Rock and Soil Mechanics

Volume 44 | Issue 6 Article 2

10-3-2023

Strength deterioration characteristics of lime-metakaolin improved earthen site soil under freeze-thaw cycles

Xin-ming LI
School of Civil Engineering and Architecture, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China; Research Center of Environmental Geotechnical Engineering and Underground Engineering Disaster Control Engineering of Henan Province, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China, xinmingli01@163.com

Hao-yang ZHANG
School of Civil Engineering and Architecture, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China; Research Center of Environmental Geotechnical Engineering and Underground Engineering Disaster Control Engineering of Henan Province, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China

Di WU
School of Civil Engineering and Architecture, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China; Research Center of Environmental Geotechnical Engineering and Underground Engineering Disaster Control Engineering of Henan Province, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China

Yan-rui GUO
School of Civil Engineering and Architecture, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China; Research Center of Environmental Geotechnical Engineering and Underground Engineering Disaster Control Engineering of Henan Province, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China

See next page for additional authors

Recommended Citation

LI, Xin-ming; ZHANG, Hao-yang; WU, Di; GUO, Yan-rui; REN, Ke-bin; and TAN, Yun-zhi (2023) "Strength deterioration characteristics of lime-metakaolin improved earthen site soil under freeze-thaw cycles," *Rock and Soil Mechanics*: Vol. 44: Iss. 6, Article 2.
DOI: 10.16285/j.rsm.2022.6193
Available at: https://rocksoilmech.researchcommons.org/journal/vol44/iss6/2

Strength deterioration characteristics of lime-metakaolin improved earthen site soil under freeze-thaw cycles

Abstract

The Central Plains are located in an area that experiences seasonal freeze-thaw cycles, which can have significant effects on the soil structure of soil relics. To determine if lime-metakaolin (L-MK) is a feasible alternative to natural hydraulic lime (NHL) for earth site restoration work, tests were conducted using lime, metakaolin and silty sand from the site as main raw materials. Mass loss, unconfined compressive strength and splitting tensile strength tests were carried out on L-MK improved silty sand soil undergoing different numbers of freeze-thaw cycles to study its strength characteristics in depth. X-ray diffraction (XRD) thermogravimetry (TG), and scanning electron microscope (SEM) microscopic tests were also performed on some samples to reveal the internal mechanism of strength deterioration law of L-MK improved soil. Results indicate that L-MK improved soil has better freeze-thaw cycle resistance than NHL improved soil under the experimental mix ratio. Increasing the content of metakaolin improves the strength of L-MK improved soil. As the number of freeze-thaw cycles increases, the strain softening characteristics of L-MK improved soil show a weakening trend, and unconfined compressive strength and tensile strength decrease monotonically. After 30 freeze-thaw cycles, the unconfined compressive strength and splitting tensile strength of L-MK improved soil are about 3.79 and 1.16 times higher than that of NHL improved soil, respectively. The variation of strength is consistent with hydration products such as CSH and C4AH13 generated by hydration reaction under the influence of freeze-thaw cycle for L-MK and NHL improved soil.

Keywords

earthen sites, freeze-thaw cycle, lime-metakaolin, hydraulic lime, microstructure

Authors

Xin-ming LI, Hao-yang ZHANG, Di WU, Yan-rui GUO, Ke-bin REN, and Yun-zhi TAN

Rock and Soil Mechanics 2023 44(6): 1593−1603 ISSN 1000−7598
https: //doi.org/10.16285/j.rsm.2022.6193 http://rocksoilmech.researchcommons.org/journal

Strength deterioration characteristics of lime-metakaolin improved earthen site soil under freeze-thaw cycles

LI Xin-ming[1, 2], ZHANG Hao-yang[1, 2], WU Di[1, 2], GUO Yan-rui[1, 2], REN Ke-bin[3], TAN Yun-zhi[4]

1. School of Civil Engineering and Architecture, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China
2. Research Center of Environmental Geotechnical Engineering and Underground Engineering Disaster Control Engineering of Henan Province, Zhongyuan University of Technology, Zhengzhou, Henan 450007, China
3. Henan Provincial Architectural Heritage Protection and Research Institute, Zhengzhou, Henan 450007, China
4. Key Laboratory of Geological Hazards on Three Gorges Reservoir Area of Ministry of Education, China Three Gorges University, Yichang, Hubei 443002, China

Abstract: The Central Plains are located in an area that experiences seasonal freeze-thaw cycles, which can have significant effects on the soil structure of soil relics. To determine if lime-metakaolin (L-MK) is a feasible alternative to natural hydraulic lime (NHL) for earth site restoration work, tests were conducted using lime, metakaolin and silty sand from the site as main raw materials. Mass loss, unconfined compressive strength and splitting tensile strength tests were carried out on L-MK improved silty sand soil undergoing different numbers of freeze-thaw cycles to study its strength characteristics in depth. X-ray diffraction (XRD) thermogravimetry (TG), and scanning electron microscope (SEM) microscopic tests were also performed on some samples to reveal the internal mechanism of strength deterioration law of L-MK improved soil. Results indicate that L-MK improved soil has better freeze-thaw cycle resistance than NHL improved soil under the experimental mix ratio. Increasing the content of metakaolin improves the strength of L-MK improved soil. As the number of freeze-thaw cycles increases, the strain softening characteristics of L-MK improved soil show a weakening trend, and unconfined compressive strength and tensile strength decrease monotonically. After 30 freeze-thaw cycles, the unconfined compressive strength and splitting tensile strength of L-MK improved soil are about 3.79 and 1.16 times higher than that of NHL improved soil, respectively. The variation of strength is consistent with hydration products such as CSH and C_4AH_{13} generated by hydration reaction under the influence of freeze-thaw cycle for L-MK and NHL improved soil.

Keywords: earthen sites; freeze-thaw cycle; lime-metakaolin; hydraulic lime; microstructure

1 Introduction

Earthen sites are humanistic heritages of historical, artistic and scientific value built with soil as the main material. The earthen sites are affected by the meteorological environment, geological environment, and human factors in the area where they are located and are constantly subjected to damage from various sources, and their bodies exhibit many diseases[1−2]. For example, in the Central Plains region, which is a seasonally frozen soil zone, most of the earthen sites are mostly compacted with strong to extremely strong frost heaving silt or silty sand. The earthen sites are susceptible to disasters such as undercutting, peeling and even collapsing under repeated freezing and thawing[2]. The rational choice of restoration materials is the key to the preventive conservation of earthen sites. Therefore, it is important to research restoration materials for earthen sites to slow down the rate of damage and extend the effective life of earthen sites.

Following the principle of “minimal intervention” in heritage conservation, traditional restoration materials should be used as far as possible. Inorganic materials such as lime[3], cement[4] and natural hydraulic lime (NHL)[5] are currently used for the restoration of earthen sites. Among them, air-hardening materials such as lime have the shortcoming of unstable mechanical properties in a water environment, which leads to the adverse situation of repeatedly repairing earthen sites[3]. Hydraulic materials such as cement have the characteristics of early-strength and stable mechanical properties, but they are often used less in the repair of earthen sites due to poor compatibility[4]. Since its discovery in 1756, NHL has been widely used in Europe and the United States for its moderate mechanical strength, good water permeability and air permeability, and its ability to maintain good compatibility with protected buildings, as well as its strong resistance to wind and rain erosion and repeated changes in temperature and humidity[5]. However, NHL is limited by the construction process, reliance on imports and high prices, which are not conducive to the promotion of the use of large quantities in the restoration of earthen sites in China. Other studies showed that anhydrous aluminium silicate (SiO_2-$2Al_2O_3$),

---

Received: 1 August 2022 Accepted: 23 October 2022
This work was supported by the Henan Provincial College Young Backbone Teacher Project (2019GGJS142), the Basic Research Project of Henan Provincial Key Scientific Research Project (20ZX009), the National Nature Science Foundation of China (51509274) and the Scientific and Technological Project of Henan Province (202102310584, 222102320060).

