Effect of Protective Coatings on Frost Resistance of Concrete Structures in Northeast Coastal Areas

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Abstract: Dalian is located in the northeast coastal area, and the complex environment has caused severe freezing and thawing damage to the marine concrete. The experiment used polyurea, polyurethane, epoxy mortar to protect the concrete surface, and then carried out indoor rapid freeze-thaw test to analyze the effect of coating on the antifreeze performance of concrete. The concrete samples were subjected to mercury intrusion test before and after the freeze-thaw cycle to analyze the pore structure changes of the concrete before and after erosion. The test results show that the concrete covered by protective coating has a lower mass loss rate and a higher dynamic elastic modulus than the unprotected concrete, the order of anti-freezing performance of the protective coating from strong to weak is: epoxy mortar > polyurethane > polyurea. By isolating the concrete from the corrosive environment, the protective coating can delay the ingress of corrosive materials, slow the tendency of harmless pores in the concrete to multiple the harmful holes and harmful pores, improve the frost resistance of the concrete, and prolong the use of the concrete structure life.

1. Introduction
Freezing and thawing damage is one of the main forms affecting the destruction of concrete buildings. Concrete structures damaged by freeze-thaw damage are mainly characterized by loose surfaces, exfoliated and exposed aggregates. The structure of freeze-thaw damage in China is mainly concentrated in the northeast, north and northwest regions, especially in the northeastern coastal areas. There are almost local or large-scale freeze-thaw damages in the northeastern coastal areas, and the freeze-thaw damage accelerates the deterioration of concrete caused by other factors such as salt ion erosion, wave impact, etc., seriously affecting the long-term use and operational safety of buildings [1].

Concrete protective coatings are one of the measures that have been developed in recent years to improve the durability of concrete. By spraying or brushing the concrete surface with anti-corrosion and anti-penetration coating, it penetrates into the concrete to form a hydrophobic protection layer. Or form a waterproof seal on the surface, seal the micro cracks, pores and other defects on the concrete surface to prevent the outside air, water, salt ions from contacting the concrete. This can effectively prevent the reduction of the bearing capacity of the concrete structure, improve the safety and reliability of the engineering structure, and prolong the service life of the concrete structure [2,5].

Based on the actual situation of projects in Dalian, In this paper, three kinds of coating materials are selected to protect the surface of concrete for accelerated freeze-thaw test in laboratory. Compare the effects of different protective coatings on the frost resistance of concrete and conduct microscopic test analysis to determine the preferred coating for the protection of Dalian offshore concrete buildings.
2. Experiment

2.1. Raw material

2.1.1 Concrete material. (1) Cement, PO grade 42.5 ordinary Portland cement produced by Dalian Cement Factory; (2) Fly ash, Grade II ash of Dalian Huaneng Power Plant; (3) Mineral powder, grade S95; (4) Slag, natural river sand with good particle size gradation in Dalian, medium sand, fineness modulus 2.3; (5) Crushed stone, continuous graded gravel with a particle size of 5mm~31.5mm; (6) Water reducing agent, Superplasticizer of polycarboxylic acid, provided by Dalian Architectural Science Research Institution Co., Ltd.

2.1.2 Concrete protective coating material. The concrete protective coatings in this paper are organic film-forming coatings, which are classified as follows:

   (1) Polyurethane system, with high-permeability epoxy resin as primer, medium-paint and topcoat with one-component polymer polyurethane waterproof coating, brushing thickness one millimeter;

   (2) Epoxy mortar system, based on polymer epoxy resin as primer, polymer epoxy cement as medium paint, high weather resistance polyurea coating for topcoat, brushing thickness one millimeter;

   (3) Polyurea system, with high-permeability epoxy resin as primer, one-component high-toughness polyurea coating for intermediate paint and topcoat, brushing thickness one millimeter.

2.2. Concrete mix ratio

Concrete mix ratio and 28d strength are shown in Table 1.

For ease of analysis and discussion, the concrete specimens used in this test are numbered as shown in Table 2.

