Composite Structures

Beyond Time: Enhancing Corrosion Resistance of Geopolymer Concrete and BFRP Bars in Seawater
--Manuscript Draft--

Abstract:	To improve the durability of Basalt fiber reinforced polymer (BFRP) bars reinforced geopolymer concrete (GPC), it is important to study the time-dependent variation of the corrosion resistance ability of GPC and BFRP in a seawater environment. This paper presents an experimental investigation to study the time-dependent mechanical properties and durability of BFRP bars and geopolymer materials synthesized.The resulting GPC and Portland cement (PC) concrete were exposed to artificial seawater. The corrosion resistance of geopolymer (GP) mortar and PC mortar was evaluated by studying the migration ability and pore structure in corrosive ions attack in artificial seawater. In addition, the dual interface transition zones (ITZs) characteristics of BFRP reinforced GPC under artificial seawater were also investigated by SEM and BSE tests. The results showed that the volume expansion rate and strength loss rate of GPC decreased by 77.6% and 8.7%, respectively. In addition, the effect of seawater corrosion on the tensile strength of BFRP bars increases with the increase of bars' diameter, and the ultimate strengths of BFRP bars with diameters of 6 mm and 8 mm were 695 MPa and 663 MPa, respectively. This research can provide a theoretical basis for the service life prediction of BFRP reinforced geopolymer concrete.

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Response to Reviewers:	

Dear Prof. Heng Hu
Editor-in-Chief
Composite Structures

We wish to re-submit the manuscript titled titled "*Beyond Time: Enhancing Corrosion Resistance of Geopolymer Concrete and BFRP Bars in Seawater*".

The manuscript has been rechecked and appropriate changes have been made in accordance with the reviewers' suggestions. The responses to their comments have been prepared and attached herewith. The manuscript has been proofed by language edit center.

We thank you and the reviewers for your thoughtful suggestions and insights, which have enriched the manuscript and produced a better and more balanced account of the research. We look forward to working with you and the reviewers to move this manuscript closer to publication in COMSTR.

Thank you for your consideration. We look forward to hearing from you.

Sincerely,
Yunchao Tang
State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures
Guangxi University
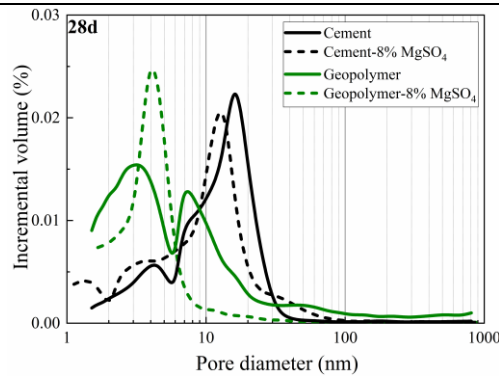Email: joshua0115@gxu.edu.cn

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Title: "Beyond Time: Enhancing Corrosion Resistance of Geopolymer Concrete and BFRP Bars in Seawater"

Authors: Zheng Chen; Jiamin Yu; Yumei Nong; Yongmin Yang; Hexin Zhang; and Yunchao Tang

Serial No.	Comments	Authors' Response	Action Taken
	Comments from **Reviewer #1**		
Comment 1	The citation format should follow the journal's guidelines. To improve the research depth of the paper, it is recommended that the author refer to some of the latest relevant papers, such as: https://doi.org/10.1016/j.jmrt.2022.11.135 https://doi.org/10.1016/j.ocecoaman.2022.106038 https://doi.org/10.1016/j.jobe.2021.103828 https://doi.org/10.1016/j.compstruct.2020.113078 https://doi.org/10.1016/j.conbuildmat.2020.121399 https://doi.org/10.1016/j.conbuildmat.2020.122195 https://doi.org/10.1016/j.conbuildmat.2021.123218	The authors thank this comment from the reviewer. Some of the suggested articles have now been added to the Introduction	Some of the suggested articles have now been referred as [37-40] in the Introduction, to suitably address this comment.
Comment 2	Was the equipment shown in Figure	The authors appreciate the valuable	The Section 3.1.2, (lines 296-305,

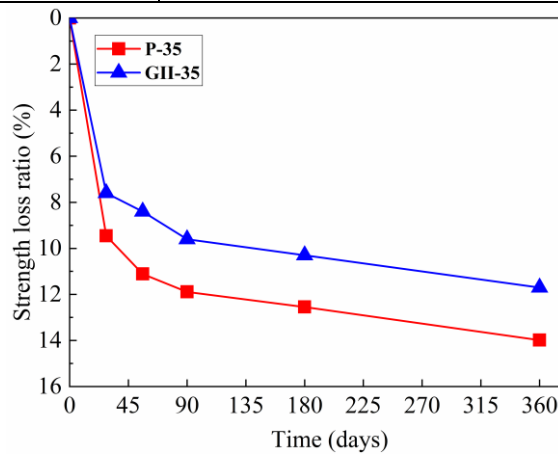|			
	2designed and developed by the authors themselves? It is indeed an interesting aspect of this study. However, the device lacks a detailed description of the equipment. It would be helpful if the authors could provide a more comprehensive explanation of the design, components, and functioning of the equipment. This would allow readers to better understand its novelty and relevance to the research conducted in this study.	comment from this reviewer. The suggested detailed description of the equipment has now been added to the Section 3.1.2, (lines 296-305, page 11)	page 11) has now been improved to address this comment.
Comment 3	The meaning of symbols $F_c(t)$ and $F_w(t)$ in Eqs.(4) and Eqs. (5) need to be clarified.The meaning of symbols C and C_0 in Eqs. (8) and Eqs. (9) need to be clarified.	The authors appreciate this comment from the reviewer. $F_c(t)$ is strength retention rate of concrete in marine environments in immersion time t. $F_w(t)$ is strength retention rate of GPC in marine environments in immersion time t. C_0 is the chloride concentration on the exposed surface of concrete. C is the free chloride concentration in diffusion time t	The meaning of $F_c(t)$ and $F_w(t)$ in Eqs. (4) and (5) have now been clarified in Section 4.2 to address this comment. The meaning of C and C_0 in Eqs. (8) and (9) have now been clarified in Section 4.3 to address this comment.
Comment 4	The label of the curve in Figure 7(c) is mislabeled	The authors thank this comment from the reviewer. The new Figure 7(c) in the revised manuscript also is attached below.	To suitably address this comment, the new Figure 7(c) are changed in the revised manuscript.

(c) Pastes with MgSO$_4$

Fig.7. Pore size distribution of geopolymer and cement pastes with NaCl, Na$_2$SO$_4$ and MgSO$_4$

Comment 5	The authors studied the effect of Cl$^-$, SO$_4^{2-}$ and Mg^{2+} on the pore structure of geopolymers under seawater erosion. However, the article has less analysis of magnesium ions, please explain further the effect of magnesium ion erosion on geopolymers in chapter 4.4.	In order to help address this comment, the author has now been added at lines 483-491 on page 19. This may be due to the fact that in the early stage of erosion, the erosion products of SO$_4^{2-}$ first fill the pores, thus leading to a decrease in the median pore size like of the cement paste. In addition, the addition of 8% Mg^{2+} resulted in a significant increase in the number of macropores in the cement paste and a significant decrease in the percentage of macropores in the geopolymer. This suggests that the erosive effect of Mg^{2+} may be more likely to convert the hydration product C-S-H gel to M-S-H, leading to the appearance of loose macropores in the structure. These results indicate that geopolymers have good resistance to penetration of erosive materials due to their compact pore structure.	A detailed analysis has now been added at lines 484-492 on page 19 to suitably resolve this comment in the revised manuscript.
Comment 6	The graphs, tables and figures are of very good standard.	The authors thank this comment from the reviewer	No action taken at this stage.
Comment 7	The data and analysis provided in the paper are extensive and detailed. However, I believe that the content could be slightly	We have adjust the tables and charts based on the reviewer's comment.	Figure 7 has been modified.

	condensed by removing some secondary data tables and charts.		

Serial No.	Comments	Authors' Response	Action Taken
		Comments from **Reviewer #2**	
Comment 1	The introduction of other studies is summarized thoroughly in the preface, but it would be beneficial to provide further explanation of the content and significance of this paper's study.	The content and significance of this paper's study has now been lines 211-220 on page 7.	The manuscript was left unchanged in respect to this comment.
Comment 2	In Table 9, the authors investigated the impact of different dosages of NaCl, Na_2SO_4, and $MgSO_4$ added into the GP paste. However, the text does not provide a basis for the chosen dosage of marine corrosive substances. Please provide further reasons for this choice of dosage in chapter 3.3.3.	The authors thank this comment from the reviewer. In Table 9, the purpose of mixing NaCl, Na_2SO4 and $MgSO_4$ inside the slurry is only to compare the corrosion ion migration resistance of GP with that of ordinary cement slurry, so the dosage is not selected according to the content of marine corrosive substances. Secondly, the content of corrosive ions in the actual marine environment is low, and the effect of studying the ion migration performance in a short time is not obvious. In the existing research literature [1-5], the content of chloride ion is basically taken as 0%~5% and sulfate ion is basically taken as 0%~10%, but the reason for the selection of dosage has not been shown. Therefore, in this paper, the content of sodium chloride is taken as 3.5% and 5%, and the content of sodium sulfate and magnesium sulfate is taken as 3% and 8%. [1]https://doi.org/10.1016/j.conbuildmat.2018.12.168 [2]https://doi.org/10.1016/j.conbuildmat.2021.122970 [3]https://doi.org/10.1016/j.conbuildmat.2017.09.159 [4]https://doi.org/10.1061/(ASCE)MT.194	No action taken at this stage.

		3-5533.0001618 [5]https://doi.org/10.1016/j.compositesb.2019.107689	
Comment 3	In Figure 4.(b), it is suggested to change the strength loss ratio from 0-16 to 16-0. This change would present a clearer representation of the intensity loss between GPC and PC concretes.	The authors thank this comment from the reviewer. the new Figure 4(b) in the revised manuscript also is attached below.	To suitably address this comment, the new Figure 4(b) are changed in the revised manuscript.

(b) Strength loss

Fig. 4. The corrosion resistance of GPC and PC concretes

Comment 4	Discussion about the limitations of the study is suggested	Yes, the authors agree fully with this reviewer here Yet, the present study focuses on analyzing the ionic attack resistance of BFRP reinforced geopolymer concrete by simulating seawater environment in the laboratory. However, in real marine environments, the migration of ions is not only by diffusion, but there may be convective effects under hydrostatic pressure. Certain key questions are still waiting to be considered: How to simulate more realistic ocean conditions is further investigated through systematically designed experiments? What is the effect of competing antagonistic effects on the	As advised by Reviewers 2, the Section 5 on "Conclusions" summarizes and lists the limitations from the present study. As well, the future direction is also detailed in the revised manuscript.

		performance of BFRP reinforced geopolymer concrete under multiple-ion combined attack in marine environments? Further studies, with systematically designed experiments and research including long-term observation that will help tune the proposed mathematical models will address the above questions.	

Declaration of interests

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

CRediT authorship statement

Zheng Chen: conceptualization, software, validation, and writing the original draft. **Jiamin Yu**: reviewing and editing. **Yumei Nong, Yongmin Yang**: software, data curation and editing. **Hexin Zhang**: investigation, data curation and validation. **Yunchao Tang**: Supervision, conceptualization and editing.

1   **Beyond Time: Enhancing Corrosion Resistance of Geopolymer Concrete and**
2   **BFRP Bars in Seawater**

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35

36 **ABSTRACT:** To improve the durability of Basalt fiber reinforced polymer (BFRP)

37 bars reinforced geopolymer concrete (GPC), it is important to study the time-

38 dependent variation of the corrosion resistance ability of GPC and BFRP in a seawater

39 environment. This paper presents an experimental investigation to study the time-

40 dependent mechanical properties and durability of BFRP bars and geopolymer

41 materials synthesized by granulated blast furnace slag (GGBFS), fly ash, and silica

42 fume. The resulting GPC and Portland cement (PC) concrete were exposed to

43 artificial seawater. The mechanical properties of GPC were evaluated by analyzing

44 and comparing the volume expansion and strength loss rates of GPC and PC concrete

45 in an artificial seawater environment. The corrosion resistance of geopolymer (GP)

mortar and PC mortar was evaluated by studying the migration ability and pore structure in corrosive ions attack (Cl^-, SO_4^{2-}, Mg^{2+}) in artificial seawater. Moreover, the time-dependent tensile strength of BFRP was comparatively investigated by immersing in different solutions (tap water, artificial seawater, and alkaline simulated seawater). In addition, the dual interface transition zones (ITZs) characteristics of BFRP reinforced GPC under artificial seawater were also investigated by SEM and BSE tests. The results showed that the volume expansion rate and strength loss rate of GPC decreased by 77.6% and 8.7%, respectively, after 360 days of seawater corrosion compared with PC concrete. This enabled the development of a time-dependent strength model of GPC in marine environments. The coefficient of ions diffusion in GP mortar is much lower than that of PC mortar, and GP mortar shows excellent resistance to ion migration. In addition, the effect of seawater corrosion on the tensile strength of BFRP bars increases with the increase of bars' diameter, and the ultimate strengths of BFRP bars with diameters of 6 mm and 8 mm were 695 MPa and 663 MPa, respectively. The tensile strength degradation model of BFRP bars in geopolymer concrete under seawater corrosion was established. After 360 days of seawater immersion, the average porosity of the ITZ between geopolymer and aggregates, and the average porosity of the ITZ between geopolymer and BFRP bars increased insignificantly compared to that of PC concrete. This research can provide a theoretical basis for the service life prediction of BFRP reinforced geopolymer concrete within marine environments.

Keywords: Geopolymer concrete, Basalt fiber reinforced polymer (BFRP) bars, Seawater, Time-dependence, Interface characteristic.

1 Introduction

Geopolymer concrete (GPC) has attracted extensive attention from researchers due to its excellent characteristics, such as stable hydration products, compact paste structure, adjustable setting time, early strength, and high strength [1-4]. Meanwhile, it can effectively reduce energy consumption and greenhouse gas emissions of ordinary Portland cement (OPC) production[5-10]. The process of preparing GPC is given in Fig.1. In addition, GPC has excellent seawater corrosion resistance, enabling the use of local materials and sea sand as aggregate, to solve the problem of insufficient river

79 sand resources. Therefore, GPC is suitable for the characteristics of marine
80 engineering construction, and it can address issues such as the shortage of materials
81 and fresh water, the influence of tidal action in the construction process, and the
82 corrosion from harmful ions in seawater in the service process of buildings.
83 Experimental results show that the mechanical properties of seawater sea sand
84 concrete (SWSSC) are similar to those of traditional concrete[11]. However, seawater
85 and sea sand contain high concentrations of chloride ions, which will lead to the
86 corrosion of steel bars in SWSSC structures [12, 13]. Corrosion and expansion of steel
87 bars cause durability problems such as cracking and peeling of the protective concrete
88 layer. These problems seriously reduce the safety of SWSSC structures and lead to
89 high maintenance costs. However, fiber reinforced polymer (FRP) bars are believed to
90 be another effective way to solve these problems, potentially eliminating the
91 limitation that seawater sea sand cannot be directly used as concrete raw material [14].
92 Recently, basalt fiber reinforced polymer (BFRP) bars have been used in some
93 concrete structures subjected to extreme environmental conditions due to their
94 superior chemical resistance [15-17]. There is no corrosion and expansion problem in
95 marine environments, so BFRP reinforced geopolymer concrete (hereafter called
96 BFRP GPC) has broad application prospects in marine engineering construction.
97 However, it is worth noting that BFRP GPC has double interface transition zones
98 (ITZs), and the transport of corrosive ions in seawater in the GPC is time-dependent.
99 Existing research results do not reveal the time-dependence variation of corrosive ions
100 transported in GPC under seawater corrosion and the influence of the time-
101 dependence variation on the performance of BFRP bars. Thus, it is necessary to study
102 the time-dependence mechanism of GPC and BFRP bars under seawater corrosion as
103 it can provide a basis for service life prediction of BFRP GPC in marine environments.
104   In previous studies, there have been numerous research efforts on the seawater
105 corrosion resistance of GPC, including Cl^- permeability resistance, sulfate resistance
106 (SO_4^{2-} and Mg^{2+}), and the variation of properties in artificial seawater. On Cl^-
107 permeability resistance of GPC, Thomas et al. [18] studied the chloride ion
108 permeability of alkali-activated fly ash, alkali-activated slag, and PC concrete
109 immersed in 3% NaCl for 90 days. In general, alkali-activated slag concrete has better
110 chloride ion permeability resistance, slightly better than PC concrete. Gunasekara et al.
111 [19]studied the corrosion of fly ash-based geopolymers and PC concrete immersed in

112 3% NaCl for 540 days. Test results indicated that the three-dimensional N-A-S-H and

113 C-A-S-H crosslinking formed in the fly ash-based geopolymers reduces the diffusion

114 of chloride ions into the depth of the concrete, resulting in a lower corrosion rate

115 compared to PC concrete. Amorim Junior et al. [20] showed that metakaolin GPC has

116 similar or higher durability than OPC concrete by the migration test of chloride.

117 Therefore, GPC has excellent resistance to chloride ion penetration, which is related

118 to the type of activator, alkali content, and curing mode in GPC. In addition, the

119 presence of sulfate ions and magnesium ions can also affect the durability of concrete

120 structures in the marine environment. Krivenko et al. [21] proposed that slag-based

121 geopolymer concrete has better sulfate resistance than PC paste, even better than

122 sulfate-resistant cement pastes, and sodium sulfate is beneficial to promote the

123 polymerization of GPC continuous reaction, making the structure more compact.

124 Dzunuzovic et al. [22] studied the influence of 5% sodium sulfate solution on the

125 mechanical properties and microstructure properties of fly ash-slag base binder (FA-

126 BFS) and PC concrete for 180 days. During the whole immersion period, the strength

127 loss index was higher than 1, and the compressive strength of specimens exposed to

128 the sulfate solution developed slowly. XRD (X-ray diffractometer) analysis shows that

129 there were no new substances produced by the alkali-activated material and sulfate

130 reaction. Sanghamitra Jena [23] used silica ash to partially replace fly ash to prepare

131 GPC. Specimens were respectively immersed in 5% NaCl and 2% $MgSO_4$ corrosive

132 solution for 28 days. The experimental results showed that adding fly ash and silica

133 fume can improve the strength of GPC. Hafez E. Elyamany et al. [24] compared the

134 corrosion resistance of GP mortar with added slag and silica fume substituted for fly

135 ash, GP mortar with fly ash, and OPC mortar after immersion in 10% $MgSO_4$ solution

136 for 48 weeks. The results showed that the corrosion resistance of GP mortar mixed

137 with slag and silica fume is higher than that of GP mortar mixed with fly ash only, and

138 both are higher than that of OPC mortar. Valencia Saavedra et al. [25] studied the

139 performance of GPC (composed of 80% fly ash and 20% mineral powder) and OPC

140 concrete after curing in 5% $MgSO_4$ solution for 360 days. The results showed that the

141 expansion rate of FA/GBFS (Class fly ash and granulated blast-furnace slag) concrete

142 is 0.04% and the mechanical resistance is reduced by 33%, while the expansion rate

143 of OPC concrete is 0.08% and the mechanical resistance is reduced by 48% under the

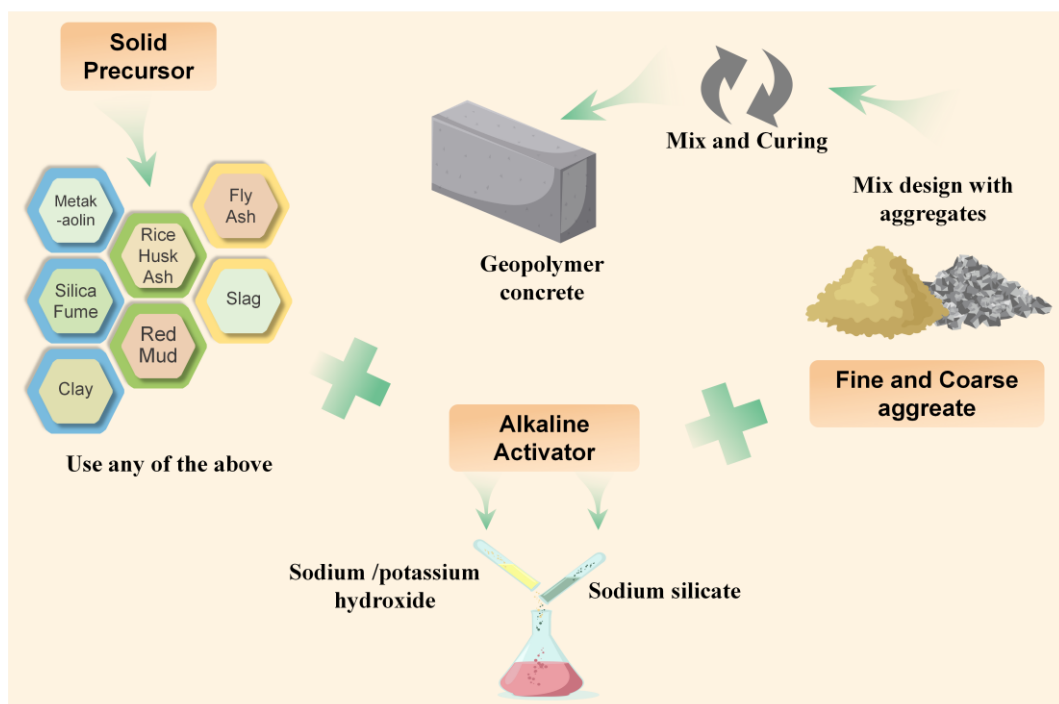144 same conditions. Therefore, FA/GBFS concrete has better resistance to $MgSO_4$

corrosion than OPC concrete. The above research shows that all kinds of GPC have better sulfate resistance than OPC concrete, as the reaction products are difficult to corrode and the microstructure is compact. However, existing research on the seawater corrosion resistance of GPC does not consider the time-dependence of corrosive ion transport, and the influence mechanism of the dynamic transport process of corrosive ions in GPC on their macroscopic properties and microstructure evolution has not been determined. In addition, the corrosion resistance of GPC in marine environments is an important problem to understand to enable their successful application [20, 26, 27].