First author: LI Xin-ming, male, born in 1987, PhD, Associate Professor, research interests: special soils mechanics and conservation of earth sites.
E-mail: xinmingli01@163.com

the main active component of metakaolin, can react with calcium hydroxide ($Ca(OH)_2$), the main component of slaked lime, in the presence of water in a volcanic ash reaction to produce a hydration product similar to that of cement hydration[6]. Based on this, the author found that the lime-metakaolin (L-MK) material retained both the good air-hardening properties of lime and the hydraulicity of cement, while also having moderate mechanical strength. This has a non-negligible advantage in the preservation of earthen sites[7]. In addition, both lime and kaolin are common natural mineral materials in China and have the advantages of being widely available at low cost. Therefore, the development of inorganic materials based on lime and kaolin as alternatives to NHL is important to improve the preservation of earthen sites in China and to enrich the materials for the conservation and restoration of cultural relics.

Durability is one of the key characteristics required for materials used in the preservation of earthen sites, and the freeze-thaw cycle is an important tool to evaluate its effect on the mechanical properties of earthen sites and their meso- and micro-structure during temperature changes. Sauer et al.[8] and Necmi et al.[9] studied the mechanical and dynamic properties of lime-treated silty clay and coarse-grained soils before and after freeze-thaw cycles, respectively, and concluded that lime could effectively improve the freeze-thaw resistance of soils. However, Olgun et al.[3] found that the freeze-thaw cycle properties of lime-improved expansive soils did not change significantly. Pavía et al.[10] evaluated the frost resistance of lime mortar and weakly hydraulic lime (NHL2) mortar using a saturation factor and found that lime mortar had superior durability compared to NHL2, and NHL2 had a higher risk of decomposition of particles aggregates. Song et al.[11] believed that the durability and strength growth rate of hydraulic lime as building materials were relatively slow, which limits its engineering applications. Whereas Kalagri et al.[12] deemed that hydraulic lime (NHL5) exhibited approximately three times the compressive and flexural strength of lime mortar and cement mortar in terms of durability. Yurdakul et al.[13] pointed out that the compressive strength of metakaolin composites increased after 56 freeze-thaw cycles but decreased after 300 cycles. Forster et al.[14] found that both the dosage and grade of hydraulic lime affected its durability in building restoration applications in conjunction with engineering practice. Li et al.[15] and Sun et al.[16] demonstrated that NHL outperformed lime in terms of durability and mechanical strength of improved silt soils based on extensive test results. Tan et al.[6, 17] carried out a systematic study on the physical and mechanical properties of lime-improved silty sand and red clay in conjunction with metakaolin and found that the durability of the soils was improved significantly with the addition of metakaolin. Hence one can see that the patterns of mechanical properties of lime and hydraulic lime improved soils with the number of freeze-thaw cycles are not consistent, and they are closely related to the method of freeze-thaw cycles, the properties of the base-material(soil), and the mixing ratio. Therefore, it is necessary to study the effect of freeze-thaw cycles on the mechanical properties of L-MK and NHL-improved soils and their microscopic mechanisms under the conditions of specific base-material and environments so as to provide material support and theoretical basis for the restoration of earthen sites.

The Central Plains region is a seasonally frozen soil zone, and periodic freezing and thawing significantly affects the structure of the earthen site soil. Based on the previous research on the mechanical properties of L-MK improved soils[7], this paper designed a laboratory freeze-thaw cycle test in accordance with the environment of the earthen site, using typical silty sand as the base material. Mass loss tests, unconfined compressive tests, and splitting tensile tests were carried out on L-MK and NHL-improved soil specimens that had undergone 0, 5, 15 and 30 freeze-thaw cycles to analyze the changes in strength against freeze-thaw cycles. Then, microscopic tests such as X-ray diffraction analysis (XRD), thermogravimetric-differential thermal analysis (TG-DTA), and scanning electron microscopy (SEM) were carried out on some representative specimens to explore the correlation between the mechanical properties and microstructural characteristics of the improved soil under freeze-thaw cycles so as to support the feasibility of replacing NHL with L-MK for the preservation of earthen sites.

2 Materials and test methology

2.1 Raw materials and specimen preparation

The test raw materials included silty sand, lime, metakaolin and hydraulic lime. The physical materials are shown in Fig. 1 and the XRD test results are shown in Fig. 2. The chemical compositions of the four materials were determined by X-ray fluorescence (XRF), and the test results are shown in Table 1. Among them, the silty sand used in the test was taken from the scattered soil of the former city site of Yuanling in Zhengzhou city, Henan province, and its main chemical composition was 67.89% of silicon dioxide (SiO_2), followed by 11.58% of aluminium oxide (Al_2O_3), and the basic physical properties are shown in Table 2. The lime was supplied by Jiangxi Xinyu Huihui Industrial Co., Ltd. with a CaO content of 95.60%; the metakaolin was supplied by Chenyi city Refractory Material

Abrasive Co., Ltd, Gongyi city, Zhengzhou, Henan province, with a 28 d volcanic ash activity index of 122% and an amorphous aluminosilicate phase ($Al_2(Si_2O_5)(OH)_4$) with a small amount of quartz and kaolinite. The hydraulic lime (NHL2) was sourced from Shanghai Desalberg Materials Co. Ltd. and the main mineral phases include dicalcium silicate (C_2S), calcium carbonate $CaCO_3$ and calcium hydroxide $Ca(OH)_2$.

(a) Silty sand (b) Lime

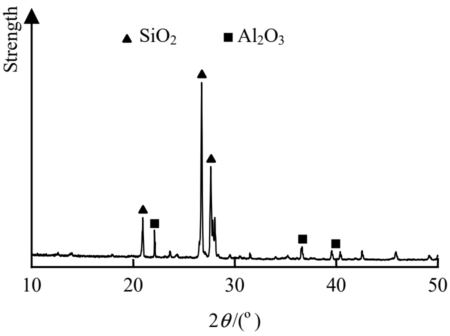
(c) Metakaolin (d) Hydraulic lime

Fig. 1 Raw materials

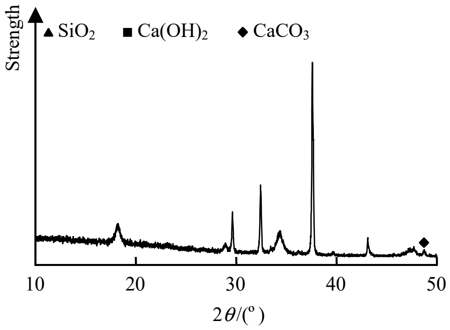
On the basis of the previous research[7], and combining the relevant requirements of tabia and three-to-seven lime-soil (volume ratio) in the protection of ancient buildings, three lime mixing ratios of 6%, 8% and 10% and three metakaolin mixing ratios of 4%, 8% and 12% (where both lime and metakaolin mixing ratios followed internal mixing method) were set, such as 6%L+4% MK meant 6% lime+4% metakaolin+90% silt. In the control groups, the improved soil samples mixed with 8% or 10% NHL were prepared. The size of the sample had a diameter of 50 mm and a height of 50 mm, and the degree of compaction was controlled at 98%. The de-moulded samples were cured for 28 days under constant temperature and humidity conditions (temperature was controlled at 20 ℃±2 ℃, and humidity was at 95%±2%).

