547 to 0.535, while that of 1.5% NF samples decreases from 0.543 to 0.526 at 800 kPa to 1600 kPa. It fully indicates that the addition of different kinds of nano-oxides causes the differential changes in the internal pore structure of samples.

To further characterize the compressive properties of solidified soil, the double logarithm method (ln(1 + *e*)-lg*p*) proposed by Butterfield[19] is used to determine the yield stress of solidified soil, as shown in Fig. 3. It can be seen that the slope of the compression curve of solidified soil changes more obviously with the vertical load under the double logarithmic coordinates, and thus the yield stress at the intersection of the gentle slope section and the steep decline section can be obtained, as shown in Table 4. The analysis shows that the 28 d yield stress of each solidified soil is greater than the 7 d yield stress, indicating that increasing curing age can improve the compression properties of solidified soil. Meanwhile, at the same curing age, the increase of nano-oxide content improves the yield stress. For example, when the NS content increases from 0.5% to 2.5%, the 28 d yield stress of the sample increases from 1032.9 kPa to 1371.6 kPa, with a growth rate of 32.8%. This growth phenomenon also appears in the NF and NA modified solidified soil samples. However, in the NM modified cement solidified soil sample, the yield stress first increases and then decreases, further indicating that the compressive properties of solidified soil are affected by the types of nano-oxides.

The difference in compressive properties is due to the excellent filling, adsorption and nucleation of nano-oxides, which improves the hydration reaction rate of cement and the amount of hydration products to a

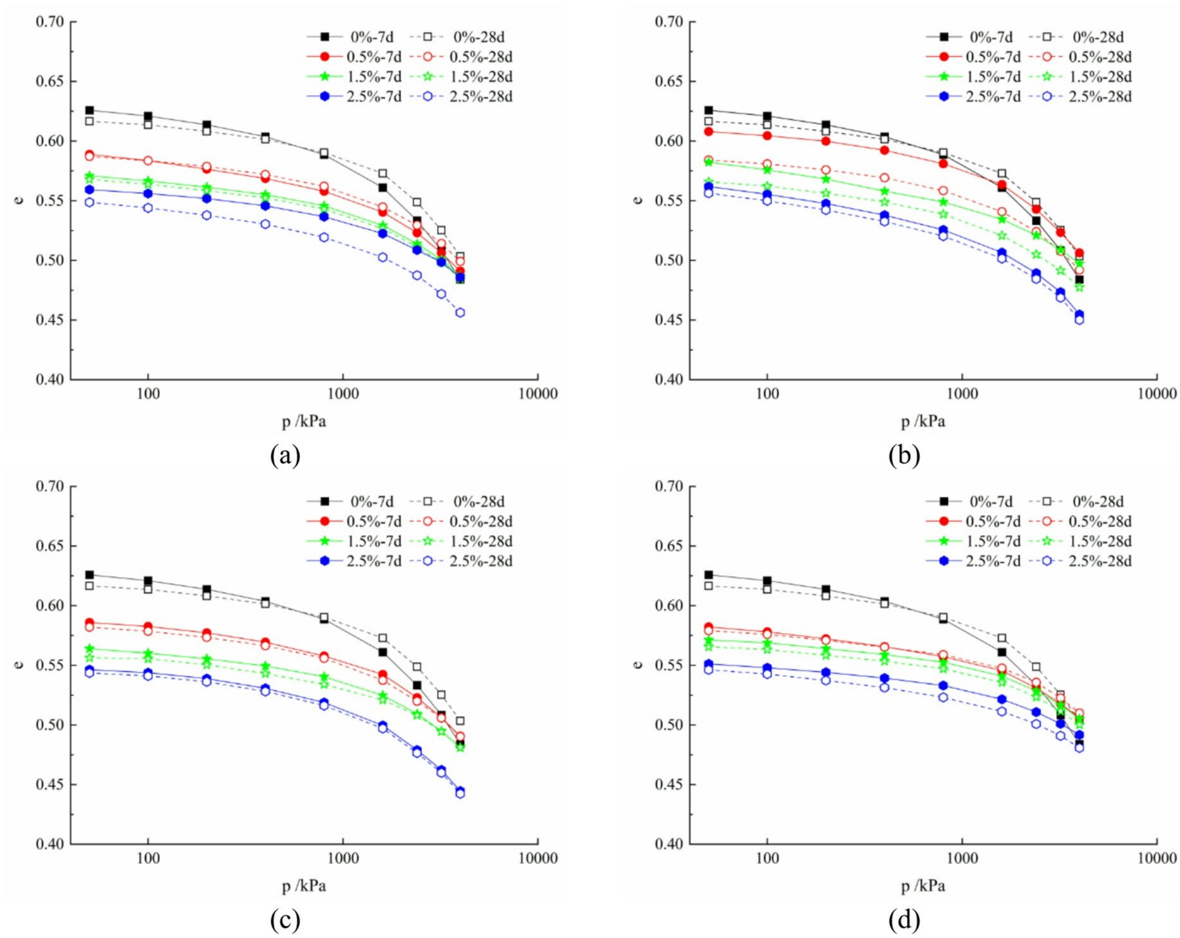


Fig. 2. Compression curves of nano-oxide modified cement solidified silty soft soil. (**a**) NA, (**b**) NF, (**c**) NM, (**d**) NS.

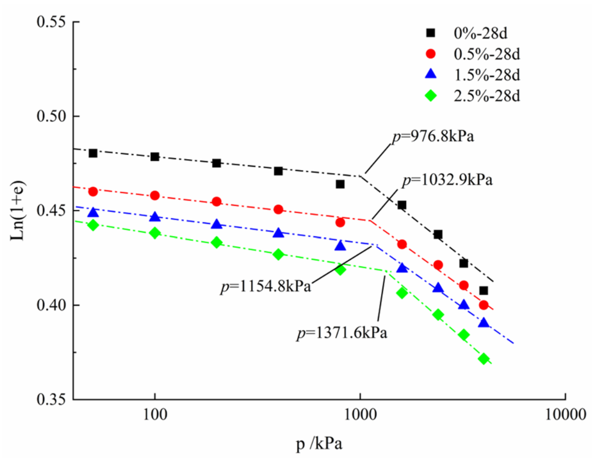


Fig. 3. Yield stress diagram of NS modified cement solidified soil (28 d).