Some researchers have studied the corrosion resistance of steel bars in GP mortars and concrete in marine environments [21, 28-32], but few articles have evaluated the long-term performance (such as durability and strength degradation) of BFRP bars. Yan et al. [14] concluded that the tensile strength of BFRP bars in an alkaline concrete pore solution decreases much faster than in distilled water, salt, or acid environments. In addition, they found that the long-term performance degradation of BFRP bars in alkaline solutions was more obvious than in seawater because OH$^-$ broke the Si-O-Si bonds in the basalt fibers [13]. Z. Wang et al. [32]conducted accelerated corrosion tests on BFRP bars under different pH values, immersion temperatures, and durations. Subsequently, they used Arrhenius degradation theory to predict the long-term behavior of BFRP bars under service conditions. The study [33] evaluated the residual tensile properties of BFRP bars coated with different SWSSC thicknesses exposed to tap water, simulated seawater, and alkaline solution at 28℃, 40℃, 60℃. It was found that the alkaline solution has a more harmful effect on the tensile properties of BFRP bars than tap water or seawater. Alkalinity is the key factor leading to the deterioration of BFRP bars. Therefore, thicker SWSSC-coated BFRP bars have higher resistance in alkaline environments, and their tensile strength retention is lower than bare BFRP bars. To sum up, although BFRP bars have an excellent ability to resist chloride corrosion, the high alkaline environment in concrete will deteriorate their performance [33-36]. Therefore, it is important to evaluate the long-term durability of BFRP bars in marine environments. Existing studies have not revealed the time-dependence mechanism of the mechanical properties and microstructure of BFRP under seawater corrosion, so further research work is necessary to establish the strength degradation model of BFRP under seawater corrosion.

178   Many studies[37-40] have focused on the macroscopic analysis of the bonding

179   properties of BFRP bars and concrete, while less research has been done on the

180   microscopic mechanism of the interface. Furthermore, interface transition zones (ITZs)

181   play a crucial role in BFRP GPC, both between aggregates and pastes and between

182   pastes and BFRP bars. While the ITZ between GP pastes and aggregates is denser

183   than that between OPC pastes and aggregates[41], it remains a weak area prone to the

184   development of microcracks and is key to controlling the overall strength, chemical

185   corrosion resistance, permeability, and other macro properties of GPC [42]. Current

186   research on the ITZ between pastes and aggregates primarily focuses on PC concrete,

187   with limited investigation on GPC. Luo [35] compared the performance of ITZs in PC

188   concrete and GPC, finding that the interface bond between the GPC matrix and

189   aggregates is stronger than in PC concrete. In PC concrete, the ITZs contain numerous

190   crystalline hydration products, whereas in GPC, the ITZs consist of a gelate-rich paste

191   with a denser microstructure. Tian et al. [43] examined the interface characteristics and

192   mechanical behavior of slag aggregates and GPC, comparing different GPC/steel slag

193   interface systems. They observed that the interface interaction between GPC and steel

194   slag aggregates significantly influenced the interface properties and mechanical

195   behavior. Xin Ren et al. [44] conducted comparative experiments to study the bond

196   strength of ITZs between GPC and aggregate, as well as OPC and aggregate. Their

197   experiments suggested that the development of ITZ bond strength in GPC appeared to

198   be more rapid than in OPC concrete after 7 days. In summary, both domestic and

199   international scholars have investigated the microstructure, composition, and bond

200   strength of the ITZ in GPC. However, it should be noted that previous research

201   primarily relied on qualitative analyses, lacking quantitative characterization, and the

202   mechanism of deterioration remains unclear, making it difficult to establish the

203   regulatory influence of ITZ microstructure on mesoscopic and macroscopic properties.

204   Furthermore, the double interface transition zone of BFRP reinforcement geopolymer

205   concrete has not been adequately considered.

206   As a result, the time-dependent strength model of GPC and the tensile strength

207   model of BFRP in marine environments have yet to be established. Additionally, the

208   changes in composition and microstructure of reaction products with GPC when

209   exposed to corrosive ions in seawater environments are not well understood. The

210   mechanism by which corrosive ions affect the properties of double interface transition

zones in BFRP GPC has not been confirmed. Consequently, this study aims to investigate the volume and strength loss rates of GPC in a simulated seawater environment during various immersion periods. The migration of corrosive ions (Cl^-, SO_4^{2-}, Mg^{2+}) in seawater will be evaluated. Simultaneously, the tensile strength of all BFRP bars will be tested after immersion in artificial seawater and alkaline simulated seawater for different durations, considering the effects of GP mortar wrapping on the properties of BFRP bars. The research will analyze the microstructural changes of BFRP bars in artificial seawater environments. Ultimately, this study aims to provide a theoretical basis for predicting the service life of BFRP GPC in marine environments.

Fig. 1. Production of geopolymer concrete

2 Experimental Design

2.1 Materials

The feasibility of utilizing a Geopolymer in marine environments was investigated using a composition comprising 70% granulated blast-furnace slag (GGBFS), 12% fly ash, 5% silica fume, and 13% activator, which consisted of a solid mixture of sodium silicate and sodium carbonate. The composites and chemical composition of the Geopolymer are provided in Table 1 and Table 2 [45]. By

231 considering the results of MgO compensation GPC volume shrinkage, stability, and
232 mortar strength, it was possible to prepare a Geopolymer with minimal volume
233 shrinkage (referred to as GII) by incorporating 6% MgO (in a ratio of 60 seconds: 220
234 seconds = 1:1) into the GPC [45]. This formulation was then used to assess its
235 suitability for marine environments. The mixture ratio and mechanical properties of
236 the GPC and PC concrete are presented in Table 3 and Table 4, respectively. The sand
237 was sourced from Huilai County, Guangdong Province and is natural sea sand. Table
238 5 provides information on the performance and ion content of the sea sand.
239 Additionally, Table 6 presents the basic physical properties of limestone gravel. The
240 BFRP bars were supplied by Sichuan Aerospace Tuoxin Basalt Industry Co., LTD, an
241 industrial manufacturer. Table 7 displays the initial physical properties of the BFRP
242 bars.

243 **Table 1**. Composition of Geopolymer (wt%)

Material	Composites				Blaine specific surface area, m^2/kg	Density, g/cm^3	Flexural strength, MPa		Compressive strength, MPa	
	GGBFS	Fly ash	Silica fume	Activator			3 d	28 d	3 d	28 d
Geopolymer	70%	12%	5%	13%	375	2.90	4.5	7.9	30.6	50.2

244 **Table 2** Chemical composition of geopolymer binder /wt%

Composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	P_2O_5	K_2O	Na_2O	LOI
Geopolymer	30.56	19.56	2.22	0.85	34.40	3.23	1.23	0.05	2.09	4.88	0.93

245 **Table 3** Mix proportions of geopolymer and Portland cement concretes

Sample ID.	Strength grade	W/C	ρ /%	Binder /(kg/m³)	Sand /(kg/m³)	Aggregate /(kg/m³)	Superplastictizer /(kg/m³)	Water /(kg/m³)
P-35	C35	0.40	42	440	760	1050	7.92	176
GII-35		0.40	42	440	720	1000	/	176

246 **Table 4** Physical and mechanical properties of geopolymer and Portland cement
247 concretes

Sample ID.	Workability		Compressive strength /MPa		
	Slumps/cm	Slump flow/mm	3 days	7 days	28 days
P-35	14.0	170	30.5	38.5	45.0

| GII -35 | 18.0 | 220 | 39.6 | 45.0 | 56.5 |

248   **Table 5** Performance of sea sand from Huilai County of Guangdong Province

Fineness modulus	Particle size range	Apparent density/(kg/m^3)	Bulk density/(kg/m^3)	Shell /(wt%)	Cl^- (wt%)	Mg^{2+} (wt %)	SO_4^{2-} /(wt %)
2.52	II	2590	1520	2.5~3.6	0.1008	0.0098	0.0090

249   **Table 6** Physical properties of aggregate

Percentage of flat-elongated particles /%	Crushing index/ %	Bulk density/(kg/m³)	Apparent density/(kg/m³)	Voidage/%
7.5	9.1	1560	2750	43.3

250   **Table 7** Physical properties of BFRP bars

Type	Length/ （mm）	Diameter/(mm)	Tensile strength/(MPa)	Anchorage length/(mm)
BFRP	1000	$\dfrac{6}{8}$	800~1100	400

251

2.2 Exposure condition

253   In this study, two immersion environments were employed for testing purposes.
254 The GPC specimens were immersed in tap water, while the bare BFRP bars were
255 immersed in artificial seawater. The composition of the artificial seawater solution
256 was designed based on ASTM D 1141-98 and is outlined in Table 8. Considering the
257 alkaline nature of the concrete environment, the BFRP bars were additionally
258 immersed in alkaline simulated seawater. This simulated seawater was prepared using
259 a saturated $Ca(OH)_2$ solution, following the composition specified in Table 8. To
260 facilitate comparative analysis, BFRP bars coated with GP mortar were also immersed
261 in artificial seawater. The exposure periods for all specimens were 28 days, 56 days,
262 90 days, 180 days, and 360 days.

263   **Table 8** The composition of artificial seawater

Ion types	NaCl	$MgCl_2$	Na_2SO_4	$CaCl_2$
Concentration （g/L）	4.53	20	4.09	1.16

3 Test methods

3.1 Seawater resistance of geopolymer concrete

3.1.1 Volume expansion and strength loss of geopolymer concrete

The specimens were prepared according to the mix proportions specified in Table 3. They were cast in the form of $150 \times 150 \times 150$ mm blocks and cured at room temperature for 24 hours. After demolding, the specimens were transferred to a standard curing chamber maintained at a temperature of 25 °C and a relative humidity of 95% for a period of 28 days.

Following the curing period, any loosely adhering portions at the corners of the test blocks were removed, and the resulting volume was measured using the drainage method. This initial volume measurement was recorded as the original volume of the specimens.

During the immersion and corrosion period, the volume and compressive strength of the specimens were measured after a certain duration denoted as "t" days. The Vt (volume corrosion resistance coefficient) and St (strength corrosion resistance coefficient) were utilized to characterize the seawater corrosion resistance of the concrete. The physical meanings of these parameters are as follows:

$$V_t = \frac{v_t - v_{28}}{v_{28}} \qquad (1)$$

Where, V_t is coefficient of the volume corrosion resistance at time, t; v_t is the volume of the concrete specimens at t age (mm^3); v_{28} is the volume of the concrete specimens at 28 days (mm^3).

$$S_t = \frac{s_{28} - s_t}{s_{28}} \qquad (2)$$

Where, S_t is coefficient of the strength corrosion resistance at time, t; s_t is the compressive strength of the concrete specimens at t age (MPa); s_{28} is the compressive strength of the concrete specimens at 28 days (MPa).

3.1.2 Ion migration resistance of geopolymer mortar

In order to further investigate the transport performance of corrosive ions in GP mortar, a mortar mixture was prepared by incorporating artificial seawater containing corrosive ions such as Cl^-, Mg^{2+}, and SO_4^{2-}. Once the mortar reached a specific age,

293 ion content measurements were conducted in each layer of the mortar along the

294 direction of hydrostatic pressure. These measurements were used to calculate the

295 migration coefficient of the GP mortar. For the ion migration tests, a self-made ion

296 migration testing device was utilized, as depicted in Figure 2. The device includes a

297 water tank ①, which is connected to an air co mpressor ② through a pipe. the valve is

298 set on the pipeline, the air pressure machine ② is connected to the specimen

299 mounting device ⑤ through the pressure pipe ③. The pressure gauge ④ is set on the

300 pressure pipe ③, and the specimen mounting device ⑤ is installed with an osmotic

301 liquid collector ⑥ on the upper part of the specimen mounting device. After migrating

302 for a certain period of time, the liquid in the collector ⑥ is poured into a measuring

303 cylinder to measure its volume, and the ion concentration in the liquid is measured by

304 ion chromatography to calculate the amount of ions migrating for a certain period of

305 time. Cylindrical mortar specimens with a bottom diameter of 100 mm, top diameter

306 of 80 mm, and height of 100 mm were employed as migration specimens. The

307 cement-to-sand ratio was 1:3, and the water-to-cement ratio was 0.5. After curing for

308 28 days, the specimens were subjected to testing under standard conditions with a

309 relative humidity (RH) of at least 95% and a temperature of 20±2℃.

310
311 **Fig. 2.** The schematic diagram of device for testing ion migration in mortar specimens
312

3.2 Tensile performance of BFRP bars

After being immersed in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution), the BFRP bars were removed and the surfaces were dried. The tensile specimens of the BFRP bars were designed and manufactured following the guidelines outlined in ACI440.3R-04 "Guide to Test Methods for FRP Bars Reinforced Concrete Structures". The total length of the tensile specimen, denoted as "L," was set to 1000 mm.

To prevent shear damage caused by the tensile machine fixture, adhesive anchors were incorporated at both ends of the tensile test sample within a length of 200 mm, as depicted in Fig. 3. These anchors were constructed using galvanized steel pipes with a bottom diameter of 30 mm, top diameter of 35 mm, and thickness of 3 mm. The steel sleeves were bonded to the BFRP bars by pouring epoxy resin.

Following the specifications outlined in the "Test Method for Basic Mechanical Properties of Fiber Reinforced Composite Bars" (GB/T 30022-2013), the prepared BFRP bars were subjected to a tensile test using an electro-hydraulic servo universal testing machine. This test aimed to measure the ultimate tensile strength and tensile strain of the specimens. A displacement control method was employed to ensure that the specimens were destroyed within a timeframe of 1 to 10 minutes.

Fig. 3. BFRP specimen for tension test（mm）

3.3 Microscopic analysis

The microstructural tests conducted in this study included scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and backscattering electron (BSE) imaging. To investigate the impact of marine corrosive substances on the microstructure of GPC, different dosages of NaCl, Na_2SO_4, and $MgSO_4$ were added into the GP paste, as detailed in Table 9. The MIP method was employed to examine the pore structure characteristics of GPC after 28 days of exposure to corrosive substances. The microstructure of the BFRP bars was analyzed using SEM after 180

days of immersion in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution).

Table 9 Dosage of corrosion ions in geopolymer

Groups	Dosage of corrosion ions (%)								
	NaCl			Na_2SO_4			$MgSO_4$		
1	0	3.5	5	-	-	-	-	-	-
2	-	-	-	0	3	8	-	-	-
3	-	-	-	-	-	-	0	3	8

3.3.1 Scanning electron microscopy (SEM) tests

The hardened paste samples were fractured into pieces after being cured for a specific duration, and some of these fragments underwent gold-plating treatment. The BFRP bars were immersed in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution) until reaching a predetermined age. Subsequently, the bars were taken out and the surfaces were dried. The microstructures of these samples were analyzed using EVO18 scanning electron microscopy (SEM) equipment, manufactured by Carl Zeiss Germany.

3.3.2 Mercury Intrusion Porosimetry (MIP) tests

MIP was employed to assess the total porosity and pore size distribution of the mortars. The samples were crushed into small pieces measuring 5×5×5 mm and soaked in ethanol for over 24 hours, with a volume ratio of approximately 1:4 for the sample to ethanol. The pore structure of the hardened paste was determined using an AutoPore IV 9500 mercury porosimeter.

3.3.3 Backscattering electron (BSE) tests

The samples were analyzed using backscattered electron imaging with an S-3400N Scanning Electron Microscope. The sample preparation process is as follows: Initially, the fractured samples were immersed in epoxy resin and left to demold for 24 hours. Subsequently, the samples solidified with epoxy resin were polished using an automatic Polish-grinding machine, employing sandpapers of various mesh sizes including 60, 120, 320, 500, 2000, and 4000. Prior to testing, the samples were coated with a layer of gold to enhance conductivity.

4 Result and discussion

4.1 Time-Dependent Behavior of Geopolymer Concrete: Volume and Strength

Figure 4 illustrates the seawater resistance of GPC (GII-35) and PC concrete (P-35) over an exposure period of up to 360 days. It can be observed that, compared to GPC, PC concrete exhibited a significantly higher volume expansion ratio at 180 and 360 days, with increases of 384.6% and 430.0% respectively (Figure 4a). Similarly, the strength loss ratio of PC concrete at 180 and 360 days increased by 10.4% and 9.6% respectively (Figure 4b). Conversely, GPC demonstrated a remarkable reduction in both volume expansion ratio and strength loss ratio, which decreased by 77.6% and 8.7% respectively after 360 days of seawater corrosion. These results indicate that GPC exhibits superior resistance to seawater corrosion compared to PC concrete.

(a) Volume expansion   (b) Strength loss

Fig. 4. The corrosion resistance of GPC and PC concretes

4.2 Time-dependent strength model of GPC in marine environments

Concrete strength will change with service time under the influence of environmental factors and sustained loads. Based on the strength data of long-term concrete in actual marine engineering, scholars have analyzed its degradation pattern using regression methods and proposed a time-dependent decay model for the average strength of concrete in marine environments, as presented in Eq. (3).

$$f_c(t) = f_0 \times 1.248 e^{-0.0340 \times (\mathrm{Int} - 0.3468)^2} \tag{3}$$

Where $f_c(t)$ represents the compressive strength of concrete after t years, MPa; f_0 represents the average value of initial concrete strength, MPa.

The time-dependence equation of concrete strength retention rate in marine

390 environments can be determined by Eq.(4). $F_c(t)$ is strength retention rate of concrete

391 in marine environments in immersion time t.

$$392 \qquad F_c(t) = \frac{f_c(t)}{f_0} = 1.248e^{-0.0340\times(\text{Int}-0.3468)^2} \times 100\% \qquad (4)$$

393   In Fig. 5, the fitting curve illustrates the seawater corrosion resistance test results

394 of GPC (GII-35) and PC concrete (P-35). As time approaches infinity, the strength

395 retention rate of GII-35 and P-35 reaches 84.9% and 77.9%, respectively. Thus, the

396 time-dependent degradation equation for the strength retention rate of GPC in marine

397 environments can be expressed as Eq. (5). $F_w(t)$ is strength retention rate of GPC in

398 marine environments in immersion time t

$$399 \qquad F_w(t) = \frac{84.9}{77.9} \times F_c(t) = 1.360e^{-0.0340\times(\text{Int}-0.3468)^2} \times 100\% \qquad (5)$$

400   The decay equation for the mechanical properties of GPC in marine

401 environments can be expressed as Eq. (6).

$$402 \qquad f_w(t) = f_{w0} \times 1.248e^{-0.0340\times(\text{Int}-0.3468)^2} \qquad (6)$$

403 Where $f_w(t)$ is the compressive strength of GPC after t years, MPa; f_{w0} is the average

404 initial strength of GPC, MPa.
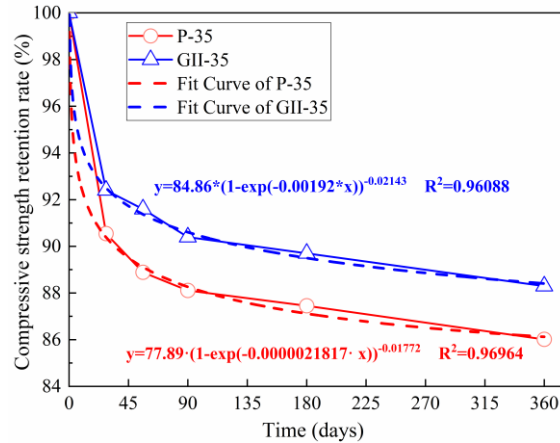
406 **Fig.5.** Compressive strength of PC (P-35) and GPC (GII-35) in seawater for different

407 immersion periods

408 **4.3 Transport performance of ions in seawater in GP mortar**

409   Under the hydrostatic pressure (1.4 MPa), the water samples of mortar specimens

410 (mixed with artificial seawater) at different exposure ages were analyzed. By

411 measuring the contents of Cl^-, SO_4^{2-} and Mg^{2+} in the water samples, the amount of

412 ions permeation migration ΣA_n at different ages were obtained. Based on the ratio of

413   chemical bonding and physical adsorption, A_0 was calculated and $\Sigma A_n/A_0$ was obtained.

414   The cumulative leaching fraction of ions can be calculated using Eq. (7). The leaching

415   rate and cumulative leaching fraction of PC mortar and GP mortar were obtained, as

416   shown in Table 10 and Table 11.

417
$$P_t = \frac{\sum A(t)}{A_0} \times \frac{V}{S} \qquad (7)$$

418   Where P_t is the cumulative leaching fraction of ions, cm; t is exposure time; $\sum A(t)$ is

419   the accumulated leaching amount of the first n ions, g; A_0 is the amounts of ions that

420   can migrate in the sample, g; V is the volume of sample, cm^3; S is the geometrical area

421   of the solidified sample in contact with water, cm^2.

422   **Table 10** Leaching ratio and cumulative leaching fraction of ions from Portland
423   cement mortar

Time (d)	$\frac{\sum A_n}{A_0}$ (Cl$^-$)	P_t (Cl$^-$/cm)	$\frac{\sum A_n}{A_0}$ (SO$_4^{2-}$)	P_t (SO$_4^{2-}$/cm)	$\frac{\sum A_n}{A_0}$ (Mg^{2+})	P_t (Mg^{2+}/cm)
1	0.0138	0.1168	0.0050	0.1111	0.0131	0.1161
2	0.0966	0.8178	0.0190	0.4222	0.0291	0.2589
3	0.1494	1.2648	0.0305	0.6778	0.0852	0.7572
5	0.2691	2.2781	0.0455	1.0111	0.1073	0.9541
7	0.3207	2.7149	0.0665	1.4778	0.1984	1.7639
10	0.3981	3.3702	0.1050	2.3333	0.2306	2.0500
15	0.4672	3.9551	0.1567	3.4811	0.2909	2.5861
20	0.5463	4.6248	0.1792	3.9822	0.3853	3.4244
25	0.5953	5.0396	0.2005	4.4556	0.4206	3.7383
30	0.6244	5.2859	0.2250	5.0000	0.4809	4.2744
35	0.6534	5.5314	0.2475	5.5000	0.5902	5.2461
40	0.6625	5.6085	0.2517	5.5933	0.6605	5.8711
50	0.6806	5.7617	0.2681	5.9567	0.7511	6.6767
60	0.7288	6.1697	0.2700	6.0000	0.8408	7.4733

424   **Table 11** Leaching ratio and cumulative percentage of ions from geopolymer mortar

Time (d)	$\sum A_n/A_0$ (Cl$^-$)	P_t (Cl$^-$/cm)	$\sum A_n/A_0$ (SO$_4^{2-}$)	P_t (SO$_4^{2-}$/cm)	$\sum A_n/A_0$ (Mg^{2+})	P_t (Mg^{2+}/cm)
1	0.0066	0.0512	0.0060	0.0636	0.0030	0.8830
2	0.0593	0.4572	0.0350	0.3719	0.0068	2.0000
3	0.0879	0.6781	0.0455	0.4833	0.0101	2.9415
5	0.1182	0.9117	0.0864	0.9190	0.0165	4.8246
7	0.1507	1.1622	0.1136	1.2083	0.0219	6.4152
10	0.1984	1.5303	0.1353	1.4385	0.0340	9.9415

15	0.2585	1.9932	0.1943	2.0659	0.0473	13.8304
20	0.3029	2.3358	0.2173	2.3099	0.0664	19.4152
25	0.3661	2.8234	0.2472	2.6279	0.0815	23.8304
30	0.4094	3.1567	0.2746	2.9196	0.1006	29.4152
35	0.4426	3.4130	0.2900	3.0837	0.1157	33.8304
40	0.4858	3.7463	0.3009	3.1998	0.1328	38.8304
50	0.5123	3.9503	0.3105	3.3019	0.1670	48.8304
60	0.5387	4.1542	0.3192	3.3937	0.2012	58.8304

425   The following hypotheses are proposed for ion migration in the solidified sample:

426   1) The leaching process of the three ions occurs through one-dimensional leaching

427   along the diameter of the solidified sample; 2) The hardened paste is a homogeneous

428   system; 3) The diffusion coefficient is constant; 4) The permeable water is a

429   homogeneous semi-infinite medium; 5) Ions bound by chemical bonding or physical

430   adsorption remain stable during osmotic dissolution; 6) Hardened pastes will not be

431   damaged by corrosion. According to Fick's 2nd law, the equation for ion osmosis

432   migration and diffusion can be obtained. C_0 is the chloride concentration on the

433   exposed surface of concrete. C is the free chloride concentration in diffusion time t.