2.2 Freeze-thaw cycle test

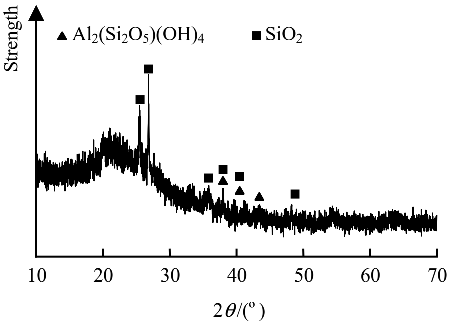
Bing[18] showed that the lower the freezing temperature of the soil was, the more its strength decreased after thawing. When the freezing temperature was lower than −10 °C, the soil strength reached a stable state. In addition, referring to the meteorological data over the years in the Central Plains area[19], the freezing temperature was set to −15 °C and the thawing temperature was set to 10 °C.



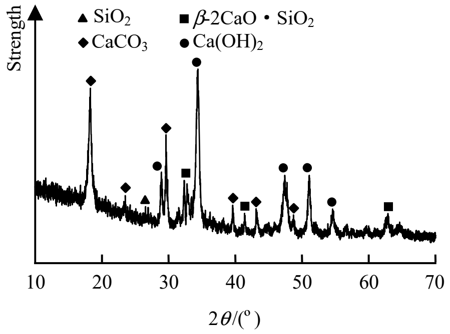
(a) Silty sand



(b) Lime



(c) Metakaolin



(d) Hydraulic lime

Fig. 2 X-ray diffraction patterns of silty sand, lime, metakaolin and hydraulic lime

After the curing of the samples, the laboratory freeze-thaw cycle test was carried out. To approximate the climate conditions of the earthen site in the natural environment to the greatest extent, an open freeze-thaw cycle test was carried out without considering the water loss of the sample during the freeze-thaw process. The samples were placed in a constant temperature and humidity box, frozen at a cooling temperature of −15 °C for 12 h, and

Table 1 Chemical composition of silty sand, lime, metakaolin and hydraulic lime

Materials	Chemical composition /%								
	SiO_2	CaO	Fe_2O_3	TiO_2	Al_2O_3	K_2O	MgO	SO_3	Other
Silty sand	67.89	3.04	5.97	2.86	11.58	1.75	2.82	0.46	3.63
Metakaolin	49.73	1.72	2.23	1.56	41.18	0.17	0.13	0.09	3.19
Hydraulic lime	13.33	75.36	1.60	0.14	2.62	0.99	2.16	0.67	3.13
Lime	1.01	95.60	0.21	—	1.55	—	0.16	0.06	1.41

Table 2 Basic properties of silty sand

Optimum moisture content w_{ot} /%	Maximum dry density ρ_{dmax} /(g • cm^{-3})	Liquid limit ω_L /%	Plastic limit ω_P /%	Plasticity index I_p	Particle composition /%		
					Sand (0.075−2 mm)	Silt (0.075−0.005 mm)	Clay (<0.005 mm)
9.3	1.96	19.2	8.2	11.0	65.66	32.48	1.86

Note: Liquid limit ω_L, plastic limit ω_P and plasticity index I_p are test data for the fine-grained portion of the silty sand.

then thawed at 10 °C for 12 h. This was a freeze-thaw cycle, which took 24 h, and the mass change of the sample was monitored during the freeze-thaw process. Studies have shown that 8−12 cycles could meet the requirements of analyzing the effects of freeze-thaw cycles on the mechanical properties of fine-grained soil strength[18]. However, considering the high weather resistance requirements for the protection of earthen sites, the number of freeze-thaw cycles was increased to 30, that is, the number of freeze-thaw cycles was set to 0, 5, 15, and 30 times, respectively. When the number of freeze-thaw cycles reached the given value, the unconfined compression test and splitting tensile strength test were carried out after the samples were saturated for 24 hours. The number of samples in the same test was not less than 6, and the average value was taken as the test value. Additionally, the microscopic test was carried out after sampling the damaged sample. For the convenience of subsequent expression, FT was used to represent the number of freeze-thaw cycles, such as FT = 5 meant that the samples experienced 5 freeze-thaw cycles.

2.3 Macroscopic mechanical test

The unconfined compressive test and the splitting tensile test were carried out using a modified California bearing ratio tester, and the axial strain rate was maintained at 1%/min during the test. The estimation was made in accordance with the *Standard for Geotechnical Testing Method* (GB/T 50123—2019)[20].

2.4 Microscopic test

The hydration product composition, hydration product content and microscopic morphology of L-MK and NHL improved soils were tested by X-ray diffraction analysis (XRD), thermogravimetric-differential thermal analysis (TG-DTA), and scanning electron microscopy (SEM).

2.4.1 XRD test

After 0 and 30 freeze-thaw cycles, 50 g samples were taken, dried in a vacuum, crushed into powder, and passed through a 0.15 mm sieve until there were no obvious particles. A Bruker D8 Advance (40 kV/40 mA) ray diffractometer, at a constant step size of 0.02° and a rate of 8 (°) /min, within the 2θ testing range of 5° to 80°, was used to measure the mineral phase composition of each proportion sample under different freeze-thaw cycles.

2.4.2 TG-DTA test

Synchronous thermal analyzer (DSC/TG-DTA) STA 499 F5 was used to conduct comprehensive thermo-gravimetric-differential thermal analysis on samples that had undergone 0 and 30 freeze-thaw cycles. The disposal method of the sample was the same as that in section 2.4.1. In order to ensure the stability of the sample during the test, it was necessary to start the instrument 3 hours in advance before starting the TG and DSC test and use nitrogen (N2) with an output pressure of 0.04 MPa to protect the sample. TG-DTA test was performed at a heating rate of 20 °C /min, and the lower and upper limits of the temperature are 0 and 1 000 °C.

2.4.3 Microscopic morphology observation

The sample, a fresh cross-section slice with a size of about 1 cm^2, was placed into −190 °C liquid nitrogen for cooling, then vacuumed for 24 h to ensure that the water in the sample was completely sublimated to a dry state, and the morphology of the sample was observed by SEM (SU-8010).

3 Analysis of test results

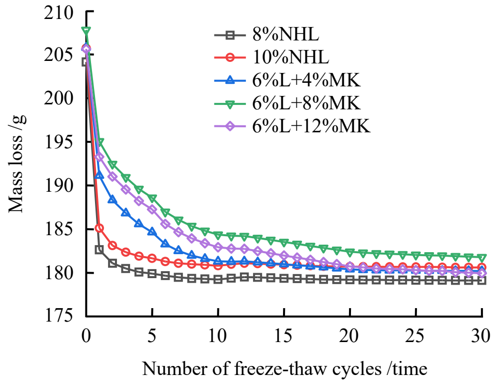
3.1 Mass loss

The mass of each specimen was weighed after each freeze-thaw cycle to obtain the mass change and mass loss rate before and after the freeze-thaw cycle, as shown in Figs. 3 and 4. The mass loss rate is the ratio of the difference between the mass of the specimen before the freeze-thaw cycle and the mass of the specimen after 30 freeze-thaw cycles to the mass of the soil sample before the freeze-thaw cycle.