certain extent. Specifically, NS and NA are potential hydraulic and pozzolanic materials, which generate H_3SiO^- and $AlOH_4^-$ ions after encountering water. Additional C-S-H and C-A-S-H gels are formed in the alkaline environment created by the hydration by-product $Ca(OH)_2$, forming a denser clay matrix and enhancing the compressive properties of the soil. NF mainly plays the role of filling and ion exchange, weakens the thickness of soil particles combined with water film, and reduces the pores between particles. However, NM reacts rapidly with water to form $Mg(OH)_2$ crystals, resulting in volume expansion. It enhances the alkalinity of the solidified

Nano-oxide	Content	Curing age		Nano-oxide	Content	Curing age	
		7d	28d			7d	28d
NS	0.5	997.5	1032.9	NM	0.5	1012.6	1136.8
	1.5	1086.9	1154.8		1.5	1154.7	1394.4
	2.5	1193.2	1371.6		2.5	1084.3	1298.6
NA	0.5	968.7	1024.5	NF	0.5	904.5	1032.6
	1.5	1084.5	1132.6		1.5	1056.7	1142.3
	2.5	1145.1	1284.7		2.5	1098.5	1284.1

Table 4. Yield stress table of nano-oxide modified cement solidified silty soft soil.

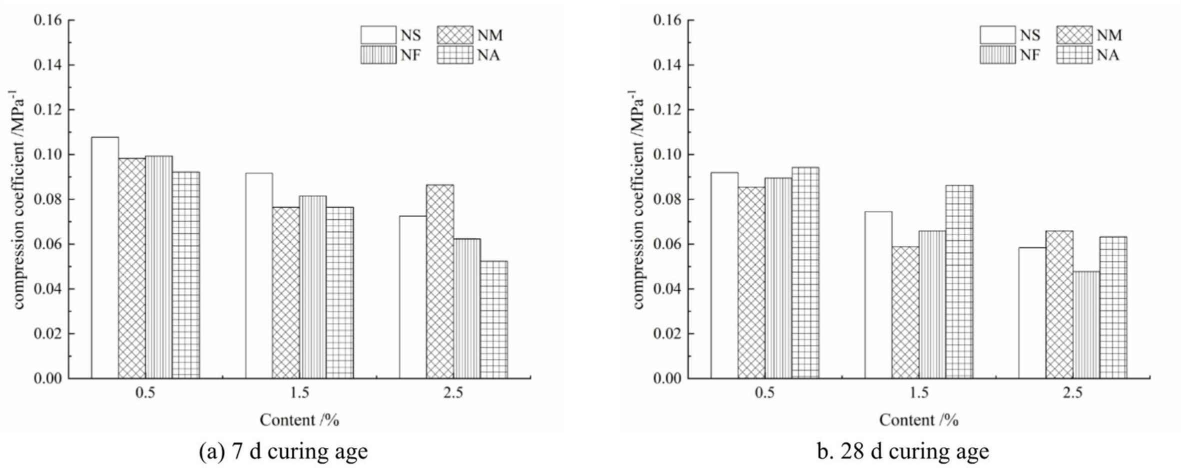


Fig. 4. Compression coefficient of nano-oxide modified cement solidified silty soft soil.

soil system while filling, and promotes the pozzolanic reaction and the formation of additional M-S-H gel. However, $Mg(OH)_2$ crystals do not have cementitious characteristics[20]. Excessive addition of nano-magnesium oxide into cement solidified soil can easily cause excessive expansion, resulting in an increase in the porosity of the sample, which is macroscopically manifested by the weakening of compressive properties.

The compression coefficient a_{1-2} in the pressure range of 100 ~ 200 kPa is used to discuss the evolution law of the compression properties of solidified soil, as shown in Fig. 4. On the whole, the compressive coefficient of 28 d samples is lower than that of 7 d samples, indicating that the increase of curing age can enhance the compressive properties of solidified soil. Except for the 0.5% NS modified solidified soil sample with 7 d curing age, the compressive coefficients of other samples are all lower than 0.1 MPa^{-1}, indicating that the solidified soil belongs to low compressibility soil, and the nano-oxide modified cement solidified silty soft soil has excellent compression properties. The compressive coefficients of NS, NA and NF modified solidified soil tend to increase gradually with the increase of content, while that of NM modified solidified soil shows a trend of first increasing and then decreasing, which is also consistent with the law of unconfined compressive strength. By comparing the compressive coefficients of four kinds of nano-oxides, it can be concluded that the order of the improvement of the compressive properties of modified solidified soil is NS > NA > NF > NM.

Water stability test

To explore the influence of rainfall or humid environment on the mechanical properties of nano-oxide modified cement solidified silty soft soil, the unconfined compressive strength of samples before and after immersion was studied, as shown in Fig. 5. It can be seen from the analysis that the strength of the sample generally shows a downward trend with the increase of immersion time, which is obviously lower than that of the standard curing sample at the same period. Under the immersion time of 3 d, 7 d, 14 d and 28 d, after immersion, the strengths of the solidified soil with 1.5% NM content were 2014.5 kPa, 1958.7 kPa, 1895.7 kPa, and 1789.2 kPa after different immersion periods, all of which were significantly lower than the pre-immersion strength (2085.3 kPa), corresponding to strength reductions of 3.4%, 6.1%, 9.1%, and 14.2%, respectively. This phenomenon also appears in other nano-oxide solidified soil samples, indicating that the strength of nano-oxide modified cement solidified silty soft soil decreases continuously with the increase of immersion time. The reason is that water infiltration will cause the thickening of the bound water film of the soil particles in the samples and the decrease of system alkalinity, and weaken the bonding and pore filling effects of hydration products on soil particles, which is macroscopically manifested as strength attenuation.