434
$$\frac{C}{C_0} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$
（8）

435   The amount of ions penetration and migration in a solidified sample can be

436   obtained by Fick's 1st law:

437
$$J(t) = -D\frac{\partial C}{\partial x}\Big|_{x=0} = -C_0\sqrt{\frac{D}{\pi t}}$$
（9）

438   The amount of ions migration in a solidified sample per unit area at t migration

439   period can be expressed as:

440
$$A_n(t) = \int_0^t J(t)dt = 2A_0\sqrt{\frac{Dt}{\pi}}$$
（10）

441   Where A_n is the accumulated amount of ions dissolved in t migration period, g; A_0 is

442   the initial amount of transferable ions in the solidified sample, g; D is the surface

443   migration coefficient, mm^2/s.

444   According to the above equations and the cumulative migration fraction, P_t , of

445   the ions in the solidified sample, Eq.(11) can be obtained:

446
$$\frac{\sum A_n}{A_0} = 2(\frac{S}{V})\sqrt{\frac{Dt}{\pi}}$$
（11）

447   Where ΣA_n is the cumulative dissolution amount of ions in t migration period, g; A_0 is

the initial amount of transferable ions in the solidified sample, g; D is the permeability

diffusion coefficient of ions migration, cm^2/d.

The migration diffusion coefficient, D, can be obtained from the slope of the line

formed by $\Sigma A_n/A_0$ and $t_n^{1/2}$:

$$D = \pi(\frac{mV}{2S})^2 \qquad （12）$$

The cumulative leaching rate ($\Sigma A_n/A_0$) of Cl^-, SO_4^{2-} and Mg^{2+} in the PC mortar and

GP mortar solidified samples obtained by the test is shown in Table 10 and Table 11.

The result obtained by curve fitting and $t^{1/2}$ is shown in Fig 6.

(a) Cl^-

(b) SO_4^{2-}

(c) Mg^{2+}

Fig. 6. Relationship between $\Sigma A_n/A_0$ and $t_n^{1/2}$

According to the fitting results in Fig. 6, the ions diffusion coefficient D of GP

and PC mortar in seawater can be calculated by Eq. (12). Table 12 shows that the

chloride diffusion coefficient of GP mortar is only 6.15×10^{-4} mm^2/s, which is 61.2%

of that of PC mortar. The sulphate diffusion coefficient of GP mortar is about 1.84×10^{-4} mm^2/s, which is 81.1% of that of PC mortar. The Magnesium ion diffusion

464   coefficient of GP mortar is 0.73×10^{-4} mm^2/s, which is only 5.3% of that of PC mortar.

465   In other words, GP shows excellent performance to resist ions migration.

466   **Table 12** Diffusion coefficient of Cl$^-$, SO$_4^{2-}$ and Mg^{2+} in GP mortar and PC mortar

Material type	D（Cl$^-$）/ （$\times10^{-4}$ mm^2/s）	D（SO$_4^{2-}$）/ （$\times10^{-4}$ mm^2/s）	D（Mg^{2+}）/ （$\times10^{-4}$ mm^2/s）
GP mortar	6.15	1.84	0.73
PC mortar	10.06	2.30	1.39

467   **4.4 Effect of corrosive ions on pore structure of GP pastes**

468   The pore size distributions of cement paste and geopolymer paste with a 28-day

469   curing age were measured using MIP. The influence of NaCl, Na$_2$SO$_4$, and MgSO$_4$ on

470   pore distribution is presented in Fig. 7. The results demonstrate that the pore size and

471   total porosity of the geopolymer are much smaller than those of the cement. In the

472   geopolymer pastes, the pore size after 28 days of age is typically smaller than 20 nm.

473   Fig. 7(a) shows that the introduction of 5% NaCl has a minimal effect on the

474   total porosity of the cement paste but refines the pore size. On the other hand, the pore

475   size of the geopolymer pastes remains relatively unchanged, but the total porosity

476   decreases significantly with the introduction of 5% NaCl. When considering the initial

477   and final setting times of the geopolymer pastes, it can be observed that the

478   introduction of 5% Cl$^-$ delays the reaction speed and increases the reaction degree,

479   resulting in a decrease in total porosity.

480   Fig. 7(b) and Fig. 7(c) demonstrate that the median pore size of the geopolymer

481   paste increases with the addition of 8% SO$_4^{2-}$, while the median pore size of the

482   cement paste decreases. It is worth noting that the results indicate a decreasing trend

483   in the number of large pores in the geopolymer paste with the addition of SO$_4^{2-}$, while

484   the number of small pores increases significantly. The observed phenomena can be

485   attributed to the early-stage erosion process, where the erosion products of SO$_4^{2-}$ tend

486   to initially fill the pores, resulting in a reduction of the median pore size in the cement

487   paste. Furthermore, the introduction of 8% Mg^{2+} causes a notable increase in the

488   number of macropores in the cement paste, while simultaneously leading to a

489   significant decrease in the percentage of macropores in the geopolymer. This

490   observation suggests that Mg^{2+} erosion converts the hydration product C-S-H gel into

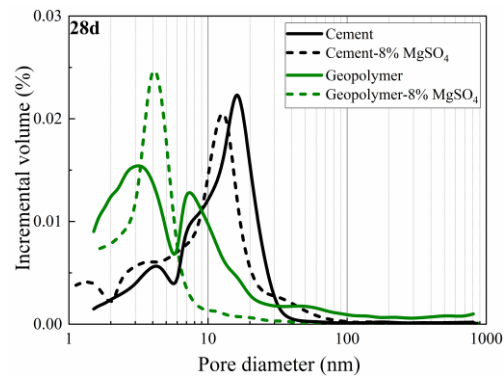491   M-S-H, leading to the formation of loosely structured macropores. As a consequence

492 of these findings, it can be inferred that geopolymers exhibit favorable resistance to
493 the penetration of erosive materials, which can be attributed to their compact pore
494 structure.
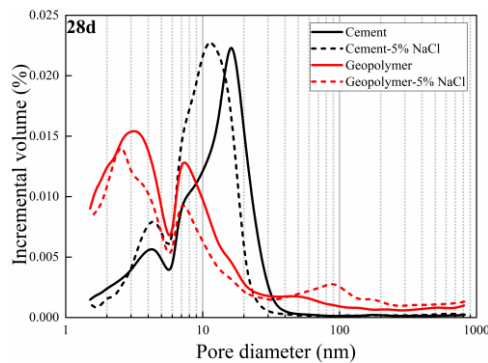
(a) Pastes with NaCl
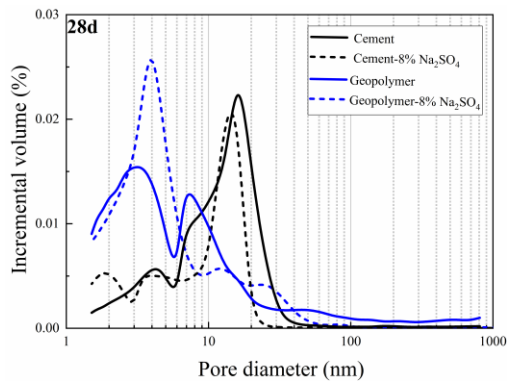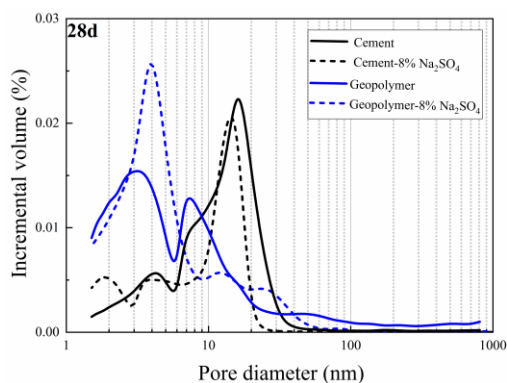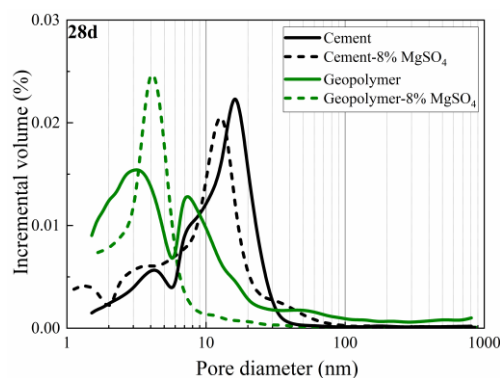
(b) Pastes with Na$_2$SO$_4$ (c) Pastes with MgSO$_4$

495 **Fig.7.** Pore size distribution of geopolymer and cement pastes with NaCl, Na$_2$SO$_4$ and
496 MgSO$_4$

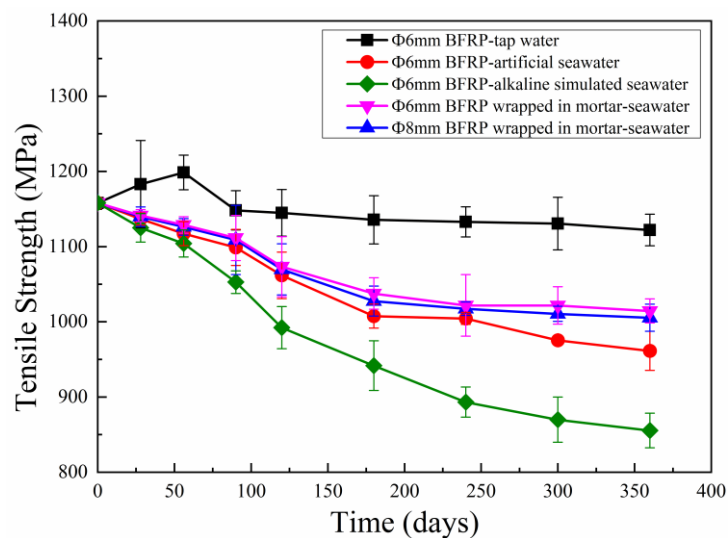## 4.5 Time-dependence regulation of mechanical properties of BFRP bars in seawater

499   Fig. 8 illustrates the degradation of tensile strength for bare BFRP bars with
500 diameters of Φ 6mm and Φ 8mm when immersed in different media (tap water,
501 artificial seawater, and alkaline simulated seawater). It also shows the degradation of
502 BFRP bars with a diameter of Φ 6mm that were wrapped in mortar and immersed in
503 artificial seawater for varying periods of time. In all solutions, the tensile strengths of
504 BFRP bars initially decrease rapidly and then exhibit a slower decrease as the
505 exposure period increases.
506   One possible explanation for this phenomenon is that the corrosion medium
507 reaches equilibrium after diffusing to a certain depth within the BFRP bars, causing

508 the corrosion reaction to slow down due to the accumulation of reaction products.
509 Notably, the degradation is significantly accelerated in alkaline environments. The
510 trend of tensile strength retention for BFRP bars under the same conditions follows
511 this order: tap water immersion > artificial seawater immersion > alkaline seawater
512 immersion.

513   It is important to mention that the tensile strength degradation of BFRP bars
514 wrapped in mortar and immersed in seawater for 360 days was found to be 6%
515 stronger compared to bare BFRP bars. Additionally, when comparing the tensile
516 strength of Φ 6mm and Φ 8mm BFRP bars wrapped in mortar, it is observed that the
517 degradation of tensile strength is more pronounced in the larger diameter bars.

518

519

520   **Fig.8.** Variation of tensile strength of BFRP bars in different corrosive solutions

521 **4.6 Microstructure of BFRP bars in seawater**

522   Fig. 9 presents SEM images of the cross section of Φ 6mm BFRP bars immersed
523 in different media for a period of 180 days. In Fig. 9(a), which represents immersion
524 in tap water, it is evident that a significant amount of resin remains bonded to the
525 surface of the fibers. This bonding facilitates the formation of tight bundles as the
526 fibers combine with each other.

527

528   In Fig. 9(b), corresponding to immersion in artificial seawater, the outer fibers
529 display the presence of pores at the edge of the cross-section, and the surface structure

530   appears to have loosened due to corrosion.

531

532   Fig. 9(c) illustrates the cross section of BFRP bars after immersion in alkaline
533   simulated seawater. The damage process is visibly pronounced, characterized by fiber
534   ruptures, resin degradation, and debonding of the resin-fiber interface. This results in
535   an increased loose area and noticeable protrusion of fibers.

536

537   These SEM images provide insight into the changes and damage experienced by
538   the BFRP bars under different immersion conditions, highlighting the effects of
539   various media on the surface and structural integrity of the bars.

(a) BFRP bar immersed in water

(b) BFRP bar immersed in artificial seawater

(c) BFRP bar immersed in saturated Ca(OH)$_2$ seawater

540   **Fig.9.** Microstructure of cross section of BFRP bars after 180 days corrosion

541   Fig. 10 displays SEM micrographs of the longitudinal section of Φ 6mm BFRP

bars subjected to different immersion media for a duration of 180 days. In Fig. 10(a), representing immersion in tap water, the surface of the fiber and resin remains unchanged. The fiber maintains a smooth and flat appearance, tightly connected to the resin.

In Fig. 10(b), following immersion in seawater, the intermediate resin that bonded the fibers together disappears, leading to a further loosening of the fiber bundles. Additionally, a significant amount of salt crystals can be observed attached to the surface.

Fig. 10(c) reveals that after immersion in alkaline simulated seawater, very little resin remains bonded to the fiber surface. The fibers exhibit evident corrosion, with signs of detachment and noticeable damage defects. This phenomenon can be attributed to the gradual penetration of the corrosive medium along the radial direction of the bars. Initially, the shedding of fiber and resin occurs, followed by fiber surface corrosion in the later stages. These factors contribute to a significant decrease in the tensile strength of the BFRP bars.

The observations presented in Fig. 10, along with those in Fig. 9, demonstrate the decisive influence of alkaline environments on the degradation of tensile strength in BFRP bars. This finding aligns with the results obtained from the tensile strength tests.

(a) BFRP bar immersed in water (b) BFRP bar immersed in artificial seawater

(c) BFRP bar immersed in saturated Ca(OH)$_2$ seawater

Fig.10. Microstructure of vertical section of BFRP bars after 180d corrosion

4.7 Degradation model of tensile strength of BFRP bars in marine environments

Through microscopic analysis of BFRP bars, the degradation mechanism in a seawater environment is identified as fiber-resin matrix interface split and separated failure. This mechanism can be expressed as follows [46]:

$$f_f = (100 - Y_\infty)exp\left(-\frac{t}{\tau}\right) + Y_\infty \qquad (13)$$

Where, Y_∞ is the residual tensile strength of BFRP bars when the corrosion time tends to infinity; τ is the characteristic time determined by corrosion temperature.

The corrosion of BFRP bars that are wrapped in GPC in marine environments is primarily caused by seawater corrosion and the alkaline environment within the GPC. Therefore, Eq (13) is modified as follows:

$$f_f = Y_\infty \times exp(-b \times t)^c + Y_\infty \qquad (14)$$

To verify the modified Eq. (14), the time-dependent variation of tensile properties of Φ 6 mm and Φ 8 mm BFRP bars wrapped in GP mortar under seawater immersion is fitted, as shown in Fig. 11. The fitting parameters are presented in Table 13. In the seawater environment, the final strengths of Φ 6 mm and Φ 8 mm BFRP bars are 695 MPa and 663 MPa, respectively. The established tensile strength degradation models for the BFRP bars are as follows:

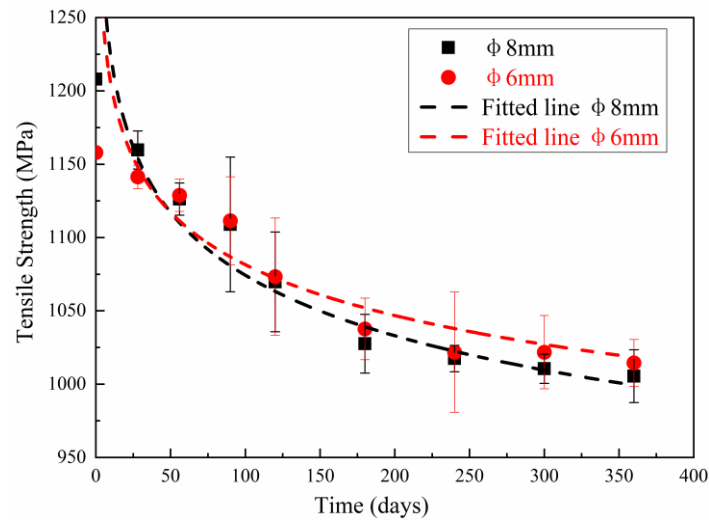Φ 6 mm BFRP bar：

$$f_f = 695.38 \times (1 - exp(-8.19958E - 7 \times t))^{-0.04694} \qquad (15)$$

Φ 8 mm BFRP bar：

$$f_f = 663.76 \times (1 - exp(-1.98349E - 6 \times t))^{-0.04248} \qquad （16）$$

583

584 **Fig.11.** Tensile strength of BFRP immersed in a marine environment

585 **Table 13** Parameters of the fitting equation to describe the degradation of BFRP bars

	Φ6 mm	Φ8 mm
Y∞	695.38	663.76
b	8.19958E-7	1.98349E-6
c	-0.04694	-0.04248
R^2	0.92197	0.95115

586 **4.8 Microstructure characteristics of the interface of BFRP bars reinforced**
587 **geopolymer in seawater**

588 4.8.1 Microscopic properties of the interface between geopolymer and aggregate in
589 seawater

590   The microscopic morphology of hardened samples of GPC and PC concrete after
591 immersion in tap water and artificial seawater for 360 days is depicted in Fig. 12 and
592 13. The backscattered electron (BSE) images of the hardened samples reveal certain
593 characteristics. The brightly colored irregular blocks represent unreacted clinker or
594 slag, while the brightly colored globular particles indicate unreacted fly ash. The gray
595 areas correspond to the reaction products formed during the reaction, and the black
596 areas represent pores within the hardened samples.

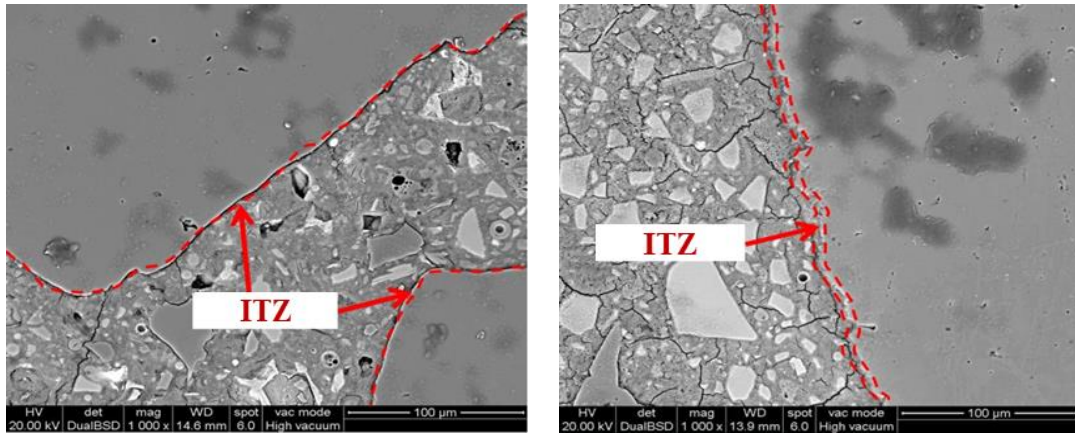597   Fig. 12(a) demonstrates that in tap water for 360 days, the GP mortar exhibits a
598 tight bond with the aggregate, without a distinct boundary of interfacial transition. Fig.
599 12(b) shows that after immersion in artificial seawater for 360 days, the interface area

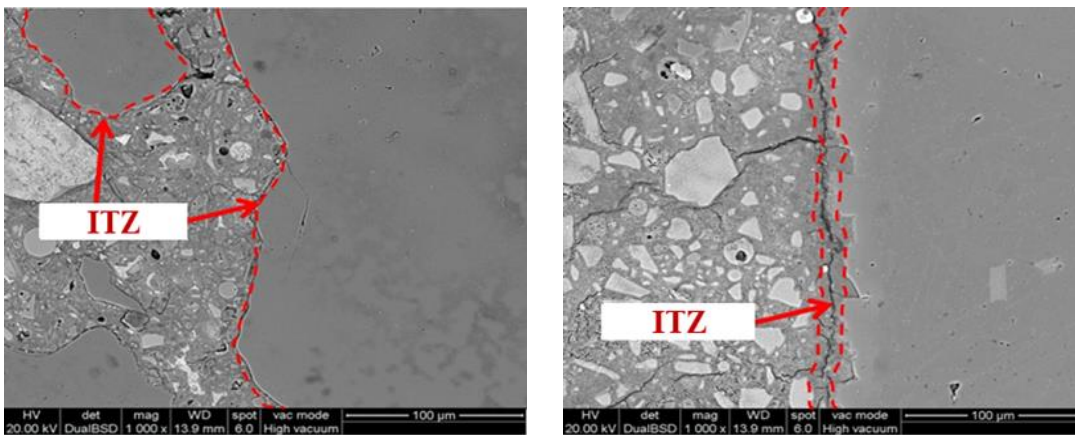between the GP mortar and aggregate does not show a significant increase, but some areas exhibit fine cracks.

Fig. 13(a) illustrates that in the PC concrete samples, there is a wide black area accompanied by a distribution of porosity between the PC mortar and aggregate. This indicates the presence of an obvious interfacial transition zone (ITZ) in the PC concrete samples, which is more pronounced compared to the GPC samples. Fig. 13(b) further demonstrates that the ITZ of the PC concrete samples becomes more apparent after seawater corrosion, along with a higher proportion of pores and cracks.

