

Research Article

Chloride Transport Performance of Basalt-Polypropylene Fiber Reinforced Concrete under Drying-Wetting Cycles

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This study investigated the chloride transport performance of basalt-polypropylene fiber reinforced concrete (BPFRC) subjected to drying-wetting cycles. The effects of the strength grade, basalt fiber (BF), polypropylene fiber (PF), and hybrid BF-PF on the pore solution pH, chloride concentration distribution, chloride peak concentration (C_{max}), and apparent chloride diffusion coefficient (D_a) of the BPFRC were analyzed, and a multifactor model of D_a was established. Moreover, the microstructures of BPFRC were studied to explore the effect of fibers on chloride transport performance of concrete in terms of theoretical pore volume, fiber-matrix interface, fiber bonding properties, and corrosion morphology. The results showed that the chloride concentration of the BPFRC increased and the pore solution pH of the BPFRC decreased with the increase in the exposure time. The chloride concentration and D_a of the BPFRC decreased with the increase in the strength grade. At a fiber volume content of 0.1%, the addition of BF and PF reduced the chloride concentration and D_a of the BPFRC; at a fiber volume content of 0.2%, the addition of hybrid BF-PF increased the chloride concentration and D_a of the concrete. The chloride peak concentration appeared at the depth of 2 mm inside the concrete, and the change of the chloride peak concentration with exposure time followed the power function model. The theoretical pore volume of the BPFRC specimens decreased initially and then increased with the increase in the exposure time. FE-SEM observed that the bonding property between BF and matrix was better than that of PF, which could effectively control the development of microcracks.

1. Introduction

Concrete is one of the most widely used building materials in the world [1]. However, its typical quasibrittle characteristics, low tensile strength, and low strain capacity have a significant effect on the application and development of concrete structures [2, 3]. The addition of short and disorderly distributed fibers can inhibit the generation and development of microcracks in concrete, control the stress at the crack tip, and play a bridging role, thereby significantly improving the toughness of the concrete [4–6] and increasing its application. At present, two types of fibers are mixed into concrete—rigid fibers and flexible fibers. Rigid fibers, such as steel fiber, carbon fiber, and basalt fiber (BF), have high elastic modulus and can improve the strength and bearing capacity of concrete, and steel fiber can increase the ductility of concrete [7, 8]. Flexible fibers, such as polyethylene fiber and polypropylene fiber (PF), have a low elastic modulus and good chemical stability and ductility and can significantly improve ductility and restrain cracking in concrete [9, 10].

To realize the benefits of various types of fibers and save costs, hybrid fibers of similar or different types and sizes have become an important area of research. Hybrid steelpolypropylene fibers are one of the most widely used hybrid fibers at present, and their synergistic effect can significantly improve the mechanical properties and toughness of concrete, while also improving its impermeability [11, 12]. However, hybrid steel-polypropylene fibers have an inherent fatal defect—the chemical composition of steel fiber is similar to that of steel bars and is prone to rust in marine environments. Consequently, there is an urgent need to find other rigid fibers to replace steel fibers.

BF is a new type of environment-friendly fiber that has the advantages of excellent chemical stability, large elastic modulus, good wear resistance, and low cost [13]. It is a suitable replacement for steel fibers in hybrid fiber systems in marine environments. Due to differences in their physical and mechanical properties, the addition of BF and PF to concrete can reduce the brittleness of concrete, restrain the development of internal cracks, and improve impermeability [14]. The dispersion of the hybrid fibers in a hybrid fiber system is another important consideration. The addition of admixtures can increase the uniformity of the dispersion of hybrid fibers, improve the bond properties between the fibers and the concrete matrix [15], and improve the durability of concrete [16].

One of the main factors that threaten the durability of concrete structures in marine environments is chloride erosion. Based on the location of a building in a marine environment, the chloride erosion environment can be further divided into marine underwater zone (full immersion) and tidal zone (drying-wetting cycles). Owing to the action of the drying-wetting cycles, the deterioration rate of the structural performance of concrete structures in tidal zone is significantly higher than that in underwater zone, and the diffusion rate of chloride in concrete structures in tidal zone is higher than that in the underwater zone as well [17–19]. Consequently, the time required to reach the chloride concentration limit of steel bar corrosion in concrete is reduced [20], which is very easy to cause steel bar corrosion and shortens the service life of buildings.

At present, most researchers study the durability of basaltpolypropylene fiber reinforced concrete (BPFRC) through rapid chloride permeation and water absorption [16, 21-24]. However, very few studies exist on the chloride transport performance of BPFRC subjected to drying-wetting cycles. In this study, the long-term chloride transport performance of BPFRC subjected to drying-wetting cycles was investigated. The free chloride concentration and pore solution pH in the BPFRC were measured at various depths, and the effects of the strength grade, BF, PF, and hybrid BF-PF on pore solution pH, chloride concentration, chloride peak concentration (C_{max}) , and apparent chloride diffusion coefficient (D_{a}) were analyzed. In addition, a multifactor model of D_a was established considering the effects of the exposure time, strength grade, and fibers content (BF and PF). Finally, the microstructures of BPFRC before and after erosion, such as theoretical total pore volume (P), the bonding performance between fiber and concrete matrix, and corrosion morphology, were evaluated by thermogravimetry (TG) and field emission scanning electron microscope (FE-SEM).

