Effect of surface treatment materials on frost resistance of damaged concrete

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Abstract. In order to study the effect of silicate infiltration agent, tetraethyl orthosilicate and nano-SiO₂ surface treatment materials on the freezing resistance of damaged concrete, the peeling condition of damaged concrete after soaking in salt water was tested by single-side freeze-thaw method. The results showed that tetraethyl orthosilicate and silicon infiltration agent can effectively improve the damaged concrete frost resistance and can reduce the 7 d water quantity of concrete, the most significant is the effect of tetraethyl orthosilicate, 7 d water quantity reduced rate of 65%, after 28 times freeze-thaw cycle exfoliation volume is 679 g/m². Silicon infiltration agent surface treatment also has a good effect, can increase the number of freeze-thaw cycles 8 times. Nano-SiO₂ has the worst treatment effect and can not improve the number of freeze-thaw cycles of damaged concrete.

1. Introduction

In the north of China, pavement concrete is easily affected by freezing. Concrete pavement will suffer from cracks, surface shedding and other diseases under the action of freezing, resulting in pavement surface damage and reduced bearing capacity [1]. At present, in order to reduce the influence of icing on pavement surface, airport usually sprinkles deicing salt on concrete surface. Although deicing salt can eliminate snow and icing, it also accelerates surface spalling, posing new challenges to the frost resistance of pavement concrete.

At present, the main measures to improve the freezing resistance of concrete include adding different admixtures and admixtures into concrete [2]. However, for the existing concrete structure, strengthening the surface is a simple, economical and reliable method. Surface strengthening treatment can form a protective layer on the surface or block the pores of concrete, improve the compactness, prevent the invasion of water and ions in the external environment, prevent the freeze-thaw damage in the concrete, and also play a role in the resistance to sulfate, chloride ions and other erosion [3]. Therefore, it is of great significance to select suitable surface treatment materials for improving the frost resistance of airport pavement concrete.

Zhang He et al. [4] explored the influence of the composite solution of lithium silicate solution and sodium silicate on the surface performance of concrete, and the results showed that the composite sol filled the micro-pores on the surface of mortar, formed a dense microstructure, improved the surface rebound value and reduced the surface permeability. Moon et al. [5] confirmed that inorganic treatment materials with calcium silicate as the basic component can improve concrete's carbonization resistance, chloride penetration resistance and freezing damage resistance, and the effect is more obvious when multi-layer treatment is adopted.

Hou Tao [6] systematically discussed the effect of tetraethyl orthosilicate as the surface treatment
material of cement concrete, and the results showed that when the volume ratio of ethyl silicate to ethanol was 1:1, the treatment effect was the best, and tetraethyl orthosilicate treatment had obvious long-term effect, which could improve the frost resistance of concrete. Barberena et al.\cite{7} analyzed the reaction of concrete cured by tetraethyl orthosilicate using FTIR, and found that tetraethyl orthosilicate could react with hydroxytraverite to generate C-S-H gel, and could also react with the existing C-S-H gel in hydration products to generate a longer C-S-H chain than the original material chain. The surface curing treatment of tetraethyl orthosilicate reduces the porosity of cement mortar, especially the pore size larger than 1μm.

Barberena et al.\cite{8} also added nano-SiO\textsubscript{2} into TEOS to treat the surface of cement mortar. Compared with the non-doped nano-SiO\textsubscript{2}, the incorporation of nano-SiO\textsubscript{2} can reduce the porosity and water absorption at the same time. Scarfato et al.\cite{9} mixed nanoparticles into epoxy resin for surface treatment of concrete. Nanofillers can improve the water permeability resistance of cured concrete by blocking the pores of concrete and reducing the diffusion performance of polymer matrix. Hou et al.\cite{10} systematically studied the properties of cement mortar cured on the surface of nano-SiO\textsubscript{2} and TEOS, and the results showed that both TEOS and nano-SiO\textsubscript{2} can effectively reduce the water absorption, water vapor transfer coefficient and porosity of cement mortar. Comparatively, TEOS had better treatment effect.

The above studies are based on undamaged concrete, but in actual engineering, due to construction, natural erosion and other reasons will inevitably lead to different degrees of concrete damage. In this paper, silica infiltration agent, tetraethyl orthosilicate and nano-SiO\textsubscript{2} were selected as surface treatment materials, and the peeling condition of damaged concrete after surface treatment under salt solution immersion was tested by single-side freeze-thaw method, and the influence of three surface treatment materials on the frost resistance of damaged concrete was discussed.

2. Methods and materials

2.1 materials

Table 1 shows concrete mix ratio and basic performance. 42.5 ordinary Portland cement is used for cement, limestone is used for coarse aggregate, Ba river sand is used for fine aggregate, and ordinary tap water is used for water.

| Material           | Cement (kg/m\(^3\)) | Water (kg/m\(^3\)) | Fine aggregate (kg/m\(^3\)) | Coarse aggregate (kg/m\(^3\)) | Vebe consistometer /s | Flexural strength at 7d /MPa | Flexural strength at 28d /MPa |
|--------------------|----------------------|---------------------|-------------------------------|-----------------------------|----------------------|-----------------------------|-----------------------------|
|                    | 330                  | 135.3               | 630                           | 1328                        | 22                   | 5.2                         | 5.6                         |

Silicon infiltration agent is the product of Hunan Fenghang New Material Company, it is a mixture of lithium silicate as the main component; The tetraethyl orthosilicate adopts the products of Shandong Fengpan New Materials Company, and the nano-SiO\textsubscript{2} adopts the nano silicon curing agent of Shanghai Zhichuang Fine Chemical Company, as shown in Table 2-4. In this paper, B, S, N and T were used to represent concrete specimens treated with untreated, silicate infiltration agent, tetraethyl orthosilicate and nano-SiO\textsubscript{2}, respectively.

