Prediction model for carbonation depth of concrete subjected to freezing-thawing cycles

QianHui Xiao*, Qiang Li, Xiao Guan, YingXian Zou

Institute of Architecture and Civil Engineering, Xi’an University of Science and Technology, Xi’an 710054, China

*Corresponding author e-mail: xiaohui_99@126.com

Abstract: Through the indoor simulation test of the concrete durability under the coupling effect of freezing-thawing and carbonation, the variation regularity of concrete neutralization depth under freezing-thawing and carbonation was obtained. Based on concrete carbonation mechanism, the relationship between the air diffusion coefficient and porosity in concrete was analyzed and the calculation method of porosity in Portland cement concrete and fly ash cement concrete was investigated, considering the influence of the freezing-thawing damage on the concrete diffusion coefficient. Finally, a prediction model of carbonation depth of concrete under freezing-thawing circumstance was established. The results obtained using this prediction model agreed well with the experimental test results, and provided a theoretical reference and basis for the concrete durability analysis under multi-factor environments.

1. Introduction

In general atmospheric environment, the concrete carbonation is the main factor for the corrosion of reinforcement, the degradation of structural performance and durability deterioration. Theoretical research and engineering investigation revealed that the concrete carbonation is closely related to the steel corrosion initiation condition and corrosion speed (rate). The environmental factor can be cited as the primary factor affecting the concrete carbonation, among many others factors, and therefore it requires that researches on concrete carbonation model should not be established based on only an specific environmental condition. In recent years, researches on the carbonation of concrete structures in marine environment have been carried out[1-9], however, research on concrete carbonation in cold environment in the North area is still limited[10-12]. Therefore, it seems very necessary to establish the numerical model of the concrete carbonation depth under the combine action of freezing-thawing cycles and carbonation, which has a great significance for predicting the corrosion initiation time of the reinforcing bar as well as the prediction of concrete structure’s life. Based on concrete carbonation mechanism and the concrete porosity investigations, this paper analyzed the variation regularity of concrete carbonation depth under the combine action of freezing-thawing cycles and carbonation, and established the prediction model of the carbonation depth of concrete under freezing-thawing environment.
2. Experimental investigation

2.1. Material and mixture ratio
The ordinary PO42.5R Portland cement with 3.4% of fineness (80μm square hole screen sieve), produce by Shaanxi Qinling Cement General Factory is used with the Class II fly ash with 18% of fineness (45μm square hole sieve screening) produce by Weihe Power Plant. The fine aggregates used are the Xi'an Pa River sand. The coarse aggregates are the limestone hammer crushed stone (diameter: 5~20mm) from Yangyang Town in Shaanxi province; while the air-entraining agent used is the SJ-3 type high performance air-entraining agent developed in Tongji University with natural wild plant soap as the main original material, and the tap water is used for the mixture.
After pouring, the concrete was cured for 24 hours and then moved to a standard curing room (temperature: 20 ± 1 °C; humidity: more than 95%) for 30 days, and then naturally cured until a predetermined age of 90 days.

Table 1. Mixture ratio per m³ of concrete for the standard specimen C2

| Water - cement ratio | Cement/kg | Fly ash/kg | Sand/kg | Stone/kg | Water/kg |
|----------------------|-----------|------------|---------|----------|----------|
| 0.45                 | 280       | 120        | 637     | 1183     | 180      |

2.2. Experimental test design

Table 2. Test specimens grouping for the carbonation and freezing-thawing combined action test

| No  | Water - cement ratio | Fly ash amount | Air content (%) | Number of specimens | Number of test pieces | Curing time (day) |
|-----|----------------------|----------------|-----------------|---------------------|-----------------------|-------------------|
| C1  | 0.35                 |                | 3.7             | 3+3                 | 24                    |                   |
| C3  | 0.45                 | 30%            | 4.4             | 3+3                 | 24                    | 90                |
| C4  | 0.55                 |                | 4.5             | 3+3                 | 24                    |                   |