2. Materials and Experimental Methods

2.1. Raw Materials. The cementitious materials used to prepare the BPFRC specimens included P. O. 42.5 ordinary Portland cement (C), fly ash (FA), silica fume (SF), and granulated blast furnace slag (GGBS). The chemical

composition and physical properties of the cementitious materials are listed in Tables 1-3. The appearance of the BF and PF are shown in Figure 1. The length, diameter, density, tensile strength, elastic modulus, elongation, and aspect ratio of the BF, prepared by Aerospace Tuoxin Basalt Industry Co., Ltd., Sichuan, China, were 18 mm, $15 \mu m$, 2.56 g/cm^3 , 4500 MPa, 75000 MPa, 3.15%, and 1200, respectively, and those of the PF, prepared by Subote New Material Co., Ltd., Jiangsu, China, were 19 mm, $30 \,\mu$ m, $0.91 \,\text{g/cm}^3$, 270 MPa, 3000 MPa, 40%, and 633, respectively. The coarse aggregate (CA) was limestone gravel with a particle size of 5-20 mm and an apparent density of 2.7 g/cm³. River sand with a fineness modulus and apparent density of 2.8 and 2.63 g/cm^3 , respectively, was used as the fine aggregate (S). The mixed water (W) was laboratory tap water. A polycarboxylate superplasticizer (PBS) with a water-reducing rate of 30% was used.

2.2. Mix Proportions and Specimen Preparation. Seven groups of BPFRC specimens were fabricated. The detailed mix proportions of the BPFRC specimens are shown in Table 4. Groups 1-3 were used to compare the effects of different strength grades using the optimal mix proportions obtained from an orthogonal test. Groups 2 and 4-7 were used to compare the effect of single and hybrid fiber on the chloride transport performance of concrete and were fabricated based on the optimal mix proportion of the strength grade C40. HC, BC, PC, and BPC represent concrete without fiber, BF reinforced concrete, PF reinforced concrete, and hybrid BF-PF reinforced concrete, respectively. BF and PF are mixed such that equal volume content is obtained. The first group of numbers after the letters indicates the concrete strength grade and the second group of numbers indicates the fiber volume content. For example, BPC-30-0.1 denotes the fact that the fiber type is hybrid BF and PF, the concrete has a strength grade of C30, and the fiber volume content is 0.1%.

The mixing process of the BPFRC was as follows:

- (i) The dried CA and S were poured into the mixer and mixed for 30 s;
- (ii) Cementitious materials (C, FA, SF, and GGBS) were added and stirred for 2 min;
- (iii) PF and BF were added to the mix and stirred for 2 min and 3 min, respectively;
- (iv) W and PBS were poured into the mixture and stirred for 2 min.

The evenly mixed concrete mixtures were poured into $100 \text{ mm} \times 100 \text{ mm} \times 100 \text{ mm}$ cube molds and vibrated on a shaking table for 15 s. After 24 h, the specimens were demolded and placed in a standard curing room maintained at a temperature of $(20 \pm 2)^{\circ}$ C and a humidity of 95% for 28 d. Subsequently, the chloride diffusion test was conducted.

2.3. Experiment and Testing Methods

2.3.1. Chloride Drying-Wetting Cycle Test. High temperature and drying-wetting cycles were used to simulate the extreme

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TABLE 1: Chemical composition of cementitious materials.

Composition (wt. %)	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	MnO
С	21.18	5.02	3.14	63.42	3.12	2.3	0.65	0.42	0.05
FA	35.71	16.57	8.92	21.14	1.41	1.94	2.18	1.02	0.1
SF	85.04	0.97	1.04	1.63	0.32	—	0.81	0.19	0.32
GGBS	34.65	14.21	0.49	34.11	11.15	1.01	0.30	0.35	0.21

TABLE 2: Physical and mechanical properties of cement.

Density (g/cm ³)	Specific area surface (m²/kg)	Fineness (%)	Ignition loss (%)	Setting time (h)		Compressive strength (MPa)		Flexural strength (MPa)	
				Initial	Final	3 d	28 d	3 d	28 d
3.10	334	3.8	2.79	2.3	3.4	28.8	48.6	6.4	8.6

TABLE 3: Physical properties of admixtures.

Туре	FA	SF	GGBS
Water content (%)	0.2	0.06	0.7
Density (g/cm ³)	2.35	2.10	2.86
Ignition loss (%)	2.85	5.48	0.31
Specific area surface (m ² /kg)	340	23000	410
Fineness (%)	17	—	—
Average particle size (µm)	—	0.12	14.5



FIGURE 1: Morphology of fibers. (a) Basalt fiber. (b) Polypropylene fiber.

	Mixture	С	SF	FA	GGBS	PBS	W	W/C	S	CA	BF	PF
1	BPC-30-0.1	234.2	22	73.2	36.6	3.66	161	0.44	683	1162.9	1.3	0.5
2	BC-40-0.1	241.6	15.8	79.2	59.4	3.96	150.5	0.38	683.4	1163.6	2.6	0
3	BC-50-0.05	333.1	29	48.3	72.4	4.83	140	0.29	774.1	1026.1	1.3	0
4	HC-40	241.6	15.8	79.2	59.4	3.96	150.5	0.38	683.4	1163.6	_	_
5	PC-40-0.1	241.6	15.8	79.2	59.4	3.96	150.5	0.38	683.4	1163.6	_	0.9
6	BPC-40-0.1	241.6	15.8	79.2	59.4	3.96	150.5	0.38	683.4	1163.6	1.3	0.5
7	BPC-40-0.2	241.6	15.8	79.2	59.4	3.96	150.5	0.38	683.4	1163.6	2.6	0.9

