Research Article

Chloride Diffusion and Induced Reinforcement Corrosion in Concrete with Fly Ash and Ground-Granulated Blast-Furnace Slag Exposed to Marine Submerged Zone

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This paper investigates the influence of mineral admixtures fly ash (FA) and ground-granulated blast-furnace slag (GGBS), the byproducts of industry, on chloride ions migration and corrosion resistance performance. A novel preparation method of wire beam electrode (WEB) was also introduced to explore the excellent corrosion-resistant capacity of concrete with mineral admixtures. By comparing concrete specimens with and without FA and GGBS, the test result of wire beam electrode, rapid chloride migration (RCM), and electrochemical tests highlight the positive impact of fly ash and GGBS against chloride ions migration, respectively. Concrete with fly ash and GGBS supplies an advanced protection effect of ordinary Portland cement; meanwhile, CO2 emission amount can be significantly reduced. Moreover, homemade wire beam electrode was proved to be a novel and reliable test method against corrosion, which has agreement with the test result of an electrochemical device.

1. Introduction

It is widely acknowledged that when a ton of ordinary Portland cement (OPC) was produced, it would consume 4 GJ of energy and emit almost 0.85 tons of carbon dioxide into the atmosphere [1, 2]. The global carbon dioxide which is produced by cement industry accounts for about 7% among which produced by entire human activities per year. In the year 2016, about 2.4 billion tons of cement were produced in China, which is about 60% of the worldwide cement production [3]. Construction of infrastructure facilitates the rapid development of the economy. However, it also triggers tremendous harm against environment, resulting from the emitted nearly 1.7 billion tons of CO2. In UK, the legislation is restricted that 80% of CO2 emissions should be reduced by 2050. Therefore, alternative low-carbon cement concrete is of great significance to the sustainable development of construction industry.

From the physical point of view, the cement content which participates in hydration process is no more than one half of the entire cement proportion. In other words, 50% of cement proportion can be replaced by other mix materials [4–6]. Class I or II fly ash from solid waste discharged from the power plant after separation and GGBS from the solid waste discharged after water quenching and pulverization of blast-furnace furnace slag both have a good secondary hydration capacity and also fill in concrete pores, which can be used to replace clinker. However, by replacing of 25% and 30% clinker with mineral additions such as fly ash and GGBS, CO2 emission is reduced by 24.6% and 29% [7]. In addition, it was reported that mineral admixture could enhance the corrosion resistance ability of steel bars inside concrete and therefore could extend the service life of concrete structures under chloride-rich environment [8].

Migration of chloride ions is a serious problem when evaluating the durability performance of concrete, which may cause reinforcement corrosion in concrete. Han et al.
investigated the behavior of high-performance concrete pastes with different mineral admixtures in simulated seawater environment. They found that mineral admixtures can significantly reduce the chloride migration coefficient. Gopalakrishnan and Chinnaraju [10] analyzed the durability of ambient-cured alumina silicate concrete based on slag/fly ash blends against sulfate environment. Wang et al. [11] proposed the concrete durability performance containing fly ash and silica fume against combined freezing-thawing and sulfate attack. Besides, Hawileh et al. [12] evaluated the performance of reinforcement concrete beams cast with different percentages of GGBS replacement to cement. McNally et al. [13] came up with a kind of probability-based assessment of the durability characteristics of concrete manufactured using CEM II and GGBS binders. Babaee et al. [14] took deep insight into the passivity of embedded reinforcement in carbonated low-calcium fly ash-based geopolymer concrete. Ramakrishnan et al. [15] carried out the experimental study on the mechanical and durability properties of concrete with glass powder and ground granulated blast-furnace furnace slag as supplementary cementitious materials. Qin et al. [16] explored the influence of mineral admixtures on carbonation curing of cement paste. Golewski et al. [17] measured the fracture mechanics parameters of concrete containing fly ash, thanks to the use of digital image correlation (DIC) method. Kumar et al. [18] applied ultrafine GGBS and calcium nitrate as concrete admixtures for improved mechanical properties and corrosion resistance. Shang et al. [19] alternated traditional cement mortar using fly ash-based geopolymer mortars modified by slag. Gholampour et al. [20] summarized the performance of sustainable concrete containing very high volume Class-F fly ash and ground-granulated blast-furnace furnace slag. Ganesh et al. [21] argued tensile behavior and durability aspects of sustainable ultrahigh performance concrete incorporated with GGBS as cementitious material. Moreover, for service life prediction, Yu and Ye [22] put forward a new perspective of service life prediction of fly ash concrete. Attari et al. [23] suggested a probabilistic assessment of the influence of age factor on the service life of concrete with limestone cement/GGBS binders. Bucher et al. [24] established a service life model of metakaolin-based concrete exposed to carbonation, which contains fly ash, blast-furnace slag, and limestone filler. And slowly, hydration of mineral admixture would decrease the hydration heat and improve the shrinkage resistance capacity of concrete, fly ash, and GGBS which have been used widely to replace cement in concrete engineering in the past twenty years in China.

