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Research Article

Experimental Investigation of Neutralisation of Concrete with Fly Ash as Fine Aggregate in Freeze-Thaw Environment

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To study the durability of concrete with fly ash as fine aggregate under alternate freeze-thaw and carbonation, freeze-thaw and carbonation cyclic tests are conducted to explore variation characteristics such as relative dynamic modulus of elasticity and neutralisation depth. The influence coefficient (λ_C) of carbonation on concrete freeze-thaw damage and the influence coefficient (λ_F) of freeze-thaw on concrete neutralisation are introduced. In addition, scanning electron microscopy is performed to reveal the deterioration mechanism of the alternating effect. Finally, through a regression analysis of test data, the mathematical expression of the composite damage coefficient k_F under alternate freeze-thaw and carbonation is obtained. Based on these findings, a prediction model of the neutralisation depth of concrete is established with number of freeze-thaw cycles and water-cement ratio as parameters. The values calculated through this model and the values measured in the tests are highly correlated. This provides a theoretical reference and basis for the analysis of concrete durability in a multifactor environment.

1. Introduction

Currently, concrete-structure service life prediction has attracted significant attention. It is known that concrete durability is an important consideration in reducing the social cost of new buildings and maintenance of infrastructures [1]. From the perspective of concrete durability, freeze-thaw is a major cost of aging infrastructure that results in concrete deterioration in cold climates. Hence, freeze-thaw is often considered in structural design [2–4]. Meanwhile, concrete neutralisation is closely related to durability, which is a primary cause of steel corrosion [5].

Considerable research has been performed locally and abroad to study concrete in single-factor environments, such as freeze-thaw cycles and carbonation, and significant achievements have been attained. The conclusions and empirical formulas obtained have been widely recognised in academia and extensively applied and verified in practical engineering [2–4, 6–10]. However, in practical engineering, the coexistence of multiple erosion environments or phased superposition of a single factor typically results in the failure of concrete structures. This applies particularly in severely cold areas where freeze-thaw damage, accompanied by the effect of carbonation, is typical [11]. Therefore, in the design of concrete materials, alternate deteriorations caused by multiple factors should be considered. Hitherto, some preliminary and fragmentary studies have been performed to study the combined effect of freeze-thaw and carbonation on ordinary concrete and fly ash concrete [11–15]. Because research into concrete with fly ash as fine aggregate is restricted to the mechanical properties or effect of a single factor [16–20], conclusions of studies under single-factor conditions are limited.

For many years, fly ash was considered as a supplementary cementitious material or a cement replacement material with a proportion of up to 30–40% [21, 22]. As a byproduct of industrial production, the use of fly ash for solving the challenges of sustainable construction has progressed. However, the positive utilisation of fly ash is impossible when it is used as an alternative cementitious material of cement owing to its early delayed strength development [23]. Hence, a method of replacing fine aggregate with fly ash was proposed [24–30]. Because fly ash replaces part of the fine aggregate, part of the fly ash act as a cementitious material to fill pores and increase the compactness, while the remaining produce a volcanic ash effect, which is attributed to the presence of SiO_2 and Al_2O_3. It reacts with calcium hydroxide to form additional calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH), which effectively constitute a compact matrix [31–33]. As such, the early strength of concrete with part of the fine aggregate replaced by fly ash is superior to that of concrete with cement fully replaced by fly ash [26, 28–30].

In this study, the durability cyclic test of concrete under the alternation of carbonation and freeze-thaw is conducted. During the test, the relative dynamic modulus of elasticity and neutralisation depth is measured. The results are compared with the measured results under the single effect and alternating effect. In addition, the prediction model of the neutralisation depth of concrete in a freeze-thaw environment is established, which is significant for evaluating the durability of concrete in cold areas.

2. Materials and Methods

2.1. Raw Materials. The cement used in this study was ordinary Portland cement P.O 42.5R, which was produced by Ningxia Saima Industry Co., Ltd, with the performance indexes presented in Table 1. Class III fly ash used in this study was produced by the Ningxia Xixia Thermal Power Plant, and the physical and chemical properties are presented in Tables 2 and 3, respectively. Continuous-graded crushed stone (5–31.5 mm) collected from the town of Zhenbeibao in Ningxia Province was used as coarse aggregate, and natural medium sand (fineness modulus of 2.71) was collected from Zhenbeibao and used as fine aggregate. Tap water was used to mix the materials, and polycarboxylate superplasticizer was used as a chemical additive.

2.2. Design of Mix Proportion. The water-cement ratios of the three concrete specimens (S1, S2, and S3) are 0.36, 0.42, and 0.48, respectively. Table 4 presents the mix proportions of the specimens. Some fine aggregates are substituted by fly ash with the same volume. The unit dosage of fly ash is calculated according to:

$$M_{\mathrm{FA}} = \frac{M_{\mathrm{s}} \cdot R \cdot \rho_{\mathrm{FA}}}{\rho_{\mathrm{s}}}, \tag{1}$$

where ρ_{S} and ρ_{FA} are the densities of fine aggregate and fly ash, respectively; M_{S} and M_{FA} are the unit consumptions of fine aggregate and fly ash, respectively [33]; R is the substitution rate of fly ash, which is 15% in this test.

2.3. Experimental Protocol. The size of the specimens was 100 mm × 100 mm × 400 mm. After being moulded, the specimens were stored under curing with moulds for 24 h. After the moulds were removed, the specimens were cured for 56 days in a curing room.

In real engineering, concrete often experiences alternate seasons of autumn and winter and alternate seasons of winter and spring. Hence, the tests were implemented in four modes:

(1) Alternative freeze-thaw and carbonation (FC mode): (1) Immerse the specimens in water (20 ± 2°C) for four days before the test such that they become water saturated. Subsequently, remove them, clean the surface water, and measure their dynamic modulus of elasticity. (2) Clean the surface water of the specimens every 25 freeze-thaw cycles and measure their dynamic modulus of elasticity. (3) When the number of cycles reaches 50, remove the specimens and air-dry them for one day. (4) Store the specimens in an oven (60°C) for two days, and subsequently place them in a carbonation chamber to conduct the five-day rapid carbonation test. Finally, remove them to measure their neutralisation depths. This is a complete cyclic process of freeze-thaw and carbonation that will be repeated for six cycles.