TABLE 4: Mix proportions of BPFRC (kg/m³).

heat and humidity of ocean tidal zones. Before the experiment, an epoxy resin was used to seal each specimen, leaving only one surface free as the erosion surface, to study the chloride transport in one-dimensional space. The specimens were immersed in a closed box filled with NaCl solution (at a temperature of 28°C and a concentration of 3.5%) for 1 d and then dried at 50°C for 1 d, as shown in Figure 2. Five drying-wetting cycle durations were simulated, including 30 d (15 cycles), 60 d (30 cycles), 90 d (45 cycles), 120 d (60 cycles), and 180 d (90 cycles). As the immersion temperature was higher than the general environment, the NaCl solution was replaced every 5 d to ensure a constant concentration of solution. After the drying-wetting cycles test, the specimens were ground in layers using a grinder (1–10 mm, 1 layer/1 mm; 11–20 mm, 1 layer/2 mm) and passed through a 0.16 mm sieve. The powder was stored in a sealed bag for chloride concentration, pore solution pH, and TG testing.

2.3.2. Chloride Concentration and Pore Solution pH Testing. The free chloride concentration and pore solution pH in the BPFRC were measured using the solid-liquid extraction method [25] and the potentiometric method [26]. Solid-liquid extraction is the operation of separating substances from solids by liquid; that is, the eroded concrete powder is soaked in deionized water, the chloride ion is dissolved in deionized water after soaking for a corresponding time, and the filtrate is extracted by filtration. The test procedure is shown in Figure 3. The chloride ion concentration in the filtrate was measured using PXSJ-216F titrator with chloride ion electrode and saturated potassium sulfate reference

electrode. The free chloride concentration in the BPFRC was calculated as follows:

$$W_{Cl^{-}} = \frac{M \times 10^{-pX} \times V}{G} \times 100\%,$$
 (1)

where W_{Cl}^{-} is the concentration of free chloride in the BPFRC specimen, %; *M* is the molar mass of a chloride ion, 35.45 g/mol; *pX* is the negative logarithm of the free chloride concentration; *V* is the deionized water volume during immersion, 100 ml; and *G* is the mass of the soaked powder, 5.000 g.

2.3.3. Thermogravimetric Testing. The thermogravimetric differential scanning of the BPFRC samples subjected to various drying-wetting cycle durations was performed using a METTLER TOLEDO TGA/DSC 2. The mass of the test sample was 15 mg, the heating rate was 10 °C/min, the heating range was 30–900°C, and the protective gas used during the test was N₂ (99% purity).

2.3.4. Porosity Testing. Diamond [27] demonstrated that the theoretical total pore volume of concrete can be evaluated based on the mass loss of the sample measured by TG. Although the detailed pore size distribution is not obtained, this method serves as an evaluation method to characterize the pore structure of concrete [27, 28]. The theoretical pore volume calculation method established by Diamond is only suitable for mortar specimens; for concrete specimens, the influence of the coarse aggregate must be considered. Consequently, the equation to calculate the theoretical pore volume of concrete is as follows:

$$P(\%) = \frac{V_p}{V_w + V_G} \times 100\% = \frac{M_w - (BW/1.3)}{M_w + (M_G/\rho_G)} \times 100\%,$$

$$\frac{M_G}{\rho_G} = \frac{M_c}{\rho_c} + \frac{M_{FA}}{\rho_{FA}} + \frac{M_{SF}}{\rho_{SF}} + \frac{M_{GGBS}}{\rho_{GGBS}} + \frac{M_{CA}}{\rho_{CA}} + \frac{M_S}{\rho_S},$$

$$BW(\%) = \frac{M_{50} - M_{550}}{M_{550}} \times 100\%,$$

(2)

where *P* is the theoretical pore volume, V_P is the volume of pores, V_W is the volume of the mixing water, V_G is the volume of the other components (including C, FA, SF, GGBS, CA, and S), M_W is the mass of the mixing water, M_G is the mass of all the other components except water (including C, FA, SF, GGBS, CA, and S), ρ_G represent the density values of the C, FA, SF, GGBS, CA, and S), ρ_G represent the average density of BW [29], M_C , M_{FA} , M_{SF} , M_{GGBS} , M_{CA} , and M_S are the masses of the C, FA, SF, GGBS, CA, and S, respectively, ρ_C , ρ_{FA} , ρ_{SF} , ρ_{GGBS} , ρ_{CA} , and ρ_S are the densities of C, FA, SF, GGBS, CA, and S, respectively, ρ_C , ρ_{FA} , ρ_{SF} , ρ_{GGBS} , ρ_{CA} , and ρ_S are the densities of C, FA, SF, GGBS, CA, and S, respectively, and M_{50} and

 M_{550} represent the mass values of sample measured by TG at 50°C and 550°C.

2.3.5. Microscopic Testing. After 0 d and 180 d of erosion, the BPFRC specimens were broken, and the mortar fragments with diameter of approximately 5 mm and smooth neat surface were selected as the test samples. During the test, the sample was first adhered to the bracket with double-sided conductive adhesive, and then the sample was sprayed with gold. Finally, the distribution of fibers in concrete and the microstructure of eroded concrete were observed using Zeiss GeminiSEM 500 FE-SEM.



FIGURE 2: Schematic diagram of drying-wetting cycle test.