The abovementioned results of the experimental studies indicated that a suitable dosage of fly ash and GGBS is beneficial to improve the durability of concrete. However, in the actual service environment, the concrete with fly ash and mineral powder is submerged in the ocean. This long-term water-filled environment is conducive to full hydration of fly ash and mineral powder in the later period, so as to improve the density of concrete. On the other hand, long-term contact of concrete with high concentration of seawater may also lead to surface corrosion and lower pH value at the concrete surface, which affects the transport and binding ability of chloride ions. Also, the amount of cement in the hydration process is no more than half of the total dose, which means that the rest can be replaced by fly ash or GGBS. Therefore, the reasonable amount of fly ash and GGBS in the marine submerged zone still needs to be further studied. In addition, corrosion of reinforced bars is a persistent process, and the elastic modulus of corrosion products obtained by acceleration test and diffusion process is significantly different from natural corrosion, so there is still a gap to release the corrosion behavior of steel in marine environment. Hence, a series of experiments were designed and put into effect at the marine submerged zone. Meanwhile, several test methods were applied which includes wire beam electrode (WBE), rapid chloride migration (RCM), and electrochemical impedance spectroscopy (EIS).

2. Materials

2.1. Materials and Specimen Preparation. The binding materials include P.I. 52.5 Portland cement, Class I fly ash, and S95 GGBS. Meanwhile, 5–25 mm crushed granite and river sand were used as aggregates. The superplasticizer and air-entraining agent were used to decrease water dosage and improve frost resistance capacity of concrete. Concrete using fly ash or GGBS substitutes cement at 15–65% by weight of binder to declare the effect of mineral admixture on chloride diffusion and binding capacity of concrete. The mixture proportions of the concrete and their compressive strength and air content are given in Table 1.

The concrete cube specimens for each mix proportion with a size of 100 mm × 100 mm × 100 mm and cylinder specimens with a size of $\phi$ 100 mm × 50 mm were cast and placed at room temperature, demoulded, and cured for 28 d at the condition of 20 ± 3°C and 95% relative humidity. Four sides of the cube specimens were sealed by using epoxy resin to ensure one-dimensional diffusion. And reinforced concrete specimens with a size of 100 mm × 100 mm × 300 mm were also cast. Carbon reinforced bar with a diameter of 10 mm was used, and its effective cover of 25 mm was set in reinforced concrete. The copper wire was connected at the end of reinforced bar and used to measure the electrochemical properties of reinforced concrete. The effective exposure length of the steel bar was 250 mm. The stainless steel sheets were inserted in the fresh concrete and pulled out before final setting to preset transverse cracks with 0.2 mm. The molding and curing methods were same as the abovementioned way.

2.2. Wire Beam Electrode Preparation. Ordinary carbon steel wire with a diameter of 1.0 mm was selected as the electrode material. The individual electrodes were insulated from each other and sealed with epoxy resin into an 11 × 11 matrix electrode, and the distance between the electrodes was 0.5 mm. Before the experiment, the electrode surface of the silk bundle was polished with 240, 360, 600, and 800 water abrasive paper, respectively, until smooth, cleaned, and dried with anhydrous ethanol and acetone successively and then
put into the dryer for standby use. The diagram of electrode is shown in Figure 1. Custom-made PVC pipe with an inner diameter of 40 mm, a wall thickness of 3 mm, and a height of 40 mm were used. The connection between PVC pipe and the wire bundle electrode was treated with gouge and coated with special waterproof adhesive. Finally, it was tightly combined with the wire bundle electrode to ensure that the connection is free of water leakage through pretest. In the middle position of the wire beam electrode for location #56–#66, a crack was prefabricated by inserting a stainless steel plate with a thickness of 0.2 mm. The stainless steel surface was glued with a small amount of solid lubricant, which was fixed by a PVC tube. Later, casting with OPC and HPC concrete ratio of mortar, fully vibrating in order to ensure the protective layer thickness is 25 mm.