The strength residual coefficient (the ratio of sample strength under immersion condition to sample strength under standard curing at the same curing age) is used to evaluate water stability, and the calculation results are

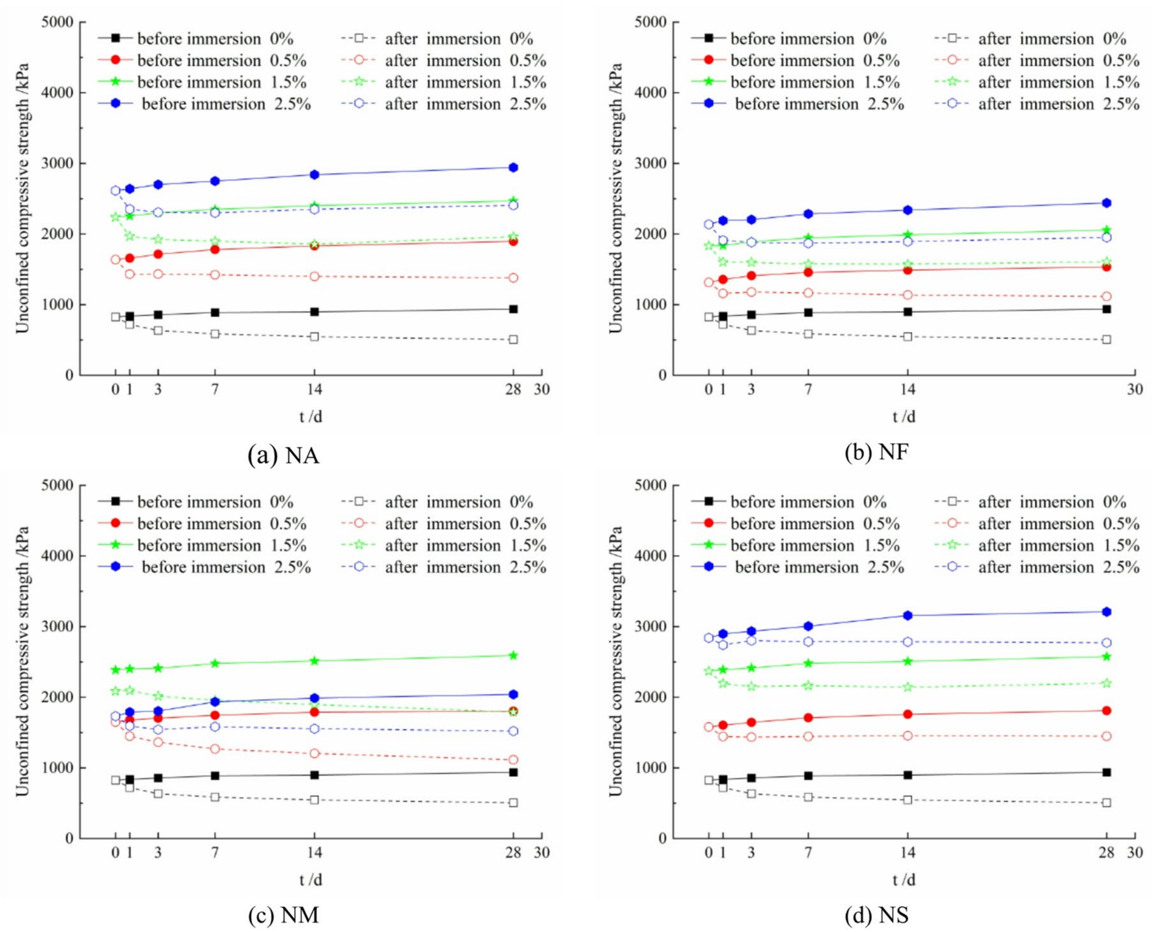


Fig. 5. The strength change of solidified soil under water immersion condition.

shown in Fig. 6. It can be seen that after immersion, the strength residual coefficient of nano-oxide modified cement solidified silty soft soil ranges from 0.62 to 0.90, and shows a decreasing trend with immersion time, indicating that immersion causes significant deterioration in the strength of the solidified soil. After 28 days of immersion, the strength residual coefficients of NS modified cement solidified soil with 0.5%, 1.5% and 2.5% contents are 0.796, 0.845 and 0.863, respectively, which are significantly higher than those of pure cement soil (0.56). This rule also occurs in other nano-oxide modified solidified soil samples, which shows that the addition of nano-oxides helps to improve the water stability of cement solidified silty soft soil, and the larger the content, the better the improvement effect. After comprehensive comparison of samples, it is found that the order of nano-oxides to improve the water stability of cement solidified silty soft soil is NS > NA > NF > NM.

Micro-mechanism research and analysis

Phase analysis

To explore the phase composition of nano-oxide modified cement solidified silty soft soil, the X-ray diffraction test was carried out on the sample cured for 28 d, and the results are shown in Fig. 7. Overall, the diffraction peak intensity of secondary minerals such as kaolinite, quartz and mica in the solidified soil samples is basically unchanged. The addition of nano-oxides promotes the enhancement of the diffraction peaks of hydration products, and the product types are more abundant. Further analysis shows that the addition of NS increases the peak strength of C-S-H in the sample, which indicates that NS improves the hydration reaction and pozzolanic reaction rate in the cement solidified soil. The addition of NA promotes the formation of C-A-S-H gel. In the alkaline environment created by cement hydration, active aluminum enters C-S-H gel analysis structure to generate a more stable network C-A-S-H gel. M-S-H diffraction peak and $Mg(OH)_2$ crystal diffraction peak appear in the NM sample, which indicates that NM induces the formation of M-S-H gel in cement solidified soil. Compared with pure cement solidified soil, the addition of NF leads to a slight increase in the C-S-H peak strength in solidified soil samples, indicating that NF can promote the hydration reaction of cement and generate more C-S-H gels. This fully demonstrates that nano-oxides can promote the hydration reaction of cement solidified soil, which causes differences in the types and quantities of hydration products, and then exhibits different macroscopic engineering characteristics.

