EFFECT OF SALT-SCALING RESISTANT ADMIXTURE ON FREEZE-DEICING SALT RESISTANCE AND MICROSTRUCTURE OF CONCRETE

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Abstract

A new type of salt-scaling resistant admixture was adopted to improve the freeze-deicing salt resistance of cement concrete pavement. According to CDF test — Test method for the freeze-thaw resistance of concrete-tests with sodium chloride solution (CDF), the deicer salt scaling resistance and microstructure of three kinds of concrete were investigated in this paper. The results show that after painted with AS scaling-salt resistant admixture, the scaled mass of three kinds of concrete in water-cement ratio (0.40, 0.36 and 0.32) were only 0.09% - 0.07% of those of concrete without AS admixture and all decreased 99% and the loss rate of dynamic elastic modulus of concrete with AS admixture reduce by 79% - 86% of the control concrete after 56 freeze-thaw cycles. SEM observations demonstrated that AS scaling-salt resistant admixture distinctly decrease the formation of cubic NaCl crystals and microcracks inside concrete and on the surface of concrete. Painted with AS anti-icing salt admixture on the surface the ordinary concrete pavement can be applied in cold regions.

1. INTRODUCTION

Concrete pavement is one of the most important pavement structures and it has been widely used due to its better strength and durability than the asphalt pavement. In cold regions the deicer-salt is used to melt the ice and snow in order to keep the traffic safe. However, it can lead scaling and cracking of concrete pavement and decrease the service life of pavement. Many technical methods [1-4] have been used to improve the deicing-frost resistance of the pavement concrete such as adding the air-entraining agent, superplasizer and fibre into concrete in order to increase air content of concrete, decrease the water cement ratio and reduce the cracking tendency of concrete pavement. Nevertheless, the internal damage of concrete, scaling and cracking on the surface of the concrete pavement still happened in cold regions [5, 6]. In 1986, experts from sixteen countries of North America, Europe and Asia underwent a test for a great number of pavements and bridges in their countries, and a consistent conclusion was given that the scaling and cracking of concrete induced by the deicer was the main destructive pattern of concrete pavement in cold regions. In this paper the
freeze-deicing salt resistance and microstructure of concrete painted with the AS scaling-salt resistant admixture were studied.

2. EXPERIMENT

2.1 Raw materials

Grade 42.5 Portland cement from Jidong Co., Ltd. according to Chinese Standards was used and its chemical composition was shown in Table 1. The maximum size of the coarse aggregates used was 25 mm. River sand with a fineness modulus of 2.80 was used as fine aggregate. A naphthalene-based superplasticizer Mighty-100 (M) from Shanghai Huawang Chemical Corporations was used. The used retarding agent was Sodium gluconate (P). Tap water was used for mixing the concrete. The AS scaling-salt resistant admixture was researched and developed in our lab.

<table>
<thead>
<tr>
<th>Table:1 Chemical composition of cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>SO₃</td>
</tr>
<tr>
<td>R₂O</td>
</tr>
</tbody>
</table>

2.2 Testing equipment

(1) Ultrasonic testing instrument

The NM-4A-I Ultrasonic testing instrumentation was used in this experiment, which was produced by Beijing Concrete Testing Technology Co., Ltd.

(2) Automatic freeze-thaw testing machine

This equipment was designed by Harbin Institute of Technology and it includes two parts which is the intelligent control device and the fridge for freezing and thawing cycle.

2.3 Test procedure

Fig.1 Frozen-thawing cycles process of the CDF test method
In this experiment the CDF test methods was conducted. The process of the freeze-thaw cycles was showed in Fig.1. Size of the specimens for the freeze-deicing salt test was 150×150×55mm and 5 specimens were tested for each mix. After demoulded, specimens were cured in the standard curing room (20 °C, 98% RH) until 28 days, then the specimens were removed and desiccated for 24 hours in drying cabinet at 80 °C. The specimens were sealed on their lateral surfaces with aluminous foil with butyl rubber. The AS scaling-salt resistant admixture was painted on the surface of the specimens (0.25 kg/m^2). The specimens were placed in the test containers and there was 5 mm high space between the test surface and the container bottom. Subsequently, the test liquid (97% by weight of distilled water and 3% by weight of NaCl) is filled into the container to a height of 10 mm without wetting the specimen's top and the test container must be closed with a cover. After 6 days the specimens were removed from containers and the transit time of ultrasonic wave must be determined before starting the freeze-thaw cycles. In addition, measurements should be carried out after every 14 freeze-thaw cycles along two perpendicular transit axes.