2.3. Chloride Ions Content Testing. After curing, the cubic, cylinder concrete and reinforced concrete specimens were transferred to the marine exposure field, Qingdao Mai Island, and placed to the submerged zone for 3 years (Figure 2). Cylinder concrete specimens were used to test chloride diffusion coefficient by means of rapid chloride migration (RCM) test. Cubic concrete samples were delivered to the laboratory after various corrosion times. In the laboratory, the powder samples were gained by polishing the specimen’s surface at depths of 1–2 mm step by step. The free chloride ion and total chloride ion content of concrete specimens were tested.

Considering the relationship between free chloride ion content and total chloride ion content, it could be expressed as follows [25]:

\[ C_f = aC_t + b. \]  

The binding chloride ion concentration is

\[ C_b = C_t - C_f = (1 - a)C_t. \]  

So, the bound chloride ion rate can be calculated by

\[ R = \frac{C_b}{C_t} = 1 - a, \]

where \( C_t \) is the total concentration of chloride ion; \( C_f \) represents the concentration of free chloride ion; \( a \) is the linear correlation coefficient; \( C_b \) is the concentration of the combined chloride ion; and \( R \) represents the bound chloride ion rate, respectively.

Additionally, uncontaminated cubic concrete, which is cured for 28 d, was grounded as a powdered sample. And then, 10 g concrete powder was stored to 1% NaCl solution and Qingdao seawater for 1 h, 5 h, 12 h, 1 d, 3 d, 7 d, 28 d, and 60 d respectively, and the chloride ions content of solution at initial and also different corrosion time were tested, and the bound chloride ions content by concrete powder could be calculated by

\[ C_b = C_0 - C_t, \]

where \( C_0 \) is the initial chloride ion concentration of immersion solution; \( C_t \) represents the chloride ion concentration of immersion solution in different time; and \( C_t \) is the concentration of the combined chloride ion, respectively.

Reinforced concrete was exposed to the marine submerged zone for 28 d, 56 d, 90 d, 150 d, 180 d, 330 d, and 700 d. The electrochemical impedance spectroscopy (EIS) measurement was performed at constant room temperature using a PARSTAT4000A potentiostat/galvanostat (Princeton Applied Research, Oak Ridge, USA). EIS measurements were carried out in the frequency ranging from 100 kHz to 10 MHz at steady open-circuit potential with a disturbance amplitude of 10 mV. The EIS data were analyzed by ZsimpWin software (Echem software, USA). The electrochemical measurements were carried out at room temperature (25 ± 3°C) with a three-electrode system. The reinforced bar electrode, Pt foil, and saturated calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively (Figure 3(a)). The charge transfer resistance of steel bar \( R_{ct} \) could be regressed according to the abovementioned circuit, and the corrosion current density \( i_{corr} \) could be calculated based on the Stern–Geary relationship as follows:

\[ i_{corr} = \frac{B}{R_p}, \]

where \( R_p \) is the polarization resistance which is generally equal to \( R_{ct} \), \( B \) is a constant as a function of anodic and cathodic Tafel slopes. For steel in concrete, the \( B \) value is equal to 26 mV for active state and 52 mV for passive state, respectively.