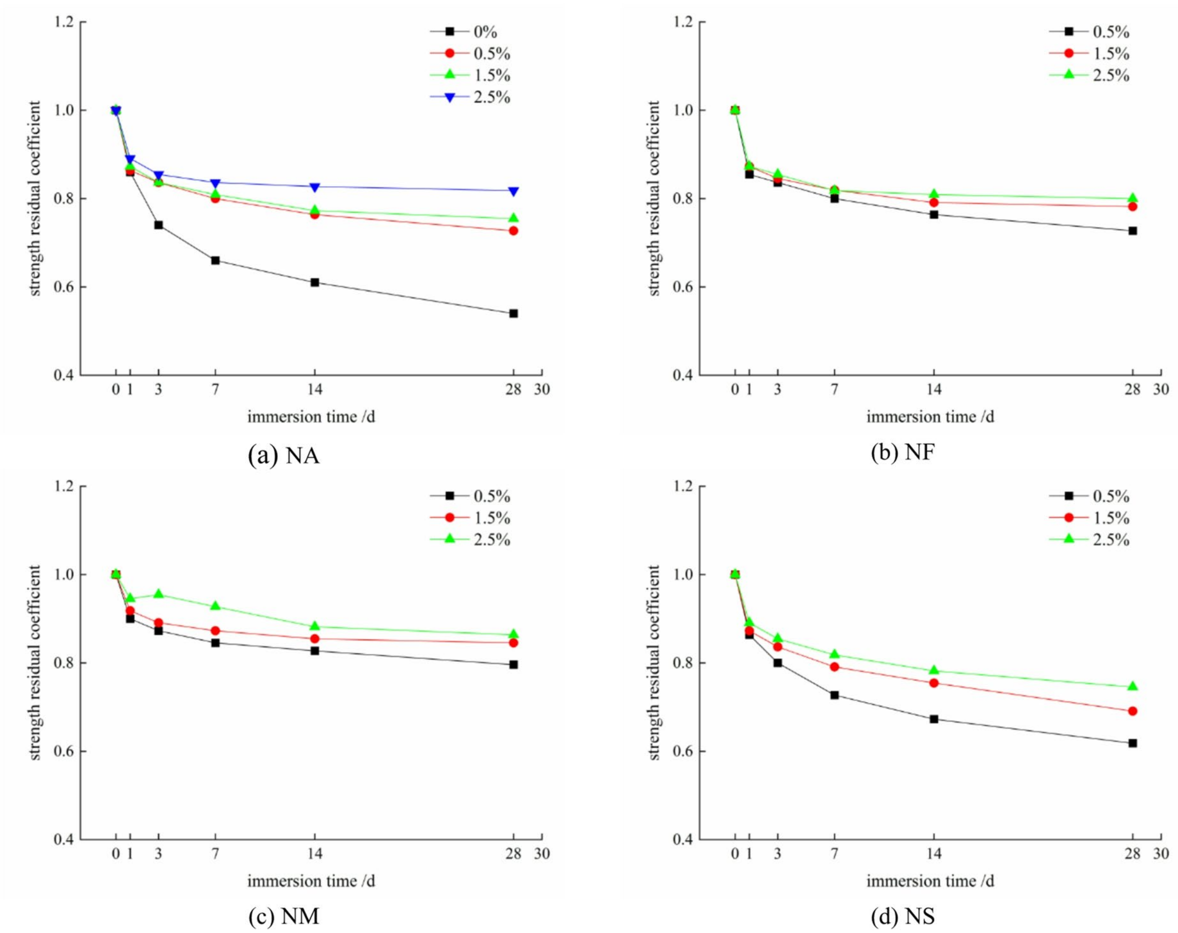


Fig. 6. Strength residual coefficient diagram of solidified soil.

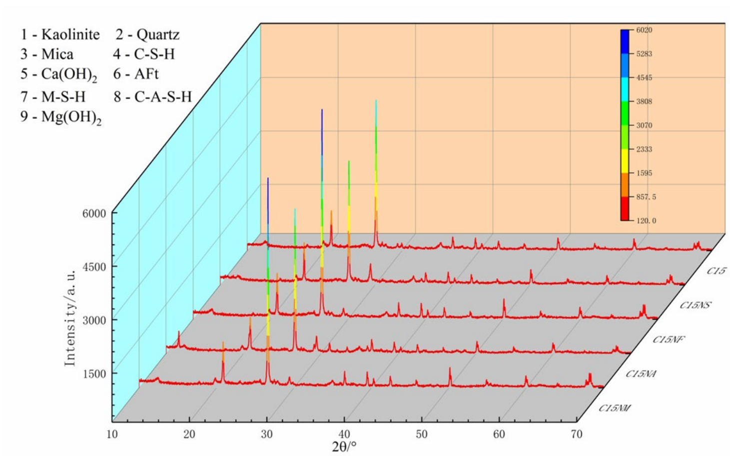
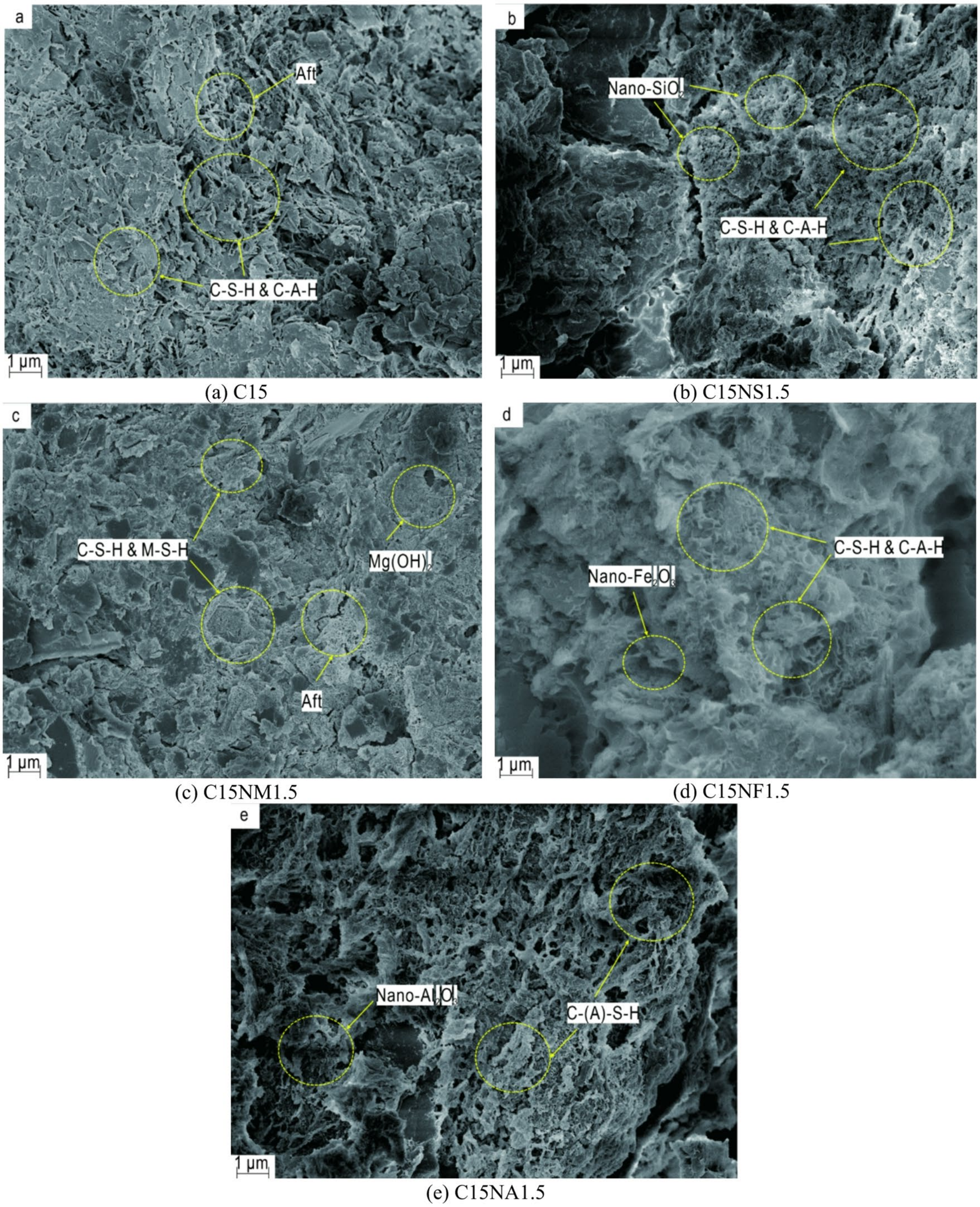