FIGURE 3: Testing process of pore solution pH and chloride concentration.

3. Results and Discussion

3.1. Pore Solution pH of BPFRC Subjected to Drying-Wetting Cycles

3.1.1. Effect of Strength Grade on Pore Solution pH. The pore solution pH of the BPFRC specimens with different strength grades is shown in Figure 4. As shown, the pH gradually decreases with an increase in the exposure time. This is because, in order to balance the anion charge during the erosion, OH⁻ ions dissolve out while chloride ions enter the concrete through capillary adsorption and diffusion, leading to a continuous decrease in the pore solution pH [30]. The higher strength grade for the BPFRC results in a higher pH value. The pH value at the 1 mm depth of C50 concrete is 2.43%-3.77% higher than that of the C30 concrete. During the drying-wetting cycle, the rate of reduction in the pH is slower, and the rising range of pH is small. After 180 d of exposure time, the pH value at a depth of 2 mm on concrete surface decreases from 11.92 of C50 concrete (BP-50-0.05) to 11.60 of C30 concrete (BPC-30-0.1). With the decrease in the strength grade, the porosity increased. During the drying process, the water in the pores evaporated more easily, and the concrete saturation decreased. During the subsequent wetting process, capillary adsorption was enhanced, and chloride ion exchange increased. Therefore, the pore solution pH of the low-strength grade BPFRC decreased rapidly.

3.1.2. Effect of Fibers on Pore Solution pH. The effect of BF, PF, and hybrid BF-PF on the pore solution pH of C40

concrete is shown in Figure 5. It can be seen from Figure 5 5(a) that the pH value of HC-40 concrete after 180 d of erosion is significantly lower than that after 120 d, especially at the depth of 3-10 mm. The main reason is that chloride enters into the concrete through capillary adsorption and diffusion in the process of continuous drying-wetting cycle, and the chloride concentration at different depths increases with the increase of erosion time. When chloride ions enter into the concrete, Ca²⁺ in the alkaline material will dissolve, which makes the hydration products decompose due to decalcification, resulting in the pH value of concrete to be greatly reduced in the later stage of erosion. With the addition of fiber, the pore size distribution of concrete is wider, which leads to the more prominent "ink bottle effect" in the process of drying-wetting cycle, and the more difficult evaporation and adsorption of water in concrete. Therefore, the decline of pH of fiber concrete is uniform in the process of erosion. At a depth of 2 mm below the surface of the specimen, the pH value of the specimen without fiber was the highest at 30 d of erosion time, which was 12.13, and the pH value of the specimen with 0.1% BF was the highest at 180 d of erosion time, which was 11.75. When the fiber volume content was 0.1%, the addition of BF, PF, and hybrid BF-PF increased the pH value at 180 d of exposure time, while a hybrid fiber content of 0.2% reduced the pH value of the concrete. The results demonstrate that an appropriate fiber content, whether BF or PF alone, or hybrid BF-PF, can inhibit the decrease in the pore solution pH during the later stages of erosion. This is because an appropriate amount of fiber can optimize the pore size distribution and reduce the



FIGURE 4: Pore solution pH of BPFRC with different strength grades. (a) BPC-30-0.1. (b) BC-40-0.1. (c) BC-50-0.05.

porosity and degree of anion exchange. With a high fiber content, the interface between the fiber and the matrix increases, a loose matrix and pores are formed around the fiber, the compactness of the concrete decreases, the capillary pore increases [31, 32], the chloride diffusion rate increases, the dissolution of alkaline substances increases, and the pore solution pH decreases rapidly during the process of erosion.

3.2. Chloride Concentration of BPFRC Subjected to Drying-Wetting Cycles

3.2.1. Effect of Strength Grade on Chloride Concentration. The chloride concentration distribution in the BPFRC specimens with different strength grades is shown in Figure 6. The chloride concentration increased from the concrete surface, and the C_{max} and convection zone appeared at a depth of 2 mm from the concrete surface; subsequently, it decreased and stabilized. The chloride concentration at each depth gradually increased the exposure time, but the increasing range gradually decreased. At a depth of 4 mm in BPC-30-0.1 specimen, the chloride concentration after 60 d of erosion was 15.72% higher than that after 30 d of erosion, while the chloride concentration after 180 d of erosion was 4.83% higher than that after 120 d of erosion. This is because the hydration of cementitious materials was still in progress during the drying-wetting cycles, decreasing the penetration rate of the chloride ions [33].

As the strength grade increased, the chloride concentration at a given depth in the concrete decreased, the chloride distribution curve was smoother, and the chloride diffusion range was smaller. After 30 d of erosion, the



FIGURE 5: Pore solution pH of C40 concrete with different fiber type and content. (a) HC-40. (b) BC-40-0.1. (c) PC-40-0.1. (d) BPC-40-0.1. (e) BPC-40-0.2.



FIGURE 6: Chloride concentration distribution of BPFRC with different strength grades. (a) BPC-30-0.1. (b) BC-40-0.1. (c) BC-50-0.05.

chloride concentration at a depth of 2 mm decreased from 0.32% of C30 concrete (BPC-30-0.1) to 0.21% of C50 concrete (BC-50-0.05), a decrease of 34.4%. However, after 180 d of erosion, the chloride concentration decreased from 0.48% of C30 concrete (BPC-30-0.1) to 0.36% of C50 concrete (BC-50-0.05), a decrease of 25%. The porosity of BPFRC with low strength is higher, and the transport rate of chloride is faster in the wetting process. In the drying process, the water in the pores of low-strength concrete is greater, and the capillary negative pressure is higher. Therefore, in the next wetting process, the capillary adsorption is obvious, and more chloride ions enter into the concrete [34].