### 2.4 Mix proportion of concrete

The mix proportion of the concrete in this test is shown in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cement/ (kg/m^2)</th>
<th>Sand/ (kg/m^2)</th>
<th>Gravel/ (kg/m^2)</th>
<th>W/C</th>
<th>P/C (%)</th>
<th>M/C (%)</th>
<th>AS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.40</td>
<td>0.02</td>
<td>0.65</td>
<td>—</td>
</tr>
<tr>
<td>0.40+AS</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.40</td>
<td>0.02</td>
<td>0.65</td>
<td>T</td>
</tr>
<tr>
<td>0.36</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.36</td>
<td>0.02</td>
<td>0.72</td>
<td>—</td>
</tr>
<tr>
<td>0.36+AS</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.36</td>
<td>0.02</td>
<td>0.72</td>
<td>T</td>
</tr>
<tr>
<td>0.32</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.32</td>
<td>0.02</td>
<td>0.75</td>
<td>—</td>
</tr>
<tr>
<td>0.32+AS</td>
<td>414</td>
<td>642</td>
<td>1195</td>
<td>0.32</td>
<td>0.02</td>
<td>0.75</td>
<td>T</td>
</tr>
</tbody>
</table>

Note: T — surface of the specimens was painted with the AS scaling-salt resistant admixture; P/C — the proportion of retarding agent to cement; M/C — the proportion of superplasticizer to cement.

### 2.5 Evaluation of the damage

The change in the relative dynamic modulus of elasticity and surface scaling mass are used as a determined index of the deicing-frost damage. The dynamic modulus of elasticity is calculated from the transit time of ultrasonic waves as described in equation (1) and (2).

\[
m_a = \frac{\sum \mu_s}{A} \quad \quad (1)
\]

\[
\Delta E_{\text{dyn}} = \left[1 - \left(\frac{t_{\text{cs}} - t_{\text{c}}}{t_{\text{nfte}} - t_{\text{c}}}\right)^2\right] \cdot 100\% \quad \quad (2)
\]
where $m_n$ is the cumulative amount of scaled material per unit area after the n cycles (Kg/m$^2$), $\mu_s$ is the mass of scaled material after n cycles(Kg), A is the area of the test surface(m$^2$), $\Delta E_{dyn,n}$ is change in relative dynamic modulus of elasticity(%), n is the number of freeze-thaw cycles, $t_{tc}$ is the total transit time before starting the freeze-thaw cycles(μs), $t_{tftc}$ is the total transit time after n freeze-thaw cycles(μs), $t_c$ is the transit time in coupling medium(μs).

3. RESULTS AND DISCUSSION

3.1 Properties of concrete

Table 3 shows the slump of fresh concrete and the bending strength of harden concrete. It can be seen that the bending strength of concrete at 3d and 28d is increased with the decrease of water-cement ratio. The slump of fresh concrete is not changed obviously due to adjusting the dosage of superplasticizer. The slump of all concrete is controlled at the range of 50mm to 60 mm.

Table 3 Properties of concrete

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slump(mm)</th>
<th>Air content (%)</th>
<th>M/C(%)</th>
<th>Bending strength(Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>55</td>
<td>1.6</td>
<td>0.65</td>
<td>3.67 5.93</td>
</tr>
<tr>
<td>0.40+AS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>54</td>
<td>1.6</td>
<td>0.72</td>
<td>3.69 6.32</td>
</tr>
<tr>
<td>0.36+AS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.32</td>
<td>56</td>
<td>1.6</td>
<td>0.75</td>
<td>3.99 6.70</td>
</tr>
<tr>
<td>0.32+AS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Deicer salt scaling resistance of concrete

![Fig.2 Effect of water cement ratio on the freeze-deicing salt resistance of control concrete](image)

414
It can be seen from Fig.2 that the scaled mass and the loss rate of dynamic elasticity modulus tend to decrease with the reduction of water cement ratio. When the water cement ratio is reduced from 0.40 to 0.32, the scaled mass of the control concrete is decreased from 5.33 kg/m\(^2\) to 3.99 kg/m\(^2\) and the loss rate of dynamic elasticity modulus is decreased from 42.7% to 27.2% after 56 cycles. So the scaled mass is decreased by 25% and the loss rate of dynamic elasticity modulus is decreased by 36%.

From the test results of Fig.2 and Fig.3, when water cement ratio is 0.40 the scaled mass of the concrete(0.40+AS) is decreased from 5.33 kg/m\(^2\) to 0.041 kg/m\(^2\) and the loss rate of dynamic elasticity modulus is decreased from 42.7% to 6.1% compared with the control concrete (0.4) due to the AS agent. When water cement ratio is 0.36 the scaled mass of the concrete(0.36+AS) is decreased from 4.46 kg/m\(^2\) to 0.038 kg/m\(^2\) and the loss rate of dynamic elasticity modulus is decreased from 37.9% to 5.9% compared with the control concrete (0.36). when water cement ratio is 0.32 the scaled mass of the concrete(0.32+AS) is decreased from 3.99 kg/m\(^2\) to 0.028 kg/m\(^2\) and the loss rate of dynamic elasticity modulus is decreased from 27.2% to 5.6% compared with the control concrete(0.32). From the above datum, the scaled mass of all concretes is decreased by 99% and the loss rate of dynamic elasticity modulus is decreased by 79% to 86%. So the freeze-deicing salt resistance of the pavement concrete is improved obviously.