(a) GPC in water for 360 days   (b) GPC in artificial seawater for 360 days

Fig. 12. Interfacial transition zone of GPC after 360 days corrosion

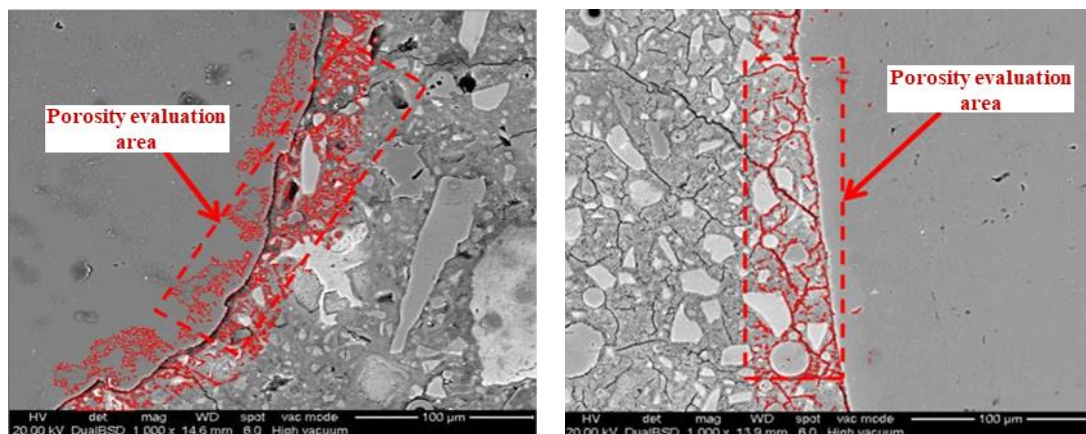(a) PC concrete in water for 360 days   (b) PC concrete in artificial seawater for 360 days

Fig. 13. Interfacial transition zone of PC concrete after 360 days corrosion

The porosity of the interfacial transition zone (ITZ) in concrete was further calculated using the fractal theory with the aid of Image-Pro Plus (IPP) image

612   processing software. Fig. 14 and 15 display the IPP image processing photos of the

613   ITZ in GPC and PC concrete, respectively, while Table 14 presents the statistical

614   results of porosity.

615   After immersion in tap water for 360 days, the average porosity of the ITZ in

616   GPC and PC concrete samples is approximately 27.89% and 37.97%, respectively.

617   This indicates that the average porosity of the ITZ in GPC is approximately 36.0%

618   lower than that in PC concrete.

619   Following 360 days of artificial seawater corrosion, the average porosity of the

620   ITZ in GPC samples only increases by 4.44%, reaching approximately 29.13% in total.

621   In contrast, the average porosity of the ITZ in PC concrete increases from 37.97% to

622   40.74%, exhibiting a 7.29% increase compared to 360 days of tap water corrosion.

623   These findings indicate that GPC possesses a smaller porosity and a lower proportion

624   of porosity increase compared to PC concrete after seawater corrosion. This

625   demonstrates the excellent resistance of GPC to seawater corrosion.
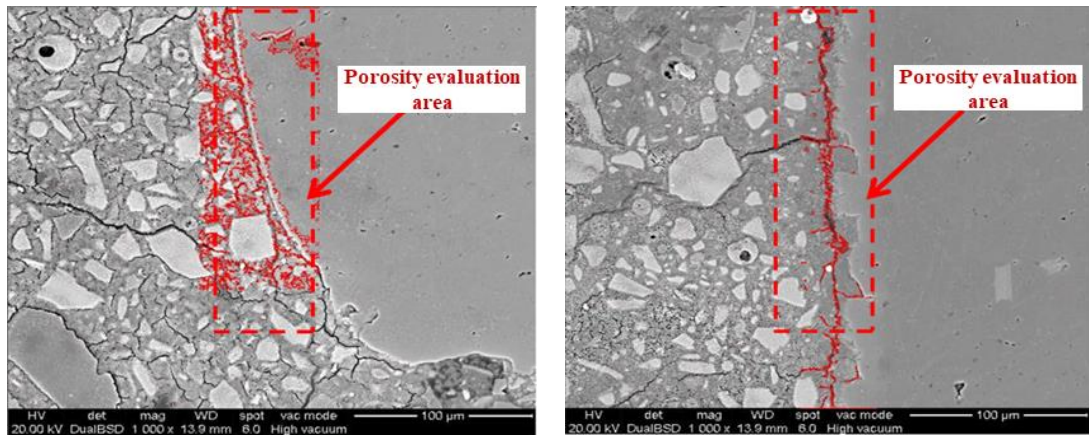

(a) GPC in water for 360 days   (b) GPC in artificial seawater for 360 days

626   **Fig. 14.** Interfacial transition zone of GPC after corrosion

(a) PC concrete in water for 360 days

(b) PC concrete in artificial seawater for 360 days

Fig. 15. Interfacial transition zone of PC concrete after corrosion

Table 14 Porosity of interfacial transition zone in concrete after corrosion

Porosity	GPC		PC concrete	
	water for 360 d	artificial Seawater 360 d	Reference	artificial Seawater 360 d
Range	23.25~31.43	22.53~33.30	32.03~43.26	34.06~47.06
Average value(%)	27.89	29.13	37.97	40.74

Note. 10 images were selected to analyze the porosity of the interfacial transition zone of concretes.

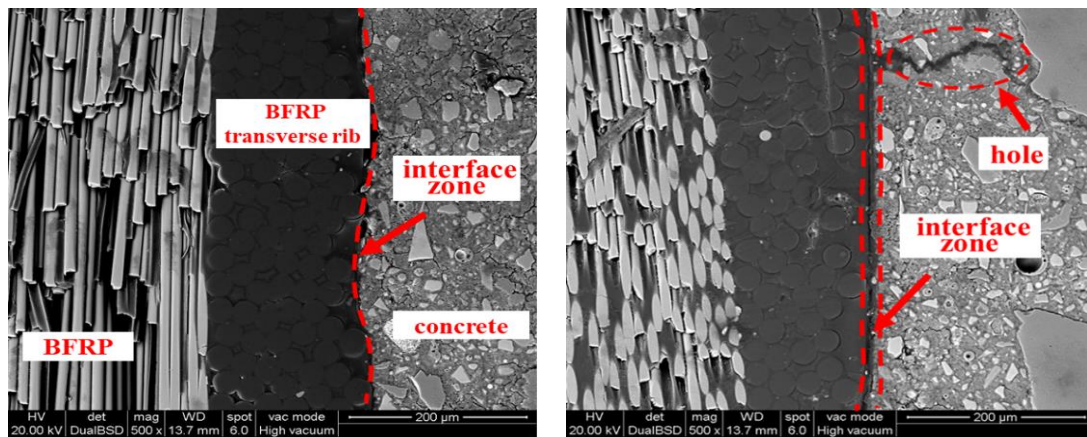4.8.2 Microstructure characteristics of interface between BFRP bars and geopolymer in seawater

In the seawater environment, the microstructure characteristics of the interface between BFRP bars and GPC were examined. Fig. 16 (a) illustrates that the BFRP bars consist of basalt fibers bonded with resin and are further reinforced with transverse ribs. The interface between the BFRP bars and GPC exhibits a tight bond without any distinct interfacial transition zone (ITZ) or noticeable interfacial pores.

After 360 days of seawater corrosion, as shown in Fig. 16 (b), the interface between the BFRP bars and GPC slightly expanded. Some cracks and pores appeared in the GPC, but the bond between the GPC and BFRP bars remained relatively tight.

These observations suggest that even after seawater corrosion, the bond between the BFRP bars and GPC remains intact, indicating the favorable compatibility and

643   durability of the interface in the seawater environment.

644   Fig. 16 (a) shows that BFRP bars are composed of resin bonded basalt fibers and
645   then wound with transverse ribs. BFRP bars are tightly bonded to GPC with no
646   obvious ITZ and no obvious interfacial pores. Fig. 16 (b) shows that the interface
647   between BFRP bars and GPC was slightly enlarged after 360 days of seawater
648   corrosion, and GPC appear some cracks and pores. It is noted that the bond between
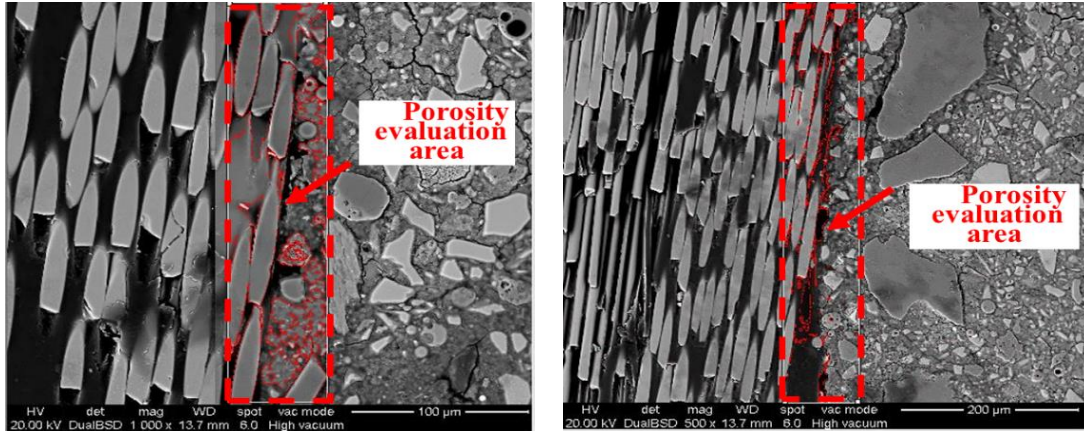649   the GPC and BFRP bars is still relatively tight.

      (a) Before corrosion   (b) After artificial seawater for 360 days

650   **Fig. 16.** Interface between BFRP bars and GPC before and after corrosion

651   To analyze the porosity of the interface area between the BFRP bars and GPC,
652   IPP image processing software was utilized. Fig. 17 presents the results of porosity
653   analysis before and after artificial seawater corrosion. The statistical data of porosity
654   are summarized in Table 15.

655   Before seawater corrosion, the interface between the BFRP bars and GPC
656   exhibited a tight bond, and the average porosity of the interfacial transition zone (ITZ)
657   was measured to be 27.88%. Following seawater corrosion, the average porosity of
658   the ITZ increased slightly to 29.06%, which represents a 1.2% increment compared to
659   the pre-corrosion condition. These results indicate that seawater corrosion has a
660   negligible impact on the porosity of the ITZ between the GPC and BFRP bars.

(a) GPC in water   (b) GPC in artificial seawater for 360 days

661   **Fig. 17.** Interfacial transition zone of BFRP bars in GPC after corrosion

662   **Table 15** Porosity of interface between BFRP bars and GPC after corrosion

Porosity/%	GPC	
	Reference	Immersed in artificial seawater for 360 days
Range	24.10~31.58	24.90~33.30
Average value/%	27.88	29.06

663   Note. 10 images were selected to analyze the porosity of the interface between BFRP

664   and GPC.

665   **5 Conclusion**

666   This study focused on investigating the corrosion resistance and interface

667   characteristics of GPC and BFRP bars in a seawater environment. The main emphasis

668   of this research was on analyzing the ionic attack resistance of BFRP reinforced

669   geopolymer concrete using laboratory-simulated seawater conditions. However, it is

670   essential to acknowledge that in actual marine environments, ion migration occurs not

671   only through diffusion but also potentially involves convective effects under

672   hydrostatic pressure.

673   Several critical questions remain to be addressed: How can we simulate ocean

674   conditions more realistically through systematically designed experiments? What are

675   the effects of competing antagonistic processes on the performance of BFRP

676   reinforced geopolymer concrete when subjected to multiple-ion combined attack in

677   marine environments? To answer these questions, further studies employing

678   systematically designed experiments and long-term observations will be crucial. Such

679   research endeavors will not only help refine the proposed mathematical models but

680   also enhance our understanding of the behavior of BFRP reinforced geopolymer

681 concrete under realistic marine conditions.

682 Based on the findings of the present study, the following specific conclusions

683 may be drawn:

684 (1) The corrosion resistance of GPC exhibited an initial sharp increase, followed by a

685 slower increase, and finally reached a stable state after 90 days of exposure. The

686 volume corrosion resistance coefficient and strength corrosion resistance

687 coefficient of GPC after 360 days of immersion were 0.06 and 0.085, respectively,

688 indicating excellent resistance to seawater corrosion. A degradation model for the

689 mechanical performance of GPC in a marine environment was established.

690

691 (2) GP mortar demonstrated superior resistance to ion migration compared to PC

692 mortar. The migration properties of chloride ions (Cl^-), sulfate ions (SO_4^{2-}), and

693 magnesium ions (Mg^{2+}) were evaluated, with Cl^- showing the highest migration,

694 followed by SO_4^{2-} and Mg^{2+}.

695

696 (3) The tensile strength degradation of BFRP bars in seawater combined with an

697 alkaline environment was more pronounced than in seawater alone. Wrapping

698 BFRP bars in GP mortar mitigated the reduction in tensile strength in seawater,

699 and a smaller BFRP diameter resulted in reduced deterioration. The ultimate

700 strengths of BFRP bars with diameters of 6 mm and 8 mm were 695 MPa and 663

701 MPa, respectively. A degradation model for the tensile strength of BFRP bars in

702 marine environments was established.

703

704 (4) Microscopic analysis revealed that seawater corrosion had little impact on the

705 porosity of the dual interfaces in BFRP bars reinforced with geopolymer concrete.

706 The average porosity of the interfacial transition zone (ITZ) between GP paste

707 and aggregate was significantly lower than that of PC concrete. The ITZ between

708 BFRP bars and GP paste exhibited a slight increase in porosity, but still

709 maintained tight interfacial bonding and narrow interface widths. Seawater

710 corrosion did not significantly affect the ITZ structure of BFRP reinforced

711 geopolymer concrete.

712

713 These findings contribute to a better understanding of the corrosion behavior and

interface characteristics of GPC and BFRP bars in seawater environments, and provide valuable insights for the development of corrosion-resistant and durable concrete structures.

REFERENCE

[1]   Zhang B, Zhu H, Li F Z, Dong Z Q, Zhang P. Compressive stress-strain behavior of seawater coral aggregate concrete incorporating eco-efficient alkali-activated slag materials [J]. Construction and Building Materials, 2021, 299.

[2]   Zhang B, Zhu H, Cao R M, Ding J M, Chen X H. Feasibility of using geopolymers to investigate the bond behavior of FRP bars in seawater sea-sand concrete [J]. Construction and Building Materials, 2021, 282.

[3]   Zhang B, Zhu H, Lu F. Fracture properties of slag-based alkali-activated seawater coral aggregate concrete [J]. Theoretical and Applied Fracture Mechanics, 2021, 115.

[4]   Chen G, Zheng D P, Chen Y W, Lin J X, Lao W J, Guo Y C, Chen Z B, Lan X W. Development of high performance geopolymer concrete with waste rubber and recycle steel fiber: A study on compressive behavior, carbon emissions and economical performance [J]. Construction and Building Materials, 2023, 393.

[5]   Elahi M M A, Hossain M M, Karim M R, Zain M F M, Shearer C. A review on alkali-activated binders: Materials composition and fresh properties of concrete [J]. Construction and Building Materials, 2020, 260.

[6]   Morsy A M, Ragheb A M, Shalan A H, Mohamed O H. Mechanical Characteristics of GGBFS/FA-Based Geopolymer Concrete and Its Environmental Impact [J]. Practice Periodical on Structural Design and Construction, 2022, 27(2).

[7]   Perumal P, Sreenivasan H, Luukkonen T, Kantola A M, Telkki V V, Kinnunen P, Illikainen M. High strength one-part alkali-activated slag blends designed

751   by particle packing optimization [J]. Construction and Building Materials,
752   2021, 299.

753 [8] Shehata N, Sayed E T, Abdelkareem M A. Recent progress in environmentally
754   friendly geopolymers: A review [J]. Science of The Total Environment, 2021,
755   762: 143166.

756 [9] Wang A G, Zheng Y, Zhang Z H, Liu K W, Li Y, Shi L, Sun D S. The
757   Durability of Alkali-Activated Materials in Comparison with Ordinary
758   Portland Cements and Concretes: A Review [J]. Engineering, 2020, 6(6): 695-
759   706.

760 [10] Zhang B, Zhu H, Wang Q, Shah K W, Wang W. Design and properties of
761   seawater coral aggregate alkali-activated concrete [J]. Journal of Sustainable
762   Cement-Based Materials, 2022, 11(3): 175-84.

763 [11] Xiao J Z, Qiang C B, Nanni A, Zhang K J. Use of sea-sand and seawater in
764   concrete construction: Current status and future opportunities [J]. Construction
765   and Building Materials, 2017, 155: 1101-11.

766 [12] Li J L, Xie J H, Liu F, Lu Z Y. A critical review and assessment for FRP-
767   concrete bond systems with epoxy resin exposed to chloride environments [J].
768   Composite Structures, 2019, 229.

769 [13] Lu Z Y, Li J L, Xie J H, Huang P Y, Xue L F. Durability of flexurally
770   strengthened RC beams with prestressed CFRP sheet under wet-dry cycling in
771   a chloride-containing environment [J]. Composite Structures, 2021, 255.

772 [14] Yan F, Lin Z B, Yang M J. Bond mechanism and bond strength of GFRP bars
773   to concrete: A review [J]. Composites Part B-Engineering, 2016, 98: 56-69.

774 [15] Torres L, Sharaky I A, Barris C, Baena M. EXPERIMENTAL STUDY OF
775   THE INFLUENCE OF ADHESIVE PROPERTIES AND BOND LENGTH
776   ON THE BOND BEHAVIOUR OF NSM FRP BARS IN CONCRETE [J].
777   Journal of Civil Engineering and Management, 2016, 22(6): 808-17.

778 [16] Aslani F, Sun J B, Bromley D, Ma G W. Fiber-reinforced lightweight self-
779   compacting concrete incorporating scoria aggregates at elevated temperatures
780   [J]. Structural Concrete, 2019, 20(3): 1022-35.

781 [17] Aslani F, Sun J B, Huang G Q. Mechanical Behavior of Fiber-Reinforced Self-
782   Compacting Rubberized Concrete Exposed to Elevated Temperatures [J].
783   Journal of Materials in Civil Engineering, 2019, 31(12).

784 [18] Thomas R J, Ariyachandra E, Lezama D, Peethamparan S. Comparison of
785   chloride permeability methods for Alkali-Activated concrete [J]. Construction
786   and Building Materials, 2018, 165: 104-11.

787 [19] Gunasekara C, Law D, Bhuiyan S, Setunge S, Ward L. Chloride induced
788   corrosion in different fly ash based geopolymer concretes [J]. Construction
789   and Building Materials, 2019, 200: 502-13.

790 [20] Amorim Júnior N S, Andrade Neto J S, Santana H A, Cilla M S, Ribeiro D V.
791   Durability and service life analysis of metakaolin-based geopolymer concretes
792   with respect to chloride penetration using chloride migration test and corrosion
793   potential [J]. Construction and Building Materials, 2021, 287: 122970.

794 [21] Monticelli C, Natali M E, Balbo A, Chiavari C, Zanotto F, Manzi S, Bignozzi

795   M C. Corrosion behavior of steel in alkali-activated fly ash mortars in the light
796   of their microstructural, mechanical and chemical characterization [J]. Cement
797   and Concrete Research, 2016, 80: 60-8.

798 [22] Dzunuzovic N, Komljenovic M, Nikolic V, Ivanovic T. External sulfate attack
799   on alkali-activated fly ash-blast furnace slag composite [J]. Construction and
800   Building Materials, 2017, 157: 737-47.

801 [23] Kuri J C, Nuruzzaman M, Sarker P K. Sodium sulphate resistance of
802   geopolymer mortar produced using ground ferronickel slag with fly ash [J].
803   Ceramics International, 2023, 49(2): 2765-73.

804 [24] Elyamany H E, Abd Elmoaty A M, Elshaboury A M. Magnesium sulfate
805   resistance of geopolymer mortar [J]. Construction and Building Materials,
806   2018, 184: 111-27.

807 [25] Saavedra W G V, Angulo D E, De Gutierrez R M. Fly Ash Slag Geopolymer
808   Concrete: Resistance to Sodium and Magnesium Sulfate Attack [J]. Journal of
809   Materials in Civil Engineering, 2016, 28(12).

810 [26] Pasupathy K, Berndt M, Sanjayan J, Rajeev P, Cheema D S. Durability of low-
811   calcium fly ash based geopolymer concrete culvert in a saline environment [J].
812   Cement and Concrete Research, 2017, 100: 297-310.

813 [27] Tennakoon C, Shayan A, Sanjayan J G, Xu A M. Chloride ingress and steel
814   corrosion in geopolymer concrete based on long term tests [J]. Materials &
815   Design, 2017, 116: 287-99.

816 [28] Dong Z Q, Wu G, Zhao X L, Zhu H, Lian J L. Durability test on the flexural
817   performance of seawater sea-sand concrete beams completely reinforced with
818   FRP bars [J]. Construction and Building Materials, 2018, 192: 671-82.

819 [29] Monticelli C, Natali M E, Balbo A, Chiavari C, Zanotto F, Manzi S, Bignozzi
820   M C. A study on the corrosion of reinforcing bars in alkali-activated fly ash
821   mortars under wet and dry exposures to chloride solutions [J]. Cement and
822   Concrete Research, 2016, 87: 53-63.

823 [30] Tittarelli F, Mobili A, Giosue C, Belli A, Bellezze T. Corrosion behaviour of
824   bare and galvanized steel in geopolymer and Ordinary Portland Cement based
825   mortars with the same strength class exposed to chlorides [J]. Corrosion
826   Science, 2018, 134: 64-77.

827 [31] Wang W R, Chen H S, Li X Y, Zhu Z G. Corrosion behavior of steel bars
828   immersed in simulated pore solutions of alkali-activated slag mortar [J].
829   Construction and Building Materials, 2017, 143: 289-97.

830 [32] Wang Z K, Zhao X L, Xian G J, Wu G, Raman R K S, Al-Saadi S, Haque A.
831   Long-term durability of basalt- and glass-fibre reinforced polymer
832   (BFRP/GFRP) bars in seawater and sea sand concrete environment [J].
833   Construction and Building Materials, 2017, 139: 467-89.

834 [33] Lu C H, Ni M Z, Chu T S, He L Y. Comparative Investigation on Tensile
835   Performance of FRP Bars after Exposure to Water, Seawater, and Alkaline
836   Solutions [J]. Journal of Materials in Civil Engineering, 2020, 32(7).

837 [34] Lu Z Y, Li Y C, Xie J H. Durability of BFRP bars wrapped in seawater sea
838   sand concrete [J]. Composite Structures, 2021, 255.