3.2.2. Effect of Fibers on Chloride Concentration. The effect of BF, PF, and hybrid BF-PF on the chloride concentration distribution in the BPFRC specimens is shown in Figure 7. At a fiber content of less than 0.1%, the addition of fiber hindered the entry of chloride ions into the concrete. However, when BF and PF were mixed, and the fiber content reached 0.2%, the chloride ion entry into the concrete accelerated. Considering the various erosion times, the order of the BPFRC chloride concentration from low to high was as follows: BC-40-0.1<BPC-40-0.1< PC-40-0.1< HC-40 <BPC-40-0.2. At the same volume content, the effect of the hybrid BF-PF on the chloride concentration at a given depth in the concrete was between those of the two fibers acting







FIGURE 7: Chloride concentration distribution of C40 concrete different fiber type and content. (a) HC-40. (b) BC-40-0.1. (c) PC-40-0.1. (d) BPC-40-0.1. (e) BPC-40-0.2.

alone. After 30–180 d of erosion, the chloride concentration at a depth of 2 mm in BC-40-0.1, PC-40-0.1, BPC-40-0.1, and BPC-40-0.2 concrete was 6.07%–3.26%, 2.19%–1.11%, 4.07%–2.21%, and -3.2% to -0.91% lower than HC-40 concrete, respectively. This is because the hybrid fiber content was excessive, the fiber dispersion decreased, the BF introduced more pores, and the bond performance between PF and the concrete matrix decreased, resulting in an increase in the number of internal defects in the concrete [35]. Therefore, the capillary effect of concrete during the erosion increased, the chloride concentration in the convection zone was higher, and the diffusion driving force increased, leading to an increase in the chloride concentration at a given depth.

3.3. Chloride Peak Concentration of BPFRC. Concrete structures located in the ocean tidal zone are usually in an unsaturated state. Chloride ions accumulate on the surface due to the evaporation of pore liquids and the convection of chloride ions, forming a peak concentration in the convection zone. This acts as the driving force for chloride diffusion inside the concrete structure. The chloride concentration deep inside the concrete also increases accordingly. Figure 8 presents C_{max} of seven groups of BPFRC at different exposure times. It can be seen that although C_{max} exhibits fluctuations randomly with the strength grade, fiber type, and content varying, C_{max} of each group of concrete fluctuates within ±15% of the average value at different exposure times. With the increase of exposure time, C_{max} of BPFRC gradually increases, but the increasing range gradually decreases and finally tends to be stable. Therefore, the change of C_{max} of BPFRC is time-dependent. Some studies have shown that the variation of C_{max} with time can be described as linear, power, exponential, square root, and logarithmic functions [36–39].



FIGURE 8: Chloride peak concentration of BPFRC at different exposure time.

The above five functions were used to fit the average value of C_{max} of BPFRC specimens with the exposure time, and the fitting results are shown in Figure 9. It can be seen that the fitting accuracy of linear function, exponential function, and square root function is relatively low. Although the fitting accuracy of logarithmic function is the highest, its initial value is negative, which is not consistent with the actual situation. Therefore, the power function model was finally selected to describe the change of peak



FIGURE 9: Fitted curves of time-dependent chloride peak concentration.

chloride concentration of BPFRC with exposure time, as shown in the following equation:

$$C_{\max}(t) = 0.118t^{0.253},\tag{3}$$

where $C_{\text{max}}(t)$ is the chloride peak concentration at different exposure times (%) and *t* is the exposure time of the BPFRC (d).

3.4. Chloride Diffusion Coefficient of BPFRC

3.4.1. Analysis of Factors Influencing Chloride Diffusion Coefficient. In concrete subjected to drying-wetting cycles, the concrete is unsaturated, and the convection zone and C_{max} are formed in the surface layer after the chloride ion has entered the concrete. The value of D_a calculated using Fick's second law is unreliable. Andrade et al. [40] proposed a novel method to calculate D_a that first removes the chloride ion increase stage, then calibrates the depth position coordinates with C_{max} as the zero point, and finally fits the descending section. Chang et al. [41] verified the suitability of this method for calculating D_a in concrete subjected to drying-wetting cycle. The equation to calculate D_a is as follows:

$$C(x,t) = C_0 + \left(C_{s,\Delta x} - C_0\right) \times \left[1 - \operatorname{erf}\frac{x - \Delta x}{2\sqrt{D_a(t)t}}\right], \quad (4)$$

where C(x, t) is the chloride concentration in concrete subjected to a drying-wetting duration t and at a depth x, C_0 is the initial chloride concentration, $C_{s, \bigtriangleup x}$ is the chloride concentration at the depth of the convection zone, erf () is the error function, and $D_a(t)$ is the apparent chloride diffusion coefficient.