![Fig.3 Effect of the AS agent on the freeze-deicing salt resistance](image1)

![Fig.4 Surface of the concrete after 56 deicing-frost](image2)
As shown in Fig.4, after 56 freeze-thaw cycles the visible scaling happens on the surface of concrete without AS agent. The coarse aggregates are exposed and the surface of concrete cracks. But no visible scaling and cracking emerges on the surface of the concrete painted with the AS agent.

3.3 Microstructure observation and mechanism analysis

Reducing the water cement ratio can improve the freeze-deicing salt resistance. This is because the free water, porosity [7] and chloride ion diffusion coefficients [8] decrease with the reduction of the water cement ratio and most of the capillary pores are close, which can prevent deicer solution from diffusing into the concrete.

The AS freeze-deicing salt resistant agent is a kind of surfactant. It can be seen from Fig.5 that deicer solution forms concave in the capillary pores of the concrete without the AS agent, the wetting angle between deicer solution and concrete surface is less than 90° in Fig. 6(a). So deicer solution can easily diffuse into the concrete as a result of the physical adsorption and hydrogen bond between active hydroxyl groups in concrete and external water.

![Diagram of deicer solution in capillary pores with and without AS agent](image)

**Fig.5 Effect of the AS agent on the level of deicer solution in capillary pores**

![Diagram of wetting angle with and without AS agent](image)

**Fig.6 Effect of the AS agent on the wetting angle**

The main component of the AS scaling-salt resistant agent is methyl silanol. Methyl silanol is painted on the surface of concrete and diffuse into the concrete because of capillary phenomenon. After dehydration and condensation under the activation of alkali solution such as Ca(OH)₂, the methyl silanol produce polysiloxane. It can react with hydroxyl (-OH) inside concrete by means of physical and chemical adsorption. Because the reaction with the hydrophobic group of R can create hydrophobic layer so the wetting angle between deicer solution and concrete is greater than 90° as shown in Fig. 6(b), the deicer solution forms...
convex in the capillary pores within the concrete painted with the AS agent. Hence deicer solution will not be easy to diffuse into concrete[9]and the scaling-salt resistance of the pavement is improved obviously.

Fig. 7(a) shows a number of irregular cracks happen inside the specimens without the AS agent after 56 freeze-thaw cycles. After drying concrete specimens many cubic NaCl crystals formed inside concrete because deicer solution diffused into concrete during freeze-thaw cycles and there are a number of fine irregular cracks around the crystals. It can be also seen from Fig. 7(b) the wide cracks occur on the surface of the specimens after 56 freeze-thaw cycles. The microstructure of concrete surface is not compact and it indicates deicer solution can easily diffuse into concrete. Then a mass of scaling on the surface of concrete will increase and large numbers of cracks produces inside the concrete. Therefore, the durability of the concrete pavement will be degraded.

Fig.7 SEM observations of the concrete without AS agent after 56 cycles

Fig.8 SEM observations of concrete with AS agent after 56 cycles
As shown in Fig.8 (a), concrete is dense and there are few micro-cracks inside the specimens painted with the AS scaling-salt admixture after 56 freeze-thaw cycles. No NaCl crystals appeared inside concrete. It can be seen from Fig.8 (b) the dense microstructures inside the concrete on the surface of the specimens are observed. This was because that hydroxyl (—OH) linking to polysiloxane react with hydroxyl (—OH) inside concrete and produce the hydrogen bond or other chemical bonds. So calcium hydroxide in concrete also is not easily discomposed under freezing and thawing cycles. Therefore the scaling mass and internal damage of the pavement concrete will be decreased and the scaling-salt resistance of concrete is obviously improved.

4. CONCLUSIONS

− The scaled mass and the loss rate of dynamic modulus of elasticity decrease with reduction of the water cement ratio. The water cement ratio is reduced from 0.40 to 0.32, the scaled mass of the ordinary concrete is decreased by 25% (from 5.33 kg/m$^2$ to 3.99 kg/m$^2$) and the loss rate of dynamic elasticity modulus is decreased by 36% (from 42.7% to 27.2%).

− The AS scaling-salt resistant admixture can greatly decrease the scaled mass and loss rate of the dynamic modulus of elasticity. After 56 deicer-frost the scaled mass of the concretes painted with the AS agent decreases by 99% of the control concrete without AS admixture and the loss rate of dynamic modulus of elasticity decreases by 79% to 86% of the control concrete.

− AS scaling-salt resistant admixture distinctly decrease the formation of cubic NaCl crystals and microcracks inside concrete and on the surface of concrete.

− AS scaling-salt resistant admixture painted on the surface of concrete can produce polysiloxane after dehydration and condensation under the activation of alkali solution. It can react with hydroxyl (-OH) inside concrete by means of physical and chemical adsorption. As the result of the production with the hydrophobic group of R the hydrophobic layer can be produced on the surface of concrete. So the wetting angle between deicer solution and concrete is greater than 90° and the deicer solution forms convex in the capillary pores of the concrete. This will prevent the chloride ions and water from diffusing into the concrete and therefore the freeze-deicing salt resistance of concrete was obviously improved.

REFERENCES