839   [35]   Luo Z Y, Li W G, Wang K J, Castel A, Shah S P. Comparison on the properties
840   of ITZs in fly ash-based geopolymer and Portland cement concretes with
841   equivalent flowability [J]. Cement and Concrete Research, 2021, 143.
842   [36]   Cai Y J, Xiao S H, Chen Y W, Huang Z R, Lin J X, Guo Y C, Peng Y Q, Xie Z
843   H. Tensile behavior and durability prediction of GFRP-steel composite bars
844   under chloride environments [J]. Journal of Materials Research and
845   Technology-Jmr&T, 2023, 23: 5746-59.
846   [37]   Xiong Z, Wei W, Liu F, Cui C, Li L, Zou R, Zeng Y. Bond behaviour of
847   recycled aggregate concrete with basalt fibre-reinforced polymer bars [J].
848   Composite Structures, 2021, 256: 113078.
849   [38]   Xiong Z, Mai G, Qiao S, He S, Zhang B, Wang H, Zhou K, Li L. Fatigue bond
850   behaviour between basalt fibre-reinforced polymer bars and seawater sea-sand
851   concrete [J]. Ocean & Coastal Management, 2022, 218: 106038.
852   [39]   Zou R, Liu F, Xiong Z, He S, Li L, Wei W. Experimental study on fatigue
853   bond behaviour between basalt fibre-reinforced polymer bars and recycled
854   aggregate concrete [J]. Construction and Building Materials, 2021, 270:
855   121399.
856   [40]   Xiong Z, Wei W, He S, Liu F, Luo H, Li L. Dynamic bond behaviour of fibre-
857   wrapped basalt fibre-reinforced polymer bars embedded in sea sand and
858   recycled aggregate concrete under high-strain rate pull-out tests [J].
859   Construction and Building Materials, 2021, 276: 122195.
860   [41]   Neupane K. "Fly ash and GGBFS based powder-activated geopolymer
861   binders: A viable sustainable alternative of portland cement in concrete
862   industry" [J]. Mechanics of Materials, 2016, 103: 110-22.
863   [42]   Khan M S H, Castel A, Akbarnezhad A, Foster S J, Smith M. Utilisation of
864   steel furnace slag coarse aggregate in a low calcium fly ash geopolymer
865   concrete [J]. Cement and Concrete Research, 2016, 89: 220-9.
866   [43]   Tian Z, Zhang Z, Liu H, Zheng W, Tang X, Gui Z. Interfacial characteristics
867   and mechanical behaviors of geopolymer binder with steel slag aggregate:
868   Insights from molecular dynamics [J]. Journal of Cleaner Production, 2022,
869   362: 132385.
870   [44]   Ren X, Zhang L. Experimental study of interfacial transition zones between
871   geopolymer binder and recycled aggregate [J]. Construction and Building
872   Materials, 2018, 167: 749-56.
873   [45]   Yang Y, Chen Z, Feng W, Nong Y, Yao M, Tang Y. Shrinkage compensation
874   design and mechanism of geopolymer pastes [J]. Construction and Building
875   Materials, 2021, 299: 123916.
876   [46]   Lee S L, Wong S F, Swaddiwudhipong S, Wee T H, Loo Y H. Accelerated test
877   of ingress of chloride ions in concrete under pressure and concentration
878   gradients [J]. Magazine of Concrete Research, 1996, 48(174): 15-25.
879

1 **Beyond Time: Enhancing Corrosion Resistance of Geopolymer Concrete and**
2 **BFRP Bars in Seawater**

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35

36 **ABSTRACT:** To improve the durability of Basalt fiber reinforced polymer (BFRP)

37 bars reinforced geopolymer concrete (GPC), it is important to study the time-

38 dependent variation of the corrosion resistance ability of GPC and BFRP in a seawater

39 environment. This paper presents an experimental investigation to study the time-

40 dependent mechanical properties and durability of BFRP bars and geopolymer

41 materials synthesized by granulated blast furnace slag (GGBFS), fly ash, and silica

42 fume. The resulting GPC and Portland cement (PC) concrete were exposed to

43 artificial seawater. The mechanical properties of GPC were evaluated by analyzing

44 and comparing the volume expansion and strength loss rates of GPC and PC concrete

45 in an artificial seawater environment. The corrosion resistance of geopolymer (GP)

mortar and PC mortar was evaluated by studying the migration ability and pore structure in corrosive ions attack (Cl^-, SO_4^{2-}, Mg^{2+}) in artificial seawater. Moreover, the time-dependent tensile strength of BFRP was comparatively investigated by immersing in different solutions (tap water, artificial seawater, and alkaline simulated seawater). In addition, the dual interface transition zones (ITZs) characteristics of BFRP reinforced GPC under artificial seawater were also investigated by SEM and BSE tests. The results showed that the volume expansion rate and strength loss rate of GPC decreased by 77.6% and 8.7%, respectively, after 360 days of seawater corrosion compared with PC concrete. This enabled the development of a time-dependent strength model of GPC in marine environments. The coefficient of ions diffusion in GP mortar is much lower than that of PC mortar, and GP mortar shows excellent resistance to ion migration. In addition, the effect of seawater corrosion on the tensile strength of BFRP bars increases with the increase of bars' diameter, and the ultimate strengths of BFRP bars with diameters of 6 mm and 8 mm were 695 MPa and 663 MPa, respectively. The tensile strength degradation model of BFRP bars in geopolymer concrete under seawater corrosion was established. After 360 days of seawater immersion, the average porosity of the ITZ between geopolymer and aggregates, and the average porosity of the ITZ between geopolymer and BFRP bars increased insignificantly compared to that of PC concrete. This research can provide a theoretical basis for the service life prediction of BFRP reinforced geopolymer concrete within marine environments.

Keywords: Geopolymer concrete, Basalt fiber reinforced polymer (BFRP) bars, Seawater, Time-dependence, Interface characteristic.

1 Introduction

Geopolymer concrete (GPC) has attracted extensive attention from researchers due to its excellent characteristics, such as stable hydration products, compact paste structure, adjustable setting time, early strength, and high strength [1-4]. Meanwhile, it can effectively reduce energy consumption and greenhouse gas emissions of ordinary Portland cement (OPC) production[5-10]. The process of preparing GPC is given in Fig.1. In addition, GPC has excellent seawater corrosion resistance, enabling the use of local materials and sea sand as aggregate, to solve the problem of insufficient river

79   sand resources. Therefore, GPC is suitable for the characteristics of marine
80   engineering construction, and it can address issues such as the shortage of materials
81   and fresh water, the influence of tidal action in the construction process, and the
82   corrosion from harmful ions in seawater in the service process of buildings.
83   Experimental results show that the mechanical properties of seawater sea sand
84   concrete (SWSSC) are similar to those of traditional concrete[11]. However, seawater
85   and sea sand contain high concentrations of chloride ions, which will lead to the
86   corrosion of steel bars in SWSSC structures [12, 13]. Corrosion and expansion of steel
87   bars cause durability problems such as cracking and peeling of the protective concrete
88   layer. These problems seriously reduce the safety of SWSSC structures and lead to
89   high maintenance costs. However, fiber reinforced polymer (FRP) bars are believed to
90   be another effective way to solve these problems, potentially eliminating the
91   limitation that seawater sea sand cannot be directly used as concrete raw material [14].
92   Recently, basalt fiber reinforced polymer (BFRP) bars have been used in some
93   concrete structures subjected to extreme environmental conditions due to their
94   superior chemical resistance [15-17]. There is no corrosion and expansion problem in
95   marine environments, so BFRP reinforced geopolymer concrete (hereafter called
96   BFRP GPC) has broad application prospects in marine engineering construction.
97   However, it is worth noting that BFRP GPC has double interface transition zones
98   (ITZs), and the transport of corrosive ions in seawater in the GPC is time-dependent.
99   Existing research results do not reveal the time-dependence variation of corrosive ions
100   transported in GPC under seawater corrosion and the influence of the time-
101   dependence variation on the performance of BFRP bars. Thus, it is necessary to study
102   the time-dependence mechanism of GPC and BFRP bars under seawater corrosion as
103   it can provide a basis for service life prediction of BFRP GPC in marine environments.
104   In previous studies, there have been numerous research efforts on the seawater
105   corrosion resistance of GPC, including Cl^- permeability resistance, sulfate resistance
106   (SO_4^{2-} and Mg^{2+}), and the variation of properties in artificial seawater. On Cl^-
107   permeability resistance of GPC, Thomas et al. [18] studied the chloride ion
108   permeability of alkali-activated fly ash, alkali-activated slag, and PC concrete
109   immersed in 3% NaCl for 90 days. In general, alkali-activated slag concrete has better
110   chloride ion permeability resistance, slightly better than PC concrete. Gunasekara et al.
111   [19]studied the corrosion of fly ash-based geopolymers and PC concrete immersed in

112   3% NaCl for 540 days. Test results indicated that the three-dimensional N-A-S-H and

113   C-A-S-H crosslinking formed in the fly ash-based geopolymers reduces the diffusion

114   of chloride ions into the depth of the concrete, resulting in a lower corrosion rate

115   compared to PC concrete. Amorim Junior et al. [20] showed that metakaolin GPC has

116   similar or higher durability than OPC concrete by the migration test of chloride.

117   Therefore, GPC has excellent resistance to chloride ion penetration, which is related

118   to the type of activator, alkali content, and curing mode in GPC. In addition, the

119   presence of sulfate ions and magnesium ions can also affect the durability of concrete

120   structures in the marine environment. Krivenko et al. [21] proposed that slag-based

121   geopolymer concrete has better sulfate resistance than PC paste, even better than

122   sulfate-resistant cement pastes, and sodium sulfate is beneficial to promote the

123   polymerization of GPC continuous reaction, making the structure more compact.

124   Dzunuzovic et al. [22] studied the influence of 5% sodium sulfate solution on the

125   mechanical properties and microstructure properties of fly ash-slag base binder (FA-

126   BFS) and PC concrete for 180 days. During the whole immersion period, the strength

127   loss index was higher than 1, and the compressive strength of specimens exposed to

128   the sulfate solution developed slowly. XRD (X-ray diffractometer) analysis shows that

129   there were no new substances produced by the alkali-activated material and sulfate

130   reaction. Sanghamitra Jena [23] used silica ash to partially replace fly ash to prepare

131   GPC. Specimens were respectively immersed in 5% NaCl and 2% $MgSO_4$ corrosive

132   solution for 28 days. The experimental results showed that adding fly ash and silica

133   fume can improve the strength of GPC. Hafez E. Elyamany et al. [24] compared the

134   corrosion resistance of GP mortar with added slag and silica fume substituted for fly

135   ash, GP mortar with fly ash, and OPC mortar after immersion in 10% $MgSO_4$ solution

136   for 48 weeks. The results showed that the corrosion resistance of GP mortar mixed

137   with slag and silica fume is higher than that of GP mortar mixed with fly ash only, and

138   both are higher than that of OPC mortar. Valencia Saavedra et al. [25] studied the

139   performance of GPC (composed of 80% fly ash and 20% mineral powder) and OPC

140   concrete after curing in 5% $MgSO_4$ solution for 360 days. The results showed that the

141   expansion rate of FA/GBFS (Class fly ash and granulated blast-furnace slag) concrete

142   is 0.04% and the mechanical resistance is reduced by 33%, while the expansion rate

143   of OPC concrete is 0.08% and the mechanical resistance is reduced by 48% under the

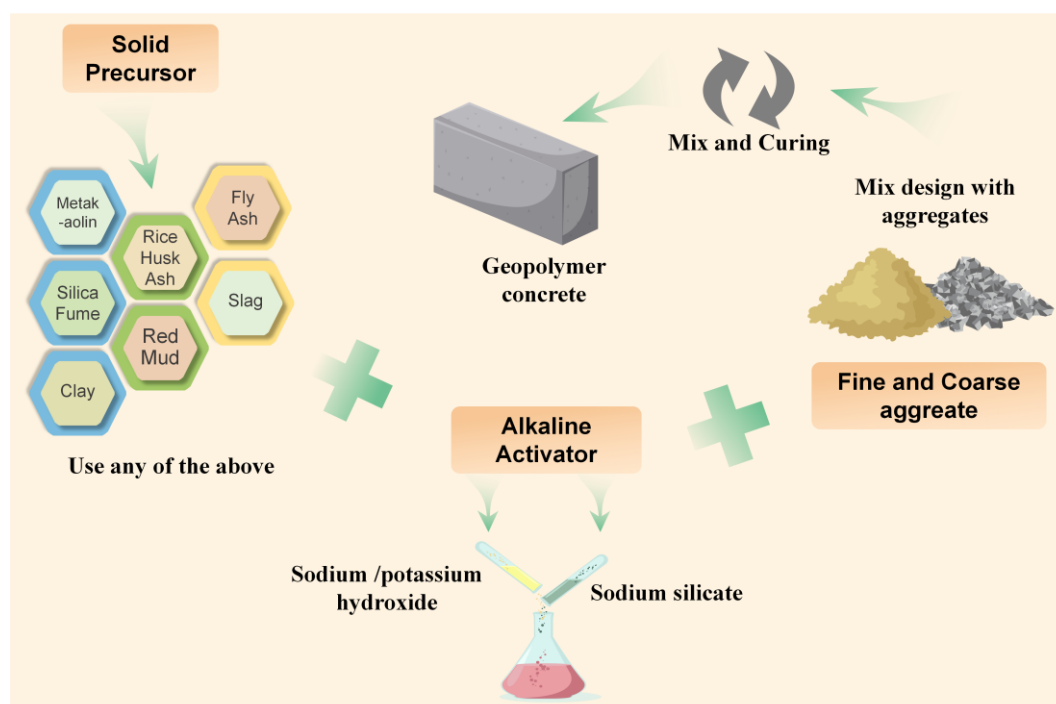144   same conditions. Therefore, FA/GBFS concrete has better resistance to $MgSO_4$

145 corrosion than OPC concrete. The above research shows that all kinds of GPC have
146 better sulfate resistance than OPC concrete, as the reaction products are difficult to
147 corrode and the microstructure is compact. However, existing research on the
148 seawater corrosion resistance of GPC does not consider the time-dependence of
149 corrosive ion transport, and the influence mechanism of the dynamic transport process
150 of corrosive ions in GPC on their macroscopic properties and microstructure evolution
151 has not been determined. In addition, the corrosion resistance of GPC in marine
152 environments is an important problem to understand to enable their successful
153 application [20, 26, 27].

154   Some researchers have studied the corrosion resistance of steel bars in GP
155 mortars and concrete in marine environments [21, 28-32], but few articles have evaluated
156 the long-term performance (such as durability and strength degradation) of BFRP bars.
157 Yan et al. [14] concluded that the tensile strength of BFRP bars in an alkaline concrete
158 pore solution decreases much faster than in distilled water, salt, or acid environments.
159 In addition, they found that the long-term performance degradation of BFRP bars in
160 alkaline solutions was more obvious than in seawater because OH^- broke the Si-O-Si
161 bonds in the basalt fibers [13]. Z. Wang et al. [32]conducted accelerated corrosion tests
162 on BFRP bars under different pH values, immersion temperatures, and durations.
163 Subsequently, they used Arrhenius degradation theory to predict the long-term
164 behavior of BFRP bars under service conditions. The study [33] evaluated the residual
165 tensile properties of BFRP bars coated with different SWSSC thicknesses exposed to
166 tap water, simulated seawater, and alkaline solution at 28℃, 40℃, 60℃. It was found
167 that the alkaline solution has a more harmful effect on the tensile properties of BFRP
168 bars than tap water or seawater. Alkalinity is the key factor leading to the deterioration
169 of BFRP bars. Therefore, thicker SWSSC-coated BFRP bars have higher resistance in
170 alkaline environments, and their tensile strength retention is lower than bare BFRP
171 bars. To sum up, although BFRP bars have an excellent ability to resist chloride
172 corrosion, the high alkaline environment in concrete will deteriorate their performance
173 [33-36]. Therefore, it is important to evaluate the long-term durability of BFRP bars in
174 marine environments. Existing studies have not revealed the time-dependence
175 mechanism of the mechanical properties and microstructure of BFRP under seawater
176 corrosion, so further research work is necessary to establish the strength degradation
177 model of BFRP under seawater corrosion.

178   Many studies[37-40] have focused on the macroscopic analysis of the bonding

179   properties of BFRP bars and concrete, while less research has been done on the

180   microscopic mechanism of the interface. Furthermore, interface transition zones (ITZs)

181   play a crucial role in BFRP GPC, both between aggregates and pastes and between

182   pastes and BFRP bars. While the ITZ between GP pastes and aggregates is denser

183   than that between OPC pastes and aggregates[41], it remains a weak area prone to the

184   development of microcracks and is key to controlling the overall strength, chemical

185   corrosion resistance, permeability, and other macro properties of GPC [42]. Current

186   research on the ITZ between pastes and aggregates primarily focuses on PC concrete,

187   with limited investigation on GPC. Luo [35] compared the performance of ITZs in PC

188   concrete and GPC, finding that the interface bond between the GPC matrix and

189   aggregates is stronger than in PC concrete. In PC concrete, the ITZs contain numerous

190   crystalline hydration products, whereas in GPC, the ITZs consist of a gelate-rich paste

191   with a denser microstructure. Tian et al. [43] examined the interface characteristics and

192   mechanical behavior of slag aggregates and GPC, comparing different GPC/steel slag

193   interface systems. They observed that the interface interaction between GPC and steel

194   slag aggregates significantly influenced the interface properties and mechanical

195   behavior. Xin Ren et al. [44] conducted comparative experiments to study the bond

196   strength of ITZs between GPC and aggregate, as well as OPC and aggregate. Their

197   experiments suggested that the development of ITZ bond strength in GPC appeared to

198   be more rapid than in OPC concrete after 7 days. In summary, both domestic and

199   international scholars have investigated the microstructure, composition, and bond

200   strength of the ITZ in GPC. However, it should be noted that previous research

201   primarily relied on qualitative analyses, lacking quantitative characterization, and the

202   mechanism of deterioration remains unclear, making it difficult to establish the

203   regulatory influence of ITZ microstructure on mesoscopic and macroscopic properties.

204   Furthermore, the double interface transition zone of BFRP reinforcement geopolymer

205   concrete has not been adequately considered.

206   As a result, the time-dependent strength model of GPC and the tensile strength

207   model of BFRP in marine environments have yet to be established. Additionally, the

208   changes in composition and microstructure of reaction products with GPC when

209   exposed to corrosive ions in seawater environments are not well understood. The

210   mechanism by which corrosive ions affect the properties of double interface transition

zones in BFRP GPC has not been confirmed. Consequently, this study aims to investigate the volume and strength loss rates of GPC in a simulated seawater environment during various immersion periods. The migration of corrosive ions (Cl^-, SO_4^{2-}, Mg^{2+}) in seawater will be evaluated. Simultaneously, the tensile strength of all BFRP bars will be tested after immersion in artificial seawater and alkaline simulated seawater for different durations, considering the effects of GP mortar wrapping on the properties of BFRP bars. The research will analyze the microstructural changes of BFRP bars in artificial seawater environments. Ultimately, this study aims to provide a theoretical basis for predicting the service life of BFRP GPC in marine environments.

Fig. 1. Production of geopolymer concrete

2 Experimental Design

2.1 Materials

The feasibility of utilizing a Geopolymer in marine environments was investigated using a composition comprising 70% granulated blast-furnace slag (GGBFS), 12% fly ash, 5% silica fume, and 13% activator, which consisted of a solid mixture of sodium silicate and sodium carbonate. The composites and chemical composition of the Geopolymer are provided in Table 1 and Table 2 [45]. By

231 considering the results of MgO compensation GPC volume shrinkage, stability, and

232 mortar strength, it was possible to prepare a Geopolymer with minimal volume

233 shrinkage (referred to as GII) by incorporating 6% MgO (in a ratio of 60 seconds: 220

234 seconds = 1:1) into the GPC [45]. This formulation was then used to assess its

235 suitability for marine environments. The mixture ratio and mechanical properties of

236 the GPC and PC concrete are presented in Table 3 and Table 4, respectively. The sand

237 was sourced from Huilai County, Guangdong Province and is natural sea sand. Table

238 5 provides information on the performance and ion content of the sea sand.

239 Additionally, Table 6 presents the basic physical properties of limestone gravel. The

240 BFRP bars were supplied by Sichuan Aerospace Tuoxin Basalt Industry Co., LTD, an

241 industrial manufacturer. Table 7 displays the initial physical properties of the BFRP

242 bars.

243 **Table 1**. Composition of Geopolymer (wt%)

Material	Composites				Blaine specific surface area, m^2/kg	Density, g/cm^3	Flexural strength, MPa		Compressive strength, MPa	
	GGBFS	Fly ash	Silica fume	Activator			3 d	28 d	3 d	28 d
Geopolymer	70%	12%	5%	13%	375	2.90	4.5	7.9	30.6	50.2

244 **Table 2** Chemical composition of geopolymer binder /wt%

Composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	P_2O_5	K_2O	Na_2O	LOI
Geopolymer	30.56	19.56	2.22	0.85	34.40	3.23	1.23	0.05	2.09	4.88	0.93

245 **Table 3** Mix proportions of geopolymer and Portland cement concretes

Sample ID.	Strength grade	W/C	ρ /%	Binder /(kg/m³)	Sand /(kg/m³)	Aggregate /(kg/m³)	Superplastictizer /(kg/m³)	Water /(kg/m³)
P-35	C35	0.40	42	440	760	1050	7.92	176
GII-35		0.40	42	440	720	1000	/	176

246 **Table 4** Physical and mechanical properties of geopolymer and Portland cement
247 concretes

Sample ID.	Workability		Compressive strength /MPa		
	Slumps/cm	Slump flow/mm	3 days	7 days	28 days
P-35	14.0	170	30.5	38.5	45.0

| GII -35 | 18.0 | 220 | 39.6 | 45.0 | 56.5 |

248 **Table 5** Performance of sea sand from Huilai County of Guangdong Province

Fineness modulus	Particle size range	Apparent density/(kg/m^3)	Bulk density/(kg/m^3)	Shell /(wt%)	Cl$^-$ (wt%)	Mg^{2+} (wt %)	SO$_4$$^{2-}$ /(wt %)
2.52	II	2590	1520	2.5~3.6	0.1008	0.0098	0.0090

249 **Table 6** Physical properties of aggregate

Percentage of flat-elongated particles /%	Crushing index/ %	Bulk density/(kg/m^3)	Apparent density/(kg/m^3)	Voidage/%
7.5	9.1	1560	2750	43.3

250 **Table 7** Physical properties of BFRP bars

Type	Length/ （mm）	Diameter/(mm)	Tensile strength/(MPa)	Anchorage length/(mm)
BFRP	1000	$\frac{6}{8}$	800~1100	400

251

252 **2.2 Exposure condition**

253   In this study, two immersion environments were employed for testing purposes.
254 The GPC specimens were immersed in tap water, while the bare BFRP bars were
255 immersed in artificial seawater. The composition of the artificial seawater solution
256 was designed based on ASTM D 1141-98 and is outlined in Table 8. Considering the
257 alkaline nature of the concrete environment, the BFRP bars were additionally
258 immersed in alkaline simulated seawater. This simulated seawater was prepared using
259 a saturated Ca(OH)$_2$ solution, following the composition specified in Table 8. To
260 facilitate comparative analysis, BFRP bars coated with GP mortar were also immersed
261 in artificial seawater. The exposure periods for all specimens were 28 days, 56 days,
262 90 days, 180 days, and 360 days.