 $D_{\rm a}$ of the BPFRC specimens under different exposure times was calculated using (4), as shown in Figure 10. $D_{\rm a}$ for all the BPFRC specimens decreased with increase in the



FIGURE 10: Apparent chloride diffusion coefficient of BPFRC.

exposure time. The strength grade had a significant effect on D_a ; the apparent chloride diffusion coefficient of BPFRC decreased with an increase in the strength grade. D_a of BPC-30-0.1 after 30 d, 90 d, and 180 d of erosion was 47.67%, 73.99%, and 77.09% higher than that of BC-50-0.05, respectively. Concrete with a high strength grade has a lower porosity and denser matrix, which slows the diffusion rate of chloride ions. Compared to HC-40, after 30 d of erosion, D_a of BC-40-0.1, PC-40-0.1, BPC-40-0.1, and BPC-40-0.2 decreased by 5.79%, 1.75%, 2.91%, and -3.53%, respectively; after 180 d of erosion, D_a of BC-40-0.1, PC-40-0.2 decreased by 5.38%, 1.54%, 3.45%, and -1.46%, respectively. This indicates that the effect of fibers on D_a of concrete decreased with increase in the erosion time.

3.4.2. Multifactor Model of Apparent Chloride Diffusion Coefficient. To investigate the effects of the exposure time, strength grade, and fiber content on D_a of BPFRC, an apparent chloride diffusion coefficient model was established based on the multifactor method, as shown in the following equation:

$$D_a(t, S, V) = D_{\text{ref}} \cdot f_1(t) \cdot f_2(S) \cdot f_3(V), \tag{5}$$

where D_a (*t*, *S*, *V*) is the apparent chloride diffusion coefficient considering the exposure time, strength grade, and fiber content, respectively; D_{ref} is the reference chloride diffusion coefficient; and f_1 (*t*), f_2 (*S*), and f_3 (*V*) are the correction coefficients of the exposure time, strength grade, and fiber content, respectively.

(1) Time-Dependent Correction Factor f_1 (t). When only considering the time-dependent coefficient of D_a , D_a model can be expressed as follows:



FIGURE 11: Relationship between apparent chloride diffusion coefficient and exposure time.

$$D_a(t) = D_{\rm ref} \left(\frac{t_{\rm ref}}{t}\right)^m,\tag{6}$$

where t_{ref} is the reference time, usually 28 d [42], and *m* is the time-dependent coefficient.

Time-dependent coefficient is an important parameter that affects the accuracy of concrete life prediction, which is usually related to strength grade, cementitious material, curing time, and exposure conditions [38]. The reference diffusion coefficient and time-dependent coefficient are calculated using (6), and the results are presented in Figure 11 and Table 5. It can be seen that the fitting accuracy values R^2 of all BPFRC specimens are greater than 0.95. The higher the strength grade, the greater the timedependent coefficient *m*, indicating that the apparent chloride diffusion coefficient of concrete decreases rapidly with the increase of exposure time, which is consistent with the research results of Huang et al. [37]. Compared with the concrete without fiber, the influence of BF, PF, or hybrid BF-PF on time-dependent coefficient is less.

All BPFRC specimens were normalized according to C40 concrete (BC-40-0.1), i. e., reference chloride diffusion coefficient $D_{ref} = D_{ref}$ (BC-40-0.1) = $12.76 \times 10^{-12} \text{ m}^2/\text{s}$. The influence factor f_1 (*t*), considering the effect of exposure time on the apparent chloride diffusion coefficient, can be defined as follows:

$$f_1(t) = \left(\frac{t_{\text{ref}}}{t}\right)^m.$$
 (7)

The influence coefficient of strength grade and fibers (BF and PF) content on time-dependent coefficient m can be expressed as follows:

$$m(S,V) = 0.81 \cdot k_S \cdot k_V,\tag{8}$$

where k_S and k_V are the correction coefficients of strength grade and fiber content.

(2) Strength Grade Correction Factor f_2 (S). The correction factor f_2 (S), considering the effect of strength grade on the apparent chloride diffusion coefficient, can be defined as follows:

$$f_2(S) = \frac{D_{\text{ref}}(S)}{D_{\text{ref}}},\tag{9}$$

where $D_{ref}(S)$ is the reference chloride diffusion coefficient with different strength grade.

(3) Fiber Content Correction Factor f_3 (V). The correction factor f_3 (V), considering the effect of fiber contents (BF and PF) on the apparent chloride diffusion coefficient, is defined as follows:

$$f_3(V) = \frac{D_{\text{ref}}(V)}{D_{\text{ref}}},\tag{10}$$

where $D_{ref}(V)$ is the reference chloride diffusion coefficient with various fiber contents of BF and PF.

Based on the regression analysis of the test results, the multifactor model of apparent chloride diffusion coefficient for BPFRC considering exposure time, strength grade, and fiber content is established as follows:

$$\begin{cases} D_{a}(t, S, V) = D_{ref} \cdot f_{1}(t) \cdot f_{2}(S) \cdot f_{3}(V), \\ D_{ref} = \frac{12.76 \times 10^{-12} m^{2}}{s}, \\ f_{1}(t) = \left(\frac{t_{ref}}{t}\right)^{0.81 (0.31S^{0.32}) \cdot (0.97 + 0.29V_{B} + 0.19V_{P})}, \\ f_{2}(S) = 2.24e^{-0.02S}, \\ f_{3}(V) = 1.08 - 0.81V_{B} - 0.37V_{P}, \end{cases}$$
(11)

where *S* is the strength grade and $V_{\rm B}$ and $V_{\rm P}$ are the BF and PF content.

The relationship between the predicted and experimental values of D_a of the BPFRC specimens at various exposure times is shown in Figure 12. The error between the predicted values of the model and the experimental values is less than 15%, which satisfies the error requirements. Therefore, the proposed model can be used to predict D_a of BPFRC subjected to drying-wetting cycles.

