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Effect of Freezing and Thawing on Chloride Ion Erosion of Fiber Concrete

B D Zhao[1,a] and Z Y Sun[1,b]

[1]School of Architectural and Civil Engineering, Shenyang University, Shenyang, 110044, China

[a]zhaobaidong@163.com; [b]zhiyousun@163.com

Abstract: the frost resistance of ordinary concrete is poor, and concrete is often destroyed in the engineering practice at low temperature. This test takes 1% polypropylene fiber concrete as an example to explore the effect of different mix ratio and different freezing thawing times on the diffusion of chloride ion. After repeated freezing and thawing, concrete members will be subjected to structural damage that can not be ignored. As the number of freeze-thaw increases, concrete shows a gradual increase in the mass loss rate and a relative decrease in relative dynamic elastic modulus. Whether or not the freeze-thaw cycle is applied, the chloride penetration of concrete increases with the increase of water cement ratio. In the freezing-thawing environment, the chloride diffusion of concrete increases rapidly with the increase of freeze-thaw times, finally, the least square method is used to fit the second law of Fick, and the mathematical solution of the new equation of chloride diffusion in concrete is obtained.

1. Introduction

In cold regions or winter climatic conditions, concrete undergoes freeze-thaw damage, causing internal micro-cracks and surface flaking; chloride ions in the environment invade the concrete and cause steel corrosion. For example, chloride ions in seawater in coastal areas and chloride ions introduced when concrete bridge decks are sprinkled with ice salts. The combination of the two ultimately leads to the destruction of the concrete structure, which is one of the reasons why many reinforced concrete structures fail prematurely before they have reached the design life.

Xie Youjun[1] et al. used the fast freezing method to explore the frost resistance of ordinary concrete in different solutions. The results showed that different concretes had different frost resistance in different solutions, and the frost resistance of concrete was affected by the chemical corrosion resistance of the concrete salt solution. Yang Wenwu[2] et al. conducted a comparison of the experimental and evaluation methods for frost resistance and atmospheric ion diffusion of concrete in the marine environment. Based on an analysis of the comparison of concrete frost resistance and ambient ion diffusion experiments and evaluation methods. The suitable experimental method for studying the frost resistance and diffusion of marine concrete was found.By simulating the severe climate environment of winter and night temperature difference during winter construction in severe cold area, Li Jianguo[3] et al. adopted the chloride diffusion coefficient as a token of the loss degree of concrete after the frost damage, and analyzed the structure development after the concrete early experience of freezing thawing cycle with different water cement ratio, thus enriching the increasingly perfect winter. Sun Congtao and Niu Yutao[4] et al. studied the chloride ion diffusion performance of fly ash concrete under ocean underwater zone, ocean tide zone, ocean atmosphere zone and freeze-thaw conditions, established a chloride ion diffusion model in fly ash concrete, and predicted the life of concrete structures under chloride ion erosion. The anti-salting performance and anti-salt freezing quantitative design of fly ash concrete were studied by experiments. Zhao Baidong and Xu Tiancheng[5], et al., by testing the chloride ion flux of self-compacting concrete with various fiber contents, it is concluded that the six-hour total electric flux of self-compacting concrete with various reference strengths is related to its fiber content. With the increase of fiber content, the six-hour total electric flux decreased first and then increased.

Based on the present study, this experiment mainly explores the effect of different water to cement ratio on the diffusion of chlorine ions in different freeze-thaw cycles, and then using the least square method to fit the second law of Fick, the mathematical solution of the new equation of chloride ion diffusion in concrete is obtained.

2. Test materials and methods

2.1. Test materials and model preparation

The water used in this experiment is drinking water for the residents of Shenyang city. The cement is a common portland cement marked 325#, with a density of 3.12g/cm3; the gravel size is 8-17mm, and its performance index is detailed in Table 1. The sand is made of medium coarse river sand in Shenyang. The fineness modulus is 2.95, and its performance is in line with the requirements of "GBT14684-2011 building sand". The fiber is made of polypropylene fiber. Polypropylene fiber has the advantages of light weight and improved durability of concrete. It is a synthetic fiber with a low elastic modulus. According to the specification[6], the concrete block made by this test is 100mm×100mm×400mm cuboid test block. Before the test block preparation, the test should check whether the materials meet the test standard, whether the cement is hydrated and whether the aggregate diameter is up to standard. The strength of the ordinary concrete is designed to be C30.