263 **Table 8** The composition of artificial seawater

Ion types	NaCl	MgCl$_2$	Na$_2$SO$_4$	CaCl$_2$
Concentration （g/L）	4.53	20	4.09	1.16

3 Test methods

3.1 Seawater resistance of geopolymer concrete

3.1.1 Volume expansion and strength loss of geopolymer concrete

The specimens were prepared according to the mix proportions specified in Table 3. They were cast in the form of 150×150×150 mm blocks and cured at room temperature for 24 hours. After demolding, the specimens were transferred to a standard curing chamber maintained at a temperature of 25 °C and a relative humidity of 95% for a period of 28 days.

Following the curing period, any loosely adhering portions at the corners of the test blocks were removed, and the resulting volume was measured using the drainage method. This initial volume measurement was recorded as the original volume of the specimens.

During the immersion and corrosion period, the volume and compressive strength of the specimens were measured after a certain duration denoted as "t" days. The Vt (volume corrosion resistance coefficient) and St (strength corrosion resistance coefficient) were utilized to characterize the seawater corrosion resistance of the concrete. The physical meanings of these parameters are as follows:

$$V_t = \frac{v_t - v_{28}}{v_{28}} \qquad (1)$$

Where, V_t is coefficient of the volume corrosion resistance at time, t; v_t is the volume of the concrete specimens at t age (mm^3); v_{28} is the volume of the concrete specimens at 28 days (mm^3).

$$S_t = \frac{s_{28} - s_t}{s_{28}} \qquad (2)$$

Where, S_t is coefficient of the strength corrosion resistance at time, t; s_t is the compressive strength of the concrete specimens at t age (MPa); s_{28} is the compressive strength of the concrete specimens at 28 days (MPa).

3.1.2 Ion migration resistance of geopolymer mortar

In order to further investigate the transport performance of corrosive ions in GP mortar, a mortar mixture was prepared by incorporating artificial seawater containing corrosive ions such as Cl^-, Mg^{2+}, and SO_4^{2-}. Once the mortar reached a specific age,

ion content measurements were conducted in each layer of the mortar along the direction of hydrostatic pressure. These measurements were used to calculate the migration coefficient of the GP mortar. For the ion migration tests, a self-made ion migration testing device was utilized, as depicted in Figure 2. The device includes a water tank ①, which is connected to an air co mpressor ② through a pipe. the valve is set on the pipeline, the air pressure machine ② is connected to the specimen mounting device ⑤ through the pressure pipe ③. The pressure gauge ④ is set on the pressure pipe ③, and the specimen mounting device ⑤ is installed with an osmotic liquid collector ⑥ on the upper part of the specimen mounting device. After migrating for a certain period of time, the liquid in the collector ⑥ is poured into a measuring cylinder to measure its volume, and the ion concentration in the liquid is measured by ion chromatography to calculate the amount of ions migrating for a certain period of time. Cylindrical mortar specimens with a bottom diameter of 100 mm, top diameter of 80 mm, and height of 100 mm were employed as migration specimens. The cement-to-sand ratio was 1:3, and the water-to-cement ratio was 0.5. After curing for 28 days, the specimens were subjected to testing under standard conditions with a relative humidity (RH) of at least 95% and a temperature of 20±2℃.

Fig. 2. The schematic diagram of device for testing ion migration in mortar specimens

3.2 Tensile performance of BFRP bars

After being immersed in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution), the BFRP bars were removed and the surfaces were dried. The tensile specimens of the BFRP bars were designed and manufactured following the guidelines outlined in ACI440.3R-04 "Guide to Test Methods for FRP Bars Reinforced Concrete Structures". The total length of the tensile specimen, denoted as "L," was set to 1000 mm.

To prevent shear damage caused by the tensile machine fixture, adhesive anchors were incorporated at both ends of the tensile test sample within a length of 200 mm, as depicted in Fig. 3. These anchors were constructed using galvanized steel pipes with a bottom diameter of 30 mm, top diameter of 35 mm, and thickness of 3 mm. The steel sleeves were bonded to the BFRP bars by pouring epoxy resin.

Following the specifications outlined in the "Test Method for Basic Mechanical Properties of Fiber Reinforced Composite Bars" (GB/T 30022-2013), the prepared BFRP bars were subjected to a tensile test using an electro-hydraulic servo universal testing machine. This test aimed to measure the ultimate tensile strength and tensile strain of the specimens. A displacement control method was employed to ensure that the specimens were destroyed within a timeframe of 1 to 10 minutes.

Fig. 3. BFRP specimen for tension test（mm）

3.3 Microscopic analysis

The microstructural tests conducted in this study included scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and backscattering electron (BSE) imaging. To investigate the impact of marine corrosive substances on the microstructure of GPC, different dosages of NaCl, Na_2SO_4, and $MgSO_4$ were added into the GP paste, as detailed in Table 9. The MIP method was employed to examine the pore structure characteristics of GPC after 28 days of exposure to corrosive substances. The microstructure of the BFRP bars was analyzed using SEM after 180

days of immersion in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution).

Table 9 Dosage of corrosion ions in geopolymer

Groups	Dosage of corrosion ions (%)								
	NaCl			Na_2SO_4			$MgSO_4$		
1	0	3.5	5	-	-	-	-	-	-
2	-	-	-	0	3	8	-	-	-
3	-	-	-	-	-	-	0	3	8

3.3.1 Scanning electron microscopy (SEM) tests

The hardened paste samples were fractured into pieces after being cured for a specific duration, and some of these fragments underwent gold-plating treatment. The BFRP bars were immersed in tap water, artificial seawater, and alkaline simulated seawater (saturated with a $Ca(OH)_2$ artificial seawater solution) until reaching a predetermined age. Subsequently, the bars were taken out and the surfaces were dried. The microstructures of these samples were analyzed using EVO18 scanning electron microscopy (SEM) equipment, manufactured by Carl Zeiss Germany.

3.3.2 Mercury Intrusion Porosimetry (MIP) tests

MIP was employed to assess the total porosity and pore size distribution of the mortars. The samples were crushed into small pieces measuring $5\times5\times5$ mm and soaked in ethanol for over 24 hours, with a volume ratio of approximately 1:4 for the sample to ethanol. The pore structure of the hardened paste was determined using an AutoPore IV 9500 mercury porosimeter.

3.3.3 Backscattering electron (BSE) tests

The samples were analyzed using backscattered electron imaging with an S-3400N Scanning Electron Microscope. The sample preparation process is as follows: Initially, the fractured samples were immersed in epoxy resin and left to demold for 24 hours. Subsequently, the samples solidified with epoxy resin were polished using an automatic Polish-grinding machine, employing sandpapers of various mesh sizes including 60, 120, 320, 500, 2000, and 4000. Prior to testing, the samples were coated with a layer of gold to enhance conductivity.

4 Result and discussion

4.1 Time-Dependent Behavior of Geopolymer Concrete: Volume and Strength

368   Figure 4 illustrates the seawater resistance of GPC (GII-35) and PC concrete (P-
369 35) over an exposure period of up to 360 days. It can be observed that, compared to
370 GPC, PC concrete exhibited a significantly higher volume expansion ratio at 180 and
371 360 days, with increases of 384.6% and 430.0% respectively (Figure 4a). Similarly,
372 the strength loss ratio of PC concrete at 180 and 360 days increased by 10.4% and
373 9.6% respectively (Figure 4b). Conversely, GPC demonstrated a remarkable reduction
374 in both volume expansion ratio and strength loss ratio, which decreased by 77.6% and
375 8.7% respectively after 360 days of seawater corrosion. These results indicate that
376 GPC exhibits superior resistance to seawater corrosion compared to PC concrete.

377

378   (a) Volume expansion   (b) Strength loss

379   **Fig. 4.** The corrosion resistance of GPC and PC concretes

4.2 Time-dependent strength model of GPC in marine environments

381   Concrete strength will change with service time under the influence of
382 environmental factors and sustained loads. Based on the strength data of long-term
383 concrete in actual marine engineering, scholars have analyzed its degradation pattern
384 using regression methods and proposed a time-dependent decay model for the average
385 strength of concrete in marine environments, as presented in Eq. (3).

386 $$f_c(t) = f_0 \times 1.248 \mathrm{e}^{-0.0340 \times (\mathrm{Int} - 0.3468)^2} \tag{3}$$

387 Where $f_c(t)$ represents the compressive strength of concrete after t years, MPa; f_0
388 represents the average value of initial concrete strength, MPa.

389   The time-dependence equation of concrete strength retention rate in marine

environments can be determined by Eq.(4). $F_c(t)$ is strength retention rate of concrete in marine environments in immersion time t.

$$F_c(t) = \frac{f_c(t)}{f_0} = 1.248e^{-0.0340\times(\text{Int}-0.3468)^2} \times 100\% \qquad (4)$$
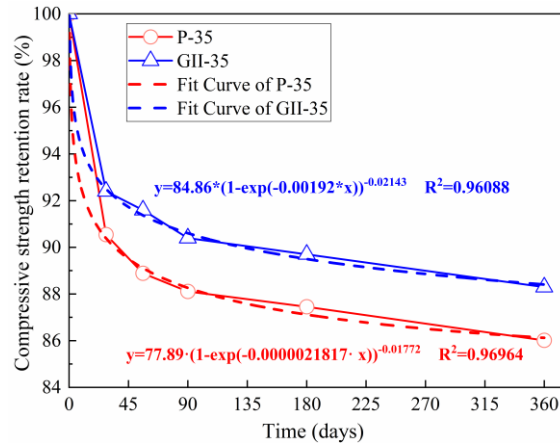
In Fig. 5, the fitting curve illustrates the seawater corrosion resistance test results of GPC (GII-35) and PC concrete (P-35). As time approaches infinity, the strength retention rate of GII-35 and P-35 reaches 84.9% and 77.9%, respectively. Thus, the time-dependent degradation equation for the strength retention rate of GPC in marine environments can be expressed as Eq. (5). $F_w(t)$ is strength retention rate of GPC in marine environments in immersion time t

$$F_w(t) = \frac{84.9}{77.9} \times F_c(t) = 1.360e^{-0.0340\times(\text{Int}-0.3468)^2} \times 100\% \qquad (5)$$

The decay equation for the mechanical properties of GPC in marine environments can be expressed as Eq. (6).

$$f_w(t) = f_{w0} \times 1.248e^{-0.0340\times(\text{Int}-0.3468)^2} \qquad (6)$$

Where $f_w(t)$ is the compressive strength of GPC after t years, MPa; f_{w0} is the average initial strength of GPC, MPa.

Fig.5. Compressive strength of PC (P-35) and GPC (GII-35) in seawater for different immersion periods

4.3 Transport performance of ions in seawater in GP mortar

Under the hydrostatic pressure (1.4 MPa), the water samples of mortar specimens (mixed with artificial seawater) at different exposure ages were analyzed. By measuring the contents of Cl^-, SO_4^{2-} and Mg^{2+} in the water samples, the amount of ions permeation migration ΣA_n at different ages were obtained. Based on the ratio of

15

413   chemical bonding and physical adsorption, A_0 was calculated and $\Sigma A_n/A_0$ was obtained.

414   The cumulative leaching fraction of ions can be calculated using Eq. (7). The leaching

415   rate and cumulative leaching fraction of PC mortar and GP mortar were obtained, as

416   shown in Table 10 and Table 11.

417
$$P_t = \frac{\sum A(t)}{A_0} \times \frac{V}{S} \qquad （7）$$

418   Where P_t is the cumulative leaching fraction of ions, cm; t is exposure time; $\sum A(t)$ is

419   the accumulated leaching amount of the first n ions, g; A_0 is the amounts of ions that

420   can migrate in the sample, g; V is the volume of sample, cm^3; S is the geometrical area

421   of the solidified sample in contact with water, cm^2.

422   **Table 10** Leaching ratio and cumulative leaching fraction of ions from Portland
423   cement mortar

Time (d)	$\frac{\sum A_n}{A_0}$ (Cl$^-$)	P_t (Cl$^-$/cm)	$\frac{\sum A_n}{A_0}$ (SO$_4^{2-}$)	P_t (SO$_4^{2-}$/cm)	$\frac{\sum A_n}{A_0}$ (Mg^{2+})	P_t (Mg^{2+}/cm)
1	0.0138	0.1168	0.0050	0.1111	0.0131	0.1161
2	0.0966	0.8178	0.0190	0.4222	0.0291	0.2589
3	0.1494	1.2648	0.0305	0.6778	0.0852	0.7572
5	0.2691	2.2781	0.0455	1.0111	0.1073	0.9541
7	0.3207	2.7149	0.0665	1.4778	0.1984	1.7639
10	0.3981	3.3702	0.1050	2.3333	0.2306	2.0500
15	0.4672	3.9551	0.1567	3.4811	0.2909	2.5861
20	0.5463	4.6248	0.1792	3.9822	0.3853	3.4244
25	0.5953	5.0396	0.2005	4.4556	0.4206	3.7383
30	0.6244	5.2859	0.2250	5.0000	0.4809	4.2744
35	0.6534	5.5314	0.2475	5.5000	0.5902	5.2461
40	0.6625	5.6085	0.2517	5.5933	0.6605	5.8711
50	0.6806	5.7617	0.2681	5.9567	0.7511	6.6767
60	0.7288	6.1697	0.2700	6.0000	0.8408	7.4733

424   **Table 11** Leaching ratio and cumulative percentage of ions from geopolymer mortar

Time (d)	$\Sigma A_n/A_0$ (Cl$^-$)	P_t (Cl$^-$/cm)	$\Sigma A_n/A_0$ (SO$_4^{2-}$)	P_t (SO$_4^{2-}$/cm)	$\Sigma A_n/A_0$ (Mg^{2+})	P_t (Mg^{2+}/cm)
1	0.0066	0.0512	0.0060	0.0636	0.0030	0.8830
2	0.0593	0.4572	0.0350	0.3719	0.0068	2.0000
3	0.0879	0.6781	0.0455	0.4833	0.0101	2.9415
5	0.1182	0.9117	0.0864	0.9190	0.0165	4.8246
7	0.1507	1.1622	0.1136	1.2083	0.0219	6.4152
10	0.1984	1.5303	0.1353	1.4385	0.0340	9.9415

15	0.2585	1.9932	0.1943	2.0659	0.0473	13.8304
20	0.3029	2.3358	0.2173	2.3099	0.0664	19.4152
25	0.3661	2.8234	0.2472	2.6279	0.0815	23.8304
30	0.4094	3.1567	0.2746	2.9196	0.1006	29.4152
35	0.4426	3.4130	0.2900	3.0837	0.1157	33.8304
40	0.4858	3.7463	0.3009	3.1998	0.1328	38.8304
50	0.5123	3.9503	0.3105	3.3019	0.1670	48.8304
60	0.5387	4.1542	0.3192	3.3937	0.2012	58.8304

425   The following hypotheses are proposed for ion migration in the solidified sample:
426   1) The leaching process of the three ions occurs through one-dimensional leaching
427   along the diameter of the solidified sample; 2) The hardened paste is a homogeneous
428   system; 3) The diffusion coefficient is constant; 4) The permeable water is a
429   homogeneous semi-infinite medium; 5) Ions bound by chemical bonding or physical
430   adsorption remain stable during osmotic dissolution; 6) Hardened pastes will not be
431   damaged by corrosion. According to Fick's 2nd law, the equation for ion osmosis
432   migration and diffusion can be obtained. C_0 is the chloride concentration on the
433   exposed surface of concrete. C is the free chloride concentration in diffusion time t.

434
$$\frac{C}{C_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{8}$$

435   The amount of ions penetration and migration in a solidified sample can be
436   obtained by Fick's 1st law:

437
$$J(t) = -D\frac{\partial C}{\partial x}\Big|_{x=0} = -C_0\sqrt{\frac{D}{\pi t}} \tag{9}$$

438   The amount of ions migration in a solidified sample per unit area at t migration
439   period can be expressed as:

440
$$A_n(t) = \int_0^t J(t)dt = 2A_0\sqrt{\frac{Dt}{\pi}} \tag{10}$$

441   Where A_n is the accumulated amount of ions dissolved in t migration period, g; A_0 is
442   the initial amount of transferable ions in the solidified sample, g; D is the surface
443   migration coefficient, mm^2/s.

444   According to the above equations and the cumulative migration fraction, P_t , of
445   the ions in the solidified sample, Eq.(11) can be obtained:

446
$$\frac{\sum A_n}{A_0} = 2(\frac{S}{V})\sqrt{\frac{Dt}{\pi}} \tag{11}$$

447   Where ΣA_n is the cumulative dissolution amount of ions in t migration period, g; A_0 is
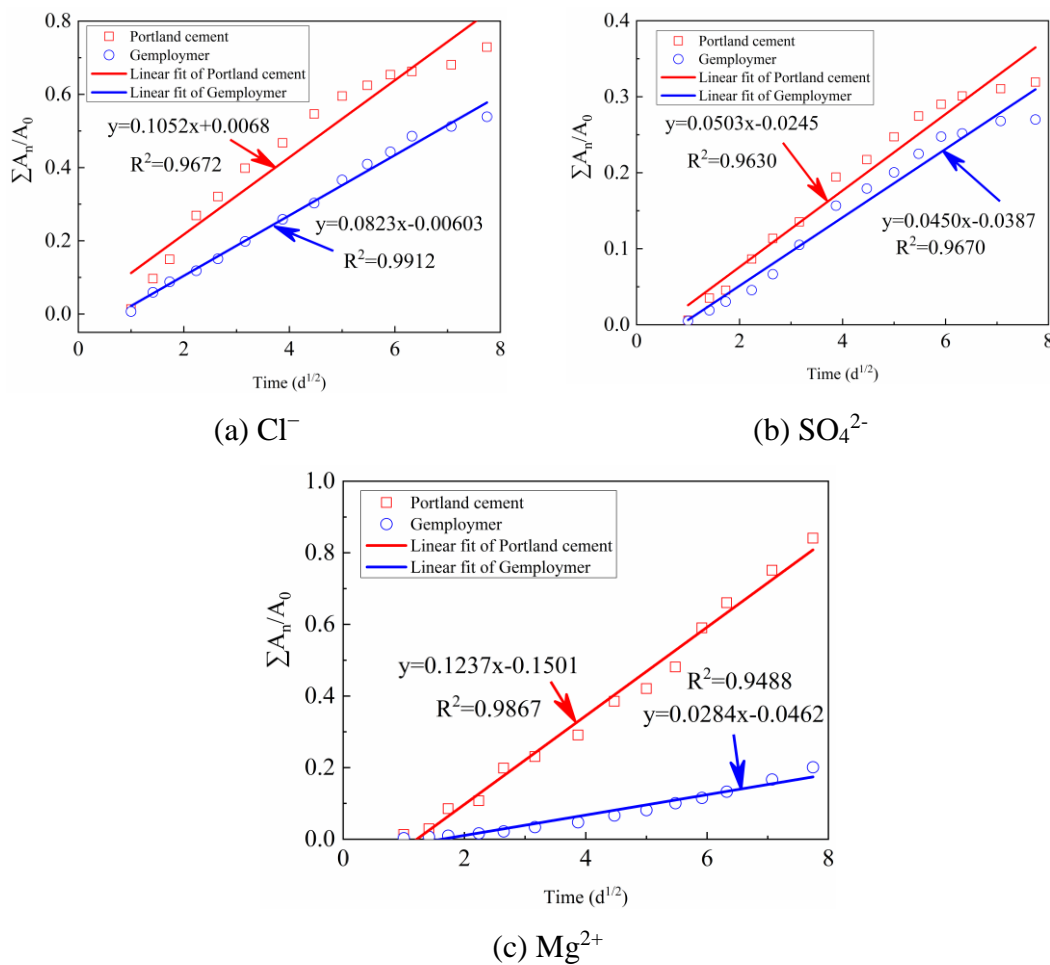
448   the initial amount of transferable ions in the solidified sample, g; D is the permeability

449   diffusion coefficient of ions migration, cm^2/d.

450   The migration diffusion coefficient, D, can be obtained from the slope of the line

451   formed by $\Sigma A_n/A_0$ and $t_n^{1/2}$:

452   $$D = \pi(\frac{mV}{2S})^2 \qquad\qquad （12）$$

453   The cumulative leaching rate ($\Sigma A_n/A_0$) of Cl^-, SO_4^{2-} and Mg^{2+} in the PC mortar and

454   GP mortar solidified samples obtained by the test is shown in Table 10 and Table 11.

455   The result obtained by curve fitting and $t^{1/2}$ is shown in Fig 6.

(a) Cl^- (b) SO_4^{2-}

(c) Mg^{2+}

Fig. 6. Relationship between $\Sigma A_n/A_0$ and $t_n^{1/2}$

459   According to the fitting results in Fig. 6, the ions diffusion coefficient D of GP

460   and PC mortar in seawater can be calculated by Eq. (12). Table 12 shows that the

461   chloride diffusion coefficient of GP mortar is only 6.15×10^{-4} mm^2/s, which is 61.2%

462   of that of PC mortar. The sulphate diffusion coefficient of GP mortar is about 1.84×10^{-4}

463   ^{4} mm^2/s, which is 81.1% of that of PC mortar. The Magnesium ion diffusion

18

464   coefficient of GP mortar is 0.73×10^{-4} mm^2/s, which is only 5.3% of that of PC mortar.

465   In other words, GP shows excellent performance to resist ions migration.

466   **Table 12** Diffusion coefficient of Cl$^-$, SO$_4^{2-}$ and Mg^{2+} in GP mortar and PC mortar

Material type	D（Cl$^-$）/ （$\times 10^{-4}$ mm^2/s）	D（SO$_4^{2-}$）/ （$\times 10^{-4}$ mm^2/s）	D（Mg^{2+}）/ （$\times 10^{-4}$ mm^2/s）
GP mortar	6.15	1.84	0.73
PC mortar	10.06	2.30	1.39

467   **4.4 Effect of corrosive ions on pore structure of GP pastes**

468   The pore size distributions of cement paste and geopolymer paste with a 28-day

469   curing age were measured using MIP. The influence of NaCl, Na$_2$SO$_4$, and MgSO$_4$ on

470   pore distribution is presented in Fig. 7. The results demonstrate that the pore size and

471   total porosity of the geopolymer are much smaller than those of the cement. In the

472   geopolymer pastes, the pore size after 28 days of age is typically smaller than 20 nm.

473   Fig. 7(a) shows that the introduction of 5% NaCl has a minimal effect on the

474   total porosity of the cement paste but refines the pore size. On the other hand, the pore

475   size of the geopolymer pastes remains relatively unchanged, but the total porosity

476   decreases significantly with the introduction of 5% NaCl. When considering the initial

477   and final setting times of the geopolymer pastes, it can be observed that the

478   introduction of 5% Cl$^-$ delays the reaction speed and increases the reaction degree,

479   resulting in a decrease in total porosity.