| Table 1: Mix proportions of concrete and their compressive strength and air content of fresh concrete. |
| --- |
| **Cement (kg·m⁻³)** | **GGBS (kg·m⁻³)** | **Fly ash (kg·m⁻³)** | **Sand (kg·m⁻³)** | **Aggregate (kg·m⁻³)** | **Water (kg·m⁻³)** | **Superplasticizer (kg·m⁻³)** | **Compressive strength (MPa)** |
| **3 d** | **28 d** | **3 d** | **28 d** | **3 d** | **28 d** | **3 d** | **28 d** |
| OPC | 470 | 0 | 0 | 760 | 1090 | 165 | 5.2 | 28.4 | 39.4 |
| HPC | 240 | 150 | 80 | 760 | 1090 | 165 | 5.2 | 30.3 | 47.1 |
| F15 | 399.5 | 70.5 | 0 | 760 | 1090 | 165 | 5.2 | 34.5 | 52.8 |
| F30 | 329 | 141 | 0 | 760 | 1090 | 165 | 5.2 | 28.7 | 51.3 |
| F50 | 235 | 235 | 0 | 760 | 1090 | 165 | 5.2 | 21.8 | 44.7 |
| K15 | 399.5 | 70.5 | 0 | 760 | 1090 | 165 | 5.2 | 26.3 | 41.3 |
| K30 | 329 | 141 | 0 | 760 | 1090 | 165 | 5.2 | 22.1 | 41.9 |
| K50 | 235 | 235 | 0 | 760 | 1090 | 165 | 5.2 | 22.1 | 41.9 |
| K65 | 165 | 305 | 0 | 760 | 1090 | 165 | 5.2 | 28.4 | 44.9 |
The WBE protected by mortar was submerged to seawater for about 300 d. When the WBE was corroded to a certain time, the surface was dried, and the current of each electrode was tested. An automatic measurement system based on modular instruments and self-designed software was employed to measure the current flowing between each wire and the remaining wires of the whole wire bundle. The WBE measurement is shown in Figure 3(b).

3. Results and Discussion

3.1. Chloride Ion Diffusion into Concrete Samples at Different times. The chloride diffusion coefficient ($D_{RCM}$) of concrete at 28 d curing age was studied, and $D_{RCM}$ of concrete exposed to the submerged zone for 3, 9, and 13 months was also tested by RCM, and their results are shown in Figure 4. When the replacement ratio of fly ash is less than 30%, $D_{RCM}$
of concrete decreased with the increasing of fly ash dosage. And $D_{\text{RCM}}$ of concrete decreased with the addition of GGBS, and the optimization replacement ration of GGBS is 30%. $D_{\text{RCM}}$ of concrete with GGBS after curing 28d is $3.16 \times 10^{-12} \text{m}^2/\text{s}$ and that of concrete with fly ash is $5.4 \times 10^{-12} \text{m}^2/\text{s}$, which indicated that high activity of GGBS might be more effective to improve chloride migration resistance capacity of concrete than fly ash. Additionally, $D_{\text{RCM}}$ of concrete decreased with corrosion time, and their relationship could be regressed as follows:

$$D_{t,\text{RCM}} = D_{0,\text{RCM}} \times \left(\frac{t_0}{t}\right)^n,$$

where $D_{t,\text{RCM}}$ and $D_{0,\text{RCM}}$ are chloride ion diffusion coefficients of concrete which was corroded for $t$ months at 28 d of curing age; $t_0$ is 28 d curing age; $t$ is corrosion time; and $n$ is age factor.

According to equation (6), the age factor of OPC was 0.54, and the average value of age factor of concrete mixed with GGBS and fly ash was 0.44 and 0.55, respectively. And $D_{t,\text{RCM}}$ of concrete with GGBS and fly ash exposed to the submerged zone for 13 months is $0.91 \times 10^{-12} \text{m}^2/\text{s}$ and $0.92 \times 10^{-12} \text{m}^2/\text{s}$, respectively. This highlights that the pozzolanic effect of fly ash can improve the long-term chloride ion diffusion resistance of concrete and can achieve the effect of mineral powder, especially in the marine submerged area.

OPC and HPC specimens were exposed to the submerged zone for 36 months, the free chloride ion content was tested, and the results are shown in Figure 5. Before 3 months of marine exposure, the convection zone of chloride profile could be observed due to unsaturation of high compaction concrete in the earlier corrosion period. The longer the corrosion time, the more the chloride ions content diffused into concrete. Meanwhile, the surface chloride content of concrete also increased with corrosion time. Comparing OPC with HPC, in the same depth and corrosion time, there is a lower concentration of chloride ions in HPC than that of OPC. After 3 years of exposure, the chloride ions content in 40 mm depth of OPC is nearly 0.25%, which is about 1.6 times of that of HPC.

Fick’s second law given by equation (7) could be used to express the chloride migration profile of concrete, and the apparent chloride diffusion coefficients $D_{\text{app}}$ of concrete in different corrosion time could be determined. It is worth mentioning that Fick’s second law is with the assumption of one-dimensional transportation of chloride ions in the saturated medium. Meanwhile, the transmission coefficient and surface concentration remain constant.

$$C(x, t) = C_s \left(1 - erf \left(\frac{x}{2\sqrt{D_{\text{app}}t}}\right)\right),$$

where $D_{\text{app}}$ represents the apparent chloride diffusion coefficients of concrete; $C_s$ is the surface chloride content; $C(x, t)$ is the chloride concentration at the depth $x$ (mm) and the exposure duration time $t$; and $x$ is depth in concrete.