Table 1. Concrete mix ratio

| Concrete material dosage / Kg·m⁻³ | Fly ash content /% | Mineral powder content /% | Water to glue ratio | 28d Compression strength /MPa |
|----------------------------------|--------------------|--------------------------|---------------------|-------------------------------|
| Water                            | 170                | 190                      | 75                  | 75                            | 850                          | 980                          | 22                             | 22                             | 0.5                            | 39.6                          |

Table 2. Concrete test piece number

| Specimen grouping                  | Test piece number | Coating type            |
|------------------------------------|-------------------|-------------------------|
| Normal environment                 | A                 | None coating            |
|                                    | B                 | None coating            |
| Freezing and thawing environment   | C                 | Epoxy mortar coating    |
|                                    | D                 | Polyurethane coating    |
|                                    | E                 | Polyurea coating        |

2.3. Test equipment and methods

2.3.1 Freeze-thaw cycle test method. The freeze-thaw test refers to the antifreeze test method in GB/T50082-2009 "Standards for Test Methods for Mechanical Properties and Durability of Conventional Concrete". A concrete specimen of 100 mm × 100 mm × 400 mm was formed according to the mixing ratio of Table 1. After standard curing for 28 days, it was taken out and placed at room temperature for 7 days. Then the concrete was coated with a protective coating according to certain requirements and placed for 7 days. The coated concrete test piece and the uncoated concrete test piece were immersed in water (20 ± 3)°C for 4 days, completely saturated with water, and then subjected to a freeze-thaw test after completion. During the test, the center temperature of Specimen was -14 ~ -18°C, the center temperature during freezing was 6 ~ 8°C, and the time of one freeze-thaw
The sample is fully saturated with water during the freeze-thaw cycle. And this specification states that you can terminate the test by one of the following conditions:
(1) The number of freeze-thaw cycles specified is up to 300 times;
(2) When the relative elastic modulus of the sample dropped to 60%, the relative dynamic elastic modulus is calculated as follows:

\[
P = \frac{f_n^2}{f_0^2} \times 100
\]  

where \(P\) is the relative dynamic elastic modulus (%) of the concrete specimen after \(N\) freeze-thaw cycles, accurate to 0.01; \(f_0\) is the initial value of the transverse fundamental frequency of the concrete specimen before the freeze-thaw cycle experiment (Hz); \(f_n\) is the transverse fundamental frequency (Hz) of the concrete specimen after \(N\) freeze-thaw cycles.

(3) When the mass loss rate of the test piece reaches 5%, the mass loss rate is calculated as follows:

\[
\Delta W = \frac{W_0 - W_n}{W_0}
\]

where \(\Delta W\) is the mass loss rate (%) of the concrete specimen after \(N\) freeze-thaw cycles, accurate to 0.01; \(W_0\) is the quality of concrete specimens before freeze-thaw cycle (g); \(W_n\) is the mass (g) of concrete specimen after \(N\) freeze-thaw cycles.

2.3.2 Mercury intrusion test. In this paper, mercury intrusion method is used to determine the structural parameters of concrete pores. The experiment used the AutoPore9500 automatic mercury intrusion meter produced by McMurray (Shanghai) Instrument Co., Ltd. The mercury intrusion meter can be used to analyze the pore size distribution, total pore volume and total pore area of powder or bulk solid. The pore size ranges from 0.006 to 300 micron. It refers to GB/T 3723-1999 "General Principles for Sampling Safety of Industrial Chemical Products" and GB/T 21650.1-2008 "Gas Pressure Method and Gas Adsorption Method for Determination of Pore Size Distribution and Porosity of Solid Materials".

![Figure 1. Curve of mass loss rate of concrete specimens.](image)

3. Results and discussion

3.1. Effects of protective coating on the mass loss rate of concrete specimens under freezing and thawing environment

The main feature of concrete freeze-thaw damage is surface erosion, which causes the surface to be uneven and the aggregate exposed. The mass loss rate is the most intuitive and reliable method for
characterizing the surface damage of the test piece. This test examined the results of the mass loss rate of concrete specimens coated with different protective coatings after undergoing freeze-thaw cycles, as shown in Figure 1.

It can be seen from Figure 1 that after 150 freeze-thaw cycles, the surface of the test piece of Group B is peeled off, coarse and fine aggregates are exposed severely, so that the mass loss rate of the test piece reaches 7.53%. The mass loss rate of the test piece group C (epoxy mortar coating), D (polyurethane coating), and E (polyurea coating) was negative and greater than -1.5%. This indicates that the protective coating relies on its own film-forming material to form a dense water-repellent paint film on the concrete surface, thereby preventing liquid from entering the interior of the concrete.

As the number of freeze-thaw cycles increases, the mass loss rate of concrete specimens coated with protective coatings shows different degrees of negative growth. Since the micropores appear in the coating after 150 freeze-thaw cycles, the negative growth rate of the mass loss of the D-specimen and the E-specimen gradually increased. As the number of freeze-thaw cycles increases, the internal pores of the test piece begin to rupture, and microcracks occur, resulting in an increase in water absorption, thereby improving the quality of the concrete test piece. The negative growth rate of the mass loss rate of the test specimens of Group C is relatively flat, because the paint film of the epoxy mortar protective coating is more dense and the frost resistance is stronger, and the protective effect on the concrete specimen is better than the other two coatings.