480   Fig. 7(b) and Fig. 7(c) demonstrate that the median pore size of the geopolymer

481   paste increases with the addition of 8% SO$_4^{2-}$, while the median pore size of the

482   cement paste decreases. It is worth noting that the results indicate a decreasing trend

483   in the number of large pores in the geopolymer paste with the addition of SO$_4^{2-}$, while

484   the number of small pores increases significantly. The observed phenomena can be

485   attributed to the early-stage erosion process, where the erosion products of SO$_4^{2-}$ tend

486   to initially fill the pores, resulting in a reduction of the median pore size in the cement

487   paste. Furthermore, the introduction of 8% Mg^{2+} causes a notable increase in the

488   number of macropores in the cement paste, while simultaneously leading to a

489   significant decrease in the percentage of macropores in the geopolymer. This

490   observation suggests that Mg^{2+} erosion converts the hydration product C-S-H gel into

491   M-S-H, leading to the formation of loosely structured macropores. As a consequence

(a) Pastes with NaCl

(b) Pastes with Na$_2$SO$_4$

(c) Pastes with MgSO$_4$

Fig.7. Pore size distribution of geopolymer and cement pastes with NaCl, Na$_2$SO$_4$ and MgSO$_4$

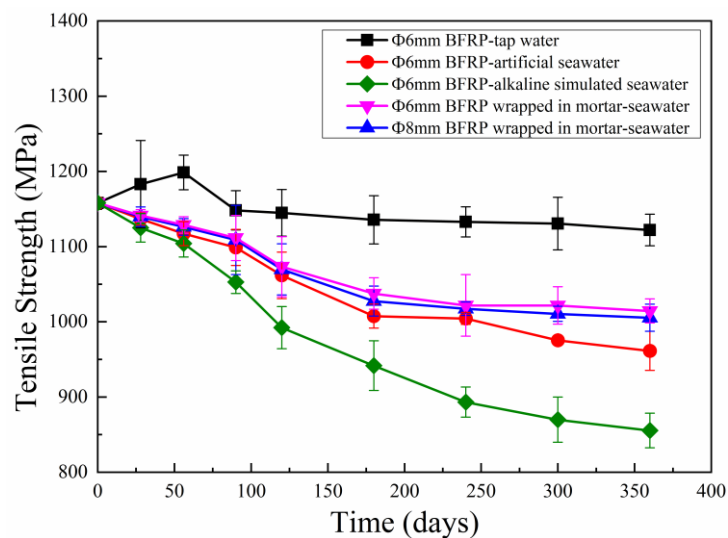## 4.5 Time-dependence regulation of mechanical properties of BFRP bars in seawater

Fig. 8 illustrates the degradation of tensile strength for bare BFRP bars with diameters of Φ 6mm and Φ 8mm when immersed in different media (tap water, artificial seawater, and alkaline simulated seawater). It also shows the degradation of BFRP bars with a diameter of Φ 6mm that were wrapped in mortar and immersed in artificial seawater for varying periods of time. In all solutions, the tensile strengths of BFRP bars initially decrease rapidly and then exhibit a slower decrease as the exposure period increases.

One possible explanation for this phenomenon is that the corrosion medium reaches equilibrium after diffusing to a certain depth within the BFRP bars, causing

508   the corrosion reaction to slow down due to the accumulation of reaction products.
509   Notably, the degradation is significantly accelerated in alkaline environments. The
510   trend of tensile strength retention for BFRP bars under the same conditions follows
511   this order: tap water immersion > artificial seawater immersion > alkaline seawater
512   immersion.

513   It is important to mention that the tensile strength degradation of BFRP bars
514   wrapped in mortar and immersed in seawater for 360 days was found to be 6%
515   stronger compared to bare BFRP bars. Additionally, when comparing the tensile
516   strength of Φ 6mm and Φ 8mm BFRP bars wrapped in mortar, it is observed that the
517   degradation of tensile strength is more pronounced in the larger diameter bars.

518

520   **Fig.8.** Variation of tensile strength of BFRP bars in different corrosive solutions

521   **4.6 Microstructure of BFRP bars in seawater**

522   Fig. 9 presents SEM images of the cross section of Φ 6mm BFRP bars immersed
523   in different media for a period of 180 days. In Fig. 9(a), which represents immersion
524   in tap water, it is evident that a significant amount of resin remains bonded to the
525   surface of the fibers. This bonding facilitates the formation of tight bundles as the
526   fibers combine with each other.

527

528   In Fig. 9(b), corresponding to immersion in artificial seawater, the outer fibers
529   display the presence of pores at the edge of the cross-section, and the surface structure
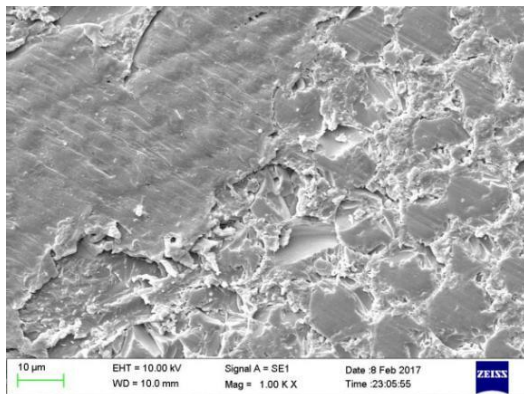
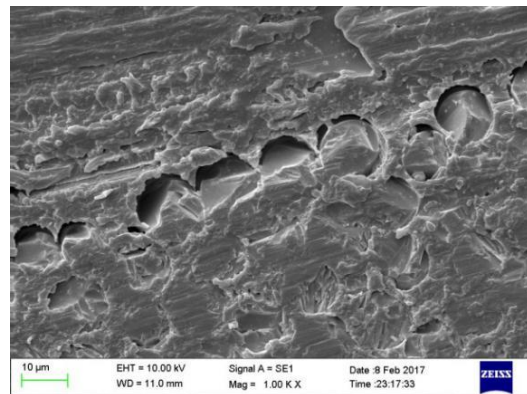530   appears to have loosened due to corrosion.

531

532   Fig. 9(c) illustrates the cross section of BFRP bars after immersion in alkaline
533   simulated seawater. The damage process is visibly pronounced, characterized by fiber
534   ruptures, resin degradation, and debonding of the resin-fiber interface. This results in
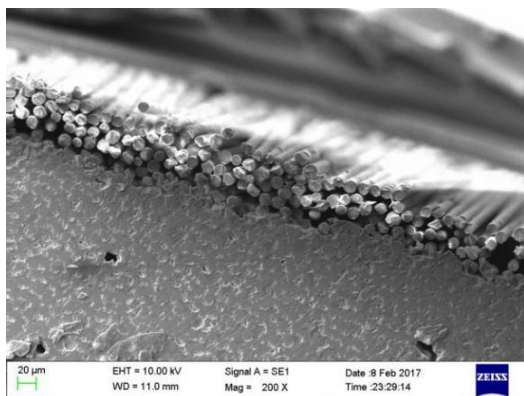535   an increased loose area and noticeable protrusion of fibers.

536

537   These SEM images provide insight into the changes and damage experienced by
538   the BFRP bars under different immersion conditions, highlighting the effects of
539   various media on the surface and structural integrity of the bars.

(a) BFRP bar immersed in water   (b) BFRP bar immersed in artificial seawater

(c) BFRP bar immersed in saturated $Ca(OH)_2$ seawater

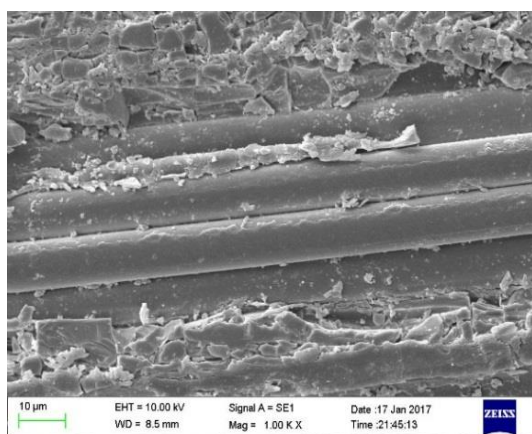540   **Fig.9.** Microstructure of cross section of BFRP bars after 180 days corrosion

541   Fig. 10 displays SEM micrographs of the longitudinal section of Φ 6mm BFRP

bars subjected to different immersion media for a duration of 180 days. In Fig. 10(a), representing immersion in tap water, the surface of the fiber and resin remains unchanged. The fiber maintains a smooth and flat appearance, tightly connected to the resin.
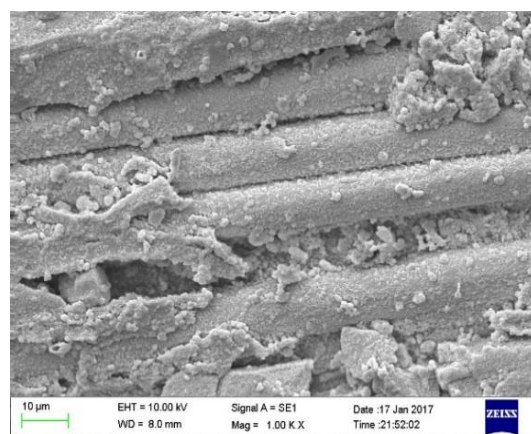
In Fig. 10(b), following immersion in seawater, the intermediate resin that bonded the fibers together disappears, leading to a further loosening of the fiber bundles. Additionally, a significant amount of salt crystals can be observed attached to the surface.

Fig. 10(c) reveals that after immersion in alkaline simulated seawater, very little resin remains bonded to the fiber surface. The fibers exhibit evident corrosion, with signs of detachment and noticeable damage defects. This phenomenon can be attributed to the gradual penetration of the corrosive medium along the radial direction of the bars. Initially, the shedding of fiber and resin occurs, followed by fiber surface corrosion in the later stages. These factors contribute to a significant decrease in the tensile strength of the BFRP bars.
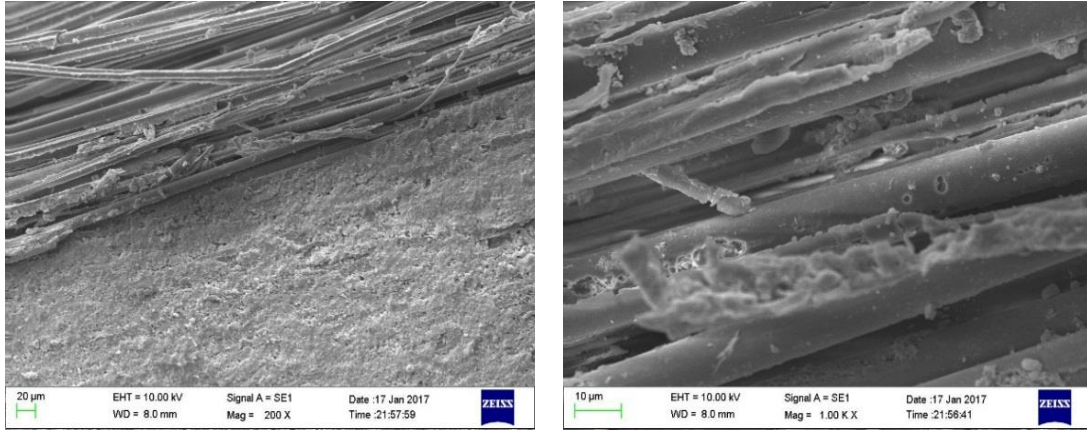
The observations presented in Fig. 10, along with those in Fig. 9, demonstrate the decisive influence of alkaline environments on the degradation of tensile strength in BFRP bars. This finding aligns with the results obtained from the tensile strength tests.

(a) BFRP bar immersed in water   (b) BFRP bar immersed in artificial seawater

(c) BFRP bar immersed in saturated Ca(OH)$_2$ seawater

561　　**Fig.10.** Microstructure of vertical section of BFRP bars after 180d corrosion

562　**4.7 Degradation model of tensile strength of BFRP bars in marine environments**

563　　　Through microscopic analysis of BFRP bars, the degradation mechanism in a

564　seawater environment is identified as fiber-resin matrix interface split and separated

565　failure. This mechanism can be expressed as follows [46]:

$$566 \qquad f_f = (100 - Y_\infty)exp\left(-\frac{t}{\tau}\right) + Y_\infty \qquad （13）$$

567　Where, Y_∞ is the residual tensile strength of BFRP bars when the corrosion time tends

568　to infinity; τ is the characteristic time determined by corrosion temperature.

569　　　The corrosion of BFRP bars that are wrapped in GPC in marine environments is

570　primarily caused by seawater corrosion and the alkaline environment within the GPC.

571　Therefore, Eq (13) is modified as follows:

$$572 \qquad f_f = Y_\infty \times exp(-b \times t)^c + Y_\infty \qquad （14）$$

573　　　To verify the modified Eq. (14), the time-dependent variation of tensile

574　properties of Φ 6 mm and Φ 8 mm BFRP bars wrapped in GP mortar under seawater

575　immersion is fitted, as shown in Fig. 11. The fitting parameters are presented in Table

576　13. In the seawater environment, the final strengths of Φ 6 mm and Φ 8 mm BFRP

577　bars are 695 MPa and 663 MPa, respectively. The established tensile strength

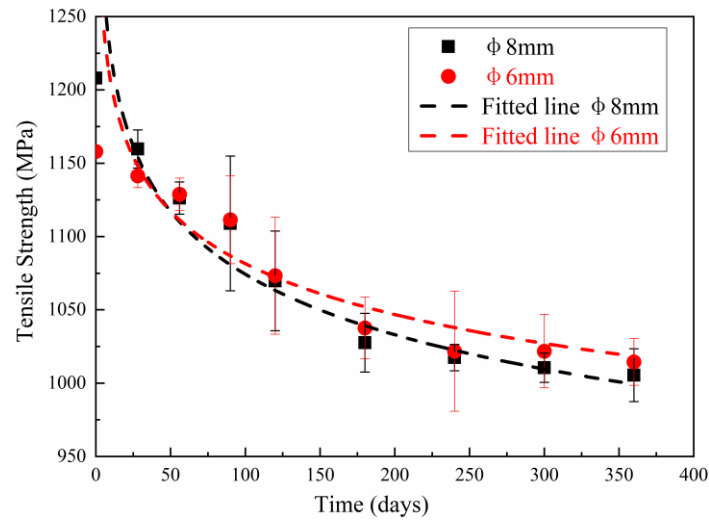578　degradation models for the BFRP bars are as follows:

579　　　Φ 6 mm BFRP bar：

$$580 \qquad f_f = 695.38 \times (1 - exp(-8.19958E - 7 \times t))^{-0.04694} \qquad （15）$$

581　　　Φ 8 mm BFRP bar：

$$f_f = 663.76 \times (1 - exp(-1.98349E - 6 \times t))^{-0.04248} \qquad （16）$$

Fig.11. Tensile strength of BFRP immersed in a marine environment

Table 13 Parameters of the fitting equation to describe the degradation of BFRP bars

	Φ6 mm	Φ8 mm
$Y\infty$	695.38	663.76
b	8.19958E-7	1.98349E-6
c	-0.04694	-0.04248
R^2	0.92197	0.95115

4.8 Microstructure characteristics of the interface of BFRP bars reinforced geopolymer in seawater

4.8.1 Microscopic properties of the interface between geopolymer and aggregate in seawater

The microscopic morphology of hardened samples of GPC and PC concrete after immersion in tap water and artificial seawater for 360 days is depicted in Fig. 12 and 13. The backscattered electron (BSE) images of the hardened samples reveal certain characteristics. The brightly colored irregular blocks represent unreacted clinker or slag, while the brightly colored globular particles indicate unreacted fly ash. The gray areas correspond to the reaction products formed during the reaction, and the black areas represent pores within the hardened samples.

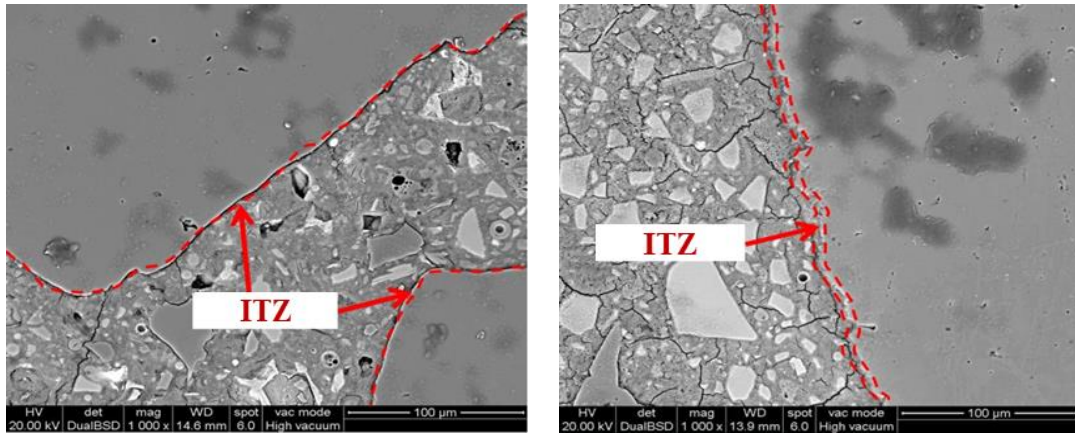Fig. 12(a) demonstrates that in tap water for 360 days, the GP mortar exhibits a tight bond with the aggregate, without a distinct boundary of interfacial transition. Fig. 12(b) shows that after immersion in artificial seawater for 360 days, the interface area

600 between the GP mortar and aggregate does not show a significant increase, but some
601 areas exhibit fine cracks.

602 Fig. 13(a) illustrates that in the PC concrete samples, there is a wide black area
603 accompanied by a distribution of porosity between the PC mortar and aggregate. This
604 indicates the presence of an obvious interfacial transition zone (ITZ) in the PC
605 concrete samples, which is more pronounced compared to the GPC samples. Fig. 13(b)
606 further demonstrates that the ITZ of the PC concrete samples becomes more apparent
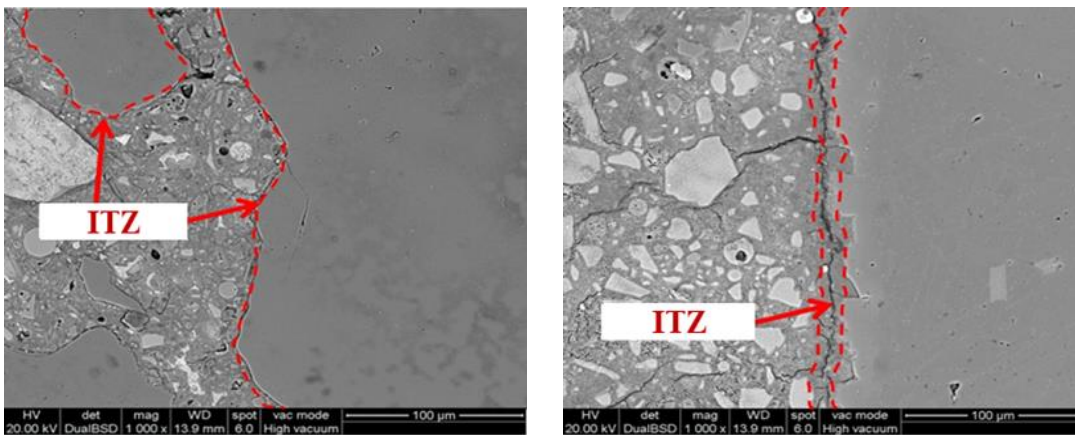607 after seawater corrosion, along with a higher proportion of pores and cracks.

(a) GPC in water for 360 days   (b) GPC in artificial seawater for 360 days

608   **Fig. 12.** Interfacial transition zone of GPC after 360 days corrosion

(a) PC concrete in water for 360 days   (b) PC concrete in artificial seawater for 360
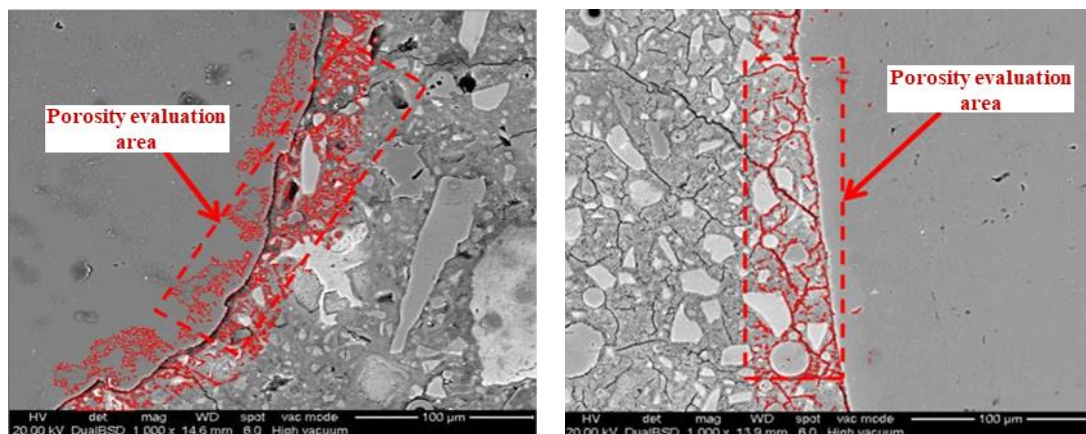   days

609   **Fig. 13.** Interfacial transition zone of PC concrete after 360 days corrosion

610 The porosity of the interfacial transition zone (ITZ) in concrete was further
611 calculated using the fractal theory with the aid of Image-Pro Plus (IPP) image

612 processing software. Fig. 14 and 15 display the IPP image processing photos of the
613 ITZ in GPC and PC concrete, respectively, while Table 14 presents the statistical
614 results of porosity.

615 After immersion in tap water for 360 days, the average porosity of the ITZ in
616 GPC and PC concrete samples is approximately 27.89% and 37.97%, respectively.
617 This indicates that the average porosity of the ITZ in GPC is approximately 36.0%
618 lower than that in PC concrete.

619 Following 360 days of artificial seawater corrosion, the average porosity of the
620 ITZ in GPC samples only increases by 4.44%, reaching approximately 29.13% in total.
621 In contrast, the average porosity of the ITZ in PC concrete increases from 37.97% to
622 40.74%, exhibiting a 7.29% increase compared to 360 days of tap water corrosion.
623 These findings indicate that GPC possesses a smaller porosity and a lower proportion
624 of porosity increase compared to PC concrete after seawater corrosion. This
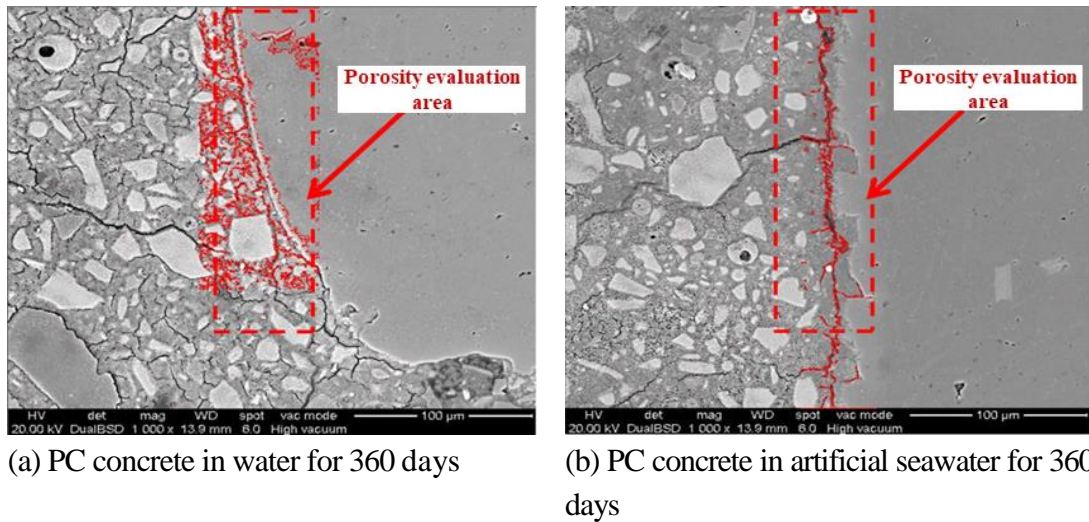625 demonstrates the excellent resistance of GPC to seawater corrosion.