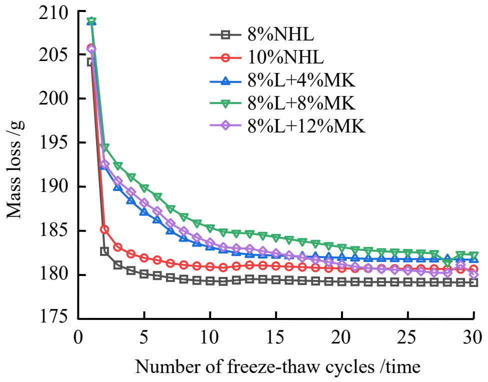
As shown in Figs. 3 and 4, the mass of both L-MK and NHL specimens decreased after freeze-thaw cycles, with the overall reduction in mass loss ranging from

12.19% to 13.37%, and mainly concentrated in the first five freeze-thaw cycles, after which the mass loss became more and more moderate. For example, the mass of the 6%L+8%MK specimen decreased from 207.8 g to 188.6 g after 5 freeze-thaw cycles, a reduction of 9.24%, and continued to decrease to 181.8 g after 30 freeze-thaw cycles, with a reduction of 3.61% between 5 and 30 cycles. The reason for this is that during the initial freezing process, the surface water first crystallizes and the internal water also moves outwards to the surface, the crystals then thaw during the temperature rise, resulting in the loss of water in soil. The loss of soil mass after 5 freeze-thaw cycles is mainly caused by the freeze-thaw effect of the frost heave force that destroys the soil structure, resulting in microcrack-induced damage to the surface of the soil, hence the relationship between the mass of the specimen and the number of freeze-thaw cycles is maintained in a slowly decreasing state.

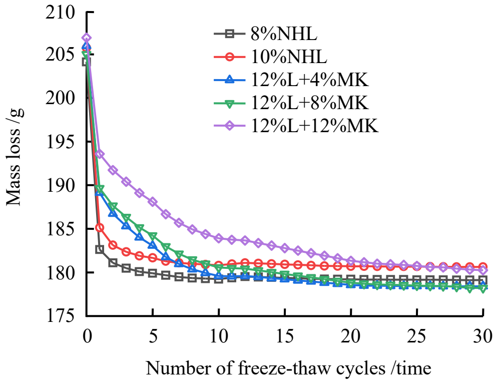
In addition, Fig. 4 shows that the mass loss of the L-MK improved soil decreased with the increase of the MK dosage when the lime dosage was higher than 8%. For example, the mass loss of the specimen after 30 freeze-thaw cycles was reduced from 12.92% to 12.47% when the lime content was 8% and the metakaolin content was increased from 4% to 12%. It suggests that when the lime content is constant, the amount of kaolinite involved in the volcanic ash reaction increases, resulting in a gradual increase in the number of hydration products, which form cementitious material and fill the soil pores, linking the soil particles together and wrapping them around the periphery of the agglomerates to form a stable structure[6,21]. As a result, the cementation between the soil particles is enhanced and the structural integrity of the soil is maintained, which reduces the magnitude of mass loss in L-MK-improved soils.



(a) 6% of lime



(b) 8% of lime



(c) 10% of lime

Fig. 3 Mass changes of samples under different freeze-thaw cycles

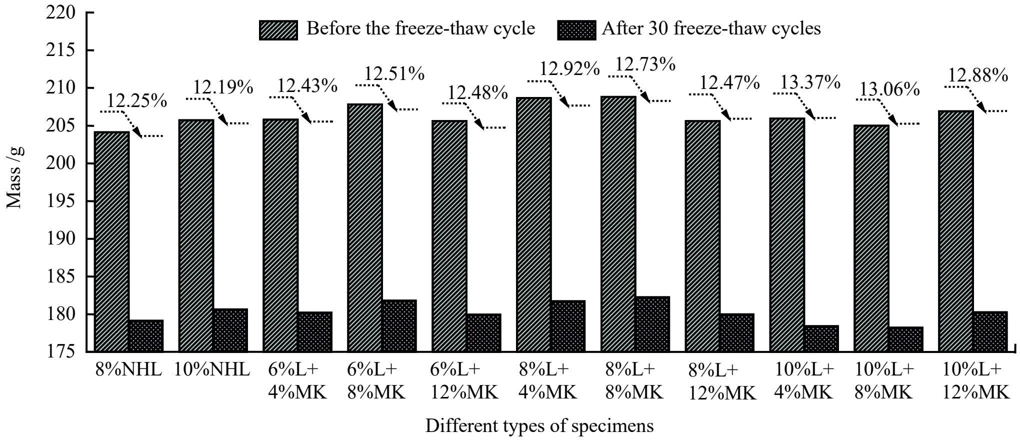


Fig. 4 Mass loss rate of samples under different freeze-thaw cycles

3.2 Unconfined compressive strength

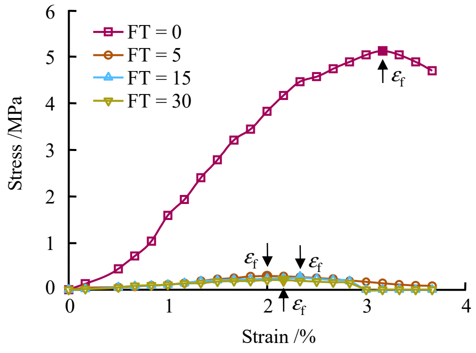
3.2.1 Axial stress−strain curve

Figure 5 shows the stress−strain curves of L-MK and NHL-improved soils at different numbers of freeze-thaw cycles. As the axial stress−strain curves for L-MK improved soils at 6%, 8% and 10% lime dosages were similar in pattern and differed merely in numerical values, only the axial stress−strain curves for L-MK at 8% lime dosages were presented here. From Fig. 5, the peak strain ε_f (the axial strain corresponding to the peak stress) of the L-MK and NHL improved soils tended to decrease with the increase of the number of freeze-thaw cycles, and gradually stabilized after five freeze-thaw cycles. For example, the ε_f of 8%L+8%MK decreased from 5.65% at FT = 0 to 1.65% (FT = 5), 1.41% (FT = 15) and 1.33% (FT = 30), respectively.

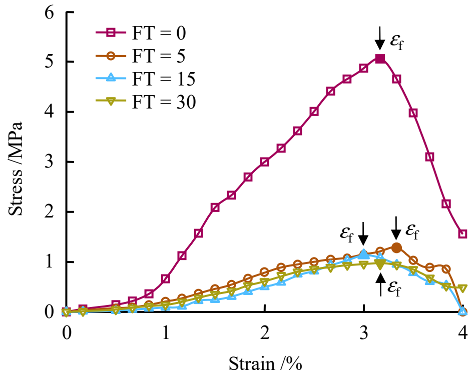
In addition, the stress−strain curve of L-MK improved soil showed an obvious peak strength without freeze-thaw cycles, which exhibited the strain-softening pattern. The softening of the specimens after freeze-thaw cycles was reduced, and with the increase in the number of freeze-thaw cycles, there was a tendency for the specimens to change from brittle damage to plastic damage. However, the softening of the stress−strain curve gradually increased after the freeze-thaw cycles as the dosage of metakaolin increased, suggesting that the brittleness of the specimens increased at this time. Due to the stronger brittleness of the soil, the greater the probability of sudden brittle failure under stress. Thus, it is necessary to determine the dosing of metakaolin reasonably in the restoration of earthen sites in the Central Plains seasonally frozen zone, i.e. to choose a lower dosing of metakaolin to meet the force and deformation requirements. The peak strain of the NHL improved soil ε_f also decreased with the increase of the number of freeze-thaw cycles, and the decrease in peak strength was greater compared to L-MK.