(2) Alternative carbonation and freeze-thaw (CF mode): (1) Store the specimens in the oven (60°C) for two days and conduct the five-day rapid carbonation test. Subsequently, remove them to measure their neutralisation depths. (2) Immerse the specimens in water (20 ± 2°C) for four days such that they become water saturated. Subsequently, remove them, clean the surface water, and measure their dynamic modulus of elasticity. (3) Clean the surface water of the specimens every 25 freeze-thaw cycles and measure their dynamic modulus of elasticity. (4) When the number of cycles reaches 50, remove the specimens and air-dry them for one day. This is a complete cyclic process of carbonation and freeze-thaw that will be repeated for six cycles.

(3) Single freeze-thaw (F mode): Clean the surface water of the specimens every 25 freeze-thaw cycles and measure their dynamic modulus of elasticity. The complete cyclic process includes 50 cycles of freeze-thaw that will be repeated for six cycles.

(4) Single carbonation (C mode): Five-day carbonation is a complete cyclic process, and it will be repeated for six cycles. After each five-day carbonation, remove the specimens to measure their neutralisation depths.

Table 5 presents the grouping of the test.

2.4. Experimental Methods

2.4.1. Freeze-Thaw Test. In this study, the cyclic freeze-thaw test was conducted in an accelerated freeze-thaw testing apparatus. Concrete samples were immersed in water

Table 1: P.O 42.5R ordinary cement indexes.

Cement setting time (min)		Rupture strength (MPa)		Compressive strength (MPa)		Fineness (retained in 80 μm) (%)	Ignition loss (%)	MgO (%)	SO_3 (%)
Initial time	Final time	3 d	28 d	3 d	28 d				
113	153	4.7	4.8	23.1	43.6	1.6	1.4	1.54	2.96

Table 2: Chemical composition of Class III fly ash.

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	P_2O_5	Na_2O	K_2O
50.35	29.65	5.85	6.61	1.83	1.72	1.13	0.335	2.11

Table 3: Physical properties of Class III fly ash.

Properties	Fly ash
Fineness (retained in 80 μm) (%)	34.3
Water demanded (%)	97
Loss on ignition (%)	5.7
Density (g/cm^3)	2.058

Table 4: Mixture proportions for a cubic meter of concrete.

Specimen code	Water cement ratio	Water (kg/m^3)	Cement (kg/m^3)	Fly ash (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Superplasticizer (kg/m^3)	Compressive strength (56 d) (MPa)
S1	0.36	185	514	80	569	1003	13.0	53.4
S2	0.42	185	440	85	608	1030	10.5	49.4
S3	0.48	185	385	90	643	1045	7.1	42.1

Table 5: Grouping of the test.

Test mode	Test program			
Freeze-thaw and carbonation (FC)	Freeze-thaw cycle 50 times	60°C, dry for 2 d	Carbonation environment 5 d	6 cycles
Carbonation and freeze-thaw (CF)	Carbonation environment 5 d	Tap water, immerse for 4 d	Freeze-thaw cycle 50 times	
Single freeze-thaw (F)		Freeze-thaw cycle 50 times		
Single carbonation (C)		Carbonation environment 5 d		

(20 ± 2°C) for four days before the test such that the samples become water saturated. The samples were removed from the apparatus, surface water was removed, and their dynamic modulus of elasticity was measured. Subsequently, the samples in the freeze-thaw chamber and the temperature in the concrete centres were controlled between (−18 ± 2)°C and (5 ± 2)°C. Every time the number of freeze-thaw cycles reached 25 or a multiple of 25, we wiped off the surface water of the samples and measured their dynamic modulus of elasticity.

2.4.2. Carbonation Test. A rapid carbonation test was performed. The prepared samples were placed in an oven (interior temperature of 60°C) and dried for 48 h. Subsequently, we sealed the five sides of all samples (not including the tops) with paraffin. Next, we placed the samples into the carbonation chamber; the spaces between them were no less than 50 mm. When the carbonation progressed to 5, 10, 15, 20, 25, and 30 d, we removed the samples to measure their carbonation depths.

2.4.3. Scanning Electron Microscopy. Scanning electron microscopy analysis of S2 samples before the test and after a 30-day carbonation in different test modes was performed using the Quanta 400 FEG scanning electron microscope.

3. Results

3.1. Relative Dynamic Modulus of Elasticity. The relative dynamic modulus of elasticity (RDME) is an important parameter of concrete freeze–thaw damage [34]. To compare the RDME in different modes, the freeze–thaw damage degree (D) is introduced, which is expressed as follows:

$$D(N) = 1 - \frac{E(N)}{E_0}, \tag{2}$$

where $D(N)$ is the damage degree of concrete after N freeze-thaw cycles, $E(N)$ is the RDME of concrete after N freeze-thaw cycles, and E_0 is the initial RDME of concrete.

In FC and F modes, the difference in the degree of freeze-thaw damage is

$$\Delta D_{FC}(N) = D_{FC}(N) - D_F(N). \quad (3)$$

In CF and F modes, the difference in the degree of freeze-thaw damage is

$$\Delta D_{CF}(N) = D_{CF}(N) - D_F(N). \quad (4)$$

The relation between RDME and the number of cycles in the FC mode is presented in Figure 1, and the RDMEs in different modes (water-cement ratio of 0.42) are presented in Figure 2. The changes in the degree of freeze-thaw damage with the number of cycles are presented in Figure 3.

