

Article

Impact of Various Erosive Environments on the Durability of POM Fiber-Reinforced Ultra-High-Performance Concrete

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Abstract: To address the durability challenges faced by traditional concrete in marine environments, this study focuses on polyoxymethylene (POM) fiber-reinforced ultra-high-performance concrete (PFUHPC) and, for the first time, systematically investigates the inhibitory effects of POM fibers on microstructural degradation and mechanical performance deterioration of ultra-high-performance concrete under various erosive environments. The results indicated the following: (1) The mass loss rate and compressive strength degradation in PFUHPC under different erosive environments initially increased and then decreased, demonstrating that the inclusion of POM fibers delayed corrosion and significantly improved the durability and stability of the material's performance. (2) Compared to the natural environment, after 180 days of immersion in different erosive environments (seawater immersion, wet–dry cycles in seawater, chloride salt immersion, sulfate salt immersion, and complex salt immersion), the compressive strength degradations were observed to be 4.8%, 9.7%, 6.8%, 11.7%, and 10.7%. (3) Microscopic analysis after 180 days revealed that the main corrosion products were gypsum, ettringite, and Friedel's salt (calcium chloroaluminate). Under the environments of seawater immersion and cyclic wetting and drying, the low concentrations of chloride and sulfate ions resulted in fewer corrosion products and a denser matrix. The primary corrosion product under the chloride salt immersion was Friedel's salt, which led to surface cracking and microporosity, while under the sulfate immersion, gypsum and ettringite were predominant, resulting in more porous and loosely bound hydration products and more severe corruptions.

Keywords: POM fiber; erosive environments; mass loss rate; strength degradation; microscopic analysis



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1. Introduction

In recent years, the oceans, abundant in resources, have increasingly become a focal point of strategic competition among nations, with a growing emphasis on construction activities aimed at enhancing military capabilities and exploiting offshore energy, and the related research has gradually become a hot spot in civil engineering. Ultra-high-performance concrete (UHPC) has a broad application prospect in offshore engineering due to its excellent mechanical properties and durability. Steel fibers are widely used as reinforcement in UHPC, and the steel fibers may be corroded by a variety of corrosive ions in seawater and cause degradation of concrete properties. In contrast, synthetic fibers, known for their high-strength elasticity and resistance to marine erosion, are being adopted as a superior alternative to steel fibers [1]. Research on synthetic fibers in UHPC primarily focuses on polyethylene (PE), polyvinyl alcohol (PVA), and polypropylene (PP) fibers [2,3]. Nevertheless, studies indicate that neither PVA nor PP fibers significantly enhance the compressive strength or toughness of UHPC [4,5]. In contrast, polyoxymethylene (POM) fibers not only demonstrate exceptional toughness but also possess excellent corrosion

resistance, thermal stability, resistance to photodegradation, low water absorption, and immunity to microbial degradation, thus preventing biofouling in marine settings.

POM fibers are a synthetic organic material [6,7], and their excellent corrosion resistance is primarily attributed to its unique chemical structure and molecular characteristics. The molecular chain of POM fibers is composed of a high-density carbon backbone, which exhibits exceptional chemical stability in alkaline and high-salinity environments. Moreover, the hydrophobic nature of the fiber surface significantly reduces the penetration ability of water molecules and corrosive ions, effectively inhibiting the occurrence of chemical reactions [8,9]. It also maintains excellent dispersibility in concrete, ensuring the matrix remains fluid [10,11] and showing that replacing high-modulus steel fibers with lower-modulus PP and POM fibers significantly enhances the fluidity of UHPC. Although this substitution results in decreases in compressive and tensile strengths, it modifies the traditional axial tensile stress–strain behavior of UHPC, substantially improving its tensile toughness. The research in [12] found that the contribution of POM fibers to UHPC positively influenced its flexural strength and high-temperature resistance. Also, it was further found through nanoindentation that POM fibers can slightly disturb the filling skeleton of UHPC and enlarge the interfacial transition zone (ITZ) between the matrix and fibers. The research in [13] found that the addition of POM fibers was beneficial to improving the fracture resistance of concrete by comparing the damage behaviors of plain concrete and POM fiber-reinforced concrete materials. The research in [14] found that sea sand concrete with POM fibers performed better in terms of mechanical properties and can improve the early cracking resistance of concrete.

Marine environments are inherently complex, not only by various corrosive inorganic salt ions, such as Cl^- , SO_4^{2-} , and Mg^{2+} , that can deteriorate the internal structure of concrete, but also by the influences of wave action, abrasion, and the cyclic wetting and drying of seawater [15]. The addition of fibers has been proven to effectively enhance the mechanical and durability properties of concrete. Numerous researchers have conducted studies on fiber-reinforced concrete's resistance to salt solution erosion. The research in [16] found that under seawater corrosion, the compressive strength of steel-fiber-reinforced concrete decreased slowly at 60 and 90 days but showed a significant reduction after 120 days. The authors of [17] developed models for mass and compressive strength losses under seawater corrosion by studying the durability of reactive powder concrete in marine environments.

In recent years, researchers have conducted a series of studies on the damage process and mechanism of UHPC in different erosion environments. While steel-fiber-reinforced concrete has been comprehensively studied, it has been found to have limitations in marine engineering and other salt-prone environments due to its high cost and susceptibility to rusting. On the other hand, POM fibers, which are compatible with inorganic materials, offer a broad application prospect in these areas, while POM fibers have good compatibility with inorganic materials, which can improve the toughness of UHPC and brittle damage characteristics. Some studies have already demonstrated that POM fibers enhance concrete performance more effectively than other types of synthetic fibers, making them a promising replacement for steel fibers in offshore engineering to mitigate the degradation of the mechanical properties of UHPC caused by corrosion [18]. However, research on the impact of POM fibers on the durability of UHPC remains limited and primarily focuses on their role in ordinary concrete. This study is the first to systematically investigate the inhibitory effects of POM fibers on the microstructural degradation and mechanical performance deterioration of ultra-high-performance concrete under various erosive environments. By integrating macroscopic performance tests and microscopic analyses, this study provides an in-depth understanding of the corrosion mechanisms of PFUHPC in complex erosive conditions and quantifies the impact of corrosion products on material performance. The findings not only fill a critical gap in the existing literature but also offer valuable insights for the practical application of novel durable materials in marine engineering.

2. Experimental

2.1. Raw Materials

The cement used was P·O 52.5 Portland cement. The silica fume was a gray–blue powder with a particle size of less than 2 μm , a density of 2.214 g/cm^3 , and a specific surface area of 18,500 m^2/kg . The fly ash was Class I, with a bulk density of 2.5 g/cm^3 and a loss on ignition of 3.9%. The sand was river sand from the Huizhou area in Guangdong Province of China, which was treated in a drying oven. The superplasticizer was a polycarboxylate-based superplasticizer with an efficiency greater than 30%. The POM fibers, produced by Chongqing Yuntianhua Tianju New Materials Co. Ltd. (Chongqing, China), were 12 mm in length and had a density of 1.4 g/cm^3 . The chemical compositions of cement, silica fume, and fly ash are shown in Table 1.

Table 1. Main chemical compositions of cementitious materials (%).

Material	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	LOI
Cement	21.30	5.21	64.39	5.11	0.89	2.38	0.72
Silica fume	94.52	0.45	0.31	0.23	1.26	-	3.23
Fly ash	52.45	24.85	7.56	5.11	2.38	1.74	5.91

2.2. Mix Proportions

Building on previous research by the research group, the water-to-binder ratio used in this study was 0.175, and the volumetric dosage of POM fibers was set at 1.8%. Fiber content was used as a variable and fiber doping of 0 was used as a control group. The specific mix proportions used in the experiments are shown in Table 2.

Table 2. Mix proportions of PFUHPC.