3.2.2 Unconfined compressive strength

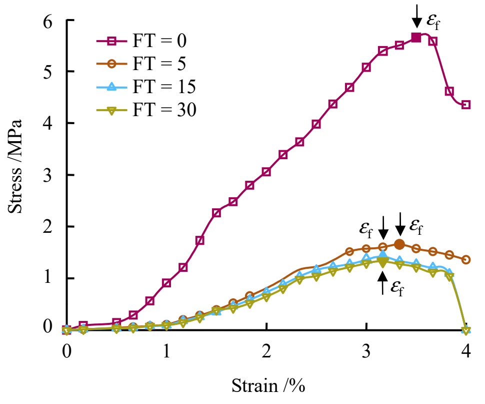
Figure 6 plots the relationship between the unconfined compressive strength of L-MK and NHL-improved soils and the number of freeze-thaw cycles. After 30 freeze-thaw cycles, the strength reduction of the L-MK improved soil was between 74.96% and 77.88%, and the absolute value of the overall compressive strength of L-MK improved soils at this time was about 5−8 times the strength values of 8% and 10% NHL improved soils. For example, the compressive strengths of 6%L+4%MK, 8%L+8%MK and 10%L+12%MK improved soils decreased from 4.45, 5.65 and 6.63 MPa at FT = 0 to 0.99, 1.33 and 1.66 MPa at FT = 30, respectively, with decreases of 77.75%, 76.46% and 74.96%. In contrast, the compressive strength of 10% NHL improved soil declined by 95.9% after 30



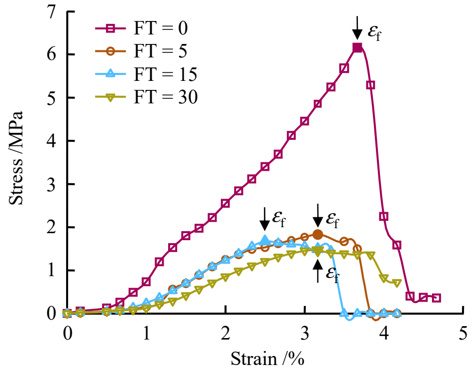
(a) 10%NHL



(b) 8%L+4%MK

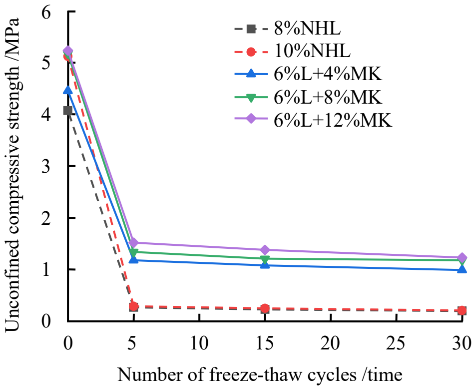


(c) 8%L+8%MK

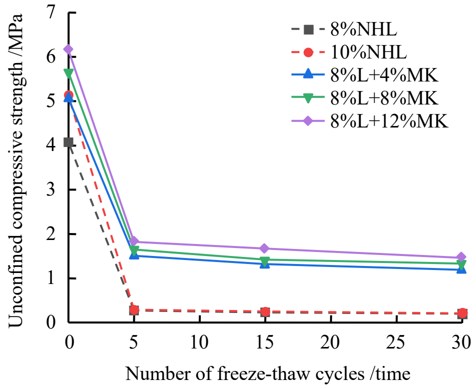


(d) 8%L+12%MK

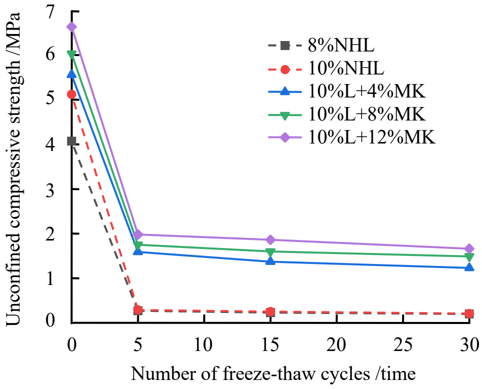
Fig. 5 Stress−strain curves of sample



(a) 6% of lime



(b) 8% of lime



(c) 10% of lime

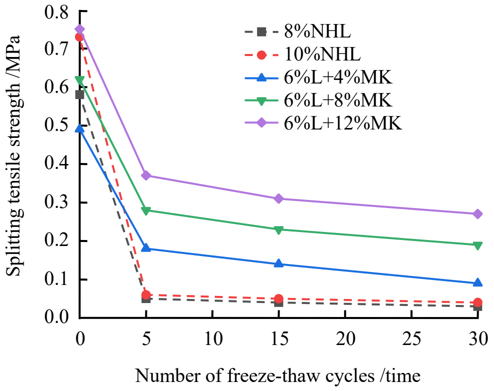
Fig. 6 Relationships between compressive strength of L-MK- and NHL-improved soils and freeze-thaw cycles

freeze-thaw cycles, with an absolute value of 0.21 MPa remaining, and the L-MK improved soil showed stronger resistance to freeze-thaw than NHL.

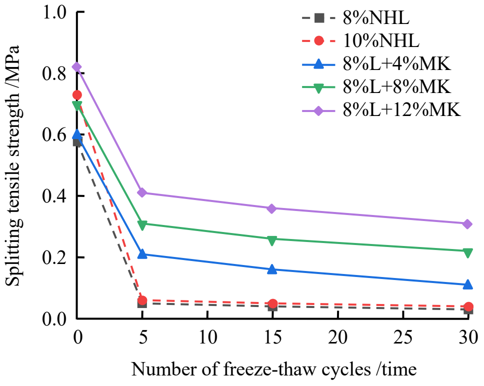
The decrease in compressive strength of the soil was most obvious when it experienced the first 5 cycles, and from the 6th to 30th freeze-thaw cycles, there was only a slight fall in compressive strength. For example, the compressive strength of 8%L+8%MK decreased by 74.88% after undergoing 5 freeze-thaw cycles, and only by 1.58% between 6th and 30th freeze-thaw cycles, indicating that the overall strength of the specimen was significantly governed by the first 5 freeze-thaw cycles.

3.3 Splitting tensile strength

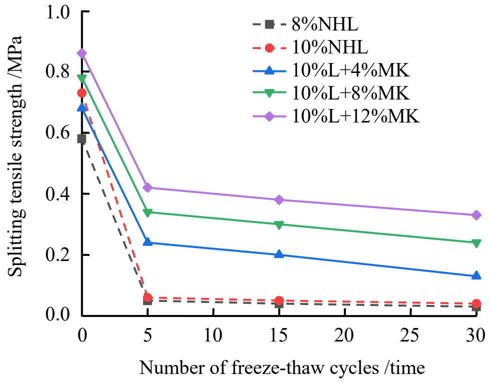
Figure 7 illustrates the relationship between the tensile strength and the number of freeze-thaw cycles for L-MK- and NHL-improved soils. Similar to the compressive strength, the tensile strength of the specimens with different proportions of additive also decreased to different degrees with the number of freeze-thaw cycles. The increase in the amount of metakaolin further boosted the tensile strength of the soil and improved its freeze-thaw resistance. The 8%L+4%MK improved soil decreased from 0.6 MPa without freeze-thaw cycles to 0.11 MPa after 30 cycles, a decline of 81.67%, while the 8%L+12%MK improved soil decreased from 0.82 MPa to 0.31 MPa, a decline of



(a) 6% of lime



(b) 8% of lime



(c) 10% of lime

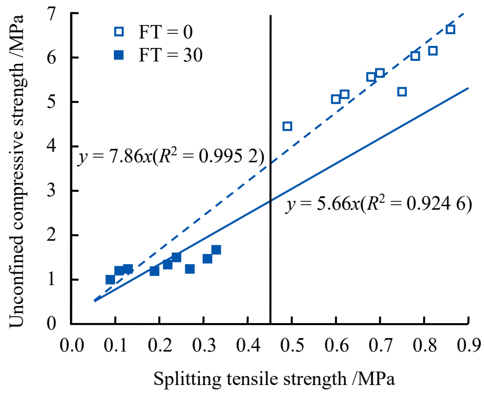
Fig. 7 Relationship between tensile strength of L-MK- and NHL-improved soils and number of freeze-thaw cycles

62.2%. The 10% NHL improved soil declined by 94.52% after 30 freeze-thaw cycles, resulting in a tensile strength of only 0.04 MPa.