The test results show that the protective coating can effectively resist the intrusion of external liquid and reduce the mass loss rate of concrete specimens. Moreover, the protective performance of epoxy mortar protective coating is superior to polyurea and polyurethane protective coating.

3.2. Effects of protective coating on relative dynamic modulus of concrete specimens under freezing and thawing environment

It can be seen from Figure 2 that as the number of freeze-thaw cycles increases, the relative dynamic elastic modulus of each group of specimens shows a downward trend. The relative dynamic modulus of the specimens of Group B decreased to 56.33% during 150 freeze-thaw cycles, and the downward trend was the steepest. After 300 freeze-thaw cycles, the relative dynamic elastic modulus curves of the C-group samples were gentle, and the relative dynamic elastic modulus decreased by only 3%. At the end of the freeze-thaw cycle, the relative dynamic elastic modulus of the D and E samples was approximately dropped to 60%. The reason is that when freezing and thawing cycles are performed, the temperature is lowered so that the water entering the capillary from the outside freezes, generating a 9% expansion volume, forcing the water in the capillary to seep elsewhere, thereby generating...
internal stress in concrete. When the tensile force exceeds a certain value, it will cause concrete cracks and elastic loss of the concrete specimen. After repeated freeze-thaw cycles, the damage is accumulated and the cracks are continuously enlarged to form large cracks that are connected to each other, resulting in a decrease in the dynamic elastic modulus of the concrete [7].

The results show that all three kinds of the protective coating can enhance the level of antifreeze concrete specimens. The relative dynamic elastic modulus of C, D, and E is 97.29%, 61.41%, 54.27% respectively. The mass loss rate of the three groups of C, D and E specimens was -1.5%, -2.97%, -3.83%. The results show that the frost resistance of concrete improved by three protective coatings was from strong to weak: epoxy mortar > polyurethane > poly.

3.3. Effects of protective coating on internal pore structure of concrete specimen under freezing and thawing environment

The distribution of pore size in concrete pores is used to analyze and evaluate the strength and durability of concrete materials. Zhongwei Wu[8] divided the pores into four grades according to the pore size: harmless pores (pore size < 20 nm), less harmful pores (pore size: 20-50 nm), harmful pores (pore size = 50-200 nm) and more harmful holes (pore size > 200nm). The structure parameters of concrete pores in freeze-thaw environment obtained by mercury intrusion test are shown in Table 3.

| Number | Average aperture/nm | Optimum aperture/nm | Total pore volume/10^2·mL·g⁻¹ | Porosity/% |
|--------|---------------------|---------------------|-------------------------------|------------|
| A      | 24.2                | 27                  | 5.56                          | 13.7589    |
| B      | 36.9                | 66.6                | 7.2                           | 14.5127    |
| C      | 20.4                | 22.8                | 5.46                          | 11.4902    |
| D      | 26.1                | 39.7                | 6.53                          | 14.8053    |
| E      | 26.6                | 49.7                | 7.31                          | 15.7324    |

Figure 3 is a comparison of cumulative mercury influx after coating concrete freeze-thaw.

Figure 3 is a comparison of cumulative mercury influx after the freeze-thaw cycle of each group of concrete specimens. The cumulative mercury inflow reflects the total pore volume inside the concrete. It can be seen from Table 3 and Figure 3 that the total pore volume is increased from 5.56 to 7.2 in Group-B specimens after 150 freeze-thaw cycles compared with Group-A specimens (indoor standard
specimens). This indicates that the interior of the concrete specimen subjected to the freeze-thaw cycle is loose, resulting in an increase in the maximum pore size and total pore volume, thereby reducing the relative dynamic elastic modulus of the concrete. After 300 freeze-thaw cycles, the total pore volume (\(10^{-2}\) mL.g\(^{-1}\)) of the C (epoxy mortar), D (polyurethane) and E (polyurea) samples was 5.46, 6.53, and 7.31 respectively. The performance of the coated concrete is still superior to ordinary concrete after 300 freeze-thaw cycles, which proves that the protective coating improves the frost resistance grade of concrete. It is consistent with the conclusions obtained above.