Group	Cement (kg/m ³)	Silica Fume (kg/m ³)	Fly Ash (kg/m ³)	Sand (kg/m ³)	POM Fiber (kg/m ³)	Water (kg/m ³)	Superplasticizer (kg/m ³)	W/B
1	722	238	90	1050	0	184	21	0.175
2	722	238	90	1050	25.2	184	21	0.175

2.3. Experimental Design

To ensure the accuracy of experimental results and minimize the influence of external factors, the following strict measures were adopted in this experiment. All raw materials were selected from the same batch, and all samples were cast on the same day. The immersion treatment of the samples also took place on the same day, with all samples being placed in an outdoor environment and the immersion solution being regularly replaced. The standard size of the samples was 100 mm $\times$ 100 mm $\times$ 100 mm. After preparation, the samples underwent standard curing for 28 days and were then placed in immersion tanks containing different solutions to simulate the actual conditions of concrete in natural environments. Both the samples and the immersion tanks were kept outdoors. To systematically evaluate the material's performance, testing intervals were set at 30 days, 60 days, 90 days, 120 days, 150 days, and 180 days, with three specimens prepared for each testing age. Tests were conducted every 30 days to measure the rate of mass loss, loss of compressive strength, and the compressive corrosion coefficient, with averages calculated for each test.

This experiment was conducted by the “GB/T 50082-2009 Standard for Test Methods of Long-Term Performance and Durability of Ordinary Concrete” [19]. Six different corrosive environments were established: natural environment (control group), seawater immersion, seawater wet–dry cycling, single chloride salt immersion, single sulfate salt immersion, and complex salt immersion, as shown in Table 3. To shorten the soaking time of salt solutions on concrete and accelerate the corrosion rate, an accelerated corrosion method was employed by increasing the concentration of the salt solution. Compared to the

standard seawater environment, every 1.5% increase in the NaCl concentration sped up the corrosion rate of the concrete by a factor of 1.43.

Table 3. Experiment identification and erosive environments.

ID	Erosive Environment	Description
ZR	Natural environment	Placed outdoors
HS	Seawater immersion	Seawater sourced from Huizhou, Guangdong
HSG	Wet–dry cycles in seawater	Seawater sourced from Huizhou, Guangdong
LY	Chloride salt immersion	5.0% NaCl solution
LSY	Sulfate salt immersion	10% Na ₂ SO ₄ solution
FHY	Complex salt immersion	Combination of 5.0% NaCl and 10% Na ₂ SO ₄

2.4. Basic Performance Indicators and Testing Methods

(1) Mass loss rate

According to the “GB/T 50082-2009 Standard for Test Methods of Long-Term Performance and Durability of Ordinary Concrete” [19], the mass loss rate of PFUHPC was tested. The mass loss rate was calculated as the ratio of the mass difference between PFUHPC before the test and after being subjected to salt solution corrosion to the mass of PFUHPC before the test, as shown in Equation (1). A negative mass loss rate indicates an increase in PFUHPC mass, while a positive mass loss rate indicates a decrease in PFUHPC mass:

$$\Delta m_n = \frac{m_0 - m_n}{m_0} \quad (1)$$

where Δm_n is the mass loss rate of PFUHPC after the corresponding test cycles, %; m_0 is the mass of PFUHPC before the test, g; m_n is the mass of PFUHPC after the corresponding test cycles, g.

(2) Compressive strength loss rate

Referring to the “GB/T 50081-2019 Standard for Test Methods of Physical and Mechanical Properties of Concrete” [20], the compressive strengths at 30 days, 60 days, 90 days, 120 days, 150 days, and 180 days were tested. The compressive strength loss rate of the specimens was then calculated using Equation (2). A negative compressive strength loss rate indicates an increase in PFUHPC compressive strength, while a positive compressive strength loss rate indicates a decrease in PFUHPC compressive strength:

$$K_n = \frac{f_{c0} - f_n}{f_{c0}} \quad (2)$$

where K_n is the compressive strength rate loss of the PFUHPC after the corresponding test cycles, %; f_{c0} is the compressive strength of the PFUHPC before testing, MPa; f_n is the compressive strength of the PFUHPC after the corresponding test cycles, MPa.

(3) Compressive corrosion resistance coefficient

Referring to the “GB/T 50081-2019 Standard for Test Methods of Physical and Mechanical Properties of Concrete” [20], the compressive strengths at 30 days, 60 days, 90 days, 120 days, 150 days, and 180 days were tested. The compressive corrosion resistance coefficient of the specimens was calculated using Equation (3). When the compressive corrosion resistance coefficient is greater than 1, it indicates an increase in the PFUHPC compressive strength, while a value less than 1 indicates a decrease in the PFUHPC compressive strength:

$$K_f = \frac{f_n}{f_{c0}} \quad (3)$$

where K_f is the compressive corrosion resistance coefficient of the PFUHPC after the corresponding test cycles; f_{c0} is the compressive strength of the PFUHPC before testing, MPa; f_n is the compressive strength of PFUHPC after the corresponding test cycles, MPa.

(4) XRD analysis

X-ray diffraction (XRD) analysis was conducted using a Bruker D8 ADVANCE X-ray diffractometer, manufactured by Bruker Corporation, Germany. Samples of the PFUHPC that had undergone the specified erosion cycles and compressive strength tests were collected. The samples were treated with ethanol to halt hydration, after which the bulk specimens were placed in a dryer. Once the ethanol had evaporated, large aggregates were removed, and the remaining material was ground using an agate mortar. The ground material was then sieved through a 0.08 mm sieve to obtain a fine powder, which was subsequently dried in a vacuum oven at 45 °C for 24 h before testing. The XRD analysis was performed using a copper target, over a 2θ range from 5° to 85°, with a step size of 0.02° per second.

(5) SEM analysis

Scanning electron microscopy (SEM) analysis was conducted using an HV-01-43 model scanning electron microscope. Samples of the PFUHPC that had completed the specified erosion cycles and compressive strength tests were prepared with surfaces as flat and edge-free as possible. The samples were preserved in anhydrous ethanol to halt the hydration reaction and then dried in a vacuum oven at 45 °C for 24 h. Before testing, the samples underwent sputter coating with gold. During the SEM analysis, the acceleration voltage was set to 20 kV, and the magnifications used were 1000×, 5000×, and 10,000×, respectively.

3. Experimental Results and Analysis

3.1. Mass Loss Rates of PFUHPC Under Different Erosive Environments

Figure 1 shows the mass loss rates of the PFUHPC in different erosion environments. It can be seen from Figure 1 that the mass loss rates of ZR0% and ZR1.8% in the control group without erosion showed slight growth trends with the increase in soaking time, reaching the maximum values of 0.27% and 0.31% at 180 days, respectively. The mass loss rates of PFUHPC without fibers and 1.8% fibers increased first and then decreased with the increase in soaking time in other different erosion environments. This is because in the early test, the materials inside the PFUHPC were not fully hydrated. As the test progressed, the materials inside the PFUHPC further hydrated and generated more hydration products, thereby increasing the mass loss rate of the PFUHPC. In addition, the formation of some corrosion products will also increase the mass loss rate of PFUHPC in various corrosion solutions [21].

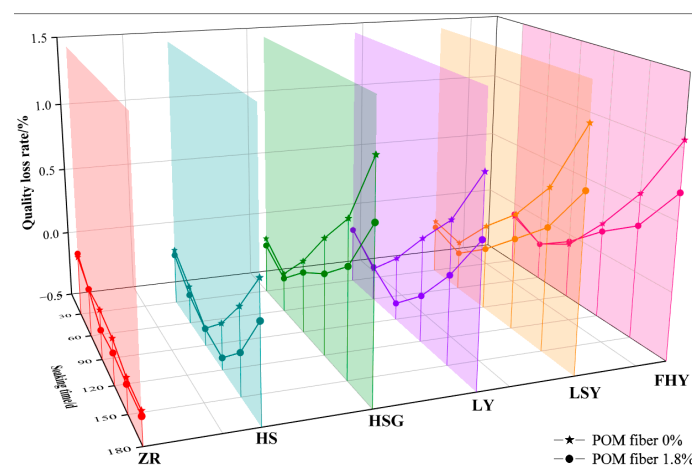


Figure 1. The mass loss rates of the fiber-free PFUHPC and the PFUHPC containing 1.8% POM fibers in different erosion environments.