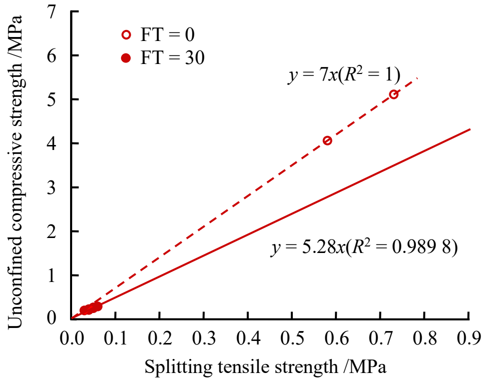
There were also turning points in the attenuation process of the L-MK- and NHL-improved soils, with the soil strength decreasing mainly in the first five freeze-thaw cycles, after which the soil strength loss became significantly smaller. It is well known that moisture in the soil plays a major destructive role in the freeze-thaw cycle of the soil. After 1 d of water saturation, the L-MK-improved soil specimens were fully hydrated and the moisture in the soil was frozen at −15 °C. The volume expanded to the point where it started to squeeze the soil particles when it came into contact with the soil particles, which gradually loosened the contact between the particles and increased the number and diameter of pores[1]. Subsequently, the ice crystals in the soil melted during the thawing process, and the water loss in the specimen was greater at this time. The plastic deformation of the soil caused by the 5 freeze-thaw cycles continued to accumulate, microfractures in the soil developed, and the internal structure of the soil was continuously destroyed until a new balance was reached[18]. As a result, the difference between the strength after 5 freeze-thaw cycles and that after 30 freeze-thaw cycles was small. However, it is important that the splitting tensile strength of the NHL-improved soil specimens stabilized after five cycles, but the strength of the L-MK-improved soil specimens still tended to decrease after the same number of cycles, indicating that the soil structure of the NHL was destroyed earlier than that of the L-MK improved soil specimens in the same test conditions under the freeze-thaw cycles.

3.4 Relationship between unconfined compressive strength and splitting tensile strength

Figure 8 gives the correlation between compressive strength and tensile strength for L-MK and NHL-improved soils, where R^2 is the correlation coefficient. It can be seen that the fitted parameter for the compressive strength of L-MK at FT = 0 was 7.86, i.e. the compressive strength was approximately 7.86 times the tensile strength, but at FT = 30 the fitted parameter decreased to 5.66. This indicated that the splitting tensile strength of the soil declined significantly more than the unconfined compressive strength, and again verified that the brittleness of the soil weakened and plasticity increased after undergoing freeze-thaw cycles, with the form of damage gradually tending towards plastic damage. The fitted parameter of NHL samples decreases from 7 before freeze-thaw cycles to 5.28 after 30 freeze-thaw cycles, but both were slightly lower than those of L-MK samples.



(a) Lime-metakaolin improved soil



(b) Hydraulic lime improved soil

Fig. 8 Relationship between the compressive and tensile strengths of L-MK- and NHL-improved soils

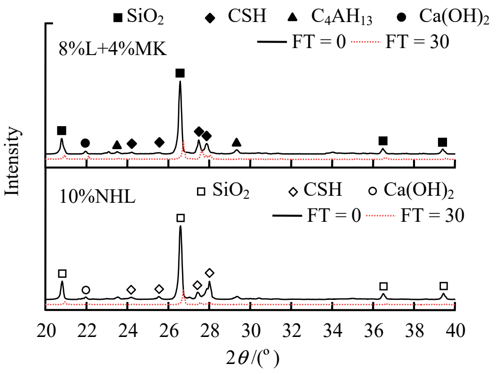


Fig. 9 XRD results of hydration products of L-MK and NHL improved soils (20°−40°)

4 Micro-mechanism analysis

4.1 XRD diffraction tests

The XRD results of the hydration products of the L-MK and NHL improved soils at 0 and 30 freeze-thaw cycles from 20° to 40° are illustrated in Fig. 9. The volcanic ash reaction of the L-MK improved soil, excluding the quartz and $Ca(OH)_2$ in the soil itself, produced hydration products similar to those of NHL, mainly including hydrated calcium silicate ($CaO\text{-}SiO_2\text{-}H_2O$, CSH) and hydrated tetra-calcium aluminate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$, C_4AH_{13}) in the non-crystalline state. In other words, the carbonation of lime produced $Ca(OH)_2$, while the Ca^{2+} and OH^- ionized from $Ca(OH)_2$ reacted volcanically with SiO_2 and Al_2O_3 in metakaolin to form CSH and C_4AH_{13}. The unreacted SiO_2 and supersaturated $Ca(OH)_2$ remained in crystalline form. The reaction equations are as follows:

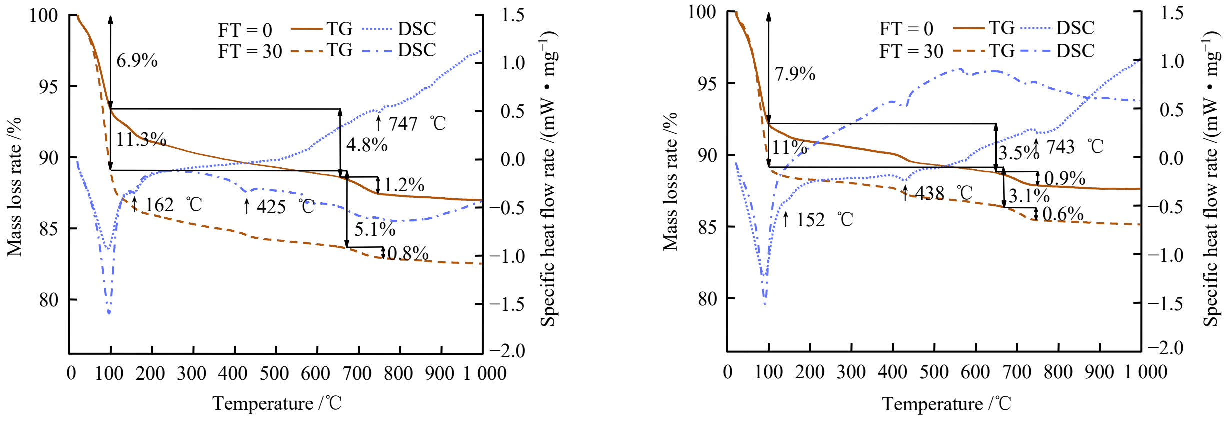
$$Al_2O_3 \cdot 2SiO_2 + 3Ca(OH)_2 + 6H_2O \longrightarrow$$
$$2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O + CaO - SiO_2 - H_2O \quad (1)$$

$$Al_2O_3 \cdot 2SiO_2 + 6Ca(OH)_2 + 9H_2O \longrightarrow$$
$$4CaO \cdot Al_2O_3 \cdot 13H_2O + 2CaO - SiO_2 - H_2O \quad (2)$$