As shown in Figure 1, the RDME of concrete is negatively correlated with the number of cycles. After 300 freeze-thaw cycles, with a water-cement ratio of 0.48, the RDME is the lowest at 0.838. With a water-cement ratio of 0.42, the RDME becomes 0.873; with a water-cement ratio of 0.36, the value is the highest at 0.904. All the RDME values of concrete after 300 freeze-thaw cycles are above 0.6; this suggests that the concrete exhibits better freeze-thaw resistance than ordinary concrete [35].

As shown in Figures 2 and 3, when the number of cycles is less than 300, the freeze-thaw damage in the FC and CF modes is more severe than the damage in the F mode, with the FC mode affecting the freeze-thaw damage to a greater extent than the CF mode. This is because in a freeze-thaw environment, the structure of concrete changes gradually from compact to porous and full of microcracks [36, 37]. In a rapid carbonation environment, permeable CO_2 will interact with $Ca(OH)_2$ in concrete to cause a neutralisation reaction, through which acid salt $CaCO_3$ is generated to fill the internal structural pores and serve as grouting. Hence, the porosity is reduced temporarily [38] and the loss rate of RDME is temporarily relieved. However, this is a vicious cycle. That is, freeze-thaw causes a greater damage effect on concrete than carbonation. With the increase in the water-cement ratio and number of cycles, the extent of the vicious circle becomes increasingly worse. Meanwhile, in terms of structural damage to concrete, during carbonation, permeable CO_2 interacts with $Ca(OH)_2$ in concrete to cause a neutralisation reaction, and the generated $CaCO_3$ can fill the internal pores to temporarily improve the internal porosity and relieve the loss rate of RDME [39]. This suggests that the carbonation reaction can inhibit the expansion of freeze-thaw degradation characteristics.

3.2. Change Law of Neutralisation Depth. To analyse the change law of the neutralisation depth of concrete in a complex environment, the relation between neutralisation depth and time in the FC mode at different water-cement ratios was studied, and the results are shown in Figure 4. The relation between neutralisation depth and time in different test modes is presented in Figure 5. The carbonation rate is controlled by diffusion, and the diffusion coefficient of carbon dioxide in carbonated concrete is a characteristic transport coefficient [40]. Assuming a constant diffusion coefficient for the carbonated layer, the depth of carbonation can be derived from Fick's first law of diffusion [41]:

$$X_c = K\sqrt{t}, \quad (5)$$

where X_c is the depth of carbonation, t is the carbonation time, and K is the carbonation velocity coefficient. Using test data, the carbonation velocity coefficient K of group S2 specimen can be obtained from equation (5), as shown in Figure 6.

As shown in Figure 4, in the coupling test mode of freeze-thaw and carbonation, the neutralisation depth is positively correlated with the water-cement ratio under different strength conditions [30]. As shown in Figures 5 and 6, in the three test modes, the neutralisation depth is

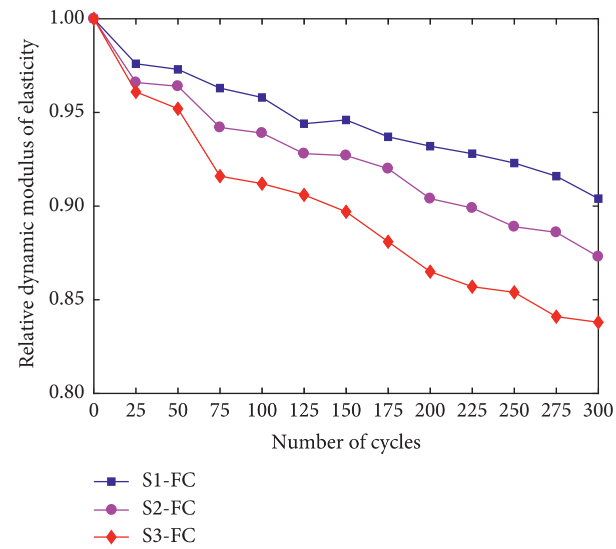


Figure 1: Relative dynamic modulus of elasticity of S1, S2, and S3 in FC mode. S2 in different testing modes.

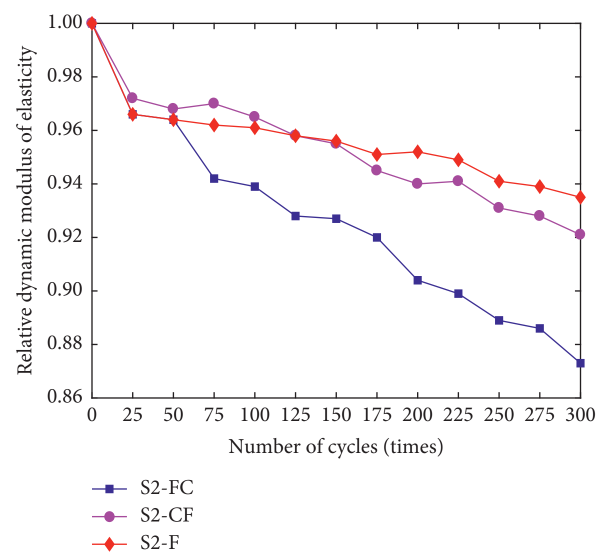


Figure 2: Relative dynamic modulus of elasticity of S2 in different testing modes.

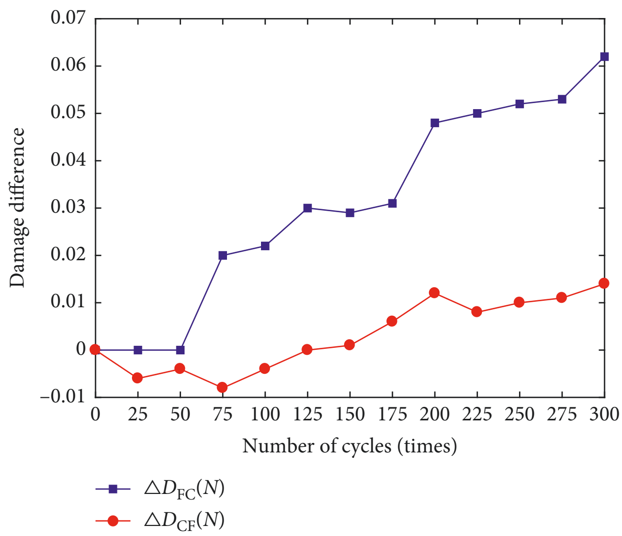


Figure 3: Damage difference of S2 between different testing modes.