It can be seen from Figure 1 that when the content of POM fiber was 0%, the mass loss rate of the HS0% group reached the maximum value of -0.37% at 90 days, and the mass loss rates of PFUHPC in other erosion solutions reached the maximum values of -0.21% , -0.25% , -0.13% , and -0.21% at 60 days, respectively. It can also be seen from Figure 1 that when 1.8% POM fiber content was added, the mass loss rate of the HS1.8% group reached the maximum value of -0.41% at 120 days, and the mass loss rate of the LY1.8% group reached the maximum value of -0.37% at 90 days. The mass loss rates of the PFUHPC in other erosion solutions reached the maximum values of -0.24% , -0.21% , and -0.22% at 60 days, respectively. This shows that the erosion effects of the seawater dry–wet cycle, sulfate immersion, and composite salt immersion on the PFUHPC were significantly greater than those of seawater immersion and chloride salt immersion. This is due to the weak erosion of seawater. When immersed in the PFUHPC, the hydration reactions of non-hydrated cementitious materials were slow, and the structural damage was limited. When immersed in chloride salt, the chemical reactions between chloride ions and the PFUHPC were relatively small. The dry–wet cycle of seawater aggravates the internal stress change of concrete. Shrinkage stress is generated during drying, and tensile stress is generated during wetting, which leads to the generation and expansion of microcracks and reduces the compressive strength. Sulfate reacts with cement in concrete to form expansive products, such as ettringite and gypsum, increasing internal stress and damage. The composite salt solution contains a variety of corrosive ions, which trigger complex chemical reactions and generate a variety of corrosive and expansive products, further aggravating the erosion and reducing the compressive strength of concrete. Therefore, the erosion effects of the seawater drying–wetting cycle, sulfate immersion, and compound salt immersion on the PFUHPC were significantly greater than those of seawater immersion and chloride immersion. Moreover, in the long term, the degree of erosion caused by composite salt solutions was less than those caused by seawater wet–dry cycles and sulfate salt immersion.

In addition, compared with the test group without POM fibers, the mass loss rate of the PFUHPC decreased to a certain extent after adding 1.8% POM fibers. The main reason is that the POM fibers strengthen the bonding inside the concrete and optimize the compactness of the structure by interfering with the micropore network and adjusting the pore distribution in the interfacial transition zone (ITZ). Specifically, the presence of POM fibers changed the distribution of hydration products and promoted the formation of ettringite and C-S-H gel around the fibers, thus preventing the further expansion of corrosion products, such as Friedel's salt and gypsum, and delaying the corrosion process [22].

3.2. Compressive Strength Loss Rates of PFUHPC in Different Erosive Environments

Figure 2 illustrates the compressive strength loss rates of the PFUHPC in various erosive environments. It can be seen from Figure 2 that in the early test, in each group with 1.8% POM fibers, the compressive strength loss rate of the HS1.8% group was -2.0% at 30 days and reached the maximum value of -4.2% at 90 days. The 30-day loss rates of the HSG1.8%, LY1.8%, LSY1.8%, and FHY1.8% groups were -4% , -2% , -3% , and -2% , respectively, and reached the maximum values of -7.2% , -5% , -7.2% , and -6% at 60 days. It can be seen that the loss rates of the HSG1.8% and LSY1.8% groups increased significantly. This may be related to the increase of microcracks in the PFUHPC caused by the dry–wet cycles of seawater, and because corrosive ions are more likely to enter the interior and react with incompletely hydrated cementitious materials to form hydration products. In addition, the water–cement ratio of PFUHPC is small, and the sulfate attack is from the outside to the inside. In the early stage of erosion, it reacts with the cementitious material to form more hydration products [23,24].

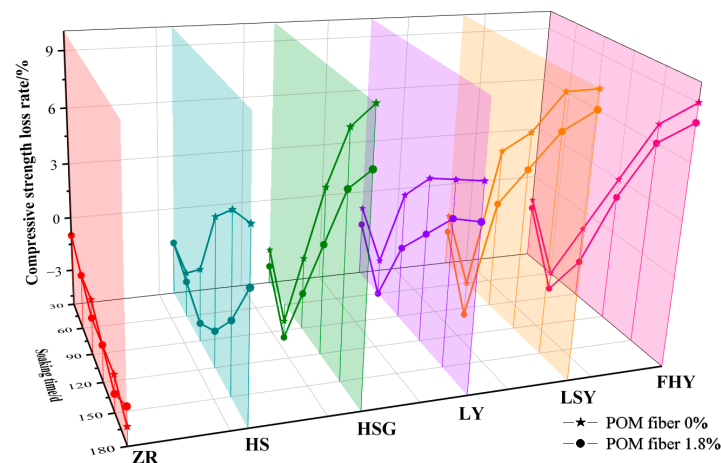


Figure 2. The compressive strength loss rates of the PFUHPC without fibers and with 1.8% POM fibers in different erosion environments.

In the middle and late stages of the tests, the erosion of the PFUHPC by each solution was further aggravated, and the compressive strength began to decrease. The HSG1.8% group, LSY1.8% group, and FHY1.8% group decreased more rapidly. Among them, the compressive strength of PFUHPC in the LSY1.8% group was lower than that before erosion at 90 days, and the compressive strengths of the other groups were lower than the initial values at 120 days. When the soaking time further increased to 180 days, the compressive strength loss rates of the HS1.8% group, HSG1.8% group, LY1.8% group, LSY1.8% group, and FHY1.8% group were 2%, 7%, 4%, 9%, and 8%, respectively. Compared with the control group ZR1.8%, the performance degradations of the PFUHPC after 180 days of different solution immersions were 4.8%, 9.7%, 6.8%, 11.7%, and 10.7%, respectively. It can be seen that the PFUHPC had little effect on the compressive strengths after 180 days of seawater immersion. This was due to the gradual stability of hydration products in the PFUHPC in the later stage of seawater immersion, and because the effect of seawater erosion was weakened. At the same time, compared with seawater immersion, the compressive strength of PFUHPC after the seawater dry–wet cycle was significantly reduced, which was attributed to the continuous evaporation and infiltration of water inside the PFUHPC during the dry–wet cycle, resulting in more serious microcracks and increased porosity. In addition, since the chemical reactions between chloride ions in chloride salt solution and the PFUHPC were relatively small, SO_4^{2-} in the sulfate solution reacted with the PFUHPC to form expansive products, like gypsum and ettringite, resulting in greater internal stress and damage. The Cl^- in the composite salt solution will inhibit the erosion of SO_4^{2-} on the concrete, so the effect of the PFUHPC soaking in the chloride salt solution for 180 days on the compressive strength will be less than that of the sulfate solution and the composite salt solution [25,26].

3.3. Compressive Corrosion Resistance Coefficients of the PFUHPC in Different Erosive Environments

Figure 3 illustrates the compressive corrosion resistance coefficients of the PFUHPC under various erosive conditions. It was observed that the control group (ZR) exhibited an increase of 3% in compressive strength by the end of 180 days. The corrosion resistance coefficients for PFUHPC after immersion in different erosive solutions generally showed initial increases followed by decreases, demonstrating patterns of resilience that diminished over time.

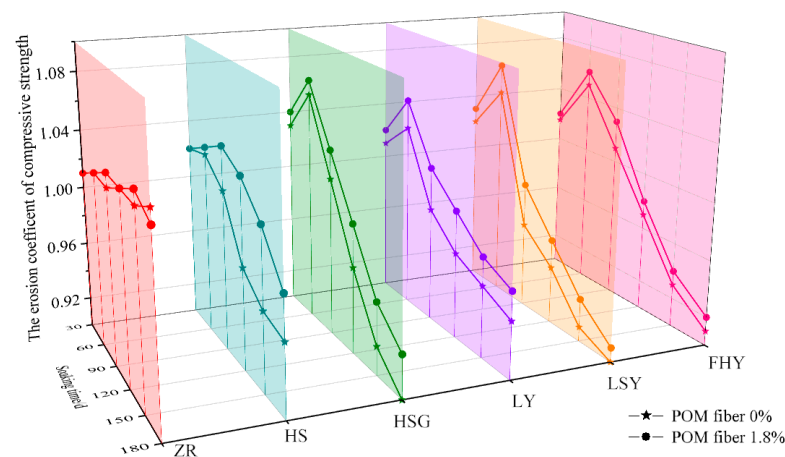


Figure 3. The compressive corrosion resistance coefficients of fiber-free and 1.8% POM fiber-reinforced PFUHPC in different corrosive environments.

At the end of the experimental period of 180 days, for the groups without POM fibers, the compressive corrosion resistance coefficients for the HS0%, HSG0%, LY0%, LSY0%, and FHY0% groups were, respectively, 0.95, 0.90, 0.94, 0.90, and 0.91. When the POM fiber content was increased to 1.8%, the compressive corrosion resistance coefficients improved, and the compressive corrosion resistance coefficients for the HS1.8%, HSG1.8%, LY1.8%, LSY1.8%, and FHY1.8% groups were, respectively, 0.98, 0.93, 0.96, 0.91, and 0.92.