| Performance parameter of silicate infiltration agent | Density/(g/cm\(^3\)) | pH | Solid content /% | Viscosity /Pa-s | Surface tension/(mN/m) |
|------------------------------------------------------|----------------------|----|-----------------|-----------------|------------------------|
|                                                      | 1.18±0.03            | 11.0±1.0 | 22±2.2         | 11.0±1.0        | ≤30.0                  |

| Performance parameters of tetraethyl orthosilicate | Silicon content/% | Acidity/ppm | Viscosity /(CPs/25°C) | Density /(g/ml) | VOC/% |
|---------------------------------------------------|-------------------|-------------|-----------------------|----------------|-------|
|                                                   | 40.61             | 40          | 5.04                  | 1.058           | <3.0  |
### Table 4 Performance parameters of nano-SiO₂

| Particle size/nm | Solid content/% | Density /(g/cm³) | pH   | Appearance     |
|------------------|-----------------|------------------|------|----------------|
| 10±1             | 12.5±1          | 1.125±0.007      | 11±0.5 | Semitransparent |

#### 2.2 Test methods

The single-side freezing-thawing method was tested according to the "Standard for Test Methods of Long-term Performance and Durability of Ordinary Concrete (GB/T 50082-2009)". Cubic specimens of 150mm×150mm× 150mm were used for 7 days of pre-water absorption and 6 freezing-thawing cycles after curing to 28 days. At this time, the cumulative amount of spalling is about 250 g/m², and the concrete surface in this state is in the pockmarked stage, which is relatively common in practical engineering. The concrete specimens were taken out and dried for 1 month in the indoor environment, then the surface was cleaned with a brush and then the surface was brushed. After curing for 7 days in the indoor environment, the concrete specimens were pre-absorbent and single-side freezing-thawing cycle, with 5 specimens in each group. Concrete quality, exfoliation quality and ultrasonic propagation time were tested every 4 cycles.

The test can be stopped when one of the following conditions is reached: (1) the number of cycles reaches 28 times; (2) The total mass of exudation reaches 1500 g/m²; (3) The relative elastic modulus of ultrasonic wave is reduced to 80%.

#### 3. Results & Discussion

Figure 1 is the amount of 7d pre-water absorption of concrete specimen, and Figure 2 is the mass of exfoliation of concrete specimen after freezing-thawing cycle. During the test, it was found that the ultrasonic relative dynamic modulus of concrete after freezing-thawing cycle was far from reaching the test termination condition, so the total mass of exudates per unit surface area of the specimen was taken as the test termination index.

It can be seen from Figure 1 that the three surface treatment materials can reduce the 7d pre-water absorption of damaged concrete. Compared with B, the 7d water absorption of S, N and T specimens decreases by 31%, 9% and 65%, respectively. The treatment effect of tetraethyl orthosilicate is the best, followed by silicon infiltration agent, and the treatment effect of nano-SiO₂ is not obvious. This is because the three kinds of surface treatment materials will product and concrete hydration reaction to generate gel, gel blocking pore and micro cracks, so as to reduce concrete water imbibition, silicon infiltration agent in concrete to form a layer of transparent film on the surface, nano-SiO₂ although there will be a lot of powder material cover surface layer, but lower strength, is the penetration of ethyl silicate strongest, And the tetraethyl orthosilicate treatment can increase the contact Angle of the concrete surface, forming a hydrophobic protective layer on the surface of the concrete and the internal aperture, so the water absorption of the tetraethyl orthosilicate surface treatment specimen is the lowest. At the same time, it can be seen that after 1 day of pre-water absorption, except for the specimens treated with ethyl silicate, the water absorption of the first day can reach more than 64% of the water absorption of the seventh day. The surface curing treatment mainly improves the water absorption of the concrete specimens on the first day after soaking, and there is a small difference in the water absorption of the specimens in the following time.

It can be seen from Figure 2 that the number of freeze-thaw cycles of damaged concrete increased from 20 times to 28 times with the surface treatment of nano-SiO₂, and the total amount of exfoliation per unit area of specimens cured by ethyl silicate was only 679 g/m² after 28 times of cycles, far from reaching the termination conditions of the test. This is because the reduction of water absorption will reduce the depth and amount of ice in concrete, while the reduction of brine infiltration will weaken the influence of accelerating deterioration, thus enhancing the frost resistance. As the powder substance formed on the concrete surface of nano-SiO₂ falls off in the freezing-thawing cycle, the treatment effect is greatly reduced.
4. Conclusions

According to the test, the following three conclusions can be drawn:

(1) The three surface treatment materials can reduce the 7d pre-water absorption of damaged concrete, among which, tetraethyl orthosilicate has the most obvious effect, and the water absorption reduction rate can reach 64%; The water absorption of concrete treated with nano-SiO₂ can only be reduced by 9%.

(2) The three surface treatment materials mainly improved the water absorption of concrete specimens on the first day after soaking, and there was little difference in the water absorption of specimens in the following time.

(3) Tetraethyl orthosilicate has the best improvement effect on freezing resistance of damaged concrete. After 28 freezing-thawing cycles, the total amount of exfoliation per unit area is only 679 g/m². Silicon infiltration agent can increase the number of freezing-thawing cycles of damaged concrete from 20 times to 28 times, while nano-SiO₂ can not improve the number of freezing-thawing cycles of concrete.

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