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Effect of Alkali-free Accelerator Containing Nano-silica on the Durability of Shotcrete

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Abstract. *The effect of nano-silica-containing alkali-free accelerator and ordinary alkali-free accelerator on the durability of C30 shotcrete was investigated by means of seepage resistance tests and frost resistance tests. The results show that under the same conditions, the C30 shotcrete with nano-silica-containing alkali-free accelerator has a lower electrical flux and a greater impermeability rating than P10. The C30 shotcrete with nano-silica-containing alkali-free accelerator maintains a mass loss rate of about 0.4% after 200 freeze-thaw cycles, a 10.5% decrease in relative dynamic modulus of elasticity, a compressive strength loss rate of less than 20%, the bubble spacing coefficient and the average bubble diameter increased by 20.9% and 60.5% respectively, showing good frost resistance performance. This indicates that alkali-free accelerator containing nano-silica can improve the durability of shotcrete. In addition, a comparison was also made between ordinary accelerator shotcrete with nano-silica, and when 5% nano-silica was added, the properties of shotcrete were comparable to those of 2% nano-silica alkali-free accelerator shotcrete.*

Keywords: *Nano-silica; Alkali-free accelerator; Durability; Shotcrete*

1. Introduction

In China, tunnel support structures are mainly composite linings. As the shotcrete is in direct contact with the surrounding rock, which is generally filled with pressurized water, the shotcrete is subject to freeze-thaw cycles under alternating positive and negative temperature changes, which can cause damage to its material, frostbite rupture and even damage destabilization. Nano silica is used in shotcrete to improve the strength and impermeability of concrete due to its excellent physical and chemical properties, filling the pores of cementitious materials, providing nucleation and optimizing the interfacial over-structure (Elsayed et al. 2023, Gao et al. 2021, Yang et al. 2023). It is often incorporated directly into concrete in larger quantities (Zhang et al. 2016). Nano silica itself has a low density and tends to agglomerate into balls, which are not easily dispersed in concrete mixing, resulting in large waste(Changcheng et al. 2022, Zhengfa et al. 2023). In this paper, we have synthesized a accelerator containing nano-silica, which is pre-dispersed in the accelerator and then incorporated into concrete. The nano-silica was found to significantly enhance the stability of aluminum sulphate-based alkali-free accelerator and to improve the strength of mortar test blocks under the same conditions. In this paper, the effect of nano-silica-containing alkali-free accelerator and ordinary alkali-free accelerator on the durability performance of C30 shotcrete was compared and studied through impermeability and frost resistance tests.

2. Experimental materials and methods

2.1 Experimental materials

The main raw materials for shotcrete are cement, stone, sand, water reducing agent, quick setting agent and water. The main performance indicators for each component are as follows:

(1) Cement: P-O42.5 cement was used. The main physical properties and mineral composition of the cement are shown in Tables 1 and 2.

Table 1. Basic physical and mechanical properties of cement physical properties

Density (g/cm^2)	Water consumption for standard consistency (%)	Specific surface area (cm^2 /g)	Coagulation time (min)		Compressive strength (MPa)		Flexural strength (MPa)	
			The initial condensation	Final condensation	7d	28d	7d	28d
3.17	25	3350	133	243	34.6	47.9	6.6	7.8

Table 2. Chemical composition of cement clinker

Chemical composition					
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
21.16	5.01	5.23	65.03	1.7	1.09

(2) Stone: 5-10mm continuously graded gravel, meeting the requirements of continuous grading.

(3) Sand: natural river sand is used.

(4) Water reducing agent: Polycarboxylic acid system high performance water reducing agent, pH 5.2, solid content 22%, water reduction rate 30%, alkali content 0.6%.

(5) accelerator, ordinary accelerator (code NS), containing nano-silica accelerator, nano-silica content of 1%, 2%, 3%, numbered in order Si1S, Si2S, Si3S. used doping amount of 8%, accelerator performance indicators are shown in Table 3.