These results indicate that the inclusion of POM fibers enhanced the corrosion resistance of the PFUHPC [27]. POM fibers not only contributed to maintaining higher structural integrity under corrosive conditions but also significantly mitigated the reduction in compressive strength over time, particularly in harsh environments, like those involving sulfates and complex salts. This enhancement is particularly crucial in applications where durability and long-term performance are critical under exposure to aggressive environmental conditions.

3.4. Microscopic Testing

3.4.1. XRD Analysis

Figure 4 shows the X-ray diffraction (XRD) patterns of the PFUHPC after 180 days of immersion in seawater and undergoing seawater wet–dry cycles, compared with samples in natural environmental conditions. The XRD patterns indicate that after 180 days of seawater immersion, various corrosion products formed within the PFUHPC, with significant increases in the diffraction peaks of ettringite and gypsum. Additionally, peaks corresponding to Friedel’s salt were also observed. These changes suggest that the corrosive ions in seawater reacted with the hydration products in the concrete, leading to the formation of more corrosion products. The formation of these corrosion products not only consumed some of the hydration products but also induced the generation and expansion of microcracks, thereby exacerbating compressive strength loss. After seawater wet–dry cycling, the diffraction peaks of these corrosion products were more pronounced than those in the samples immersed solely in seawater, particularly the characteristic peaks of gypsum, ettringite, and Friedel’s salt. This indicates that the seawater wet–dry cycles accelerated the corrosion process, causing corrosive ions to penetrate more deeply into the concrete, further promoting the formation of these corrosion products. This is consistent with the trend of compressive strength loss shown in Figure 2, where the compressive strength losses of PFUHPC were more significant under the wet–dry cycling conditions, further highlighting the close relationship between the formation of these corrosion products and strength loss.

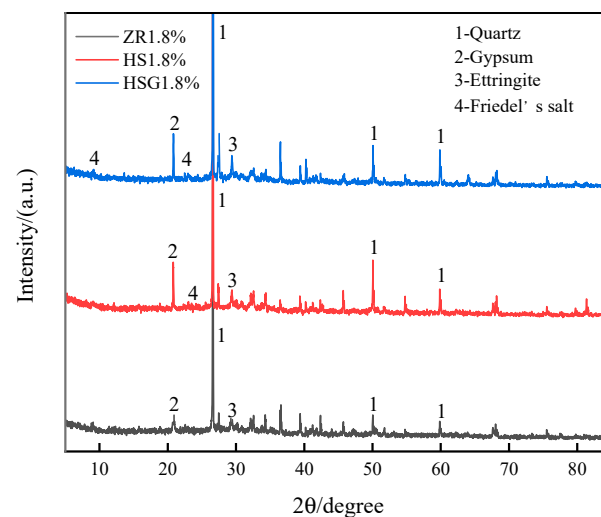


Figure 4. XRD analyses of the PFUHPC under the natural environment, seawater immersion, and wet–dry cycles in seawater conditions.

Figure 5 shows the XRD patterns of the PFUHPC after 180 days of immersion in chloride solution, sulfate solution, and composite salt solution, revealing the characteristics of corrosion products' formation and their impact on the material structure in different erosion environments. In the chloride solution, a significant diffraction peak of Friedel's salt was observed, while the peak intensity of ettringite was relatively weak. This indicates that the high concentration of Cl^- ions primarily reacted with hydration products to form stable Friedel's salt. In the sulfate solution, due to the high concentration of SO_4^{2-} ions, the diffraction peaks of expansive corrosion products, such as gypsum and ettringite, were significantly enhanced. This suggests that the sulfate ions in the sulfate solution reacted with the PFUHPC, generating more corrosion products. These corrosion products led to increased internal stress in the concrete, which in turn triggered the expansion of microcracks and an increase in porosity. This phenomenon is consistent with the trend of compressive strength reduction, indicating that the corrosion of the PFUHPC by sulfate solution was more severe. In the composite salt solution, XRD analysis showed notable diffraction peaks for ettringite, gypsum, and Friedel's salt, reflecting the synergistic effects of Cl^- and SO_4^{2-} on the structure of the PFUHPC. Specifically, Cl^- ions reacted with hydration products to form Friedel's salt, while SO_4^{2-} ions generated expansive products, such as gypsum and ettringite. It is noteworthy that chloride ions somewhat inhibited sulfate corrosion, which may be due to the preferential reaction between Cl^- and Ca^{2+} using the contact chance of SO_4^{2-} ions with hydration products. This also explains why the amount of gypsum and ettringite formed in the composite salt solution was lower than that in the sulfate solution [28–31].

Figures 4 and 5, along with Table 4, indicate that the primary corrosion products for the HS, HSG, and FHY groups were consistently ettringite, gypsum, and Friedel's salt. However, compared to seawater immersion, diffraction peaks of the main corrosion products were more pronounced in complex solutions, where high concentrations of Cl^- and SO_4^{2-} led to the formation of more corrosion products, exacerbating the degradation of the PFUHPC. Conversely, the amounts of gypsum and ettringite generated in complex solution were lower than in sulfate immersion, suggesting that Cl^- inhibited the corrosive effects of SO_4^{2-} on the PFUHPC. This inhibition may be attributed to the stronger penetration and diffusion capabilities of Cl^- , which preferentially entered the concrete, consuming part of the C-S-H and forming stable Friedel's salt, thereby mitigating the erosion caused by SO_4^{2-} [32].

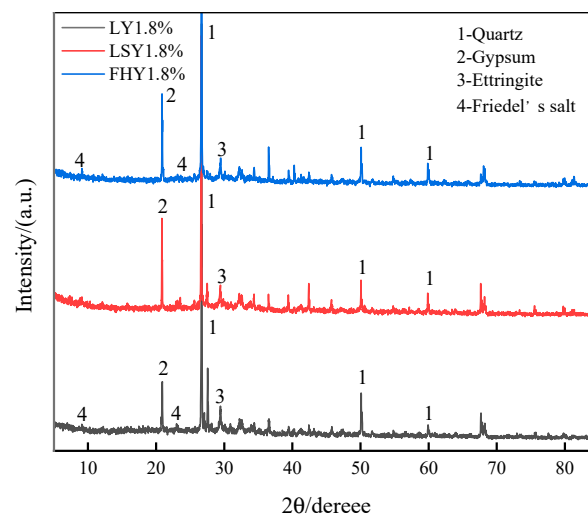
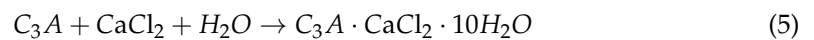
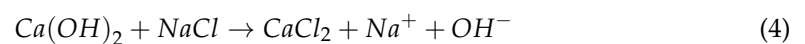


Figure 5. XRD analyses of the PFUHPC under chloride salt solution, sulfate solution, and complex solution conditions.

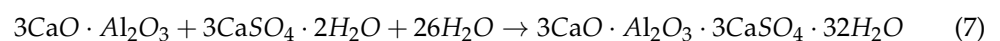
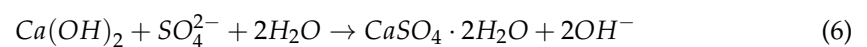
Table 4. The corrosion products of the PFUHPC in different erosive environments.

Corrosion Products	HS	HSG	LY	LSY	FHY
Gypsum	✓	✓		✓	✓
Ettringite	✓	✓		✓	✓
Friedel's salt	✓	✓	✓		✓

Cl^- will react with the hydration products to form Friedel's salt, and the main chemical reactions can be summarized as follows:



The sulfate ions in seawater mainly interact with concrete through two mechanisms. First, SO_4^{2-} reacts with calcium hydroxide in the concrete to form gypsum. Second, it reacts with tricalcium aluminate (C_3A) present in the hydration products to form ettringite, a complex expressed as $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. The main chemical reactions can be summarized as follows:



3.4.2. SEM Analysis

To further explore the degradation mechanisms of the PFUHPC under different erosion environments, this study employed SEM/EDS analysis to examine the microstructure and hydration products of the PFUHPC samples under erosion conditions over a 180-day test period. The deterioration damage mechanism of the PFUHPC was elucidated by observing the morphological changes of erosion products, pore changes, and crack changes within the concrete.