2.3. Experimental method
The freezing-thawing and carbonation test were conducted according to the Standard "Test Methods of Long-term Performance and Durability of Ordinary Concrete" (GB/T50082-2009)[13], and the sample size of 100 mm × 100 mm × 400 mm. The specific test steps are as follows:
(1) The specimens are produced in accordance with the designed concrete mixture ratios, and the air content measured before the concrete pouring using the CA-3 type concrete air content tester. 24 hours after the concrete pouring, the specimens were demolded, labeled and put into the curing room for 30 days standard curing period, follow by the natural curing period of 60 days.
(2) Four days before the test, the concrete specimens were immersed in water to obtain the saturated state. Before putting the specimens into the freezing-thawing box, the moisture on the specimen's surfaces was wiped off, and the masses and dynamic elastic modulus were measured.
(3) The specimens are placed into the freezing-thawing box and the freezing-thawing cycles set to 25 time, after which the specimens are inverted in order to reduce the error caused by the difference of temperature between the upper and lower parts of the specimens. After each 25 time freezing-thawing cycles, the specimens surfaces are wiped for the moisture and the mass and dynamic elastic modulus are measured.
(4) The specimens are removed from the free-thaw box, and allowed for air-dry during two days, and then dried in an oven for one day. The specimens are then placed into the carbonation box ensuring 50mm spacing between each the specimens. The carbonation is started when the temperature between the carbonation box is (20 ± 2)°C, the relative humidity is controlled to (70 ± 2)%, and the
CO2 concentration is kept at (20 ± 1)%. After 7 days of carbonation, the specimens are cut out to determine their carbonation depth. The above is the test procedure for a cycle of freezing-thawing and carbonation test; thereafter the above steps were repeated and a total of four cycles were performed.

3. Test results and analysis

3.1. Concrete neutralization test results

Table 3 shows the neutralization depth values measured during the combined action freezing-thawing cycles and carbonation test.

| No | Carbonation time(day) | 7   | 14   | 21   | 28   |
|----|-----------------------|-----|------|------|------|
| C1 |                       | 0.52| 0.79 | 0.94 | 2.74 |
| C3 |                       | 0.89| 1.71 | 2.46 | 4.51 |
| C4 |                       | 3.15| 4.8  | 5.68 | 6.82 |

Under the freezing-thawing cycles and carbonation interaction test mode, the neutralization depth of the concrete with water-cement ratio of 0.35, 0.45 and 0.55 varies with the carbonation time as shown in Figure 1.

![Fig.1. Concrete carbonation depth variation regularity with carbonation time for different water-cement ratios](image)

As illustrated in the figure, it can be seen that the carbonation depth of concrete specimens with less water - cement ratio is obviously smaller than that of concrete with large water - cement ratio.

4. Establishment of the prediction model of the concrete carbonation depth under freezing-thawing circumstance

4.1. Basis of the model establishment

The carbonation of concrete is the process in which the carbon dioxide in the environment diffuses into the concrete and reacts with the carbonizable substances in the concrete. During the freezing-thawing damage process, the concrete is actually an hydration element changing to dense to friable state, and the freezing-thawing cycles can cause changes in the concrete porosity, but the composition of the hydration element remained basically unchanged. Also, the change of concrete porosity will affect the diffusion of carbon dioxide in the concrete, thus affecting the carbonation rate of concrete.

Based on the concrete carbonation mechanism, the relationship between the gas diffusion coefficient and porosity in concrete is analyzed, to investigate the calculation method of the porosity in Portland cement concrete and fly ash cement concrete, considering the effect of freezing-thawing
damage on concrete diffusion coefficient. Finally, the prediction model of carbonation depth of concrete under freezing-thawing conditions is established.