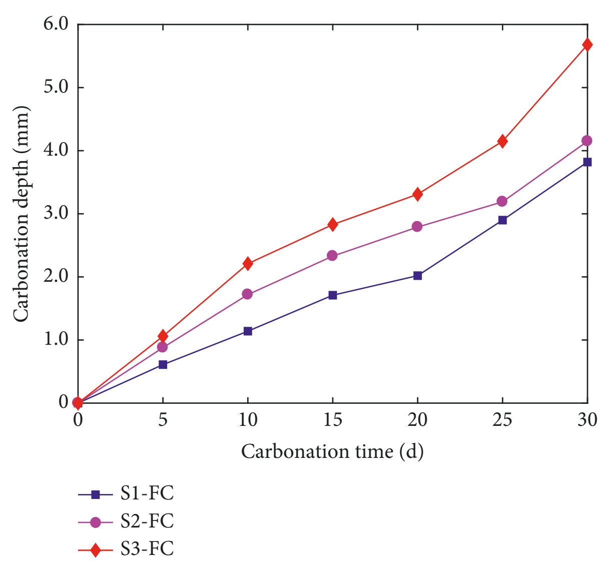


Figure 4: Carbonation depths of S1, S2, and S3 in FC mode.

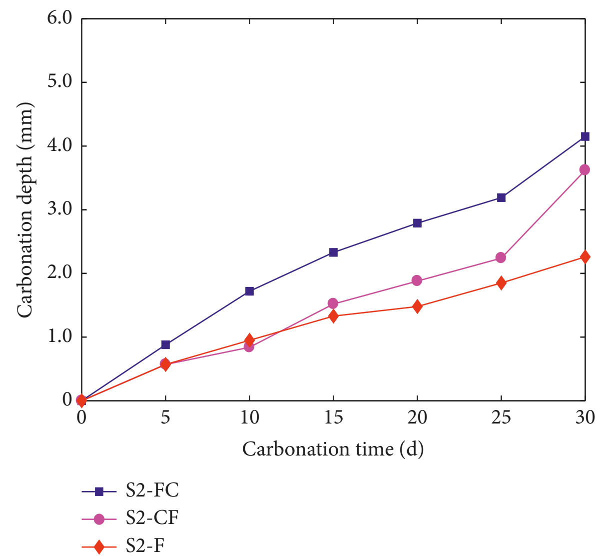


Figure 5: Carbonation depth of S2 in different testing modes.

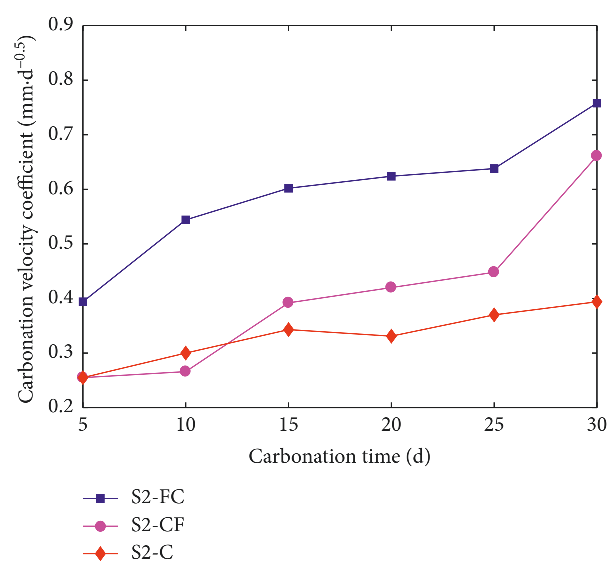


Figure 6: Carbonation velocity coefficient of S2 in different testing modes.

positively correlated with carbonation time, thus implying that the neutralisation depth increases gradually with prolonged carbonation time. At the same carbonation time, the neutralisation depths and carbonation velocity coefficient in both FC and CF modes are greater than that in the C mode. After carbonation for 20 days, the carbonation velocity coefficient of concrete in the C mode is relatively flat compared to those in the FC and CF modes. This is because the alternating effect accelerates the development and connection of microcracks on the surface of concrete, thus facilitating the diffusion of CO_2 into the concrete interior and promotes concrete neutralisation. In addition, the freeze-thaw environment is a catalyst for accelerating the carbonation corrosion of concrete [33]. It can be observed that the neutralisation depth in the FC mode is greater than that in the CF mode. This is because when the concrete is first exposed to carbonation, the carbonised products fill the internal voids of concrete, thus enhancing the compactness of concrete [5]. However, if the concrete is first exposed to freeze-thaw, the freezing effect generates many microcracks in the concrete and causes surface cracking and even peeling [42]. Micropores and microcracks can accelerate the diffusion of CO_2 in the internal structure and improve the neutralisation depth. The increase in neutralisation depth is faster with the increase in freeze-thaw cycles.

3.3. Analysis of Interaction between Freeze-Thaw Cycle and Carbonation

3.3.1. Analysis of Carbonation on Freeze-Thaw Damage. The degree of concrete damage is studied by analysing the RDME of concrete under the alternating effect. The influence coefficient (λ_C) of carbonation on the freeze-thaw damage of concrete is introduced and defined as follows [43]:

$$\lambda_C = \frac{D_{F+C}}{D_F}, \tag{6}$$

where D_{F+C} is the composite damage degree of the concrete under the alternating effect and D_F is the damage degree of the concrete under the single effect of freeze-thaw cycles.