After the freezing and thawing cycle, compared with the Group-A (indoor standard specimen), the maximum number of pore size, the average pore size and the total pore volume of the Group-D increased by 47%, 7.8% and 17.4%, and the E group (polyurea) increased by 84%, 9.9%, and 31.4%. It indicates that the freeze-thaw cycle has caused different degrees of damage to the internal pore structure of the concrete, and the protective effect of the polyurethane protective coating is better than that of the polyurea protective coating. There was no significant change in the maximum pore size and total pore volume of the Group-C sample (epoxy mortar). The results show that the epoxy mortar protective coating effectively prevents the intrusion of water molecules and reduces the damage of freeze-thaw cycle to concrete inner hole structure.

In this paper, the pore size distribution of concrete under freeze-thaw environment is obtained by mercury injection experiment, as shown in Table 4.

| Number | Aperture distribution range/\% |
|--------|-----------------------------|
|        | < 20nm | 20-50nm | 50-200nm | > 200nm |
| A      | 46.23  | 23.46   | 12.56    | 17.78   |
| B      | 18.69  | 10.01   | 14.98    | 56.45   |
| C      | 41.61  | 20.83   | 20.03    | 17.55   |
| D      | 32.93  | 21.19   | 12.43    | 33.38   |
| E      | 30.56  | 16.59   | 9.84     | 43.06   |

Figure 4 is a comparison of the amount of mercury in each group of concrete. The amount of mercury in the grade can reflect the pore size distribution of the concrete.
As shown in Table 4 and Figure 4, it is found that the harmless pores and the less harmful pores in the test specimens of Group-A occupy more than 60% of the total pore diameter, and the harmful pores in the specimens of Group-B occupy more than 50% of the total pore diameter. The proportion of harmless and less harmful pores decreased, indicating that the freeze-thaw cycle seriously damaged the internal pore structure of concrete.

After the freeze-thaw cycle, the proportion of harmless and less harmful holes in the concrete specimen coated with protective coatings decreased, which accounted for more than 50% of the total pores, indicating that the protective coating has an effective protection effect on the concrete and improves the frost resistance level of the concrete. Compared with the test piece group A which is not coated with the protective coating, the proportion of harmless pores and less harmful pores is reduced, and the proportion of harmful pores is increased. This indicates that the two concrete protective coatings protect the concrete specimens at an early stage. As the corrosion age increases, the protective coatings and the specimens are separated to different degrees, causing damage to the internal structure of the concrete caused by the freeze-thaw cycle.

4. Conclusions

(1) The rapid freeze-thaw test was carried out on the coated and uncoated concrete respectively. The test results show that the protective coating improves the frost resistance grade of ordinary concrete from F150 to above F300, which can prolong the service life of concrete structure under freezing and thawing environment.

(2) The analysis of the mass loss rate and the relative dynamic elastic modulus test data shows that the protective coating reduces the mass loss rate of the concrete specimen and improves the relative dynamic elastic modulus of the concrete specimen. At the end of the 150th freeze-thaw cycle, the mass loss rate of concrete specimens decreased from 7.53% to below -1.5%, and the relative dynamic elastic modulus increased from 56.33% to over 90%.

(3) Analysis of concrete pore structure parameters and concrete pore size distribution under freezing and thawing environment shows that the protective coating slows down the damage of the internal pore structure of the concrete caused by freezing and thawing cycles, and slows the tendency of the harmless pores in the concrete to transform into harmful pores, thereby improving the frost resistance of the concrete.

(4) Different protective coatings have different effects on the improvement of concrete frost resistance. At the end of the freeze-thaw cycle, the mass loss rate of concrete coated with epoxy mortar, polyurethane and polyurea protective coating were -1.5%, -2.97%, -3.83%, and the relative dynamic elastic modulus were 97.29%, 61.41%, 54.27%. This result indicates that the epoxy mortar coating has the best effect on improving the frost resistance of concrete, and it is viewed as the preferred coating.

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References

[1] Zhang L S, Zhang P, et al. 2010 Engineering Construction 42 1
[2] Liang H, Wang Z Q, et al. 2015 Yangtze River 46 79
[3] Han W, Du K, et al. 2011 People's Yangtze River 42 80
[4] Feng J, Han W, et al. 2012 Journal of Yangtze River Scientific Research Institute 29 (2) 64
[5] Wei T, Liao L W, et al. 2011 Journal of the Yangtze River Scientific Academy 28 (10) 175
[6] Liu G R, Liu T, et al. 2011 Journal of Nanjing University of Technology 33 (3) 22
[7] Powers 2016 Journal of American Concrete Institute 16 245
[8] Zhao T J 2004 Characterization parameters in concrete pore analysis. Proceedings of the Symposium on Science and Education for 60 Years, China Institute of Silicate