Time Dependent Chloride Diffusion Coefficient in Concrete in Cold Regions

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Abstract. Chloride and freeze-thaw cycles are two main factors which cause deterioration of reinforced concrete (RC) structure in the cold regions. In this paper, the process of chloride ingress into concrete exposed to freeze-thaw cycles is experimentally researched. From the experimental results, it appears that freeze-thaw cycles make the effective diffusion coefficient become bigger. Based on the experimental data, the concept of developing coefficient was defined to obtain the evolution equation of effective diffusion coefficient. Together with considering the effect of aging of concrete on effective diffusion coefficient, the time dependent diffusion coefficient of concrete in cold regions was obtained.

1 Introduction

In cold regions, freeze-thaw attack is one of the main factors which influence durability of RC structures [1]. Meanwhile the chloride, from deicing agent or sea water (for marine and offshore structures), ingress into concrete makes RC structures deteriorate more severely, not only to generate more micro cracks in concrete but also to accelerate the corrosion of the reinforcing steel [2-4]. The combined effects of freeze-thaw cycle and chloride ingress increase the complexity of the durability design and prediction of RC structures located in the seacoast of northern cold region or where deicing salts are used [5-7]. So the research of chloride ingress model of concrete under freeze-thaw cycle is very important for RC structures in cold regions.

There are many papers about chloride penetration into concrete in common climate, but only a few researches about chloride ingress into concrete while suffering freeze-thaw cycles [8-12]. For these few researchers, they mainly focus on comparing the penetration resistance of different type of concrete, but not the prediction method or model of chloride ingress into concrete, which is more significant for durability design such as predicting the time of pitting corrosion of reinforcing steel. However, for the model of chloride ingress into concrete under freeze-thaw cycles, the time dependent diffusion coefficient is the key problem. Only when the time dependent diffusion coefficient is obtained, the model of chloride ingress into concrete under freeze-thaw cycles can be established together with Fick's second law.

2 Experimental methods

As the feasibility of rapid chloride permeability test under freeze thaw cycles is not been verified by enough data, the natural diffusion method is chosen to study the chloride ingress process in this paper.

2.1 Specimen preparation

More than 180 concrete specimens (100 mm×100 mm×100mm) were made.The proportions of the various concrete mixes and the major parameters are listed in Table 1.

Table 1 Mix proportions and major parameters of concrete

Serie	Cement (kg/m³	Fly ash (kg/m³	Water reducer	Water (kg/m³)	Coarse aggre	Sand (kg/m³)	Air-entraining

s	³)	³)	(%cement)	gate (kg/m³)		agent
A	338	0	0.3	159	1000	874	
B	338	0	0.3	159	1000	874	0.3% cement
C	271	67.6	0.3	159	1000	874	
D	203	135.2	0.3	159	1000	874	
E	320	0	0.3	189	1000	874	
F	256	64	0.3	189	1000	874	
G	192	128	0.3	189	1000	874	
H	297	0	0.3	199	1000	874	
I	238	59.4	0.3	199	1000	874	
J	178	118.8	0.3	199	1000	874	

2.2 Ponding method

The salt solution was filled in the PVC dikes which were placed on the top surface of the specimens (as shown in Fig. 1).

Fig. 1 Specimens with dikes placed on the top surface

2.2 Salt solution

From the relationship between freezing point and concentration of calcium chloride solution as in Fig. 2, the main concentration of $CaCl_2$ solution was chosen to be 29%.
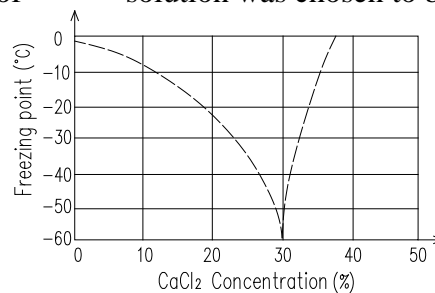

Fig. 2 Relationship between freezing point and concentration of calcium chloride solution

2.3 Freeze-thaw test

After dikes placed on the top surface, the specimens were moved into the freeze-thaw chambers(as shown in Fig. 3), and rapid freezing-thawing was carried out according to ASTM C666[13].

Fig. 3 Specimens being frozen

2.4 Chloride profiles

After some freeze-thaw cycles, samples from incremental depths were taken by sawing slices and analyzed for chloride concentration, as shown in Fig. 4.