Table 3. Accelerator performance parameters

No.	pH	Density	Solids content/%	Coagulation time		Mortar strength		
				Initial coagulation/min	Final set/min	1d compressive strength/MPa	28d compressive strength ratio/%	90d compressive strength ratio/%
NS	2.5	1.453	50.3	3.5	8.3	12.5	101	106
Si1S	3.0	1.436	50.6	3.6	8.1	13.5	105	110
Si2S	2.8	1.440	51.2	3.6	8.0	13.9	107	112
Si3S	2.8	1.442	51.3	3.4	8.0	14.3	109	113

2.2 Test methods

The ratio of alkali-free accelerator shotcrete is cement: sand: fine stone: water: water reducing agent: accelerator = 450:861:861:164:4.5:36 (kg/m^3).

Large slabs were moulded into form and cut as required for the test. Sprayed concrete strength test methods refer to the standards JGJ/T 372-201 and Standard for Test Methods for Physical and Mechanical Properties of Concrete (GB/T 50081-2019).

The concrete impermeability grade test and the electrical flux test refer to the Standard for Test Methods for the Long-term Performance and Durability of Ordinary Concrete (GB/T 50082-2009).

The frost resistance test of shotcrete is based on the fast-freezing method in GB/T 50082-2009. 200 freeze-thaw cycles are carried out, and the mass loss rate and dynamic modulus of elasticity of the specimens are measured after every 25 freeze-thaw cycles, and the compressive strength and splitting tensile strength of the specimens are measured after every 50 freeze-thaw cycles, and the loss rate of compressive strength and splitting tensile strength are calculated the rate of loss of compressive strength and the rate of loss of splitting tensile strength were calculated.

A bubble tester was used to determine the characteristic bubble parameters of the hardened concrete in accordance with ASTM C457.

3. Results and Discussion

3.1 Shotcrete impermeability

3.1.1 Electric flux

The experiments investigated the changes in the electric flux of C30 shotcrete without accelerator (recorded as blank), C30 shotcrete with different accelerator (recorded as Si1S, Si2S and Si3S respectively), and ordinary accelerator shotcrete with 3% and 5% nano-silica added during the concrete mixing process (recorded as 3SiNS and 5SiNS respectively). Table 4 shows the results of the electrical flux tests for each concrete mix ratio.

Table 4. Electrical flux of shotcrete with different accelerator

Designator	Blank	NS	Si1S	Si2S	Si3S	3SiNS	5SiNS
Electric flux/C	1350	1560	1340	1250	1130	1350	1300

Although the electrical flux of shotcrete is greater than that of spray-formed concrete after it has been moulded into shape. However, the law of generation should be the same. The electric flux of C30 shotcrete without accelerator is 1350 C. After adding ordinary accelerator, the electric flux increases to 1560 C. This is due to the prismatic AFt induced by the alkali-free accelerator, which prevents the concrete from forming a dense structure and leads to an increase in its electric flux (Choi et al. n.d., Xujiawei 2017). After the addition of an accelerator containing nano-silica, the electric flux decreases with increasing silica content. This indicates that the nano-silica in the accelerator can refine the pore structure and enhance the resistance to chloride ion penetration. The electric flux of shotcrete with 3% and 5% nano-silica is comparable to the electric flux of Si1S and Si2S shotcrete respectively. This indicates that although the external nano-silica can also play a role in enhancing the resistance to chloride ion penetration, its dispersion ability in the concrete is not as good as the pre-dispersion in the accelerator.

3.1.2 Water penetration properties

Concrete impermeability is an important physical property of concrete that can directly affect the durability of concrete. One of the most important durability concerns in the design and application of sprayed concrete is the resistance to water penetration, so it is important to study the impermeability of high-performance shotcrete. In this paper, the impermeability of shotcrete mixed with different accelerator is evaluated by testing the impermeability class, and Table 5 shows the results of the concrete impermeability class test.

Table 5. Permeability class and average seepage height of shotcrete with different accelerator

Designator	Blank	NS	Si1S	Si2S	Si3S	3SiNS	5SiNS
Impermeability class	P10	P10	P10	P10	P10	P10	P10
Average water penetration height/mm	3.5	4.7	3.6	3.1	3.0	3.8	3.6

As can be seen from the table, the shotcrete was moulded into shape with a permeability rating of P10, but its average permeation height did vary. The average permeation height of shotcrete containing silica gel decreases as the silica gel content increases. This indicates that the nano-silica has a very good filling effect on the concrete, allowing the capillaries to be further refined. Again, the performance of the externally mixed nano-silica is not as good as that of the pre-dispersed accelerator.