Fig. 7. X-ray diffraction pattern of solidified soil (28 d).

Microscopic morphology analysis

The scanning electron microscope image of solidified soil sample after curing for 28 d is shown in Fig. 8. It can be seen that the irregular hydration gel in the pure cement solidified soil sample wraps the soil particles to form a whole, and a small amount of needle-like AFt crystals fill the soil particles. The cementation and filling effect jointly promote the strength development of solidified soil. After adding nano-oxide, the number of hydration products in the solidified soil sample increases, the hydration gel encapsulates the surface of the soil particles to form a compact structure, and the pore size between the particles decreases. Meanwhile, the unreacted nano-



(a) C15 (b) C15NS1.5 (c) C15NM1.5 (d) C15NF1.5 (e) C15NA1.5

Fig. 8. SEM images of nano-oxide modified cement solidified silty soft soil (28 d).

oxide fills the inter-granular pores, prompting the soil particles to change from loose point-to-surface contact to close surface-to-surface contact, and the microstructure integrity is improved.

Further analysis shows that the strength of solidified soil sample comes from the strong cementation of C-S-H, C-A-H gel and by-product $Ca(OH)_2$ in cement hydration products, as well as the pozzolanic reaction, carbonization, ion exchange and other effects between active clay minerals[21]. By comparing the SEM images of different nano-oxide modified cement solidified soil, it can be seen that different oxide types cause obvious differences in the morphology and microstructure of hydration products inside the sample. Under the action of NS, the ratio of calcium to silicon in hydration product C-S-H decreases, the amorphous gel is more denser, and the interface transition zone between gel and soil particles becomes more complete. Hexagonal columnar crystal $Mg(OH)_2$ and scaly M-S-H gel appear in the NM sample. Under the action of NF, the C-S-H gel product covers the soil particles comprehensively, making the microstructure dense and the integrity good. The gel connection in NA sample is more specific, and the network C-A-S-H gel with three-dimensional structure is generated, further improving the cementation between particles and the integrity of microstructure. It can be seen that nano-oxides can enhance the microstructure integrity of cement solidified silty soft soil, thereby enhancing the mechanical and durability properties, and the enhancement effect is related to the types of oxides.

Pore structure analysis

The evolution of pore structure is an important way to explore the reasons for the change of soil physical and mechanical characteristics. Mercury intrusion tests were carried out on different nano-oxide modified cement solidified silty soft soil samples, and the cumulative mercury intake and pore density distribution curves are shown in Fig. 9. It can be seen that the cumulative mercury intakes of NS, NF, NA and NM modified solidified soil samples are 0.2013, 0.2214, 0.2093 and 0.2066 mL/g, respectively, which are 10.5%, 1.5%, 6.9% and 8.1% lower than those of pure cement solidified soil (0.2249 mL/g). On the whole, the addition of nano-oxides can form more gels of hydration products, and the soil particles have a better wrapping effect. Moreover, unreacted oxides fill the pore structure, promote the transformation of large pores into small pores, and further reduce the sample porosity. The above analysis is consistent with the SEM and XRD results, that is, nano oxides enhance the microstructure of soil, resulting in an increase in macroscopic strength.

From the analysis of the pore density distribution in Fig. 9b, it can be seen that the solidified soil has typical bimodal characteristics, and the pore size ranges are mainly between 0.05 ~ 0.2 μm and 0.4 ~ 4 μm. According to the pore division standard proposed by Shear et al.[22], the addition of nano-oxides results in a more concentrated pore structure in cement solidified silty soft soil. Most of the inter-particle pores are transformed into intra-particle pores, and the most probable pore size is reduced, indicating that the addition of nano-oxides improves the pore structure of cement solidified silty soft soil. Compared with NS, NA, NM and NF modified samples, it is found that the most probable pore sizes are 0.072, 0.0905, 0.0905 and 0.1104 μm, respectively, which are significantly lower than those of the cement solidified soil sample of 0.1372 μm. It can also be seen that there are obvious differences in pore structure changes caused by different kinds of nano-oxides. This conclusion effectively verifies the above test results of scanning electron microscope and XRD.

Analysis of microscopic action mechanism

Based on the above analysis results of mineral composition, pore structure and micro-morphology, combined with previous research results and findings[9–12,16,17,20,23–27], in this paper, the mechanism of nano-oxides enhancing the engineering properties of cement solidified silty soft soil is studied from the aspects of physical action and chemical activity of nano-oxides.

Physical action

The physical mechanisms of action exhibited by nano-oxides—namely filling, nucleation, and adsorption—are fundamentally governed by their intrinsic physical properties, as detailed in Table 2. The minimal particle size of NS, measuring 15 nm, significantly enhances its capacity to fill the finest micropores within the matrix. Conversely, the high specific surface area of NS, reaching 200 m²/g, affords a considerable number of active sites conducive to nucleation and adsorption processes. Furthermore, distinct surface functional groups, such as the silanol groups present on NS, critically influence their interfacial interactions with the soil-cement matrix.