3.5. Theoretical Pore Volume of BPFRC. Figure 13 presents the theoretical pore volume of the BPFRC specimens at different erosion times. It can be seen that the theoretical pore volume of the BPFRC specimens initially decreased and then increased with the increase in the erosion time. The theoretical pore volume of the BPFRC specimens was the least after 30 d of erosion. During the initial stages of the

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Mixture	$D_{\rm ref} (10^{-12} {\rm m}^2/{\rm s})$	m	R^2
BPC-30-0.1	15.92	0.71	0.98
BC-40-0.1	12.76	0.81	0.99
BC-50-0.05	10.72	0.83	0.99
HC-40	13.58	0.78	0.99
PC-40-0.1	13.32	0.79	1.00
BPC-40-0.1	13.17	0.80	1.00
BPC-40-0.2	14.05	0.79	0.99

TABLE 5: Reference chloride diffusion coefficient and time-dependent coefficient of BPFRC.



FIGURE 12: Comparison between predicted and experimental values of (D)_a for the BPFRC.



FIGURE 13: Theoretical pore volume of BPFRC. (a) Different strength grades. (b) Different fiber types and contents.



FIGURE 14: Comparison of pore volume of BPFRC [43].



FIGURE 15: Relationship between theoretical pore volume and $(D)_a$ after 30 d of erosion. (a) Different strength grades. (b) Different fiber types and contents.

erosion, the continuous hydration of concrete and the formation of Friedel's salt by the chloride ions and the hydration products reduce the theoretical total pore volume of BPFRC. As the erosion time increases, alkali substances in the concrete such as $Ca(OH)_2$, NaOH, and KOH continuously dissolved, and the concrete matrix structure becomes loose. Consequently, the theoretical total pore volume increases. As shown in Figure 13(a), the theoretical total pore

volume decreased with the increase in strength grade. After 180 d of erosion, the theoretical total pore volume of C30 concrete (BPC-30-0.1) was 1.17 times and 2.32 times that of C40 concrete (BC-40-0.1) and C50 concrete (BC-50-0.05), respectively.

The effects of BF and PF and hybrid BF-PF on the theoretical pore volume of concrete are shown in Figure 13(b). Before the erosion, the theoretical pore volume



FIGURE 16: FE-SEM micrographs of BF and PF in BPFRC. (a) The interface between the BF and matrix. (b) Failure modes of PF. (c) The interface between the PF and matrix. (d) Distribution pattern of BF and PF with 0.2% hybrid fiber.

of the BC-40-0.1, PC-40-0.1, BPC-40-0.1, and BPC-40-0.2 specimens was 13.13%, 2.91%, 5.41%, and -6.71% lower than that of HC-40, respectively. After 180 d of erosion, the theoretical pore volumes of BC-40-0.1, PC-40-0.1, BPC-40-0.1, and BPC-40-0.2 were 11.61%, 2.17%, 6.82%, and -1.74% lower than that of HC-40. Compared to the concrete with single BF, the bonding performance between the PF and the concrete matrix is poor, which increases the theoretical pore volume of PC-40-0.1. When BF and PF are mixed and the fiber content is 0.1%, the two fibers have a certain degree of influence on the mixing process, and the dispersion and cohesiveness of the fiber are reduced. Consequently, the theoretical pore volume of BPC-40-0.1 is slightly larger than that of BC-40-0.1. However, when BF and PF are mixed with a fiber content of 0.2%, the interface between the fiber and concrete matrix increases due to the excessive amount of fiber. The uneven dispersion leads to a decrease in adhesion, increasing the theoretical pore volume of the concrete.

Niu et al. [43] measured the cumulative pore volume of basalt-polypropylene fiber concrete with different fiber content by Mercury intrusion porosimetry (MIP), and the cumulative pore volume is shown in Figure 14. It can be seen that the pore volume measured by Mercury porosimetry is 11.59%–14.59%, which is larger than that calculated by TG. This is because the pore size that can be measured using MIP

technique is in the range of $0.005 \,\mu\text{m}-1000 \,\mu\text{m}$, including gel pores, capillaries, and large pores, while the total pore volume calculated by TG is the pore volume formed by free water evaporation. Fallah and Nematzadeh [44] calculated the porosity of polymer and polypropylene fiber concrete according to capillary water absorption, and the porosity is 7.0%–9.39%, which is slightly higher than that of concrete of the same strength grade in this study. In addition to the different testing methods of pore volume, in this study, the addition of mineral admixtures can improve the degree of hydration of concrete and generate more bound water, thus reducing the content of free water, which is also the reason for the decrease of porosity of concrete.

The relationship between the theoretical pore volume of the BPFRC and D_a after 30 d of erosion is shown in Figure 15. As shown, a good correlation exists between the theoretical pore volume and D_a . D_a increases with the increase in the theoretical pore volume. The lower the theoretical pore volume, the better the compactness of concrete, and the smaller the chloride ion transport rate in concrete. Therefore, concrete presents excellent chloride resistance.