Among the above reaction products, the increase in CSH and $Ca(OH)_2$ content improved the mechanical strength of the mortar[22]. The appearance of C_4AH_{13} at the beginning of the reaction was a sub-stable phenomenon caused by the supersaturation of $Ca(OH)_2$, which would be reduced or transformed into other products over time until its disappearance around 180 d[23]. A comparison with measurements taken before freeze-thaw cycles of the L-MK improved soil showed that the relative intensities of the characteristic peaks at 27.6° (CSH main characteristic peak) and 29.4° (C_4AH_{13} main characteristic peak) decreased after 30 freeze-thaw cycles, indicating a decrease in CSH and C_4AH_{13} content. The results indicate that freeze-thaw cycles reduced the content of hydration products and had a negative impact on the strength of the soil[22]. Meanwhile, the diffraction peak at 22.1° corresponds to the diffraction peak of calcium hydroxide (CH) crystals[23]. It indicated that Ca^{2+} ions and OH^- ions were produced during the $Ca(OH)_2$ hydration reaction and formed CH supersaturated mortar so that CH crystallized to form a new crystalline phase.

4.2 Thermogravimetric tests

Figure 10 presents the results of differential scanning calorimetry(DSC) and thermogravimetric (TG) analysis of L-MK and NHL-improved soils for 0 and 30 freeze-thaw cycles. The TG curves reflected the decreasing mass with increasing temperature, with mass losses of approximately 12.9% and 17.2% for the L-MK improved soil before and after 30 freeze-thaw cycles, respectively, and approximately 12.3% and 14.7% for the NHL improved soil, respectively. At the beginning of heating, the DSC curves all presented a large heat absorption peak accompanied by a uniform weight loss, which was caused by the loss of the initially adsorbed water and the removal of the gelling and interlayer water in the form of water molecules after 100 °C. In addition, three heat absorption peaks can be found in the DSC curves of L-MK improved soils, presumably caused by the decomposition of C_4AH_{13} (162 °C), $Ca(OH)_2$ (425 °C) and CSH (747 °C) to remove constitution water, and part of the decomposition of C_4AH_{13} to $Ca(OH)_2$ and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$[24]. Based on the above temperature range of water loss from the hydration products and combining the mass loss from the TG curves, the contents of CSH, $Ca(OH)_2$ and C_4AH_{13} could be estimated, as shown in Table 3.



(a) 8%L+4%MK (b) 10%NHL

Fig. 10 TG-DSC chart of 8%L+4%MK and 10%NHLimproved soil

Table 3 shows variations of hydration products content. CSH and C_4AH_{13}, of 8%L+4%MK improved soil decreased from 1.66% and 0.91% at FT = 0 to 1.45% and 0.58% at FT = 30, respectively, but the $Ca(OH)_2$ content increased by 0.22%, presumably with some $Ca(OH)_2$ decomposition from C_4AH_{13}. The changes in $Ca(OH)_2$ and CSH content of the 10% NHL improved soil under freeze-thaw cycling were the opposite of the L-MK improved soil, with a 0.03% decrease in $Ca(OH)_2$ and a 0.17% increase in CSH.

4.3 Scanning electron microscope test

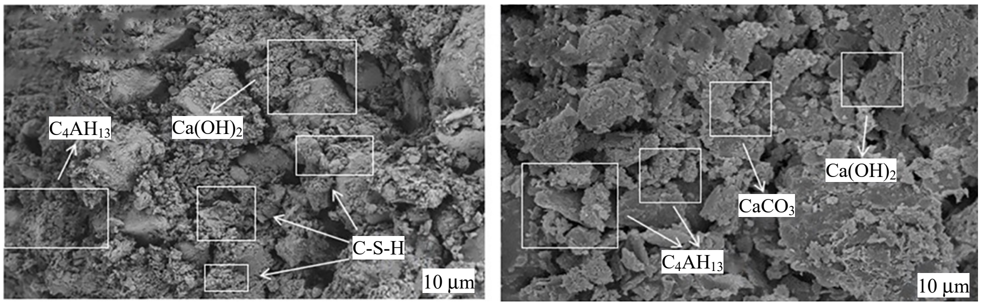
Scanning electron microscopy was used to observe the microstructure of the L-MK and NHL improved soil sections that had undergone 0 and 30 freeze-thaw cycles, and the results are shown in Fig. 11.

Figure 11 shows the SEM images of the L-MK and

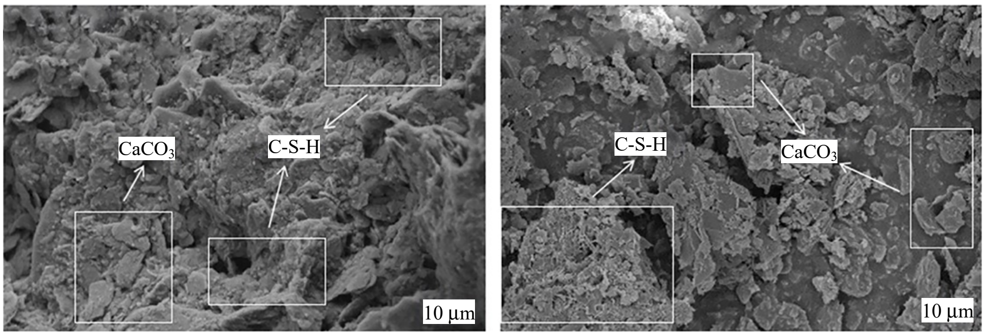
Table 3 Calculation results of CSH, $Ca(OH)_2$ and C_4AH_{13} contents

Specimen types	Freeze-thaw cycle stage	Content of hydration products /%		
		C_4AH_{13} (130−250 ℃)	$Ca(OH)_2$ (400−480 ℃)	CSH (680−750 ℃)
8%L+4%MK	Before the freeze-thaw cycle	1.66	0.36	0.91
	After the freeze-thaw cycle	1.45	0.58	0.58
10%NHL	Before the freeze-thaw cycle	—	0.69	0.63
	After the freeze-thaw cycle	—	0.66	0.80

NHL-improved soils at a magnification of 5 000. According to Fig. 11 and the XRD results, the hydration products of the L-MK improved soils before and after freeze-thaw cycles were dominated by C_4AH_{13} in laminar form, CSH in fibrous mesh form and $Ca(OH)_2$ in irregularly shaped flakes. CSH and C_4AH_{13} were distributed on the surface of $Ca(OH)_2$ or filled in the structural pores, and interwoven with $Ca(OH)_2$ to form a more complete dense structure. Figure 11(b) shows that after 30 freeze-thaw cycles, the interlocking structure between the volcanic ash reaction products and $Ca(OH)_2$ in the L-MK improved soil was significantly reduced, the filling materials between individual pores disappeared and the microstructure was severely damaged, which eventually led to a decrease in the resistance of the soil to external erosion and a corresponding deterioration of the macroscopic properties.