Filling and expansion effects The particle size of nano-oxide is extremely small, which can improve interface contact and fill internal pores, thus optimizing pore structure, promoting soil particles to change from point-to-surface contact to closer surface-to-surface contact, and making the stress structure of solidified soil skeleton more stable. Some nano-oxides expand in the alkaline environment created by cement hydration, which plays a role in squeezing the pores between particles. For example, nano-MgO hydrates to generate $Mg(OH)_2$ crystals which are attached to the surface of particles or pore walls. The micro-expansion from this crystallization can

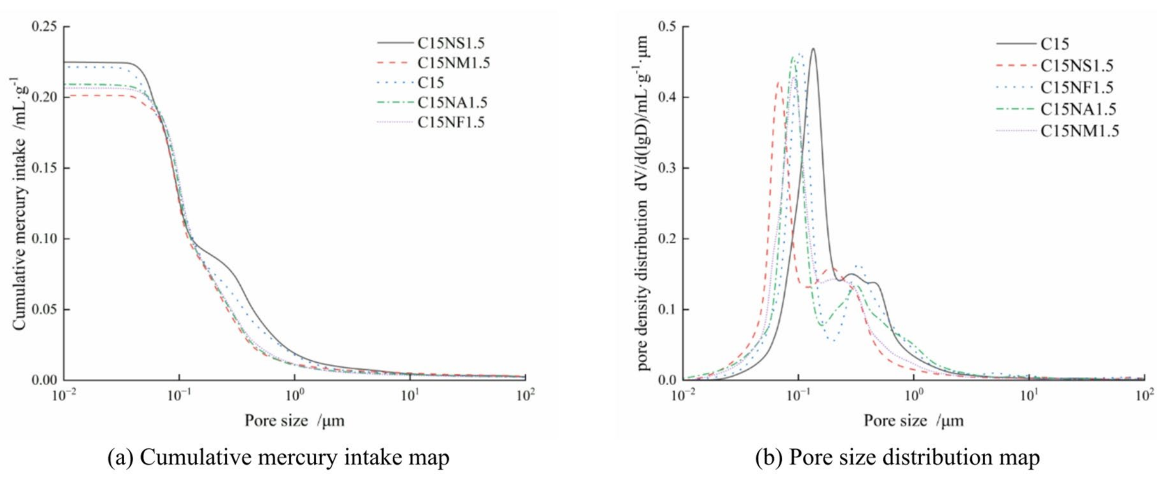


Fig. 9. MIP curves of nano-oxide modified cement solidified silty soft soil (28 d).

compact the matrix at an optimal dosage. However, beyond this optimal content, excessive crystalline growth pressure may induce micro-cracking, explaining the characteristic strength peak observed for NM-modified systems. Under the action of recrystallization, crystal growth pressure is formed to squeeze the pore wall of micropores[20]. These structural changes have improved the engineering characteristics of solidified silty soft soil to a certain extent.

Nucleation effect When the cement is added to silty soft soil, the hydration reaction occurs rapidly when cement particles meet water. The active silicon phase C_2S and C_3S release Ca^{2+}, SiO_3^{2-} and OH^- after dissolved in water. When the ion concentration increases to the critical supersaturated state, C-S-H gel precipitation is formed, which nucleates and grows with cement particles or soil particles. This process belongs to the classical nucleation process of heterogeneous occurrence[13]. Nano-oxides with high specific surface area provide more heterogeneous nucleation sites for the nucleation of C-S-H gel produced by cement hydration, effectively reduce the nucleation barrier of C-S-H gel, and accelerate its nucleation and growth rate. Thereby, it effectively shortens the cement induction period and promotes the development of cement hydration and solidified soil strength.

Adsorption and dispersion effects Previous studies have shown that the reason for the strength deterioration of cement solidified organic soil is that humic acid is adsorbed on the surface of cement and soil particles, which hinders and delays the formation of cement hydration products and its interaction with clay particles[4,23]. When nano-oxide with surface effects are added, the organic matter in silty soft soil can be effectively catalyzed, degraded or combined to reduce the hindrance to hydration reaction. For example, Fe^{2+} or Fe^{3+} in nano-iron oxide can transform insoluble organic matter into soluble organic matter by coordination and complexation with molecular functional groups of organic matter. Nanoparticles such as TiO_2 can react with the carboxyl groups of humic acid and the aromatic groups of organic matter[16]. Organic matter and most metal oxide nanoparticles can reduce the influence of organic matter on the strength deterioration of cement solidified soil through bridging flocculation under neutral or alkaline conditions.

Chemical action
Ion exchange After the introduction of nano-oxides into the cement solidified silty soft soil system, the high-valent cations (Al^{3+}, Mg^{2+}) produced by dissolution are exchanged with the monovalent cations (Na^+, K^+) in clay minerals[23]. It balances the negative charges on the surface or interlayer of clay minerals, thus reducing the ionic radius and the thickness of electric double layer structure, and promoting the self-aggregation of soil particles.

Acid-base neutralization Humus in silty soft soil accounts for about 50%~90% of the total organic matter, and the humic acid produced by decomposition has carboxyl, phenolic hydroxyl and amino groups on its surface, resulting in weak acidity of soil[25]. It destroys the cemented substance and skeleton structure after cement hydration. The addition of nano-oxides can increase the alkalinity of the curing system, and free OH^- ions can undergo acid-base neutralization with acidic ions[26]. Therefore, the content of organic matter in the soil is gradually consumed until it is exhausted, weakening the deterioration effect of humic acid on the long-term performance of solidified soil.

Pozzolanic reaction .

In the cement solidified soil system, the ways of nano-oxide promoting pozzolanic reaction are divided into the improvement of the alkalinity of the system (Ca, Mg) and the increase of the active ions (Al, Si). The former is helpful for the dissolution of active aluminosilicate in clay minerals, and further reacts with metal cations to generate secondary hydration C-S-H and C-A-H gel products. For nano-MgO (NM), the mechanism involves the formation of magnesium silicate hydrate (M-S-H) gel and $Mg(OH)_2$. Its optimal performance results from a balance: the combined positive effects of M-S-H gel formation and beneficial pore compaction from $Mg(OH)_2$ expansion must outweigh the potential structural damage caused by excessive expansion. The latter will improve the interlayer structure of C-S-H gel, replace the active ions to balance the negative charge of the network structure, and make the gel structure more stable[27]. Among the nano-oxides studied, nano-silica (NS) exhibits the most potent pozzolanic activity. Its primary contribution to long-term strength is the extensive formation of secondary C-S-H gel via the pozzolanic reaction, which densifies the matrix. Although its high specific surface area also promotes vigorous early-stage nucleation, this is considered a secondary, complementary mechanism in the context of overall strength development. Therefore, the solidified soil has excellent strength and durability. Therefore, the solidified soil has excellent strength and durability.