Figure 6 shows the microstructure images of the PFUHPC after 180 days of exposure to a natural environment. The images reveal a large number of amorphous colloidal substances and flaky crystals. Elemental composition analysis of region A indicated that the primary elements in this area were Si, Ca, and O, which correspond to the basic chemical composition of C-S-H gel. The Ca/Si ratio was 1.27, which falls within the typical range of 0.7–1.63 for C-S-H, confirming that the main hydration products in the PFUHPC under

natural conditions are C-S-H gel and C-H crystals. The formations of C-S-H gel and C-H not only filled the internal pore structure of the material, reducing the number of pores and crack widths in the matrix, but also promoted the close bonding of the interfacial transition zone, enhancing the overall structural continuity of the material. This effectively improved the compressive strength and durability of the PFUHPC, enabling it to resist external environmental erosion and thereby extending the service life of the PFUHPC concrete [33,34].

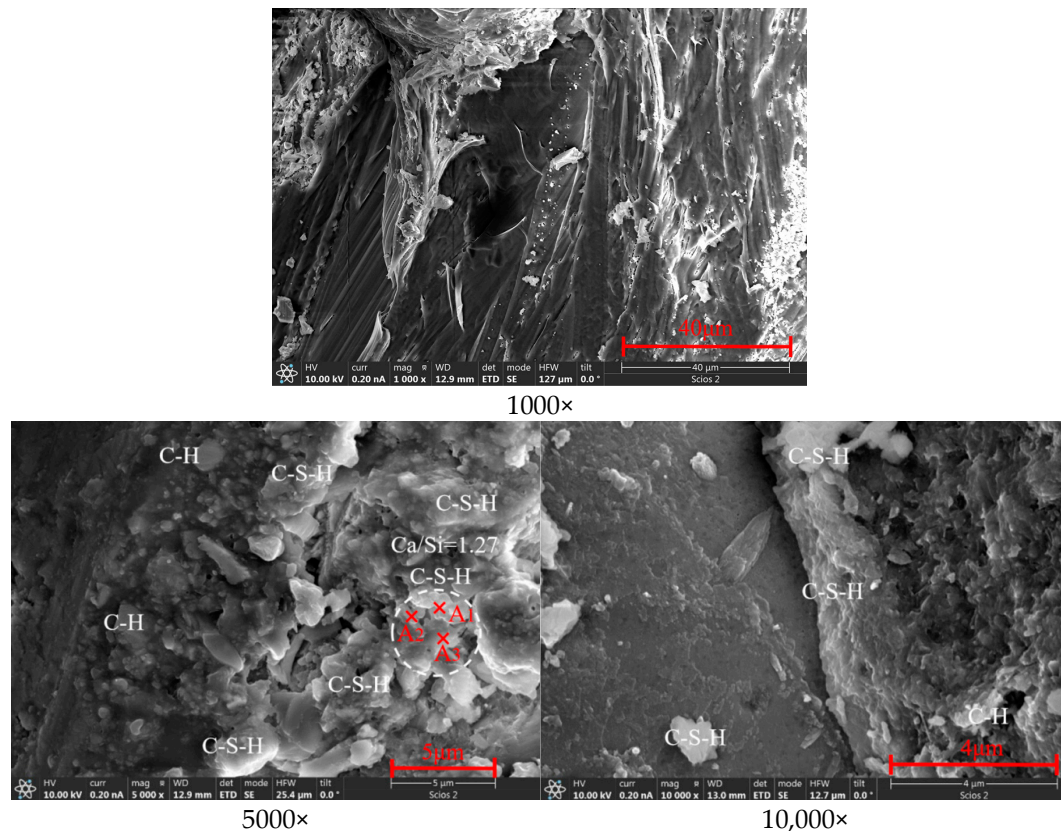


Figure 6. SEM images of the PFUHPC under natural environment conditions.

Figure 7 shows the microstructure of the PFUHPC after 180 days of exposure to seawater solution. EDS analysis revealed that the main elements in region B were Si, Ca, and O, with a Ca/Si ratio of 1.2, indicating that the primary hydration product in this region is C-S-H gel. After seawater corrosion, only minor micropores appeared at the matrix and C-S-H gel interface and the matrix remained relatively dense, suggesting that the effect of seawater corrosion on the PFUHPC was minimal. Region C contained O, Al, Si, Ca, and Cl, consistent with the basic chemical composition of Friedel's salt. The Ca/Si ratio was 8.55, which is far higher than the typical range for C-S-H gel. This suggests that the hydration product in this region is not C-S-H gel but rather Friedel's salt, with a higher calcium content. In region D, the main elements were O, Al, Si, and Ca, with a Ca/Si ratio of 6.7, corresponding to ettringite.

XRD analysis showed that SO_4^{2-} and Cl^- ions in seawater reacted with the hydration products (C-S-H gel and C-H) to form ettringite, gypsum, and Friedel's salt, causing a significant accumulation of Ca^{2+} in the corrosion products and an increase in the Ca/Si ratio. Due to the relatively low concentrations of SO_4^{2-} and Cl^- ions in seawater, only small amounts of ettringite, gypsum, and Friedel's salt formed in the concrete. In terms of compressive strength, the formation of these corrosion products generated expansive stress, which gradually accumulated and induced microcrack formation and propagation in the concrete matrix. These microcracks continued to connect and develop, reducing

the effective load-bearing area of the concrete, and leading to a gradual decrease in the compressive strength. This is consistent with the decrease in the compressive corrosion resistance coefficient of the PFUHPCC, as discussed in Section 3.3. From a durability perspective, the appearance of microcracks provides additional pathways for external corrosive media to penetrate the concrete, accelerating the infiltration of seawater and other corrosive substances, further exacerbating the degradation process and reducing the concrete's impermeability and resistance to chemical corrosion. Externally, the increase in micropores and microcracks caused the concrete surface to become rough and loose, even leading to spalling, which affected the aesthetic appearance and integrity of the concrete structure. In the long term, this may cause dimensional changes in the concrete structure, affecting its normal functionality [35,36].

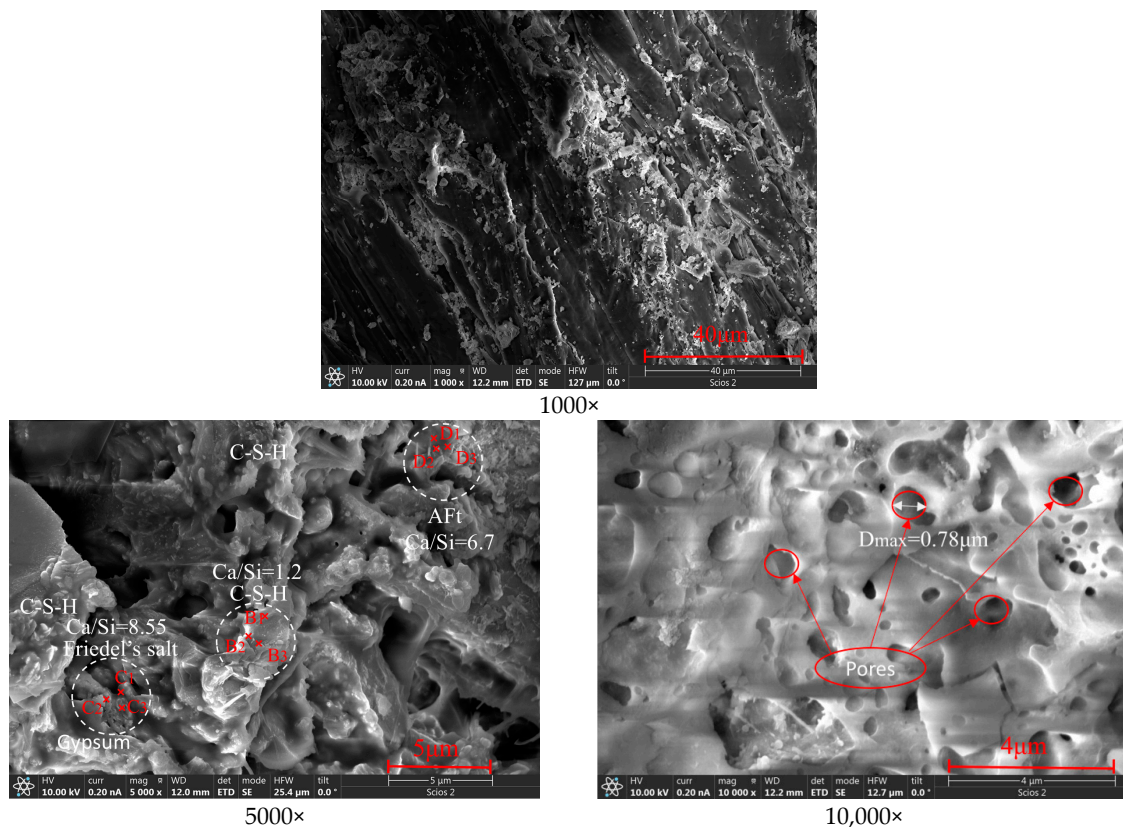


Figure 7. SEM images of the PFUHPCC under seawater immersion conditions.