(a) 8%L+4%MK, FT = 0 (b) 8%L+4%MK, FT = 30



(c) 10%NHL, FT = 0 (d) 10%NHL, FT = 30

Fig. 11 SEM images of L-MK and NHL improved soil at 5 000×magnification

In addition, a small amount of cubic $CaCO_3$ was observed, which indicated that some of the $Ca(OH)_2$ underwent a carbonation reaction to produce $CaCO_3$. By combining the small increase in $Ca(OH)_2$ content in the L-MK improved soil before and after the freeze-thaw cycle in Table 3, it could be inferred that the decomposition of C_4AH_{13} and carbonation reaction offset the effect of freeze-thaw cycles on $Ca(OH)_2$ content. From Figs. 11(c) and 11(d), there was a difference in the morphology of the hydration products of the NHL and L-MK improved soils, that is, $CaCO_3$ from the carbonation reaction gradually distributed or filled on the laminated $Ca(OH)_2$ and amorphous CSH gel, forming the main skeleton of the NHL improved soil. After 30 freeze-thaw cycles, the microstructure morphology of the soil samples also showed similar regular changes to that of L-MK-improved soil, but the area of soil particle agglomerates wrapped by the hydration products of the NHL-improved soil was significantly lower than that of the L-MK improved soil.

5 Conclusion

(1) The mass loss of L-MK and NHL specimens at FT = 30 was about 12.19% to 13.37%. When the lime dosage was higher than or equal to 8%, the mass loss of L-MK improved soil specimens tended to decrease with the increase of metakaolin dosing.

(2) Under the experimental proportion, the deterioration of the strength of the L-MK-improved soil by freeze-thaw cycles was more significant than that of the NHL-improved soil, and the increase in the amount of metakaolin improved the freeze-thaw resistance of the soil. However, the negative

effect of the increased amount of metakaolin on the increased brittleness of the L-MK-improved soil should be noted.

(3) The hydration products such as CSH and C_4AH_{13} generated by the volcanic ash reaction of lime and metakaolin intertwine with $Ca(OH)_2$ to form the main skeletal structure of L-MK. However, the C_4AH_{13} and CSH content decreased from 1.66% and 0.91% to 1.45% and 0.58% respectively when the FT was increased from 0 to 30 times, which matched the pattern of change in strength properties.

(4) The synergistic effect of lime and metakaolin can be used in earthen site conservation instead of hydraulic lime, as derived from the loss of mass, mechanical strength and microscopic mechanisms of the specimens.

The use of lime and metakaolin improved soils in the preservation of earthen sites in the Central Plains zone is feasible. However, this paper only analyses the effect of L-MK- and NHL-improved silty soil in terms of the freeze-thaw cycling characteristics of the strength of the restoration material, while the durability under the influence of other environmental factors (e.g. acid, salt, etc.) needs to be further investigated.

References

[1] YAN Geng-sheng, ZHANG Hu-yuan, WANG Xiao-dong, et al. Durability of earthen architecture ruins under cyclic freezing and thawing[J]. Rock and Soil Mechanics, 2011, 32(8): 2267−2273.

[2] REN Ke-bin, WANG Bo, LI Xin-ming, et al. Strength properties and pore-size distribution of earthen archaeological site under dry-wet cycles of capillary water[J]. Rock and Soil Mechanics, 2019, 40(3): 962−970.

[3] OLGUN M. The effects and optimization of additives for expansive clays under freeze–thaw conditions[J]. Cold Regions Science and Technology, 2013, 93: 36−46.

[4] MOROPOULOU A, BAKOLAS A, MOUNDOULAS P, et al. Strength development and lime reaction in mortars for repairing historic masonries[J]. Cement and Concrete Composites, 2004, 27(2): 289−294.

[5] MARIA APOSTOLOPOULOU, ASTERIOS BAKOLAS, MELETIS KOTSAINAS. Mechanical and physical performance of natural hydraulic lime mortars[J]. Construction and Building Materials, 2021, 290: 123272.

[6] TAN Yun-zhi, KE Rui, CHEN Jun-lian, et al. Enhancing durability of lime-cement solidified sludge with metakaolin[J]. Rock and Soil Mechanics, 2020, 41(4): 1146−1152.

[7] LI Xin-ming, LU Guang-yuan, ZHANG Hao-yang, et al. Strength characteristics and micro-mechanism of lime-metakaolin modified silty soil[J]. Journal of Building Materials, 2021, 24(3): 648−655.

[8] SAUER E K, WEIMER N F. Deformation of lime modified clay after freeze-thaw[J]. Transportation Engineering Journal, 1978, 104(2): 201−212.

[9] NECMI YARBAŞI, EKREM KALKAN, SUAT AKBULUT. Modification of the geotechnical properties, as influenced by freeze–thaw, of granular soils with waste additives[J]. Cold Regions Science and Technology, 2006, 48(1): 44−54.

[10] PAVÍA S, TREACY E. A comparative study of the durability and behaviour of fat lime and feebly-hydraulic lime mortars[J]. Materials and Structures, 2006, 39(3): 391−398.

[11] SONG Zijian, LU Zhongyuan, LAI Zhenyu. Mechanical and durability performance improvement of natural hydraulic lime-based mortars by lithium silicate solution[J]. Materials, 2020, 13(22): 5292.

[12] KALAGRI A, MILTIADOU-FEZANS A, VINTZILEOU E. Design and evaluation of hydraulic lime grouts for the strengthening of stone masonry historic structures[J]. Materials and Structures, 2010, 43(8): 1135−1146.

[13] YURDAKUL AYGÖRMEZ, ORHAN CANPOLAT, MUKHALLAD M, et al. Elevated temperature, freezing-thawing and wetting-drying effects on polypropylene fiber reinforced metakaolin based geopolymer composites[J]. Construction and Building Materials, 2020, 235: 117502.

[14] FORSTER A M, CARTER K A. Framework for specifying natural hydraulic lime mortars for masonry construction[J]. Structural Survey, 2015, 29(5): 373−396.

[15] LI Li, ZHAO Lin-yi, WANG Jin-hua, et al. Research on physical and mechanical characteristics of two traditional silicate materials in Chinese ancient buildings[J]. Chinese Journal of Rock Mechanics and Engineering, 2011, 30(10): 2120−2127.

[16] SUN Yan-zhong. Study on properties of remediation and reinforcement materials for hydraulic lime modified soil[J]. Sciences of Conservation and Archaeology, 2015, 27(Suppl.1): 27−30.

[17] TAN Yun-zhi, ZHAN Shao-hu, HU Yan, et al. Behavior of lime-laterite interaction and anti-erosion mechanism of metakaolin[J]. Rock and Soil Mechanics, 2021, 42(1): 104−112.

[18] BING Wen-shan. Road frost damage and prevention[M]. Harbin: Harbin Institute of Technology Press, 1991.

[19] WANG Ji-jun, LIU Jun-gao, CHEN Luo-cheng. Long-term trend of temperature in Central China[J]. Yellow River, 2011, 33(6): 27−29.

[20] Ministry of Water Resources of the People's Republic of China. GB/T 50123—2019 Standard for geotechnical testing method[S]. Beijing: China Planning Press, 2019.

[21] NEŽERKA V, SLÍŽKOVÁ Z, TESÁREK P, et al. Comprehensive study on mechanical properties of lime-based pastes with additions of metakaolin and brick dust[J]. Cement and Concrete Research, 2014, 64: 17−29.

[22] SANTOS SILVA A, GAMEIRO A, GRILO J, et al. Long-term behavior of lime-metakaolin pastes at ambient temperature and humid curing condition[J]. Applied Clay Science, 2014, 88−89(3): 49−55.

[23] STEPKOWSKA E T, AVILES M A, BLANES J M, et al. Gradual transformation of $Ca(OH)_2$ into $CaCO_3$ on cement hydration- XRD study[J]. Journal of Thermal Analysis and Calorimetry, 2007, 87(1): 189−198.

[24] GAMEIRO A, SANTOS SILVA A, FARIA P. Physical and chemical assessment of lime-metakaolin mortars: influence of binder: aggregate ratio[J]. Cement and Concrete Composites, 2014, 45: 264−271.