In summary, nano-oxide modified cement can effectively inhibit the interference of organic matter in silty soft soil on cement hydration reaction and the interface cementation between hydration products and clay particles, and it can also significantly improve the cementation between soil particles and microscopic pores. The specific mechanism model is shown in Fig. 10. To further clarify and compare the dominant mechanisms identified for each type of nano-oxide, a summary is provided in Table 5. A series of physical and chemical reactions of nano oxide modified cement solidified muddy soft soil promote the gel wrapped soil particles to be more complete, the microstructure pores to be further reduced, and the effective support structure between soil particles to be formed. Therefore, the engineering properties of solidified soil is significantly improved.

Conclusion

1. Nano-oxide can significantly improve the unconfined compressive strength, compressibility and water stability of cement solidified silty soft soil, and the improvement effect is related to the content, types and curing age of nano-oxide. The compressive strength of NS, NA and NF increases with the increase of the content.

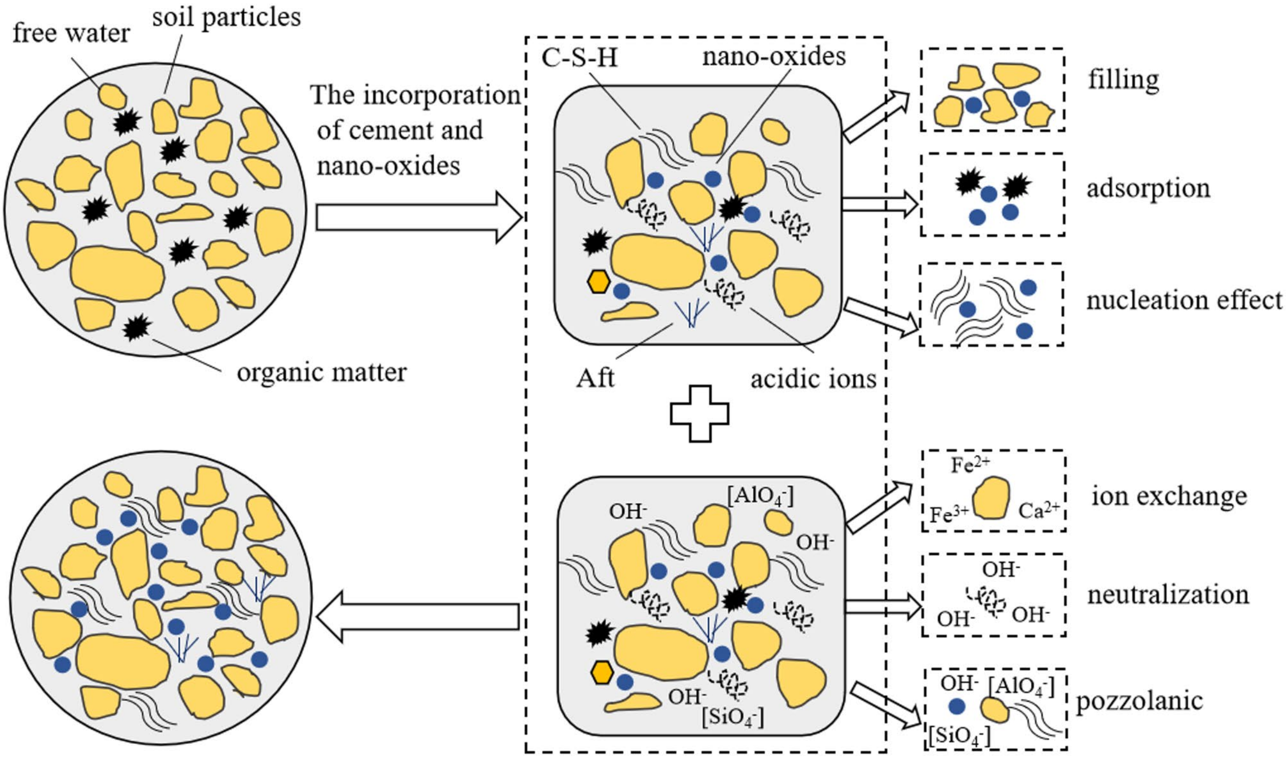


Fig. 10. Microscopic mechanism diagram of nano-oxide modified cement solidified silty soft soil.

Nano-oxide	Dominant physical mechanism	Dominant chemical mechanism	Primary effect and characteristics
NS	High-activity surface nucleation	Pozzolanic reaction (C-S-H formation)	Pore refinement & matrix densification
NA	Micro-filling	Ion exchange & C-A-H formation	Early strength gain via particle aggregation
NF	Adsorption/dispersion	Complexation & neutralization	Organic matter interference mitigation
NM	Dosage-dependent expansion	M-S-H/$Mg(OH)_2$ formation	Pore compaction at optimal content

Table 5. Dominant enhancement mechanisms of different nano-oxides.

The corresponding content of NM compressive strength peak is 1.5%. The compression coefficients of 28 d nano-oxide modified cement stabilized soil samples are all below $0.1MPa^{-1}$, and the strength residual coefficients range from 0.69 to 0.85.

2. The results of XRD and SEM show that the number and types of main hydration products of nano-oxide modified cement solidified silty soft soil are related to the types of oxides. The main products of NF modified samples are similar to those of pure cement soil, and NS and NA generate additional C-S-H and C-A-S-H gels. The main products of NM modified samples are M-S-H gel and expanded $Mg(OH)_2$ crystals. These gel products encapsulate soil particles to form a compact whole, promoting the development of engineering properties of solidified soil.
3. The analysis results of pore structure show that the pore distribution of nano-oxide modified cement solidified silty soft soil is bimodal structure, and its cumulative mercury intake and most probable pore size are lower than those of pure cement solidified soil. The internal pores are transformed from inter-particle pores to intra-particle pores, thus forming a denser and more homogeneous microstructure.
4. The lifting mechanism of nano-oxide lies in physical actions such as filling, nucleation and adsorption, as well as chemical actions such as ion exchange, acid-base neutralization and pozzolanic reaction. The microscopic mechanism model of nano-oxide modified cement solidified silty soft soil is established, and the influence mechanism of microstructure and chemical reactions on the macroscopic properties of solidified soil is revealed.