The regressed $D_{\text{app}}$ of OPC and HPC in different corrosion was plotted and compared with $D_{\text{RCM}}$ which is shown in Figure 6. Likewise, $D_{\text{app}}$ also decreased with corrosion time and that of OPC is higher than that of HPC in the same corrosion age. When corrosion time exceeded 2 years, $D_{\text{app}}$ of concrete remained roughly stable.

The chloride ion content of concrete mixed with fly ash and GGBS was tested and plotted in Figures 7 and 8 respectively. Obviously, the addition of fly ash and GGBS did not influence the law of chloride ion migration, but decreased the chloride ion content in concrete. The free chloride ions content in 40 mm depths of concrete with fly ash is 0.12–0.15% after 3 years of exposure, which is about half of that of OPC. Similarly, addition of GGBS into concrete resulted in 16–48% decrease of free

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Figure 4: RCM test result of concrete. (a) With fly ash. (b) With GGBS.
chloride ions content of concrete after 3 years of corrosion period. According to Fick’s second law, $D_{app}$ of the concrete with mineral admixture was regressed and expressed in Figure 9. $D_{app}$ of concrete with fly ash and GGBS after 3 years of exposure was $0.55 \times 10^{-12}$ m$^2$/s and $0.49 \times 10^{-12}$ m$^2$/s, which was 93% and 83% of that of control group. Moreover, $D_{app}$ of all concrete specimens was tending towards stability after 13 months of exposure to the submerged zone. In the case of concrete exposed to the tidal zone, $D_{app}$ of concrete tends to stabilize earlier because fully saturated seawater curing in the submerged zone is helpful for excited mineral admixture’s activity rapidly. And $D_{app}$ of concrete with fly ash is approximately equal to that of concrete with GGBS after 3 years of exposure to the submerged zone. It was investigated that the admixture of fly ash and GGBS can improve the chloride ions diffusion resistance capacity of concrete.

3.2. **Bound Chloride Ion Rate of Concrete.** The total chloride ion of concrete specimens exposed to the submerged zone for different time was also tested, and linear equation (1) could be used to express the relationship between total chloride ion content and free chloride ion content, which is shown in Figure 10. According to the total and free chloride ion content of concrete, the bound chloride ion rate could be regressed as shown in Figure 11. Obviously, the bound chloride ion rate of concrete decreased with corrosion age. After 3 years of exposure, the bound chloride ion rate of reference concrete is even close to zero. However, the addition of fly ash and GGBS improved the chloride binding capacity of concrete exposed to the submerged zone. The main reason of this is because both fly ash and GGBS are industrial waste residues after high-temperature treatment, which contain parts of calcium aluminate and calcium silicate minerals, but their activity is lower than ordinary Portland cement and the hydration
speed is relatively slow. After adding fly ash and GGBS, mineral admixture will react with calcium hydroxide and form secondary C-S-H and C-A-H gel respectively, which can also improve the physical binding capacity of chloride ions in concrete by physical adsorption. In addition, the active aluminum phase offered by fly ash and GGBS will also chemically combine with chloride ions to form Friedel’s salts, thus improving the chemical binding capacity of chloride ions in concrete. The bound chloride ion rate of concrete was the highest, reaching 10% and 21% respectively, when concrete mixed with 30% fly ash or GGBS was exposed to the submerged zone for 3 years. In general, the chloride ion binding capacity of concrete is in a downward trend due to the existence of sulfate ions in seawater. Therefore, the bound chloride ions should not be considered in service life prediction modeling when concrete services in marine environment, which has agreement with the result reported in reference [26, 27].

In order to further explore the influence of mineral admixtures on chloride ion binding ability, different amounts of mineral powder were submerged in 1% NaCl solution for 7 d, and afterwards, chemical titration test was applied to determine the chloride content and the result was shown as Figure 12. When the replace rate of GGBS reached 30%, the combination rate of concrete chloride ion is up to 0.7% in 1% NaCl solution and 1.3% in seawater, respectively. Similarly, when the replacement rate of fly ash is 30%, the amount of chloride ion combined with concrete hits 0.5% and 1.2% respectively. When the fly ash content brings the number to 50%, the chloride ion binding capacity is almost even comparable to that of concrete without fly ash. In addition, the amount of binding chloride ion obtained by soaking concrete powder in seawater is greater than that obtained by soaking in 1% NaCl solution. The main reason is that the concentration of chloride ion in seawater is about 1.75 and that in 1% NaCl solution is 0.61%, respectively.