If $\lambda_C = 1$, it indicates that carbonation does not affect concrete damage. If $\lambda_C < 1$, it indicates that carbonation presents an inhibiting effect on concrete damage. If $\lambda_C > 1$, it indicates that carbonation presents an acceleration effect on concrete damage, and the greater the value, the stronger the acceleration effect. The calculation results of the influence coefficient (λ_C) are presented in Table 6.

As shown in Table 6, in the FC mode, no carbonation occurs in the first 50 freeze-thaw cycles. Therefore, if $\lambda_C = 1$, it indicates that carbonation does not affect concrete damage. After 50 freeze-thaw cycles, the values of λ_C are all greater than 1, indicating that carbonation presents an acceleration effect on concrete damage, and the acceleration effect becomes more prominent with more cycles. In general, the greater the water-cement ratio, the greater the influence coefficient (λ_C). In the CF mode, during the first 100–125 freeze-thaw cycles, the values of λ_C are all less than 1, indicating that when carbonation is first exerted on concrete, the compactness of the concrete structure is enhanced and the freeze-thaw damage of the concrete is inhibited [44]. Subsequently, if the values of λ_C are still larger than 1, it indicates that in the early stage of the alternate action, carbonation can prevent the decay of the pore structure caused by partial freeze-thaw, which is beneficial in improving the frost resistance durability of concrete. However, with extended alternate periods, carbonation will accelerate the freeze-thaw damage of concrete.

3.3.2. Influence Coefficient of the Freeze-Thaw Cycle on the Development of Concrete Neutralisation Depth. The effect of the freeze-thaw cycle on concrete carbonation is analysed by studying the neutralisation depth under alternate freeze-thaw cycles and carbonation as well as the test results of neutralisation depth in the single carbonation mode. The influence coefficient (λ_F) of the freeze-thaw cycle on the neutralisation depth of the concrete is introduced, which is expressed as follows [13]:

$$\lambda_F = \frac{x_{F+C}}{x_C}, \tag{7}$$

where x_{F+C} is the neutralisation depth (mm) under the alternating effect, and x_c is the neutralisation depth (mm) under single carbonation.

If $\lambda_F = 1$, it indicates that the freeze-thaw cycle does not affect concrete neutralisation. If $\lambda_F < 1$, it indicates that the freeze-thaw inhibits the neutralisation to some extent. If $\lambda_F > 1$, it indicates that the freeze-thaw cycle accelerates concrete neutralisation, and the acceleration effect becomes more prominent with more cycles [43]. The calculation results of λ_F in different test modes are presented in Table 7.

As shown in Table 7, in the FC mode, the influence coefficient λ_F increases progressively and is always greater than 1, indicating that when freeze-thaw is first exerted on concrete, it accelerates concrete neutralisation and the acceleration effect becomes more prominent with prolonged time. In the CF mode, the influence coefficient λ_F increases gradually. However, unlike CF mode, freeze-thaw affects concrete neutralisation except for the first five days of carbonation when concrete is not subjected to freeze-thaw. In the first 10 days of carbonation, the influence coefficient λ_F still remains below 1, indicating that in the early stages of the test, the freeze-thaw cycle inhibits neutralisation, whereas it accelerates neutralisation over time.

3.4. Scanning Electron Microscopy (SEM). As an inhomogeneous porous material, the inherent defects in concrete can become a weak link for harmful substances, such as CO_2, entering the interior of the concrete. A microstructure analysis technique (SEM) was used to test the concrete of group S2 to reveal the deterioration mechanism of concrete under the alternating effect.

Figure 7 shows the microstructure of the concrete of group S2 before the test and after 30 days of carbonation in different test modes. The hydration process of concrete mixed with fly ash is as follows: First, cement clinker hydration precipitates $Ca(OH)_2$ diffuse to the surface of fly ash spherical vitreous bodies through liquid phase diffusion [45]. Subsequently, chemisorption and erosion occur, producing $Ca(OH)_2$, ettringite (AFt), and CSH gel randomly. As shown in Figure 7(a), most hydration products start to appear in gelatinous form, and a large number of hydrated calcium silicate fibrous crystals are generated on the surface of fly ash particles, which are cross connected to each other to form a high bond strength. As shown in Figure 7(b), the $CaCO_3$ generated by the reaction between the CSH gel and CO_2 gas is cross filled in the internal pores and microcracks and deposited on the surface of pores [46, 47]. The large internal pore size of concrete no longer exists, while the number and density of small pores increase. As shown in Figures 7(c) and 7(d), cracks appear on the surface of the concrete samples under the CF mode, but they do not interconnect with each other. The hydration products are loose and light flocculent. The failure of concrete is the most obvious in the FC test mode. The concrete sample surface microcracks are densely distributed and intersect with each other, and the hydration products are loose. Through comparison, it was found that carbonation facilitates in resisting freeze-thaw; however, freeze-thaw is generally more significant, which accelerates the occurrence of carbonation.

4. Prediction Model of Neutralisation Depth of Concrete in Freeze-Thaw Environment

Currently, two primary types of prediction models of the neutralisation depth of concrete exist: (1) The theoretical

Table 6: Calculation results of the influence coefficient (λ_C).

Freeze-thaw cycle times	25	50	75	100	125	150	175	200	225	250	275	300
S1-FC	1.00	1.00	1.23	1.35	1.75	1.50	1.70	1.62	1.53	1.51	1.56	1.60
S2-FC	1.00	1.00	1.53	1.56	1.71	1.66	1.63	2.00	1.98	1.88	1.87	1.95
S3-FC	1.00	1.00	1.62	1.54	1.64	1.72	1.95	2.05	1.99	1.92	1.85	1.98
S1-CF	0.79	0.85	0.87	1.00	1.13	1.11	1.27	1.21	1.17	1.14	1.11	1.12
S2-CF	0.82	0.89	0.79	0.90	1.00	1.02	1.12	1.25	1.16	1.17	1.18	1.22
S3-CF	0.87	0.75	0.83	0.88	1.25	1.28	1.36	1.33	1.24	1.25	1.13	1.33

Table 7: Calculation results of the influence coefficient (λ_F).