Table 1. Main performance index of crushed stone.

Density (kg/m^3)	Crushed value (%)	Absorption (%)	Sulfide and sulfate content (%)	Mud content (%)	Mud block content (%)
2600	16	0.04	0.3	0.35	0.27

2.2. *Polypropylene fiber additive*

Fiber reinforced concrete has attracted the attention of scholars and engineering circles due to its advantages such as good crack resistance, corrosion resistance, strong erosion resistance and good frost resistance. The damage of concrete is generally manifested as the emergence and development of cracks. Adding fiber in concrete can effectively inhibit the diffusion of cracks and improve the long-term performance of concrete structures. Many scholars at home and abroad have been relatively mature in the research of polypropylene fiber reinforced concrete. It is considered that the concrete with 0.5%-1.2% fiber parameters has better frost resistance. The design of this mix ratio is based on 1% fiber content. The fiber is made of polypropylene fiber. Polypropylene fiber has the advantages of light weight and improved durability of concrete. It is a synthetic fiber with a low elastic modulus. The basic parameters of polypropylene fiber are shown in Table 2.

Table 2. Performance parameters of fiber.

Name	Diameter /μm	Length /mm	Tensile strength /MPa	Elastic modulus /GPa	Density /(g/cm^3)
Polypropylene fiber	30	10	276	3.8	0.91

2.3. *Mix ratio design*

Many evaluation indexes of concrete are related to the water cement ratio. Whether the design of water cement ratio is reasonable or not will directly affect the quality of the test results. It should be verified in a strict sense in accordance with the steps of mix proportion design. Under the same conditions of production and standard curing, the lower the water cement ratio, the higher the strength of the specimen, the higher the density and the less the pore. When cement is hydrated, the water cement ratio has a direct effect on the porosity of hardened cement paste, and porosity affects the pore volume of concrete. The pore diameter of the concrete is expanded and connected to each other, and the reduction of the number of candidate holes leads to a reduction in the effect of relieving the heaving pressure, which causes a higher expansion pressure after freezing, which increases the volume of the pores. The quality of the aggregate mixture of 1m^3 concrete is 2450kg, as shown in Table 3. According to the concrete mix design steps, the final design and determination of concrete water cement ratio are three kinds, namely, W/C=0.40,0.45,0.50 three grades.

Table 3. Mix ratio of fiber concrete with different water/cement ratio.

Concrete number	Water cement ratio	Water	Cement	Stone	Sand	Polypropylene fiber	Collapsing degree /mm
						Unit: kg/m^3	
W_1	0.4	172	430	909	914.5	24.5	153
W_2	0.45	175	388.9	914	947.6	24.5	165
W_3	0.5	178	356	918	973.5	24.5	180

3. Freeze-thaw test and analysis

The two freeze-thaw test methods used in the experiment are quick freezing and thawing methods. This test adopts a rapid water freeze-thaw test. The freeze-thaw temperature was -20℃-20℃, and freeze-thaw time is two hours apart for one hour. The test instruments used include JCD freezing and thawing machine, TM- II dynamic instrument, electronic scale and so on. The number of freezing and thawing cycles on the whole is 200 times, and measuring the lateral frequency fm of the test piece after every 50 intervals, and the lateral fundamental frequency is measured by the dynamic elastic measuring instrument. Before the test, the surface scum was removed and the clear water was kept, and then the weight of the specimen is weighed. After testing, adjust the direction of the test block in the original test box and continue the experiment. In appearance, the external surface of concrete is mainly manifested in the reduction of the mass and the decrease of the dynamic elastic modulus, while in the mechanical properties, the compressive strength and the flexural strength are gradually attenuated. In the process of freezing and thawing test, the performance of the block can be changed in many aspects. Therefore, the following cases occur in the test process, which can end the test: the number of freezing and thawing cycle reaches the set value; the relative dynamic elastic modulus of the specimen falls to 0.6; the quality of the specimen is lower than the initial value of 95%. The test instrument and process are shown in Figure 1 and the relative elastic modulus and mass loss rate curves of this test are shown in Figure 2 and Figure 3 respectively.