Figure 7: Chloride ion profile of concrete mixed with fly ash. (a) Fly ash = 15%. (b) Fly ash = 30%. (c) Fly ash = 50%.
Figure 8: Chloride ion profile of concrete mixed with GGBS. (a) GGBS = 15%. (b) GGBS = 30%. (c) GGBS = 50%. (d) GGBS = 65%.

Figure 9: Apparent chloride ion diffusion coefficient of concrete. (a) With fly ash. (b) With GGBS.
Compared with concrete with mineral powder, the chloride ion binding capacity of fly ash concrete powder is about 0.1% lower, and the chloride ion binding ratio of concrete with mine powder is also higher than that of fly ash concrete after 3 years exposure in the submerged area. The above results all highlight that the chloride ion binding capacity of mine powder is higher than that of fly ash. Besides, for concrete which has been corroded in the marine submerged area for 3 months, the content of combined chloride ion calculated according to total and free chloride ion amount is roughly 0.05–0.3%, and the amount of combined chloride ion obtained by soaking concrete powder is 1.0–1.3%, which is more than 4 times higher than the result of marine exposure. The reason is that the concrete powder has a higher specific surface area, which is in more contact with the corrosion solution.

OPC concrete powder was immersed in 1% NaCl solution and seawater for 1 h, 5 h, 12 h, 1 d, 3 d, 7 d, 28 d, and 60 d, respectively. The chloride ion concentration before and after the corrosion was tested, respectively, and the amount of combined chloride ion was calculated and shown in Figure 13. OPC concrete powder was immersed in 1% NaCl solution, and the amount of binding chloride ion increased rapidly with the increase of soaking age in the first day. However, with the further increasing of corrosion age, the binding chloride ion concentration gradually tends to be saturated, and the relationship conforms to the Freundlich adsorption relationship. When the concrete powder was immersed in seawater solution, the amount of combined chloride ion increased rapidly in 3 d before soaking and that

Figure 10: Relationship between total chloride ion content and free chloride ion content. (a) OPC. (b) HPC. (c) Fly ash = 30%. (d) GGBS = 30%.
of combined chloride ion in the 3d reached 18.35 mg/g. Afterwards, the chloride ion binding amount began to decrease. When the immersion time was 28d, the binding amount of chloride ion decreased to 7.01 mg/g. For 60d, it dropped to 6 mg/g. The above results are consistent with the corrosion age effect on chloride ion binding capacity of concrete. The reason is that the hydration products of sulfate ions in seawater and cement-based material tricalcium aluminate reacted and formed ettringite and gypsum. Meanwhile, some Friedel’s salt particles appeared, which leads to reduction of chloride ion binding capacity [28, 29].

3.3. Reinforcement Corrosion inside Concrete Exposed to the Submerged Zone. OPC and HPC with 0.3 mm crack were exposed to the submerged zone for about 800d, and the Nyquist and Bode results are shown in Figure 14. The Nyquist plots of OPC-reinforced concrete only shifted to the right side after 800d marine environment corrosion, which indicates that the impedance was gradually increasing and gradually denser. The slope of the curve in low-frequency area becomes lower gradually, which highlights that the reinforcement tends to be corroded gradually. In Nyquist plots, the low-frequency curves of HPC-reinforced concrete decreased significantly, indicating that the passivation film of reinforcement had a destructive tendency. In Bode diagram, the absolute value of the maximum phase angle in the low-frequency area decreased from 50° at 28d to 17° at 700d, which means that the steel passivation film was gradually destroyed.

The R(QR) (QR) equivalent circuit was selected, and the impedance spectrum data were fitted by ZsimpWin...
3.4. Current Distribution of WBE Protected by OPC and HPC. The WBE with 0.2 mm cracks was protected by OPC and HPC mortar, which was immersed into seawater for 300 d, and its current distribution of WBE was tested and shown in Figures 16 and 17.