3.2 Frost resistance of shotcrete

3.2.1 Relative dynamic modulus of elasticity

As seen in Figure 1, the addition of alkali-free accelerator caused the relative dynamic elastic modulus of concrete to decrease significantly with the increase in the number of freeze-thaw cycles. The relative modulus of elasticity of concrete with nano-silica accelerator is better than that of concrete with ordinary accelerator(Huazhu et al. 2021). The relative modulus of elasticity of concrete with nano-silica accelerator is better than that of concrete with ordinary accelerator. The relative dynamic modulus of elasticity of shotcrete with 3% and 5% nano-silica is not as good as that of shotcrete with nano-silica.

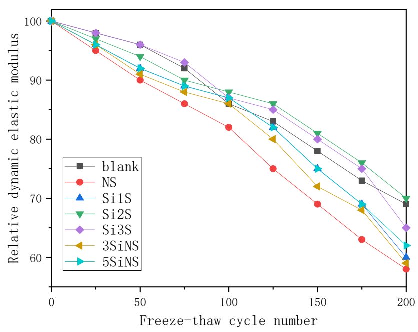

Figure 1. Relative dynamic elastic modulus variation curve under freeze-thaw cycle

3.2.2 Mass loss rate

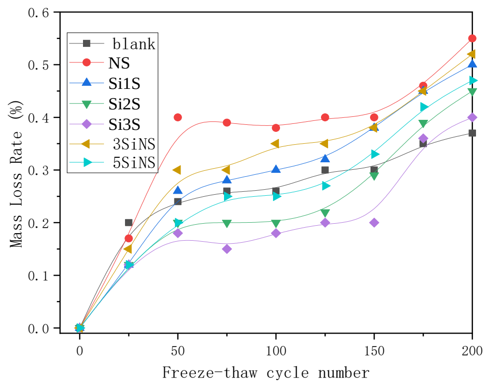

Figure.2. Mass loss rate variation curve under freeze-thaw cycle

Figure 2 shows the change curve of the mass loss rate of shotcrete under freeze-thaw cycles. As can be seen from the graph, the concrete mass loss rate continued to increase with the increase in the number of freeze-thaw cycles. During the freeze-thaw cycle, the NS test group was the first to experience a rapid increase in mass loss, and after 75 freeze-thaw cycles, the growth rate of mass loss slowed down, and at 200 freeze-thaw cycles, the mass loss rate of the specimen was 0.55%. Again, the performance of the externally doped nano-SiS was not as good as that of the pre-dispersed rapid setting agent.

3.2.3 Compressive strength

The change curve of compressive strength of shotcrete under freeze-thaw cycles is shown in Fig. 3 and the change curve of compressive strength loss rate is shown in Fig. 4. It can be seen from the graph that with the increase of the number of freeze-thaw cycles, the compressive strength loss rate of concrete gradually accelerates, the NS test group has the lowest strength and the largest loss rate, the SiS test group maintains better strength and the loss rate remains low. The compressive strength of externally mixed silica nanoparticles is not as high as that of pre-dispersed in quick setting agent.