(a) GPC in water for 360 days   (b) GPC in artificial seawater for 360 days

626 **Fig. 14.** Interfacial transition zone of GPC after corrosion

(a) PC concrete in water for 360 days　　　(b) PC concrete in artificial seawater for 360 days

Fig. 15. Interfacial transition zone of PC concrete after corrosion

Table 14 Porosity of interfacial transition zone in concrete after corrosion

Porosity	GPC		PC concrete	
	water for 360 d	artificial Seawater 360 d	Reference	artificial Seawater 360 d
Range	23.25~31.43	22.53~33.30	32.03~43.26	34.06~47.06
Average value(%)	27.89	29.13	37.97	40.74

Note. 10 images were selected to analyze the porosity of the interfacial transition zone of concretes.

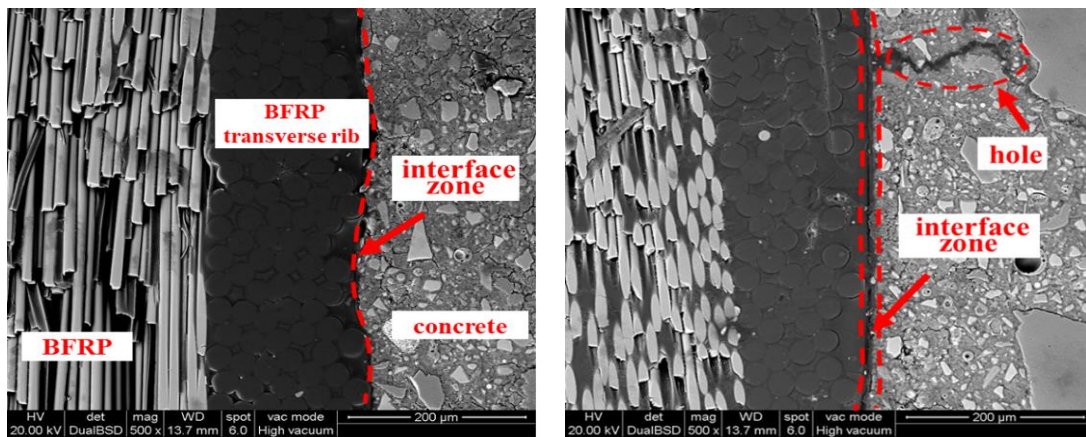4.8.2 Microstructure characteristics of interface between BFRP bars and geopolymer in seawater

In the seawater environment, the microstructure characteristics of the interface between BFRP bars and GPC were examined. Fig. 16 (a) illustrates that the BFRP bars consist of basalt fibers bonded with resin and are further reinforced with transverse ribs. The interface between the BFRP bars and GPC exhibits a tight bond without any distinct interfacial transition zone (ITZ) or noticeable interfacial pores.

After 360 days of seawater corrosion, as shown in Fig. 16 (b), the interface between the BFRP bars and GPC slightly expanded. Some cracks and pores appeared in the GPC, but the bond between the GPC and BFRP bars remained relatively tight.

These observations suggest that even after seawater corrosion, the bond between the BFRP bars and GPC remains intact, indicating the favorable compatibility and

643   durability of the interface in the seawater environment.

644   Fig. 16 (a) shows that BFRP bars are composed of resin bonded basalt fibers and
645   then wound with transverse ribs. BFRP bars are tightly bonded to GPC with no
646   obvious ITZ and no obvious interfacial pores. Fig. 16 (b) shows that the interface
647   between BFRP bars and GPC was slightly enlarged after 360 days of seawater
648   corrosion, and GPC appear some cracks and pores. It is noted that the bond between
649   the GPC and BFRP bars is still relatively tight.
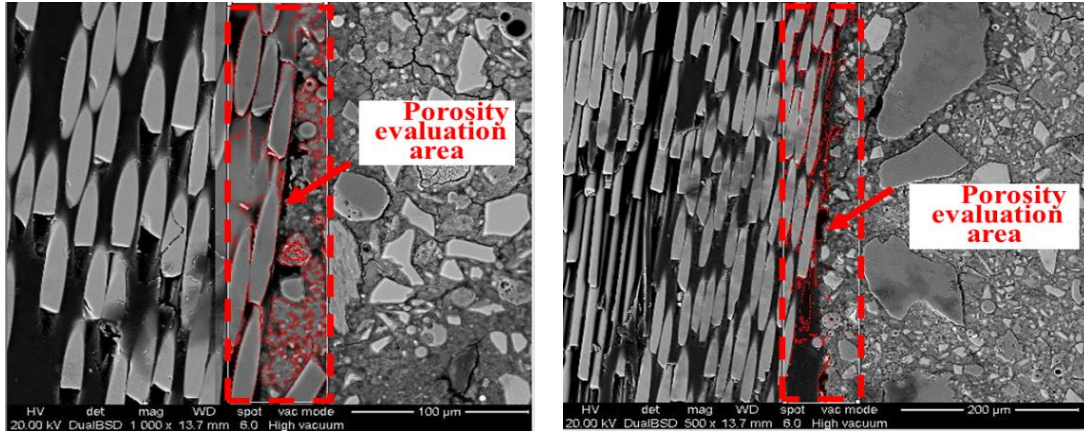

(a) Before corrosion   (b) After artificial seawater for 360 days

650   **Fig. 16.** Interface between BFRP bars and GPC before and after corrosion

651   To analyze the porosity of the interface area between the BFRP bars and GPC,
652   IPP image processing software was utilized. Fig. 17 presents the results of porosity
653   analysis before and after artificial seawater corrosion. The statistical data of porosity
654   are summarized in Table 15.

655   Before seawater corrosion, the interface between the BFRP bars and GPC
656   exhibited a tight bond, and the average porosity of the interfacial transition zone (ITZ)
657   was measured to be 27.88%. Following seawater corrosion, the average porosity of
658   the ITZ increased slightly to 29.06%, which represents a 1.2% increment compared to
659   the pre-corrosion condition. These results indicate that seawater corrosion has a
660   negligible impact on the porosity of the ITZ between the GPC and BFRP bars.

| (a) GPC in water | (b) GPC in artificial seawater for 360 days |

661 **Fig. 17.** Interfacial transition zone of BFRP bars in GPC after corrosion

662 **Table 15** Porosity of interface between BFRP bars and GPC after corrosion

Porosity/%	GPC	
	Reference	Immersed in artificial seawater for 360 days
Range	24.10~31.58	24.90~33.30
Average value/%	27.88	29.06

663 Note. 10 images were selected to analyze the porosity of the interface between BFRP

664 and GPC.

665 **5 Conclusion**

666 <mark>This study focused on investigating the corrosion resistance and interface</mark>

667 <mark>characteristics of GPC and BFRP bars in a seawater environment. The main emphasis</mark>

668 <mark>of this research was on analyzing the ionic attack resistance of BFRP reinforced</mark>

669 <mark>geopolymer concrete using laboratory-simulated seawater conditions. However, it is</mark>

670 <mark>essential to acknowledge that in actual marine environments, ion migration occurs not</mark>

671 <mark>only through diffusion but also potentially involves convective effects under</mark>

672 <mark>hydrostatic pressure.</mark>

673 <mark>Several critical questions remain to be addressed: How can we simulate ocean</mark>

674 <mark>conditions more realistically through systematically designed experiments? What are</mark>

675 <mark>the effects of competing antagonistic processes on the performance of BFRP</mark>

676 <mark>reinforced geopolymer concrete when subjected to multiple-ion combined attack in</mark>

677 <mark>marine environments? To answer these questions, further studies employing</mark>

678 <mark>systematically designed experiments and long-term observations will be crucial. Such</mark>

679 <mark>research endeavors will not only help refine the proposed mathematical models but</mark>

680 <mark>also enhance our understanding of the behavior of BFRP reinforced geopolymer</mark>

Based on the findings of the present study, the following specific conclusions may be drawn:

(1) The corrosion resistance of GPC exhibited an initial sharp increase, followed by a slower increase, and finally reached a stable state after 90 days of exposure. The volume corrosion resistance coefficient and strength corrosion resistance coefficient of GPC after 360 days of immersion were 0.06 and 0.085, respectively, indicating excellent resistance to seawater corrosion. A degradation model for the mechanical performance of GPC in a marine environment was established.

(2) GP mortar demonstrated superior resistance to ion migration compared to PC mortar. The migration properties of chloride ions (Cl^-), sulfate ions (SO_4^{2-}), and magnesium ions (Mg^{2+}) were evaluated, with Cl^- showing the highest migration, followed by SO_4^{2-} and Mg^{2+}.

(3) The tensile strength degradation of BFRP bars in seawater combined with an alkaline environment was more pronounced than in seawater alone. Wrapping BFRP bars in GP mortar mitigated the reduction in tensile strength in seawater, and a smaller BFRP diameter resulted in reduced deterioration. The ultimate strengths of BFRP bars with diameters of 6 mm and 8 mm were 695 MPa and 663 MPa, respectively. A degradation model for the tensile strength of BFRP bars in marine environments was established.

(4) Microscopic analysis revealed that seawater corrosion had little impact on the porosity of the dual interfaces in BFRP bars reinforced with geopolymer concrete. The average porosity of the interfacial transition zone (ITZ) between GP paste and aggregate was significantly lower than that of PC concrete. The ITZ between BFRP bars and GP paste exhibited a slight increase in porosity, but still maintained tight interfacial bonding and narrow interface widths. Seawater corrosion did not significantly affect the ITZ structure of BFRP reinforced geopolymer concrete.

These findings contribute to a better understanding of the corrosion behavior and

interface characteristics of GPC and BFRP bars in seawater environments, and provide valuable insights for the development of corrosion-resistant and durable concrete structures.

ACKNOWLEDGEMENTS

REFERENCE

[1] Zhang B, Zhu H, Li F Z, Dong Z Q, Zhang P. Compressive stress-strain behavior of seawater coral aggregate concrete incorporating eco-efficient alkali-activated slag materials [J]. Construction and Building Materials, 2021, 299.

[2] Zhang B, Zhu H, Cao R M, Ding J M, Chen X H. Feasibility of using geopolymers to investigate the bond behavior of FRP bars in seawater sea-sand concrete [J]. Construction and Building Materials, 2021, 282.

[3] Zhang B, Zhu H, Lu F. Fracture properties of slag-based alkali-activated seawater coral aggregate concrete [J]. Theoretical and Applied Fracture Mechanics, 2021, 115.

[4] Chen G, Zheng D P, Chen Y W, Lin J X, Lao W J, Guo Y C, Chen Z B, Lan X W. Development of high performance geopolymer concrete with waste rubber and recycle steel fiber: A study on compressive behavior, carbon emissions and economical performance [J]. Construction and Building Materials, 2023, 393.

[5] Elahi M M A, Hossain M M, Karim M R, Zain M F M, Shearer C. A review on alkali-activated binders: Materials composition and fresh properties of concrete [J]. Construction and Building Materials, 2020, 260.

[6] Morsy A M, Ragheb A M, Shalan A H, Mohamed O H. Mechanical Characteristics of GGBFS/FA-Based Geopolymer Concrete and Its Environmental Impact [J]. Practice Periodical on Structural Design and Construction, 2022, 27(2).

[7] Perumal P, Sreenivasan H, Luukkonen T, Kantola A M, Telkki V V, Kinnunen P, Illikainen M. High strength one-part alkali-activated slag blends designed

751   by particle packing optimization [J]. Construction and Building Materials,
752   2021, 299.

753 [8]   Shehata N, Sayed E T, Abdelkareem M A. Recent progress in environmentally
754   friendly geopolymers: A review [J]. Science of The Total Environment, 2021,
755   762: 143166.

756 [9]   Wang A G, Zheng Y, Zhang Z H, Liu K W, Li Y, Shi L, Sun D S. The
757   Durability of Alkali-Activated Materials in Comparison with Ordinary
758   Portland Cements and Concretes: A Review [J]. Engineering, 2020, 6(6): 695-
759   706.

760 [10]   Zhang B, Zhu H, Wang Q, Shah K W, Wang W. Design and properties of
761   seawater coral aggregate alkali-activated concrete [J]. Journal of Sustainable
762   Cement-Based Materials, 2022, 11(3): 175-84.

763 [11]   Xiao J Z, Qiang C B, Nanni A, Zhang K J. Use of sea-sand and seawater in
764   concrete construction: Current status and future opportunities [J]. Construction
765   and Building Materials, 2017, 155: 1101-11.

766 [12]   Li J L, Xie J H, Liu F, Lu Z Y. A critical review and assessment for FRP-
767   concrete bond systems with epoxy resin exposed to chloride environments [J].
768   Composite Structures, 2019, 229.

769 [13]   Lu Z Y, Li J L, Xie J H, Huang P Y, Xue L F. Durability of flexurally
770   strengthened RC beams with prestressed CFRP sheet under wet-dry cycling in
771   a chloride-containing environment [J]. Composite Structures, 2021, 255.

772 [14]   Yan F, Lin Z B, Yang M J. Bond mechanism and bond strength of GFRP bars
773   to concrete: A review [J]. Composites Part B-Engineering, 2016, 98: 56-69.

774 [15]   Torres L, Sharaky I A, Barris C, Baena M. EXPERIMENTAL STUDY OF
775   THE INFLUENCE OF ADHESIVE PROPERTIES AND BOND LENGTH
776   ON THE BOND BEHAVIOUR OF NSM FRP BARS IN CONCRETE [J].
777   Journal of Civil Engineering and Management, 2016, 22(6): 808-17.

778 [16]   Aslani F, Sun J B, Bromley D, Ma G W. Fiber-reinforced lightweight self-
779   compacting concrete incorporating scoria aggregates at elevated temperatures
780   [J]. Structural Concrete, 2019, 20(3): 1022-35.

781 [17]   Aslani F, Sun J B, Huang G Q. Mechanical Behavior of Fiber-Reinforced Self-
782   Compacting Rubberized Concrete Exposed to Elevated Temperatures [J].
783   Journal of Materials in Civil Engineering, 2019, 31(12).

784 [18]   Thomas R J, Ariyachandra E, Lezama D, Peethamparan S. Comparison of
785   chloride permeability methods for Alkali-Activated concrete [J]. Construction
786   and Building Materials, 2018, 165: 104-11.

787 [19]   Gunasekara C, Law D, Bhuiyan S, Setunge S, Ward L. Chloride induced
788   corrosion in different fly ash based geopolymer concretes [J]. Construction
789   and Building Materials, 2019, 200: 502-13.

790 [20]   Amorim Júnior N S, Andrade Neto J S, Santana H A, Cilla M S, Ribeiro D V.
791   Durability and service life analysis of metakaolin-based geopolymer concretes
792   with respect to chloride penetration using chloride migration test and corrosion
793   potential [J]. Construction and Building Materials, 2021, 287: 122970.

794 [21]   Monticelli C, Natali M E, Balbo A, Chiavari C, Zanotto F, Manzi S, Bignozzi

795　　　　M C. Corrosion behavior of steel in alkali-activated fly ash mortars in the light
796　　　　of their microstructural, mechanical and chemical characterization [J]. Cement
797　　　　and Concrete Research, 2016, 80: 60-8.
798　[22]　Dzunuzovic N, Komljenovic M, Nikolic V, Ivanovic T. External sulfate attack
799　　　　on alkali-activated fly ash-blast furnace slag composite [J]. Construction and
800　　　　Building Materials, 2017, 157: 737-47.
801　[23]　Kuri J C, Nuruzzaman M, Sarker P K. Sodium sulphate resistance of
802　　　　geopolymer mortar produced using ground ferronickel slag with fly ash [J].
803　　　　Ceramics International, 2023, 49(2): 2765-73.
804　[24]　Elyamany H E, Abd Elmoaty A M, Elshaboury A M. Magnesium sulfate
805　　　　resistance of geopolymer mortar [J]. Construction and Building Materials,
806　　　　2018, 184: 111-27.
807　[25]　Saavedra W G V, Angulo D E, De Gutierrez R M. Fly Ash Slag Geopolymer
808　　　　Concrete: Resistance to Sodium and Magnesium Sulfate Attack [J]. Journal of
809　　　　Materials in Civil Engineering, 2016, 28(12).
810　[26]　Pasupathy K, Berndt M, Sanjayan J, Rajeev P, Cheema D S. Durability of low-
811　　　　calcium fly ash based geopolymer concrete culvert in a saline environment [J].
812　　　　Cement and Concrete Research, 2017, 100: 297-310.
813　[27]　Tennakoon C, Shayan A, Sanjayan J G, Xu A M. Chloride ingress and steel
814　　　　corrosion in geopolymer concrete based on long term tests [J]. Materials &
815　　　　Design, 2017, 116: 287-99.
816　[28]　Dong Z Q, Wu G, Zhao X L, Zhu H, Lian J L. Durability test on the flexural
817　　　　performance of seawater sea-sand concrete beams completely reinforced with
818　　　　FRP bars [J]. Construction and Building Materials, 2018, 192: 671-82.
819　[29]　Monticelli C, Natali M E, Balbo A, Chiavari C, Zanotto F, Manzi S, Bignozzi
820　　　　M C. A study on the corrosion of reinforcing bars in alkali-activated fly ash
821　　　　mortars under wet and dry exposures to chloride solutions [J]. Cement and
822　　　　Concrete Research, 2016, 87: 53-63.
823　[30]　Tittarelli F, Mobili A, Giosue C, Belli A, Bellezze T. Corrosion behaviour of
824　　　　bare and galvanized steel in geopolymer and Ordinary Portland Cement based
825　　　　mortars with the same strength class exposed to chlorides [J]. Corrosion
826　　　　Science, 2018, 134: 64-77.
827　[31]　Wang W R, Chen H S, Li X Y, Zhu Z G. Corrosion behavior of steel bars
828　　　　immersed in simulated pore solutions of alkali-activated slag mortar [J].
829　　　　Construction and Building Materials, 2017, 143: 289-97.
830　[32]　Wang Z K, Zhao X L, Xian G J, Wu G, Raman R K S, Al-Saadi S, Haque A.
831　　　　Long-term durability of basalt- and glass-fibre reinforced polymer
832　　　　(BFRP/GFRP) bars in seawater and sea sand concrete environment [J].
833　　　　Construction and Building Materials, 2017, 139: 467-89.
834　[33]　Lu C H, Ni M Z, Chu T S, He L Y. Comparative Investigation on Tensile
835　　　　Performance of FRP Bars after Exposure to Water, Seawater, and Alkaline
836　　　　Solutions [J]. Journal of Materials in Civil Engineering, 2020, 32(7).
837　[34]　Lu Z Y, Li Y C, Xie J H. Durability of BFRP bars wrapped in seawater sea
838　　　　sand concrete [J]. Composite Structures, 2021, 255.

839   [35]   Luo Z Y, Li W G, Wang K J, Castel A, Shah S P. Comparison on the properties
840   of ITZs in fly ash-based geopolymer and Portland cement concretes with
841   equivalent flowability [J]. Cement and Concrete Research, 2021, 143.

842   [36]   Cai Y J, Xiao S H, Chen Y W, Huang Z R, Lin J X, Guo Y C, Peng Y Q, Xie Z
843   H. Tensile behavior and durability prediction of GFRP-steel composite bars
844   under chloride environments [J]. Journal of Materials Research and
845   Technology-Jmr&T, 2023, 23: 5746-59.

846   [37]   Xiong Z, Wei W, Liu F, Cui C, Li L, Zou R, Zeng Y. Bond behaviour of
847   recycled aggregate concrete with basalt fibre-reinforced polymer bars [J].
848   Composite Structures, 2021, 256: 113078.

849   [38]   Xiong Z, Mai G, Qiao S, He S, Zhang B, Wang H, Zhou K, Li L. Fatigue bond
850   behaviour between basalt fibre-reinforced polymer bars and seawater sea-sand
851   concrete [J]. Ocean & Coastal Management, 2022, 218: 106038.

852   [39]   Zou R, Liu F, Xiong Z, He S, Li L, Wei W. Experimental study on fatigue
853   bond behaviour between basalt fibre-reinforced polymer bars and recycled
854   aggregate concrete [J]. Construction and Building Materials, 2021, 270:
855   121399.

856   [40]   Xiong Z, Wei W, He S, Liu F, Luo H, Li L. Dynamic bond behaviour of fibre-
857   wrapped basalt fibre-reinforced polymer bars embedded in sea sand and
858   recycled aggregate concrete under high-strain rate pull-out tests [J].
859   Construction and Building Materials, 2021, 276: 122195.

860   [41]   Neupane K. "Fly ash and GGBFS based powder-activated geopolymer
861   binders: A viable sustainable alternative of portland cement in concrete
862   industry" [J]. Mechanics of Materials, 2016, 103: 110-22.

863   [42]   Khan M S H, Castel A, Akbarnezhad A, Foster S J, Smith M. Utilisation of
864   steel furnace slag coarse aggregate in a low calcium fly ash geopolymer
865   concrete [J]. Cement and Concrete Research, 2016, 89: 220-9.

866   [43]   Tian Z, Zhang Z, Liu H, Zheng W, Tang X, Gui Z. Interfacial characteristics
867   and mechanical behaviors of geopolymer binder with steel slag aggregate:
868   Insights from molecular dynamics [J]. Journal of Cleaner Production, 2022,
869   362: 132385.

870   [44]   Ren X, Zhang L. Experimental study of interfacial transition zones between
871   geopolymer binder and recycled aggregate [J]. Construction and Building
872   Materials, 2018, 167: 749-56.

873   [45]   Yang Y, Chen Z, Feng W, Nong Y, Yao M, Tang Y. Shrinkage compensation
874   design and mechanism of geopolymer pastes [J]. Construction and Building
875   Materials, 2021, 299: 123916.

876   [46]   Lee S L, Wong S F, Swaddiwudhipong S, Wee T H, Loo Y H. Accelerated test
877   of ingress of chloride ions in concrete under pressure and concentration
878   gradients [J]. Magazine of Concrete Research, 1996, 48(174): 15-25.

879