The anode area (positive current area) and cathode area (negative current area) can be divided according to the positive and negative corrosion current of the filament electrode. When the OPC mortar beam electrode with a 0.2 mm crack is immersed in seawater for 14 d, an obvious anode area is formed due to the rapid penetration of oxygen and chloride ions to the WEB surface through the crack and its oxidation. However, until 112 d, the anode area is gradually transformed into the cathode area, and the wire bundle electrode (steel bar) in the mortar is in the passivation state. However, from 240 d to 300 d, the chloride ion penetrates the surface of the wire beam electrode (steel bar) through the protective layer of the mortar, and a part of the wire beam electrode is oxidized and in a low-speed corrosion state. Therefore, the change of anode, cathode, and the development of corrosion in steel bar under concrete protection can be well observed by the wire beam electrode test. In the early stage of corrosion, oxygen and chloride ions were rapidly permeated to the surface of the steel bar due to the existent of cracks. However, when the immersed time reaches 112 d, all the steel bundle electrodes under protection of mortar are converted into the cathode area, and the steel bar comes to the passivation state. When the corrosion age reaches 300 d, the filament electrode under protection of HPC mortar is still in the cathode area, and no large range of anode can be observed. Additionally, the anode current density of the HPC-protected filament electrode was lower than that of the OPC-protected one. This shows that the high-performance concrete with fly ash and GGBS slows down the rate of steel corrosion, which is consistent with the steel corrosion in the cracked concrete exposed to natural marine exposure.

3.5. CO₂ Emission of Concrete with Mineral Admixture. As mentioned above, the chloride ions migration follows Fick’s second law which can be rewritten as equation (10). DuraCrete model is modified according to Fick’s second law, which is based on the results of international research on concrete durability while considering life prediction model, chloride permeability, service environments, curing conditions, protective layer variation coefficient, etc. [30]. The life prediction model is shown in equation (11).

\[
\frac{C_{x,t} - C_s}{C_0 - C_s} = erf\left(\frac{x}{\sqrt{4Dt}}\right),
\]

where \(C_{x,t}\) is chloride concentration of migration depth of concrete at time \(t\); \(C_0\) is initial chloride concentration; \(C_s\) is chloride ions concentration at the concrete surface; and \(D\) is the chloride migration coefficient.

According to Table 2, after 800 d of marine submerged zone corrosion, the steel reinforcement with 0.3 mm cracked concrete has entered the low-speed corrosion stage. The corrosion rate of steel bars in HPC is 0.139 μm/year, while that in ordinary concrete is 0.178 μm/year. The addition of fly ash and GGBS improves the reinforcement protection capacity for cracked concrete in marine environment.
Figure 14: Nyquist and Bode figures of OPC and HPC exposed to submerged zone. (a) Nyquist, OPC. (b) Bode, OPC. (c) Nyquist, HPC. (d) Bode, HPC.

Figure 15: RP and $i_{corr}$ of reinforced concrete exposed to submerged zone. (a) RP. (b) $i_{corr}$. 
\[ t = \left[ \frac{2}{x - D_x} \cdot \text{erf}^{-1} \left( 1 - \frac{C_c}{\gamma_1} \cdot \frac{1}{A \cdot (w/b) \cdot \gamma_2} \right) \right]^{-2} \cdot \frac{1}{D_0 \cdot k_e \cdot k_c \cdot \gamma_3 \cdot t_0^{1/1-n}}, \]  

where \( t \) is time until reinforcement depassivation (year), which means the service life of concrete in submerged zone; \( x \) is the cover thickness (mm); \( \Delta x \) is the construction deviation of the cover thickness (mm); \( C_c \) is the eigenvalue of the critical chloride ion concentration; \( \gamma_1 \) is the fractional coefficient of the critical chloride ion concentration; \( A \) is the regression coefficient of the chloride ion concentration at the concrete surface and the water/cement ratio relationship in concrete; \( w/b \) is the water/binder ratio; \( \gamma_3 \) is the fractional coefficient of the chloride concentration at the concrete

### Table 2: The corrosion time and corrosion rate of OPC and HPC.

| Concrete types | \( k \) | \( R_0 \) (kΩ · cm\(^2\)) | \( R^2 \) | \( T_1 \) (d) | \( H \) (μm/year) |
|----------------|--------|-----------------|---------|-------------|-----------------|
| OPC            | -1.494 | 1637.23         | 0.92    | 747         | 0.178           |
| HPC            | -1.554 | 1679.33         | 0.95    | 743         | 0.139           |