In order to ensure that the whole test block is immersed in the water, the experimental treatment of 3mm of water immersion concrete was taken before the freezing and thawing test to isolate the effect of air factors on the freezing and thawing test.

Figure a.

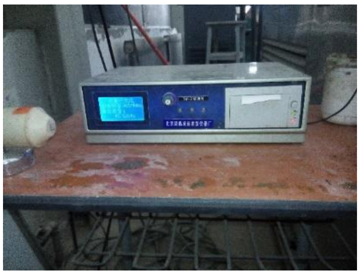

Figure b.

Figure c.

Figure d.

Figure 1. Freeze-Thaw test

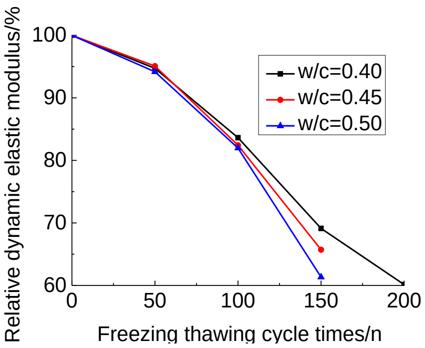

Figure 2. The relative dynamic modulus of elasticity of concrete under different mixing ratios.

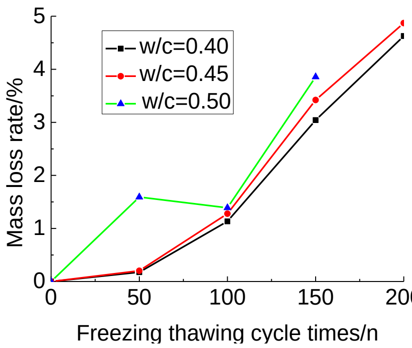

Figure 3. The quality loss rate of concrete under different mix ratios.

According to Figure 1 and Figure 2, the relative elastic modulus of concrete decreases with the increase of freeze-thaw cycles. When the freezing and thawing times are less than 100 times, the damage of concrete is not obvious, and the difference between the curves of different mix ratio is little. The possible reason is that the internal aggregate of concrete is interacted to resist the freezing and thawing. When the number of freezing and thawing times is more than 100 times, the relative dynamic elastic modulus of concrete drops faster, when the water ash is larger, the freeze-thaw resistance of concrete is relatively weak, and the relative dynamic elastic modulus of concrete with water cement ratio of 0.5 is less than 60%. The possible reason is that the number of freezing thawing times is too much, and the concrete has lost its strength.

According to Figure 1 and Figure 3, the mass loss rate has some defects as an index of freeze-thaw resistance. The quality of concrete with different mix proportioning has increased characteristics during freeze-thaw cycles. This is mainly due to a large number of micro cracks in the concrete, and the micro cracks absorb water saturated during freeze-thaw cycles. When the number of freeze-thaw cycles is low, the weight loss of concrete surface is smaller, and the quality of the specimen increases after freezing and thawing. Because of the higher density of the other test parts, the quality of the water quality in the immersed specimen is less than that of the test piece, so the quality of the specimen after the freezing and thawing cycle is heavier than that before the freeze-thaw cycle.

4. Chloride ion diffusion equation

The diffusion coefficient is the physical quantity describing the diffusion velocity. It is equal to the mass or particle number of $1m^2$ area in 1s when the concentration gradient is 1. The greater the the chloride diffusivity, the faster the diffusion rate. The chloride diffusivity (D) in concrete is an important index reflecting the durability of concrete structure to resist chloride ion. At present, the methods of detecting chloride diffusivity in concrete include natural immersion method, electromigration method and salt saturation conductivity method.