Figure 8 presents the SEM images of the PFUHPCC after 180 days of seawater wet–dry cycling. After the wet–dry cycling, the matrix exhibited a large number of pores and cracks, with the maximum pore diameter reaching 2.3 μm. EDS results indicated that region E contained O, Si, and Ca, with a Ca/Si ratio of 1.09, which corresponds to C-S-H gel. After 180 days of seawater wet–dry cycling, the Ca/Si ratio of the C-S-H gel decreased further, and the gel was eroded, causing its surface to become rougher. Ca^{2+} was leached from the C-S-H gel, leading to calcium body spalling and the formation of additional cracks and larger pores. Region F contained O, Al, Si, Ca, and Cl, with a Ca/Si ratio of 7.57, corresponding to Friedel's salt. Region G showed O, Al, Si, and Ca, with a Ca/Si ratio of 9.7, indicating ettringite.

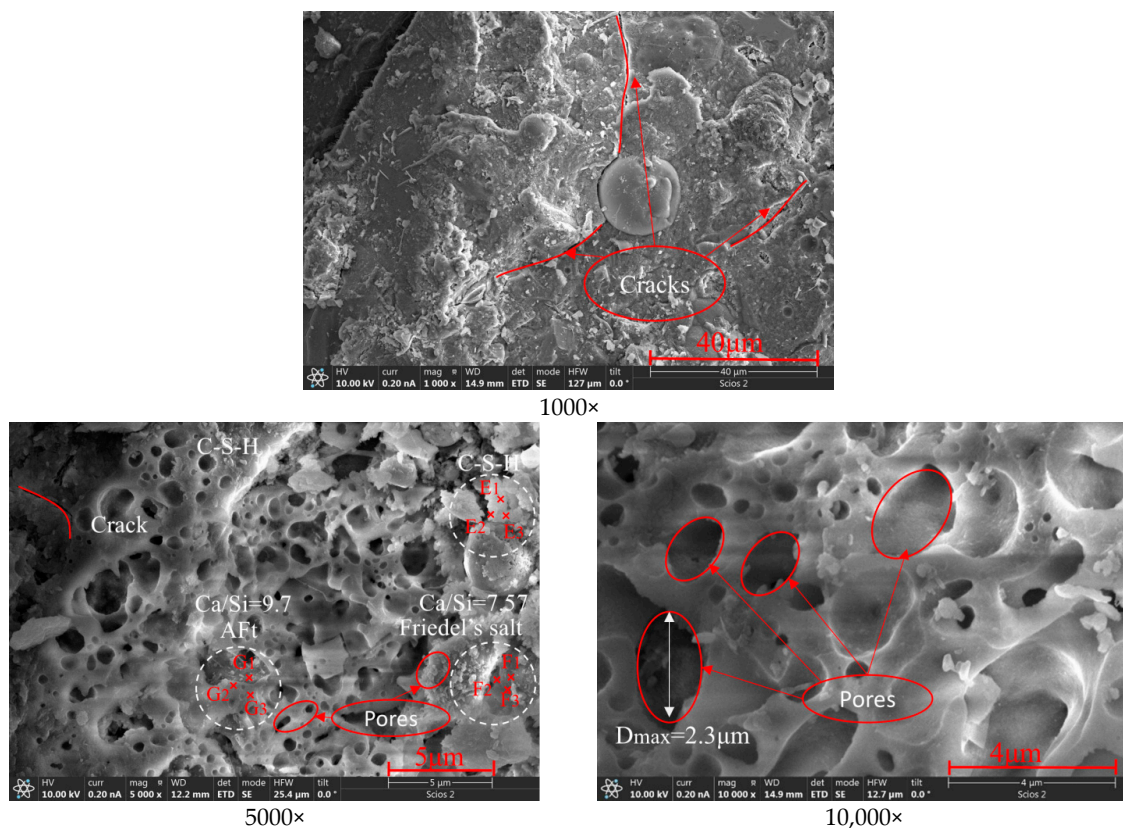


Figure 8. SEM images of the PFUHPC under seawater wet-dry cycle conditions.

The main corrosion products of the PFUHPC after seawater wet-dry cycling were ettringite, gypsum, and Friedel's salt. The matrix experienced repeated cycles of drying and wetting, leading to continuous dehydration and absorption, and accumulating more internal porosity. At this stage, the surface cracks were larger than those observed in seawater immersion, and more cracks were formed, allowing corrosive ions, such as Cl^- and SO_4^{2-} , to penetrate the concrete interior, causing greater damage to the internal structure. Therefore, after 180 days of seawater wet-dry cycling, the PFUHPC showed lower compressive strength, durability, and surface integrity compared to seawater immersion [37].

Figure 9 shows the microstructure of the PFUHPC after 180 days of chloride salt immersion. After immersion in chloride salt, the matrix showed numerous cracks and a small number of micropores, with the maximum pore diameter reaching 0.67 μm. EDS results showed that region H contained O, Si, and Ca, with a Ca/Si ratio of 1.11, corresponding to C-S-H gel. Although the Ca/Si ratio in the C-S-H gel decreased, the layered structure of the C-S-H gel remained relatively intact, and the surrounding material maintained a dense state, with minimal evidence of corrosion. Region I contained O, Al, Si, Ca, and Cl, with a Ca/Si ratio of 6.82, corresponding to Friedel's salt.

After chloride salt immersion, Cl^- reacted with C-S-H gel and C_3A , forming a large amount of Friedel's salt, leading to numerous pores and depressions on the concrete surface. The connectivity between the pores also increased. At this stage, the concrete matrix surface showed many cracks, and the increases in surface porosity and cracks reduced the effective load-bearing area of the concrete, intensifying the stress concentration and significantly reducing the compressive strength of the PFUHPC. The interface transition zone between the aggregates and the paste became blurred, and the overall adhesion worsened, making it difficult for the concrete to effectively transmit stress under load, further weakening the overall strength. The connected pores and numerous cracks provided a convenient pathway for chloride ions to enter the concrete, increasing the number of Friedel's salts

formed by ion reactions, leading to larger surface cracks and a sharp decline in the concrete structure's durability [38,39].