Carbonation time (d)	5	10	15	20	25	30
S1-FC	1.61	1.50	1.88	2.04	2.44	2.60
S2-FC	1.54	1.81	1.75	1.89	1.72	1.92
S3-FC	1.58	1.65	1.58	1.65	1.76	1.88
S1-CF	1.00	0.77	1.11	1.33	1.48	1.65
S2-CF	1.00	0.88	1.14	1.27	1.21	1.68
S3-CF	1.00	0.86	1.04	1.16	1.32	1.58

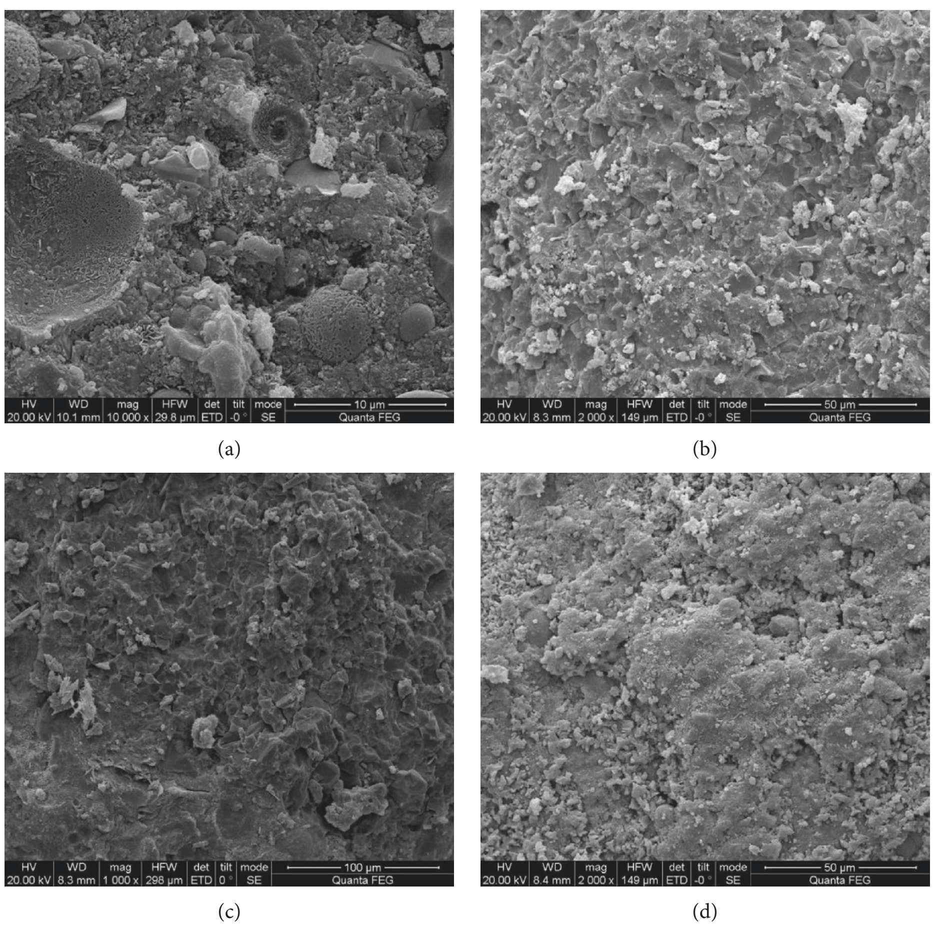


Figure 7: SEM of group S2 samples before test and after 30-day carbonation in different test modes. (a) S2, (b) S2-C, (c) S2-CF, and (d) S2-FC.

model: Papadakis et al. [48] developed an analytical model according to the mass balance conditions of CO_2 and carbonised substances during neutralisation. Yu and Jiang [49] proposed a practical mathematical model of the neutralisation depth of concrete based on the carbonation mechanism. (2) Empirical model: As different factors that affect carbonation are considered by different scholars, a variety of prediction models of neutralisation depth have been developed in accordance with actual engineering data or the results of rapid carbonation testing [50–52].

4.1. New Models. The abovementioned models were established in a typical atmosphere environment; therefore, they cannot be applied directly to the freeze-thaw environment. Herein, based on the carbonation mechanism and considering factors such as environmental temperature, relative humidity, CO_2 concentration, indoor and outdoor concrete, water-cement ratio, and number of freeze-thaw cycles, the following prediction model is proposed [53]:

$$x = k_W k_{co_2} k_T k_{RH} k_F \sqrt{t}, \tag{8}$$

where k_W is the indoor and outdoor influence coefficient of concrete; k_{co_2} is the influence coefficient of CO_2 concentration; k_T is the influence coefficient of environmental temperature; k_{RH} is the influence coefficient of relative humidity; and k_F is the composite damage coefficient under alternate freeze-thaw and carbonation.

To obtain the composite damage coefficient under the alternating effect, the test data in FC and CF modes were analysed. Subsequently, based on the positive correlation between the neutralisation depth and square root of carbonation time, the neutralisation depths measured in the test are converted into the carbonation coefficient. Using equation (5), the calculation results of the composite damage coefficient k_F in the FC mode are presented in Table 8, and the calculation results of k_F in the CF mode are presented in Table 9.

The calculation model with the number of freeze-thaw cycles (N) and water-cement ratio (w/c) as parameters can be obtained through a fitting analysis of kF in Tables 8 and 9:

In FC mode,

$$\begin{aligned} k_F = {} & 1.8479 + 0.0107N - 7.0790 \times 10^{-5} N^2 \\ & + 1.9460 \times 10^{-7} N^3 - 1.5444 \times 10^{-10} N^4 \\ & + 3.2691 \ln\left(\frac{w}{c}\right) + 1.2978 \ln\left(\frac{w}{c}\right)^2, \quad N \le 300. \end{aligned} \tag{9}$$

In FC mode,

$$\begin{aligned} k_F = {} & 1.3780 + 2.424310^{-4} N + 3.7237 \times 10^{-5} N^2 \\ & - 2.8380 \times 10^{-7} N^3 + 6.6222 \times 10^{-10} N^4 \\ & + 0.5560 \ln\left(\frac{w}{c}\right) + 1.7954 \ln\left(\frac{w}{c}\right)^2, \quad N \le 250. \end{aligned} \tag{10}$$

Comparisons of the values calculated in the model and those measured in the test are shown in Figures 8 and 9.