At present, most scholars study the diffusion of chloride ions based on the most commonly used chloride diffusion equation, that is, one dimensional diffusion equation derived from the second law of Fick is:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

Formula: t is time, x is distance from concrete surface, d is chloride ion diffusion coefficient, c is chlorine ion concentration from concrete surface x.

The mathematical equation is:

$$c_x = \left(c_s - c_0\right)\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] + c_0 \tag{2}$$

The chlorine ion concentration on the surface x of the concrete surface of the cx-t time, the chloride ion concentration at the cs-c0, the initial concentration of chloride ions in the concrete material, the D for the chloride ion diffusion coefficient and the erf(g) as the error function.

The equation (1) is simplified when the material is not composed of chlorine ions in the selection of concrete:

$$c_x = c_s\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{3}$$

At present, most studies have taken chlorine ions into the steel surface as the mark of the end of the durability life of chloride ion erosion of concrete structure, and the scholar Ma Yali[7] use formula (4) to calculate the durability of the concrete structure under chloride ion erosion environment:

$$T = \frac{X^2}{4D}\left[erf^{-1}\left(1 - \frac{c_{cr}}{c_s}\right)\right] \tag{4}$$

Type: x means the thickness of reinforced concrete protective layer; cs is the critical concentration of chloride ion.

Mangat[8] et al in the chloride diffusion equation, the relationship between chloride diffusion coefficient and time is considered:

$$D = D_i t^{-m} \tag{5}$$

In the formula: Di is the effective chloride ion diffusion coefficient when the time equals 1s; m is the empirical constant.

In-band(1), the diffusion equation considering the time dependence of chloride ion diffusion coefficient is obtained:

$$\frac{\partial c}{\partial t} = D_i t^{-m} \frac{\partial^2 c}{\partial x^2} \tag{6}$$

The mathematical solution is:

$$C_f = C_s \left[1 - erfx \left(2\sqrt{\frac{D_i}{1-m} t^{1-m}} \right)^{-1} \right] \tag{7}$$

t time away from the concrete surface of the total chlorine ion concentration of ct, free chloride ion concentration of cf, combined with the concentration of chloride ions cb, then the concrete chloride binding capacity r is defined as:

$$R = \frac{c_b}{c_f} = \frac{c_t - c_f}{c_f} \tag{8}$$

The chloride ion diffusion coefficient of concrete when t0 is the D0,t time when the chloride ion diffusion coefficient of concrete is D, the relationship between chloride diffusion coefficient and time of concrete is:

$$D_t = D_0 \left(\frac{t_0}{t} \right)^m \tag{9}$$

The effect of chloride ions on concrete diffusion is accelerated by the micro-cracks inside the concrete during the use, and the equivalent diffusion coefficient De can be expressed as:

$$D_e = KD_t \tag{10}$$

In the formula: K is the deterioration effect coefficient of chloride ion diffusion property of concrete.

The time dependence of chloride ion diffusion coefficient and the new diffusion equation of chloride ions affected by structural defects are as follows:

$$\frac{\partial c_f}{\partial t} = \frac{KD_0 t_0^m}{1+R} t^{-m} \frac{\partial^2 c_f}{\partial x^2} \tag{11}$$

Using the same initial conditions and boundary conditions as the (2) type, with the aid of mangat[9], the formula (7) can be used to obtain the most basic mathematical solution of the new diffusion equation of chloride ion in concrete:

$$c_f = c_0 + \left(c_s - c_0\right) \left[1 - erfx \left(2\sqrt{\frac{KD_0 t_0^m}{\left(1+R\right)\left(1-m\right)} t^{1-m}} \right)^{-1} \right] \tag{12}$$

5. Chlorine ion concentration test

The study of the durability of reinforced concrete began in the 20s of last century. The most representative durability problem is corrosion of steel bar, and the corrosion of chlorine salt is the main cause of corrosion of steel bar, and the long-term effect will affect the safety of the structure. Therefore, it is necessary to study the chloride penetration resistance of concrete, which provides a theoretical basis for preventing chloride ion erosion.