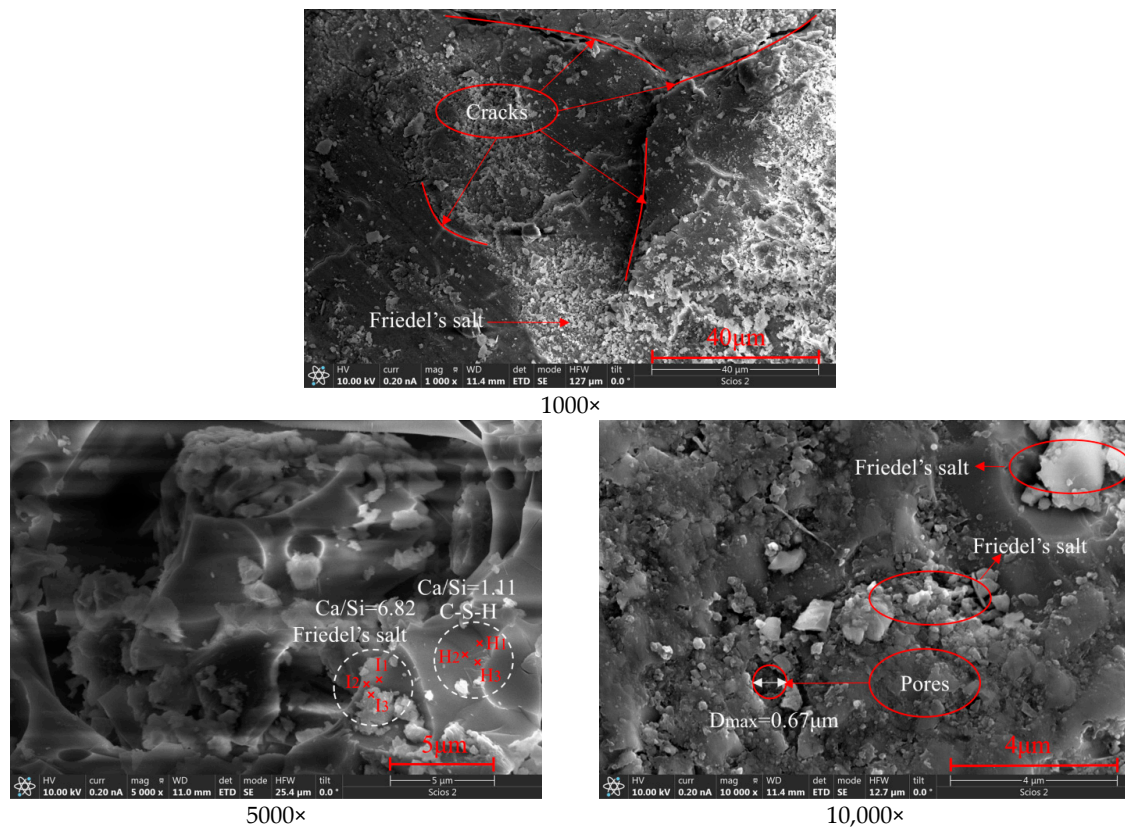


Figure 9. SEM images of the PFUHPc under chloride salt immersion conditions.

Figure 10 shows the microstructure of the PFUHPc after 180 days of sulfate solution exposure. After sulfate immersion, the number and area of internal pores increased, and the overall structure became loose and porous, with the maximum pore diameter reaching 2.37 µm. EDS results showed that region J contained O, Si, and Ca, with a Ca/Si ratio of 0.98, corresponding to C-S-H gel. At this point, decalcification in the C-S-H gel was most pronounced, with the Ca/Si ratio dropping significantly, indicating severe erosion of the C-S-H gel and extensive leaching of Ca^{2+} from it. Region K contained O, Al, Si, and Ca, with a Ca/Si ratio of 10.6, corresponding to ettringite.

SO_4^{2-} ions in the sulfate solution entered the concrete and reacted with hydration products, generating large amounts of gypsum and ettringite. As a result, Ca^{2+} ions were leached and concentrated, forming loose materials with a significant increase in the Ca/Si ratio. Due to the high concentration of SO_4^{2-} , numerous needle-like ettringite crystals and short-column gypsum crystals can be observed in the images. As the corrosion period progressed, the formation of ettringite and gypsum generated expansive stress, leading to the formation of cracks in the concrete matrix. Once microcracks formed, SO_4^{2-} ions, driven by diffusion, entered the concrete through these cracks, further compromising the integrity of the concrete structure and lowering the compressive strength and durability of the PFUHPc. Therefore, long-term immersion in sulfate solution significantly accelerated the degradation of the PFUHPc concrete [40,41].

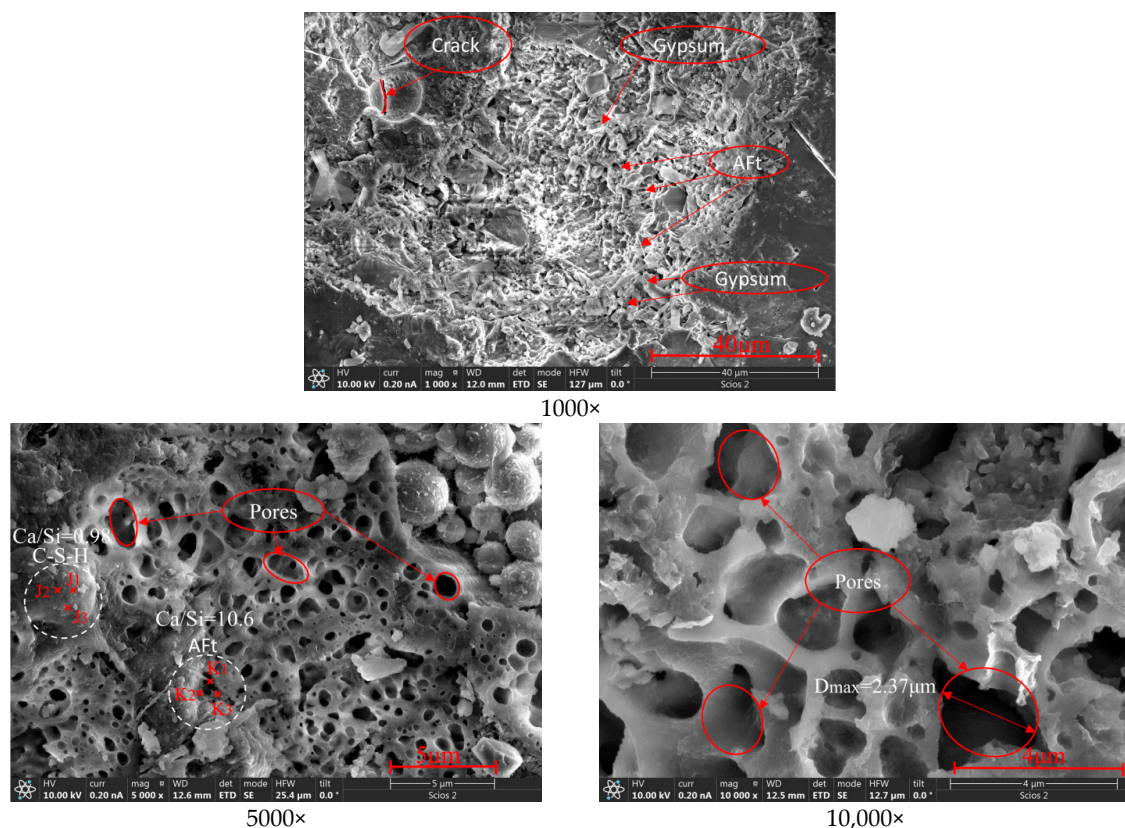


Figure 10. SEM images of the PFUHPC under sulfate immersion conditions.

Figure 11 shows the microstructure of the PFUHPC after 180 days of exposure to a composite salt solution. After immersion in a composite salt solution, the matrix developed numerous cracks and pores, and the overall structure became loose and porous, with the maximum pore diameter reaching $1.86\ \mu\text{m}$. EDS results indicated that the main elements in region L were O, Si, and Ca, with a Ca/Si ratio of 1.03, corresponding to C-S-H gel. At this stage, the C-S-H gel underwent dual erosion by Cl^- and SO_4^{2-} , further compromising its stability. The Ca/Si ratio decreased significantly, and the leaching of Ca^{2+} became more evident. Region M contained O, Al, Si, and Ca, with a Ca/Si ratio of 9.09, corresponding to ettringite, while region N contained O, Al, Si, and Ca, with a Ca/Si ratio of 6.32, corresponding to Friedel's salt.

The main corrosion products in the composite salt solution were gypsum, ettringite, and Friedel's salt. Similar to sulfate immersion, the high concentration of SO_4^{2-} corrosion products caused significant damage to the concrete. However, the severity of the corrosion was weaker than that observed in sulfate immersion. This is consistent with the earlier XRD analysis, which showed that Cl^- had a stronger penetration and diffusion ability, and preferentially entered the concrete, consuming some of the C-S-H while forming stable Friedel's salt. This process delayed the erosion effect of SO_4^{2-} . Therefore, the PFUHPC exposed to the composite salt solution demonstrated better compressive strength and durability than the PFUHPC exposed to the sulfate solution [42].

From the results of SEM and Table 5, it is evident that the primary corrosion products in seawater immersion and seawater wet–dry cycles were ettringite, gypsum, and Friedel's salt. However, due to lower chloride and sulfate ion concentrations, the formation of corrosion products was limited, resulting in minimal surface micropores and a relatively dense overall concrete matrix. Nevertheless, the erosion of the PFUHPC was exacerbated under seawater wet–dry cycle conditions. In chloride salt immersion, Friedel's salt was the main corrosion product, accompanied by the appearance of cracks and micropores on the concrete surface. In sulfate immersion, gypsum and ettringite were the principal

corrosion products, leading to a porous and loosely structured concrete surface and more severe corrosion. The quantities of gypsum and ettringite generated under the PFUHPCC composite salt immersion were less than those under sulfate immersion, resulting in lower expansion stress and reduced damage to the concrete matrix. Thus, it is evident that the presence of high concentrations of chloride ions inhibited the erosive effects of sulfates on concrete.