The comparison of the measured values and calculated values using formulas (9) and (10) shows that their standard deviation is 0.072 and the correlation coefficient is 0.934, suggesting good correlation. Therefore, the composite damage coefficient k_F proposed herein is reasonable.

Table 8: Calculated values of k_F in FC mode.

Number	Number of cycles (N)	Water cement ratio (w/c)	k_F
S1-FC	50	0.36	0.272
S2-FC	50	0.42	0.394
S3-FC	50	0.48	0.474
S1-FC	100	0.36	0.361
S2-FC	100	0.42	0.544
S3-FC	100	0.48	0.699
S1-FC	150	0.36	0.442
S2-FC	150	0.42	0.602
S3-FC	150	0.48	0.731
S1-FC	200	0.36	0.452
S2-FC	200	0.42	0.624
S3-FC	200	0.48	0.740
S1-FC	250	0.36	0.580
S2-FC	250	0.42	0.638
S3-FC	250	0.48	0.830
S1-FC	300	0.36	0.697
S2-FC	300	0.42	0.758
S3-FC	300	0.48	1.040

Table 9: Calculated values of k_F in CF mode.

Number	Number of cycles (N)	Water cement ratio (w/c)	k_F
S1-CF	0	0.36	0.170
S2-CF	0	0.42	0.255
S3-CF	0	0.48	0.300
S1-CF	50	0.36	0.231
S2-CF	50	0.42	0.266
S3-CF	50	0.48	0.364
S1-CF	100	0.36	0.261
S2-CF	100	0.42	0.392
S3-CF	100	0.48	0.483
S1-CF	150	0.36	0.295
S2-CF	150	0.42	0.420
S3-CF	150	0.48	0.523
S1-CF	200	0.36	0.352
S2-CF	200	0.42	0.448
S3-CF	200	0.48	0.624
S1-CF	250	0.36	0.444
S2-CF	250	0.42	0.661
S3-CF	250	0.48	0.873

5. Conclusions

Freeze-thaw cycle and carbonation were primary causes of concrete damage in cold areas, both of which could reduce the durability of concrete structures and affect the service life of buildings. Based on concrete durability under alternate freeze-thaw cycle and carbonation, the laws of RDME and concrete neutralisation were investigated. Conclusions drawn are as follows:

(1) In the early stage, carbonation was beneficial to concrete's frost resistance; however, over time, it accelerated the rate of freeze-thaw damage. Concrete