3.6. FE-SEM Analysis. To analyze the effect of BF and PF on chloride transport performance of BPFRC, the morphology



FIGURE 17: FE-SEM micrographs of BPC-40-0.1 concrete after 180 days of exposure time. (a) Sodium chloride crystals. (b) Corrosion products. (c) The interface between the BF and concrete matrix. (d) The interface between the PF and concrete matrix.

of BPFRC was observed by FE-SEM. Figure 16 shows the distribution of BF and PF in BPFRC without erosion. It can be seen from Figure 16(a) that a certain amount of hydration products are attached to the surface of BF, the interface structure of BF is dense, and the bond between BF and matrix is tight; there are microcracks distributed around BF, and there is no connection between microcracks, indicating that the addition of BF can effectively restrain the emergence and development of shrinkage cracks in concrete at the initial stage of hydration. The distribution of PF in concrete is shown in Figures 16(b) and 16(c). It can be seen that, compared with BF, PF has poor bonding performance with concrete matrix, and there is obvious gap between fiber and matrix. PF warps at the end after tension, and PF can consume a certain amount of fracture energy in the process of tension, which can restrain the development of cracks [45]. Figure 16(d) presents the fiber distribution of BPC-40-0.2 concrete. It can be seen that the fiber dispersion is uneven due to excessive fiber content. The bonding performance between the fibers and the concrete matrix decreases, which not only increases the weak interface between fiber and concrete matrix and reduces the compactness of concrete but also weakens the inhibition and control effect of fiber on cracks, thus providing more channels for the transport of chloride ions. Therefore, there are more chloride ions in BPC-40-0.2 concrete.

The morphology of BPC-40-0.1 concrete after 180 d of erosion is shown in Figure 17. As shown in Figures 17(a) and 17(b), a large number of sodium chloride crystals are distributed in BPFRC, and the hydration products exhibit loose and porous characteristics due to decalcification, forming many small pores. It can be seen from Figure 17(c) that salt crystallization and corrosion products are attached to the surface of BF and the fiber-matrix interface transition zone, but the bond strength between fiber and matrix decreases, which is due to the decrease of alkalinity of pore solution and serious loss of hydration products in concrete after erosion. Figure 17(d) shows the morphology of PF in concrete after erosion. Sodium chloride crystals exist on the fiber surface, but there are few hydration products attached around the fiber.

4. Conclusions

In this study, a tropical ocean tidal zone was simulated using a drying-wetting cycle test system in a high-temperature environment. The effects of the strength grade, fiber type, and fiber content on the chloride transport performance of BPFRC were investigated. The main conclusions are as follows:

- (1) The pore solution pH of the BPFRC specimens decreased with the increase in the exposure time, and the pore solution pH of the surface concrete decreased rapidly. In the process of erosion, the pH decrease rate of high strength concrete was slower, and the rising range of pH was smaller. The effects of BF, PF, and hybrid BF-PF on the pore solution pH of C40 concrete are as follows: BC-40-0.1>BPC-40-0.1>PC-40-0.1>HC-40>BPC-40-0.2.
- (2) The chloride concentration at a given depth in the BPFRC specimens increased gradually with the increase in the exposure time; it increased rapidly initially and gradually during the later stages. The strength and fiber had little effect on the depth of convection zone, and the depth of convection zone of all specimens at each erosion time was 2 mm. The chloride concentration in the BPFRC specimens decreased with the increase in strength grade. At a fiber volume content of 0.1%, the single-doped BF had the largest effect on reducing the BPFRC chloride concentration in the C40 concrete. The effect of the hybrid BF-PF on the reduction of the chloride concentration was between those of the BF alone or PF alone. When the hybrid fiber content was 0.2%, the addition of fibers increased the chloride concentration at a given depth in the concrete.
- (3) The chloride concentration of BPFRC presented a two-stage distribution, and the chloride peak concentration appeared at the depth of 2 mm. C_{max} in C30 concrete (BPC-30-0.1) was 16.78%–22.61% and 33.23%–48.84% higher than that of BC-40-0.1 and BC-50-0.05, respectively. C_{max} of C40 concrete with 0.1% BF was the lowest, which was 5.95%–3.24% lower than that of the specimen without fiber (HC-40). The addition of 0.2% hybrid fiber increased C_{max} of C40 concrete by 0.93%–3.21%.
- (4) The chloride peak concentration increased with the exposure time. The power function was regarded as the best fitting formula to describe the chloride peak concentration model of BPFRC.
- (5) D_a of the BPFRC specimens decreased with the increase of exposure time, exhibiting a power function attenuation law. D_a of C30 concrete (BPC-30-0.1) was 47.67%–77.09% higher than that of C50 concrete (BC-50-0.05). With the increase of erosion time, the decreasing effect of single fiber on D_a of concrete decreased, while that of hybrid fiber increased. A multifactor model was established considering the effects of exposure time, strength grade, and the content of BF and PF on D_a of BPFRC. The error between the calculated and experimental values of apparent chloride diffusion coefficient was within 15%.
- (6) The theoretical pore volume of the BPFRC specimens initially decreased and then increased with the

exposure time increasing. The higher the strength grade, the smaller the theoretical pore volume. BF, PF, and hybrid BF-PF had positive and negative effects on the theoretical pore volume of the C40 concrete. After 180 d of erosion, the addition of fiber reduced the porosity of C40 concrete by 11.61% to -1.74%. The theoretical pore volume demonstrated good correlation with D_{a} .

(7) FE-SEM results showed that the bond between BF and concrete matrix was better than that of PF before erosion, which could effectively control the development of microcracks. For the specimen containing 0.2% hybrid fiber, BF and PF presented agglomeration and uneven dispersion. After 180 d of erosion, a large number of salt crystals were distributed in BPFRC, and the bonding properties between fiber and matrix decreased.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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