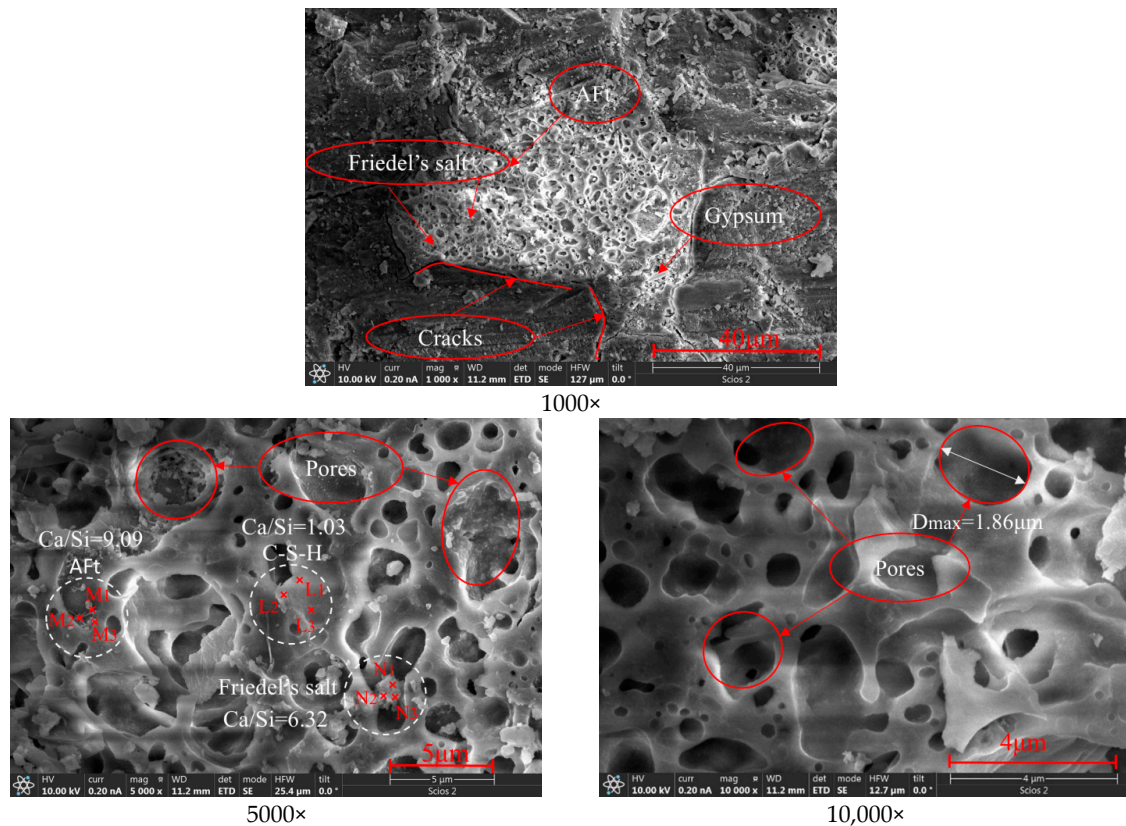


Figure 11. SEM images of the specimen under complex salt immersions.

Table 5. EDS analyses on the yielded molar mass ratios of major elements of hydration products in different erosion environments.

Sample	Area	O	Na	Al	Si	Ca	Cl	Ca/Si
ZR	A	60.5	1.1	1.4	16.3	20.7	/	1.27
	B	61.4	4.09	3.58	14.06	16.87	/	1.20
HS	C	40.87	3.65	11.54	4.3	36.77	2.87	8.55
	D	51.9	2.2	3.8	5.5	36.6	/	6.7
HSG	E	59.87	4.11	8.86	13.00	14.16	/	1.09
	F	41.63	4.25	10.38	4.7	35.58	3.46	7.57
	G	47.9	1.2	2.8	4.5	43.7	/	9.7
LY	H	61.79	5.21	5.36	13.10	14.54	/	1.11
	I	40.21	4.87	12.49	4.9	33.42	4.11	6.82
LSY	J	67.45	4.39	4.76	11.82	11.58	/	0.98
	K	45.1	1.3	3.7	4.3	45.6	/	10.6
FHY	L	66.93	5.14	3.51	12.03	12.39	/	1.03
	M	47.9	1.4	4.3	4.6	41.8	/	9.09
	N	41.27	5.03	8.94	5.6	35.37	3.79	6.32

4. Conclusions

This study investigated the mass losses and strength degradations of the PFUHPC under different erosion environments, including seawater immersion, seawater wet–dry cycles, chloride salt immersion, sulfate salt immersion, and composite salt immersion, over durations ranging from 0 to 180 days. Microscopic property tests were conducted on the PFUHPC samples after 180 days of erosion, yielding the following conclusions:

1. In erosion experiments, the mass loss of the PFUHPC exhibited trends of initial increases followed by decreases under all tested erosion environments. The addition of POM fibers delayed corruptions and reduced mass losses. After 180 days of immersion in various solutions, the mass loss percentages for the HS0%, HSG0%, LY0%, LSY0%, and FHY0% groups were 0.49%, 1.14%, 0.97%, 1.22%, and 1.05%, respectively, with 0% POM fiber content. With 1.8% POM fiber content, the mass loss percentages decreased to 0.19%, 0.72%, 0.53%, 0.78%, and 0.70%.

2. Similarly, the strength loss of the PFUHPC followed an initial increase followed by a decreasing trend under all erosion environments. The addition of POM fibers delayed corrosion and reduced compressive strength loss. After 180 days of immersion in various solutions, the compressive strength loss percentages for the HS0%, HSG0%, LY0%, LSY0%, and FHY0% groups were 5%, 10%, 6%, 10%, and 9%, respectively, with 0% POM fiber content. With 1.8% POM fiber content, the compressive strength loss percentages decreased to 2%, 7%, 4%, 9%, and 8%, respectively. Relative to the natural immersion group, the strength degradation percentages were 4.8%, 9.7%, 6.8%, 11.7%, and 10.7%.

3. Microscopic analysis of the PFUHPC samples after 180 days of erosion revealed that the predominant erosion products under different erosion environments were gypsum, ettringite, and Friedel's salt. In seawater immersion and seawater wet–dry cycle environments, where chloride and sulfate ion concentrations were low, fewer corrosion products were generated, resulting in a relatively dense concrete surface with micropores. Chloride salt immersion mainly produced Friedel's salt, leading to the appearance of cracks and micropores on the concrete surface. Sulfate salt immersion primarily resulted in gypsum and ettringite, leading to a porous and severely corroded concrete surface. In complex salt immersion, the reduced content of ettringite, coupled with the high concentration of Cl^- ions, delayed the erosion caused by SO_4^{2-} , resulting in less severe corrosion compared to sulfate salt immersion.

5. Limitations and Future Prospects

This study primarily investigated the durability of concrete without POM fibers and with 1.8% POM fiber content under different aggressive environments, and analyzed its microstructure through SEM. However, the research has certain limitations, which are outlined as follows:

1. This study only investigated concrete with a POM fiber content of 1.8%. Future research can explore the effects of different POM fiber contents and lengths, as well as conduct long-term erosion tests and studies on multi-environment interactions. These efforts would provide data support for the development of standardized design guidelines for the PFUHPC, thereby promoting its widespread application in complex environments, such as marine engineering.

2. Under various aggressive environments, the incorporation of POM fibers improved the durability of the PFUHPC, reducing the damage and repair frequency caused by erosion and lowering maintenance costs. However, POM fibers are relatively expensive, costing approximately CNY 20,000 per ton, with the material cost for POM fibers in one cubic meter of PFUHPC being about CNY 504. This cost poses a significant challenge for large-scale engineering applications. Therefore, future research should focus on the modification of POM fibers. Strategies such as adding appropriate fillers, additives, or blending with other materials could be employed to reduce the use of high-cost components in POM fibers without significantly compromising their performance, thus achieving cost reduction for practical applications.

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