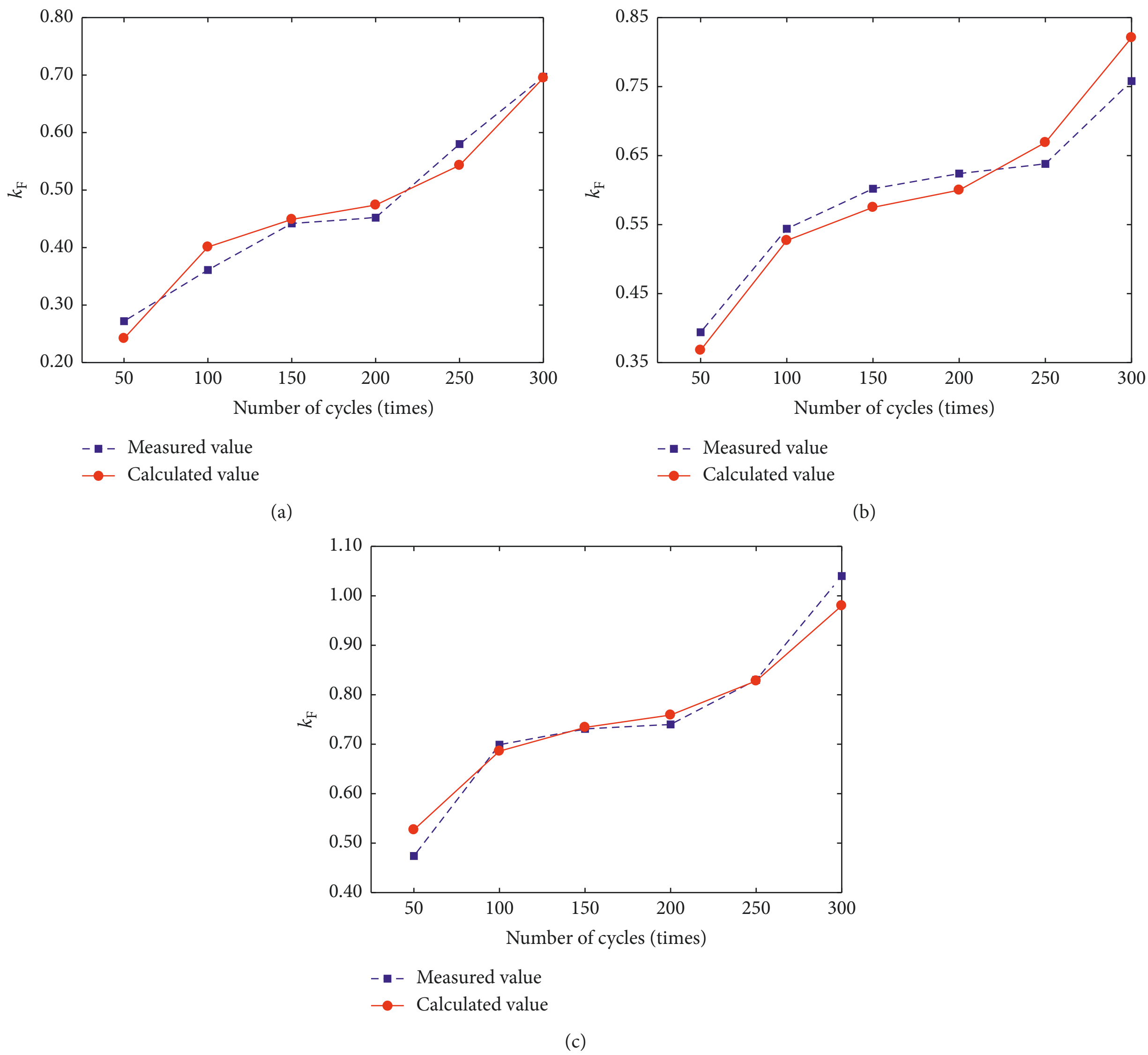


Figure 8: Comparison of measured value and calculated value of the composite damage coefficient k_F in FC mode. (a) S1-FC, (b) S2-FC, and (c) S3-FC.

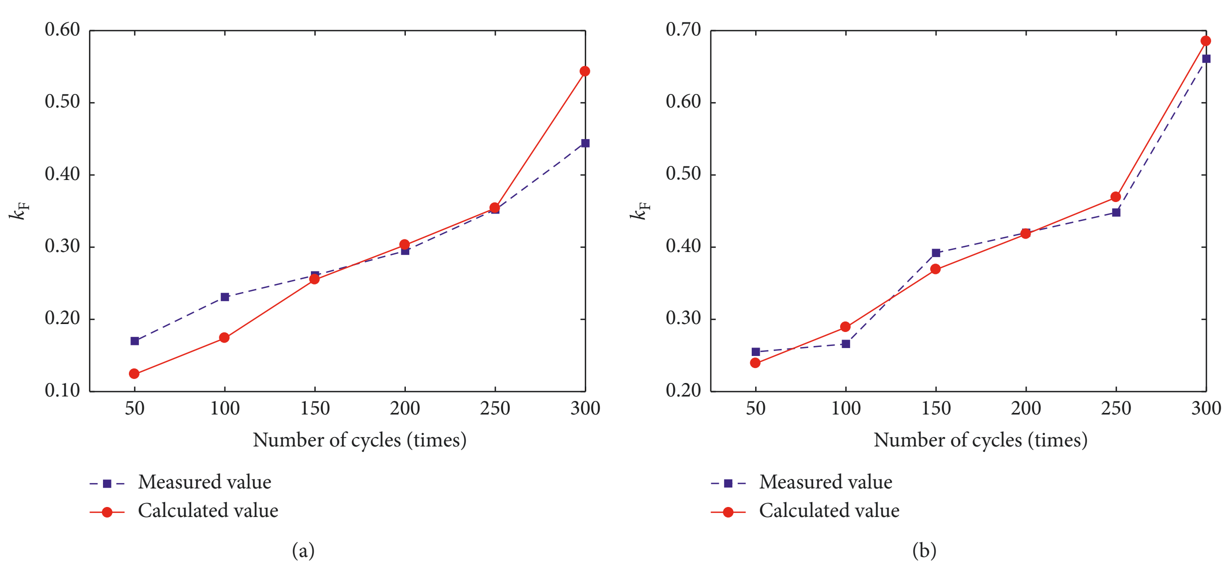
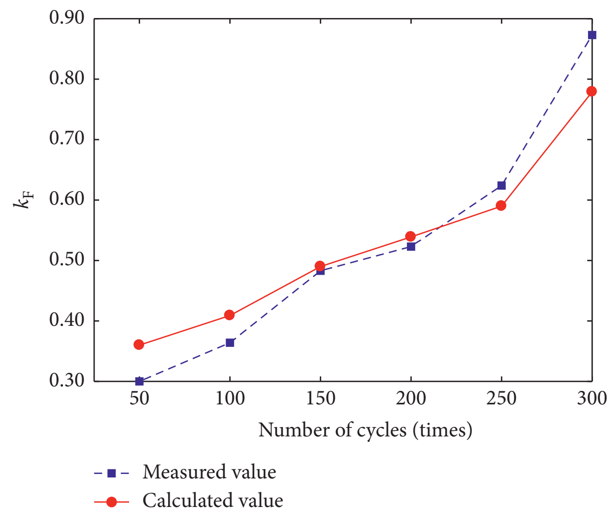


Figure 9: Continued.



(c)

Figure 9: Comparison of measured value and calculated value of composite damage coefficient k_F in CF mode. (a) S1-CF, (b) S2-CF, and (c) S3-CF.

freeze-thaw damage under the FC mode was more severe than that under the F mode. When an obvious alternating effect occurred in the actual environment, it was insufficient to consider only the single factor of the freeze-thaw cycle in the design of freeze-thaw durability; alternate freeze-thaw and carbonation must be considered and introduced as well.

(2) Under alternate freeze-thaw and carbonation, regardless of which factor was first applied to concrete, be it freeze-thaw cycle or carbonation, the RDME was lower than that of concrete in the F mode. In the FC mode, concrete exhibited the maximum deterioration at the start of the initial freeze-thaw cycle.

(3) The influence coefficient (λ_C) of carbonation on freeze-thaw damage was introduced to analyse the effect of carbonation on the freeze-thaw damage of concrete. The influence coefficient (λ_F) of freeze-thaw on concrete neutralisation was introduced to analyse the effect of the freeze-thaw cycle on the neutralisation depth of concrete.

(4) Through a regression analysis of test data, the mathematical expression of the composite damage coefficient k_F under alternate freeze-thaw and carbonation was presented. In addition, based on the analysis of influence factors of concrete neutralisation in the freeze-thaw environment, the prediction model of the neutralisation depth of concrete was established and its fitting precision was verified to be high.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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