4.2. Theoretical model of concrete carbonation

Based on Fick's first law of diffusion and the diffusion and absorption of carbon dioxide in porous materials[6], it is assumed that:

1. The diffusion of CO\textsubscript{2} in the concrete pores follows Fick's first law:

\[
N_{CO_2} = D_e \frac{d [CO_2]}{dx}
\]

Wherein: \(N_{CO_2}\) is the CO\textsubscript{2} diffusion rate, mol/(m\textsuperscript{2}s); \(D_e\) is the effective diffusion coefficient of CO\textsubscript{2}, m\textsuperscript{2}/s; \([CO_2]\) is the concentration of CO\textsubscript{2} on concrete surface, mol/m\textsuperscript{3}; \(x\) is the concrete depth, m

2. The CO\textsubscript{2} diffuses from the concrete surface to the interior, and the concentration decreased linearly.

3. Partially carbonized areas are ignored.

From the above assumptions, it follows that during a time \(dt\), the CO\textsubscript{2} diffusing into the concrete from the pores is absorbed by the carbonizable substances within a length \(dx\), and the following equation is obtained.

\[
M_0dx = N_{CO_2}dt
\]

The derivation gives:

\[
x_c = \sqrt{\frac{2 D_e [CO_2]}{M_0}} \sqrt{t}
\]

Where, \(M_0\) is the amount of CO\textsubscript{2} absorbed per unit volume of concrete.

4.3. The concrete carbonation model under freezing-thawing circumstances

According to the equation of state of ideal gas, the relationship between the carbon dioxide concentration and the carbon dioxide molar concentration is:

\[
[CO_2] = \frac{P_{\text{CO}_2} \cdot V}{R \cdot T}
\]

Substituting the above parameters into Equation (3) gives:

\[
[CO_2]_0 = 41.57 \cdot C_0
\]

\(P_{\text{CO}_2}\): Carbon dioxide gas pressure, under atmospheric pressure \(P_{\text{CO}_2} = C_0 \cdot 1\text{atm}\);
\(C_0\): Percent of Carbon Dioxide Concentration,\%;
\(V\): Carbon dioxide gas volume, unit volume of 1m\textsuperscript{3};
\(R\): Ideal gas constant, \(R = 0.0821\text{atm} \cdot \text{L}/(\text{mol} \cdot \text{K})\);
\(T\): Absolute temperature, K.

Based on test data, the calculation model of the carbonation depth of concrete under freezing-thawing circumstances can be derived as follows:

\[
x_f = \sqrt{\frac{0.45C_0(1.25 - RH)^{2.2} \rho_0^{0.08} e^{-0.0033n} \times 10^{-4}}{m_0}} \sqrt{t}
\]

Where: \(x_f\): The concrete carbonation depth under freezing-thawing environment, mm;
\(C_0\): Percentage concentration of carbon dioxide, \%;
\(RH\): Concrete humidity, %
\(\rho_0\): Concrete hole porosity before being freezed;
\(n\): Freezing-thawing cycles;
5. Conclusion

From the prediction model of concrete carbonation depth in freezing-thawing environment, the factors influencing the carbonation of concrete in freezing and thawing environment are almost all included in the calculation model of carbonation depth of concrete. And from the ambient humidity and carbon dioxide concentration it is obvious that, the porosity of concrete communication holes can be obtained through the concrete water absorption, while the amount of fly ash, the amount of cement and cement varieties are all implicitly included in the parameter \( m_0 \). Furthermore, based on the equation of concrete carbonation model in freezing-thawing, it can be observed that porosity is a function of initial porosity and freezing-thawing cycles, since the freezing-thawing cycles would increase the concrete porosity. After the carbonation reaction, the internal porosity of the concrete will be clogged to a certain degree, so the concrete porosity will decrease. However, at the same time, the calcium hydroxide solution dissolved in the pores will be dissipated by the reaction and will continue to dissolve out from the cement matrix. Part of the gel is also consumed by the carbonation reaction. In other words, these carbonizable substances are continuously dissolved and consumed from the matrix, and thereby generate new pores. Therefore, the concrete porosity will increase with the increase of freezing-thawing cycles and the carbonization time. From the above, it can be stated that the carbonation model of concrete under freezing-thawing circumstances presented in this paper is scientifically reasonable.

Acknowledgments

The authors acknowledge the support and assistance from the former master students at Xi’an University of Science and Technology during the experiments and calculations. This project is financially supported by the National Natural Science Foundation of the People's Republic of China under the grant No.51508461, and the National Natural Science Foundation of China under the grant No.51408483.

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