Fig. 4 Specimen after freeze-thaw cycles and sawing slices

3　Results and Discussion

3.1 Experimental *De*

From the experiment, the effective diffusion coefficient (De) of each specimen was obtained. Also, the relationship between De and freeze thaw cycles for each type concrete was obtained, as shown in Fig. 6.
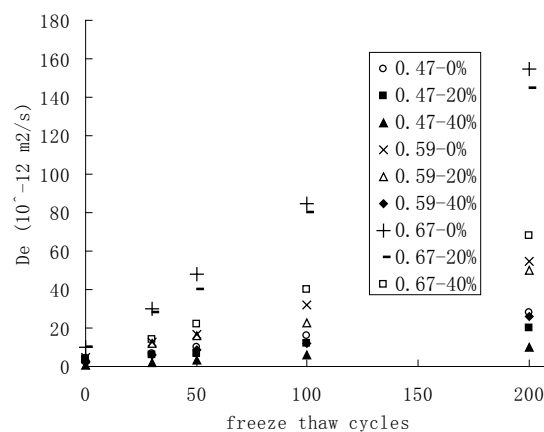

Fig. 5 Relationship between De and freeze thaw cycles for different type of concrete

3.2 Model building of chloride ingress into concrete under freeze thaw cycles

3.2.1　Developing coefficient and evolution equation of De

In order to research the process of chloride ingress into concrete under freeze thaw cycles, the relationship between De and freeze thaw cycles should be obtained first. For this purpose, in this paper, the concept of developing coefficient of De (designated as Kd) is defined. From Fig. 6, it's apparent that for each type of concrete, De increases as freeze thaw cycles increasing. So, the increment of De in one freeze-thaw cycle can be defined as the developing coefficient of De, which can be expressed as following equation:

$$K_{d(N)} = De_{(N+1)} - De_{(N)} \tag{1}$$

Therefore, the evolution equation for De can be derived:

$$De_{(N)} = De_0 + \sum_{i=1}^{N} K_{d(i)}$$
(2)

Where, $De_{(N)}$ is the effective diffusion coefficient of concrete after a certain number (N) of freeze-thaw cycles, N is the number of freeze-thaw cycles, De_0 is the initial effective diffusion coefficient.

From the experimental data in Fig. 6, we can find that De increases approximately linearly as freeze thaw cycles increasing. So, it's reasonable to use the approach of linear regression on De and freeze-thaw cycles to obtain the average developing coefficient (K_{da}).The linear regression analysis results for average developing coefficient are shown in Table 2.

4 K_{da} values of different type of concrete

ratio Fly ash \ W/C	0.47	0.59	0.67
0%	1.13E-13	2.43E-13	7.18E-13
20%	7.30E-14	2.04E-13	6.65E-13
40%	4.20E-14	1.15E-13	3.09E-13
0%（air-entrained）	9.62E-14		

From the data in Table 2, it's apparent that the values of K_{da} increase with increasing W/C ratio and decreasing fly ash content. It means that increasing W/C ratio and decreasing fly ash content can accelerate the degradation process of concrete under freeze-thaw cycles. Also, from comparing K_{da} values of specimens with and without air-entrainment, it is found that the air entrainment can improve the frost resistance of concrete.

So, with the average developing coefficient (K_{da}) instead of developing coefficient ($K_{d(i)}$) in formula(2), the following equation can be easily derived:

$$De_{(N)} = De_0 + K_{da} \times N$$
(3)

While formula (3) is used to predict De of concrete in practical engineering, the number of natural freeze thaw cycles should be equivalently transformed to the number of rapid freeze thaw cycles in laboratory first. And then, the relationship between time t and N should be established. Finally, the evolution equation can be derived:

$$De_{(t)} = De_0 + K_{da} \times N_{(t)}$$
(4)

Formula (4) is simplified evolution equation for De of concrete under freeze-thaw cycles, which can be used in practical engineering.

3.2.2 The effect of ageing of concrete on De

Observations at structures suggest that diffusion coefficient of concrete is not a constant value over time due to a gradually increasing degree of hydration[14]. Consideration must be given to the ability of the cementitious system to refine its pore structure as it matures, thereby decreasing transport rates. Due to continued hydration of cement, the porosity is reduced, which results in a reduced diffusion coefficient. Based on many years of research at concrete exposed to an outdoor climate, an equation including the effect of ageing of concrete on diffusion coefficient is given [15-17]:

$$D(t) = D_0 t^{-n}$$
(5)

Where, $D(t)$ is time-dependent diffusion coefficient, D_0 is initial diffusion coefficient, t is time (year), n is ageing parameter.

3.2.3 Time dependent De of concrete in cold regions

For concrete in cold regions, both freeze thaw cycles and ageing effect should be considered on De. So, in this paper, the time dependent model of De is assumed as follows:

$$De_{(t)} = (De_0 + K_{da}N_{(t)}) \times (\frac{1}{t})^n \tag{6}$$

Where, $De_{(t)}$ is time dependent effective diffusion coefficient, N is the number of freeze-thaw cycles, De_0 is the initial effective diffusion coefficient, K_{da} is developing coefficient, $N_{(t)}$ is equivalent number of freeze thaw cycles, t is time (year), n is ageing parameter.

With the time dependent model of De and Fick's second law, the model of chloride ingress into concrete in cold regions can be established.

4 Conclusions

In this paper, the experiment of specimens suffered both freeze-thaw cycles and chloride ingress were carried out. From the experimental results, it's apparent that after freeze-thaw cycles, the effective diffusion coefficient will increase. As w/c ratio increasing and fly ash content decreasing, effective diffusion coefficient increases. Based on the experimental data, the concept of developing coefficient was defined to obtain the evolution equation of effective diffusion coefficient. Together with considering the effect of aging of concrete on effective diffusion coefficient, the time dependent diffusion coefficient of concrete in cold regions was obtained.

Acknowledgements

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