It should be noted that the present study was conducted under standard curing conditions (20 ± 2 °C, 95% relative humidity) using soil with a specific organic matter content (3.16%). Consequently, the performance of the nano-oxide-modified cement-stabilized soil under extreme environmental conditions (e.g., freeze-thaw cycles) or with higher organic contents remains to be verified. Furthermore, the evaluation period was limited to 28 days; longer-term evolution of strength and durability (e.g., beyond 90 days) warrants further investigation. In addition, the dosage of nano-oxides was expressed as a percentage of wet soil mass—a practical approach for field application, yet one that does not account for the substantial differences in density, particle size, and specific surface area among the various oxides. For more scientifically comparable studies, future work could employ intrinsic metrics such as molar ratio or total specific surface area of the nanoparticles. These identified limitations highlight meaningful avenues for subsequent research.

Data availability

Te data presented in this study are available on request from the corresponding author.

Received: 27 June 2025; Accepted: 19 January 2026
Published online: 21 January 2026

References

1. Xia, Y. J. & He, W. Effect of Metakaolin on dynamic properties and microscopic characteristics of cement solidified soil. *Yangtze River*. **53**(6), 212–216 (2022).
2. Tang, Y. X., Liu, H. L. & Zhu, W. Study on engineering properties of cement solidified soil. *Chin. J. Geotech. Eng.* **22**(5), 549–554 (2000).
3. Zhang, Z. Y. & Yan, J. Experimental study on dredged material solidification technology for urban rivers. *Yangtze River*. **52**(12), 210–213 (2021).
4. Liang, S. H. et al. Comparative experimental on solidification of Nansha organic soft soil with cement and different admixtures. *Industrial Constr.* **49**(2), 93–97 (2019).
5. Meng, T. et al. Effect of compound nano-CaCO3 addition on strength development and microstructure of cement-solidified soil in the marine environment. *Constr. Build. Mater.* **151**, 775–781 (2017).
6. Choobbasti, A. J. & Kutanaei, S. S. Microstructure characteristics of cement-solidified sandy soil using nanosilica. *J. Rock Mech. Geotech. Eng.* **9**(5), 981–988 (2017).
7. Wang, W. et al. Direct shear mechanical behavior of cement solidified road solid waste modified by fibers and nanomaterials. *J. Zhejiang University(Engineering Science)*. **57**(9), 1727–1735 (2023).
8. Zhuang, X. S. & Kou, Q. Dynamic stress and microanalyses of the cement-soil modified by nano-SiO_2 in the seawater corrosive environment. *Hydrogeol. Eng. Geol.* **49**(2), 86–93 (2022).
9. Lang, L., Chen, B. & Duan, H. J. Modification of nanoparticles for the strength enhancing of cementsolidified dredged sludge. *J. Rock Mech. Geotech. Eng.* **13**(3), 694–704 (2021).
10. Lu, J. G. *Experimental Study on Mechanical Properties and Mechanism of Cement Soil Improved by Nano materials*(Hefei University of Technology, 2022).
11. Zhang, X. C. et al. Study on the mechanism of nano-SiO_2 for improving the properties of cement-based soil stabilizer. *Nanomaterials* **10**(3), 405 (2020).
12. Yao, K. et al. Effect of nano-MgO on mechanical performance of cement stabilized silty clay. *Mar. Georesources Geotechnol.*. **38**(2), 250–255 (2020).
13. Lang, L., Liu, N. & Chen, B. Strength development of solidified dredged sludge containing humic acid with cement, lime and nano-SiO_2. *Constr. Build. Mater.* **230**(10), 116971 (2020).
14. Ministry of Housing and Urban-. *Rural Development of the People's Republic of China. Standard for Engineering Classification of Soils: GB/T 50145 – 2007* (China Planning, 2007).
15. Ministry of Housing and Urban-Rural Development of the People's Republic of China (MOHURD). *Specification for Mix Proportion Design of Cement Soil: JGJ/T 233–2011* (China Architecture & Building, 2011).
16. Wang, Q. et al. Environmental effects of inorganic nanoparticles in soils and their influencing factors. *Acta Mineral. Sinica*. **40**(3), 289–296 (2020).
17. Wang, W. et al. Mechanical properties and micro mechanism of nano-SiO2 modified coastal cement soil at short age. *Acta Materiae Compositae Sinica*. **39**(4), 1701–1714 (2022).
18. Zhong, W. H. Compressibility behavior of cement solidified sludge combined with industrial by-products. *J. Changjiang River Sci. Res. Inst.* **41**(1), 121–127 (2024).
19. Butterfield, R. A natural compression law for soils (an advance on e-log p'). *Géotechniquee* **29**(4), 469–480 (1979).
20. Jiao, M. P. et al. Influence of s-type Magnesia expansive agent on micro-structure, shrinkage and durability of concrete. *J. Chin. Ceramic Soc.* **51**(11), 2905–2913 (2023).
21. Wang, Z. S. & Wang, D. X. propertiess of industrial residue-cement solidified soils in resisting sulfate erosion. *Chin. J. Geotech. Eng.* **44**(11), 2035–2042 (2022).
22. Shear, D. L., Olsen, H. W. & Nelson, K. R. *Effects of Desiccation on the Hydraulic Conductivity Versus Void Ratio Relationship for a Natural clay* Vol. 1369, 130–135 (National Academy, 1992).
23. Guo, Y., Xu, R. Q. & Shao, Y. C. Study on mechanism of silty soil stabilization. *J. Zhejiang Univ. (Eng. Sci.)* **6**, 1071–1075 (2008).
24. Tang, R. F. et al. ʒ-S-H Nano-seed and its promoting effect on cement hydration and hardening: a Review. *Mater. Rep.* **37**(9), 109–124 (2023).
25. Liu, J. J. et al. Compressive strength and curing mechanism of alkali-activated geopolymer curing marine silty soft soil. *J. Railway Sci. Eng.* **21**(7), 2745–2754 (2024).
26. Tan, Y. Z. et al. Effect of sludge organic treated with alkaline solution and its mechanism. *Rock. Soil. Mech.* **41**(5), 1567–1572 (2020).
27. Xie, X. J. & Wang, S. Effect of nano-alumina on rheological property, hydration and hardening strength of Portland cement paste. *Bull. Chin. Ceramic Soc.* **40**(6), 1911–1917 (2021).

Author contributions

X.D: formal analysis, conceptualization, visualization, and supervision. X.L. and Z.W.: investigation, methodology, and writing—original draft. Z.X.: supervision, writing–review and editing. R.H.: writing—review and editing. X.H. and H.F.: writing—review and editing.

Funding

This work was supported by the Natural Science Foundation of Hunan Province (No.2024JJ8020) and Hunan Xiangtan Science and Technology Bureau's Science and Technology Innovation Project (CG-YB20240009).

Declarations

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to Z.X.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.