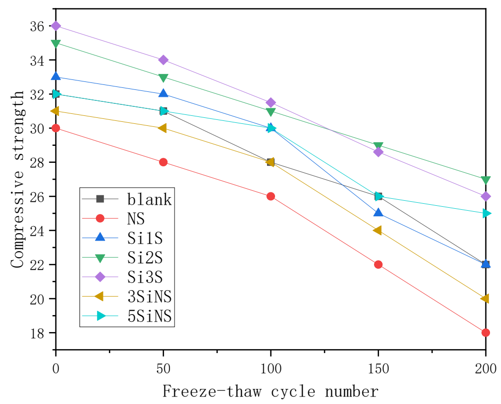

Figure 3. Compressive strength variation curve under freeze-thaw cycle

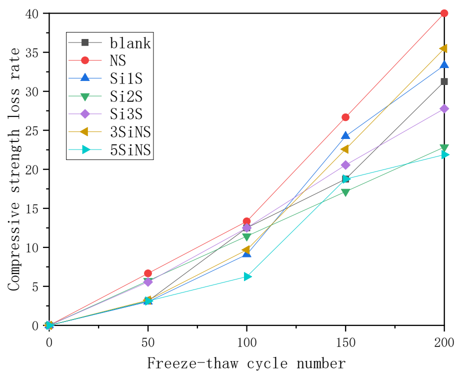

Figure 4. Compressive strength loss rate variation curve under freeze-thaw cycle

3.2.4 Bubble characterization parameters

The bubble characteristics parameters of the concrete were tested in the tests and the number of freeze-thaw cycles was chosen to be 0, 50, 100, 150 and 200. Figure 5 shows the change curve of the characteristic parameters of shotcrete bubbles under freeze-thaw cycles. After 200 freeze-thaw cycles, the bubble spacing coefficient and the average bubble diameter of ordinary quick-setting concrete increased by 40.5% and 80.4% respectively. And with nano-silica accelerator concrete bubble spacing coefficient, the average bubble diameter increased by 20.9% and 60.5% respectively. The bubble spacing coefficient and the average bubble diameter of 5SiNS concrete with nano-silica accelerator increased by 34.1% and 67.9% respectively.

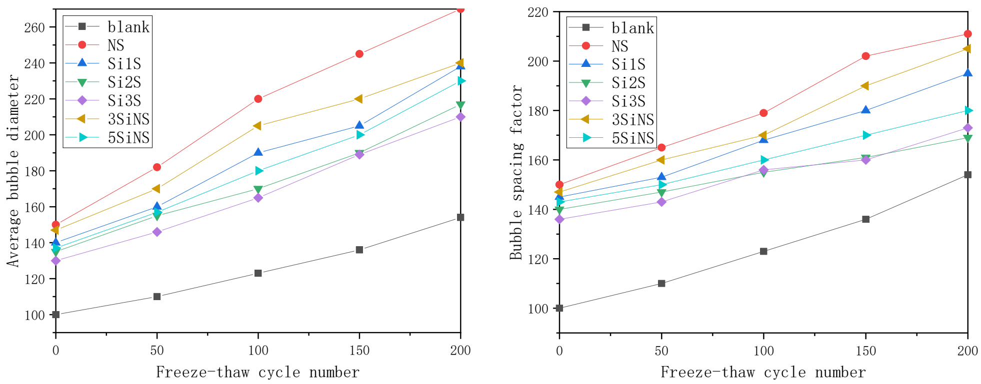

Figure 5 Variation curve of shotcrete bubble characteristics under freeze-thaw cycles

4. Conclusion

Under the same conditions, C30 shotcrete mixed with an alkali-free accelerator containing nano-silica has a lower electrical flux and a greater impermeability rating than P10.

After 200 freeze-thaw cycles, the mass loss of C30 shotcrete was greater than 0.8%, the relative dynamic modulus of elasticity was less than 60%, the loss of compressive strength was greater than 50%, and the bubble spacing factor and average bubble diameter increased by 40.5% and 80.4% respectively. In contrast, after 200 freeze-thaw cycles of C30 shotcrete with nano-silica alkali-free accelerator, the mass loss rate was maintained at about 0.4%, the relative dynamic elastic modulus decreased by 10.5%, the compressive strength loss rate was less than 20%, and the bubble spacing factor and the average bubble diameter increased by 20.9% and 60.5% respectively, showing good frost resistance performance. It indicates that alkali-free accelerator containing nano-silica can improve the durability of shotcrete.

In addition, also compared with the ordinary accelerator shotcrete mixed with nano-silica, when mixed with 5% nano-silica, shotcrete performance and Si2S containing nano-silica alkali-free accelerator shotcrete equivalent. It shows that the nano-silica pre-dispersed in the accelerator, can make the nano-silica uniformly dispersed in the concrete, play a role, but also can significantly reduce the amount of nano-silica, save materials, reduce costs.

Alkali-free accelerator shotcrete increases in durability as the number of nano-silica increases. However, the viscosity of the accelerator increases, which is not conducive to the construction of the project. On balance, the optimum amount of nano-silica is 2% of the weight of the accelerator.

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