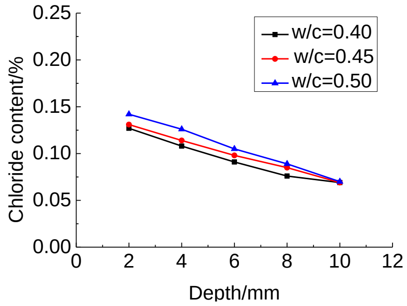

Figure 4. Chloride ion intrusion of concrete before freezing and thawing.

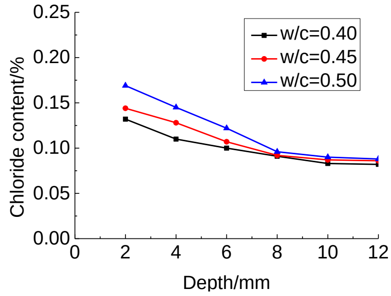

Figure 5. The penetration of chlorine ions in frozen-thawing 50 times concrete.

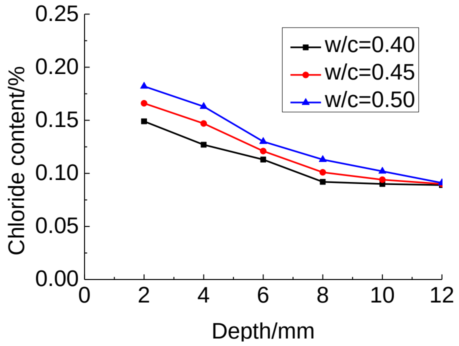

Figure 6. The penetration of chlorine ions in frozen-thawing 150 times concrete.

As shown in Figure 4, 5 and 6, the chloride penetration of concrete increases with the increase of water cement ratio, no matter whether it is freeze-thaw cycle or not. The reasons are that, on the one hand, the water cement ratio increases the internal porosity of concrete, and the diffusion of chlorine ions to the concrete is faster. On the other hand, the greater the water cement ratio, the more freeze-water content in concrete, the worse the frost resistance, and further increase the chloride ion penetration rate after the damage to the concrete surface. With the increase of the same water cement ratio, the early internal structure gradually developed, the internal porosity decreased gradually, and the chloride diffusion coefficient decreased, indicating that the increase of the pre feeding age was helpful to the formation and development of the internal structure of concrete, the development of concrete strength and the test of different water cement ratio. The greater the ratio of water to cement, the greater the diffusion coefficient of chloride ion, which shows that the concrete with large water cement ratio is relatively large, and the structure development is relatively slow because of the more water and water cement ratio. Therefore, the strength of the concrete with low water cement ratio is better than that of the concrete.

The chloride ion content of concrete after freezing and thawing cycle is obviously increased compared with the results of the chloride ion intrusion in the unthawing test block. The chloride ion mass fraction of the surface of the concrete with water cement ratio 0.45 is 0.142%, the freezing and thawing 50 times is 0.153%, and the freezing thawing increases to 0.176% when the freeze-thaw is 150 times. Freeze-thaw cycles cause cracks in concrete and accelerate chloride ion erosion. The more cycles, the more serious chloride ions attack.

6. Conclusion

(1) After repeated freezing and thawing, the concrete members will be damaged by the structure which can not be neglected, and with the increase of freezing and thawing times, the quality loss rate of concrete is improved gradually and the relative dynamic modulus of elasticity decreases gradually

with the allowable parameter range of the test.
(2) The chloride diffusion coefficient in concrete is positively correlated with the ratio of water to water cement in different specimens. The chlorine ion intrusion of concrete increases with the increase of the ratio of water to ash, which indicates that the concrete specimens with high water/cement ratio have high moisture content, so the internal porosity is relatively high, and the internal structure changes relatively slowly.
(3) In freezing-thawing environment, the diffusion of chloride ions in concrete increases rapidly with the increase of freeze-thaw times, finally, the least squares method is used to fit the second law of Fick, and the mathematical solution of the new equation of chloride ion diffusion in concrete is obtained. The mathematical solution can better reflect the actual situation of the prediction of the durability life of chloride ions.

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