Figure 16: Current distribution of WBE protected by OPC mortar with 0.2 mm cracks.
Due to the lack of long-term exposure test results, in this model, the apparent chloride ion diffusion coefficient of concrete after 3 years marine exposure is used as the long-term chloride ion diffusion coefficient of concrete without considering the age factor \( n \). In addition, the chloride ion diffusion coefficient of concrete is obtained through marine exposure experiment for three years, which has reflected the impact of corrosive environment and maintenance. Hence, \( k_c \) and \( k_e \) will not be taken into account in the model. And the surface chloride ions content \( C_s \) can be acquired by chloride ions distribution principle from three years exposure experiment, and it is considered that it will not change in the later period. Besides, concrete will chemically combine with chloride ion in the marine submerged zone, which will lead to the reduction of chloride ion diffusion coefficient. Hence, the chloride ion diffusion coefficient should be modified as \( D/(1 + R) \). The simplified model is modified as follows:

\[
t = \left( \frac{2}{x - D_x} \cdot \text{erf}^{-1} \left( 1 - \frac{C_s}{C_s \cdot y_2} \right) \right)^{-2} \cdot \frac{1}{D_{\text{app}}/1 + R \cdot y_3},
\]

(12)

where \( x \) is the cover thickness (mm) with a range from 60 to 90 mm; \( \Delta x \) is the construction deviation of the cover.
thickness (mm) while considering normal repair cost of mitigation of risk ($\Delta x$ is 14 mm); $C_c$ is the eigenvalue of the critical chloride ion concentration; and $C_s$ is surface chloride concentration of concrete. In this experiment, $C_s$ is considered as the chloride concentration at the depth of 1 mm of concrete specimen after three years of exposure. $D_{app,3}$ is the chloride ions diffusion coefficient of concrete exposed to the submerged zone for 3 years (m²/s). $R$ is chloride binding coefficient of concrete. $y_1$, $y_2$, and $y_3$ are 1.06, 1.4, and 2.35, respectively, according to normal repair cost of mitigation.

Table 3 shows several significant influencing factors when calculating the predicted service life with various cover thickness, and the result was shown as Figure 18.

Taking the cover thickness is 90 mm into consideration, and the duration time until reinforcement depassivation of OPC, HPC, F30, and K30 are 61, 132, 104, and 212 years, respectively. The corrosion rate of reinforcement under natural marine environment is 0.178 and 0.139 μm/year, which means the corrosion rate of rebar in HPC decreased by 22 percent compared with that in OPC. In other words, the service life can be expended by 22% when replacing OPC with HPC, and moreover, the entire service life can be prolonged by 50% to 120% if suitable dosage of mineral powders mixed with other conditions remains unchanged. The average price and carbon emission of raw materials in Qingdao city is shown in Table 4. Assuming that the cubic capacity of concrete in the seawater flood area of Qinglian Sea-crossing Railway is 200,000 cubic meters, the total CO₂ emissions when using the four types of concrete are listed in Table 5. Apparently, when considering high-performance concrete used in sea-crossing railway bridge, the average cost and CO₂ emission per year will be reduced by 59.6% and 73.8%, respectively. Moreover, if 30% cement was replaced by fly ash, the average cost and CO₂ emission per year will be reduced by 52.7% and 58.7% and that of 73.1% and 78.4% would be saved, respectively, if 30% cement was substituted by GGBS.

### Table 3: Significant impact factors on concrete service life prediction.

| Parameters | $x$ (mm) | $\Delta x$ (mm) | $C_{cr}$ (%) | $C_s$ (mm) | $D_{app,3}$ $(10^{-12} \text{m}^2/\text{s})$ | $R$ | $y_1$ | $y_2$ | $y_3$ |
|------------|----------|----------------|-------------|------------|--------------------------------|-----|-----|-----|-----|
| OPC        | 60–90    | 14             | 2.2         | 5.05       | 0.59                                         | 0.023 | 1.06 | 1.4  | 2.35|
| HPC        | 60–90    | 14             | 2.2         | 4.02       | 0.37                                         | 0.01  | 1.06 | 1.4  | 2.35|
| F30        | 60–90    | 14             | 2.2         | 3.38       | 0.69                                         | 0.106 | 1.06 | 1.4  | 2.35|
| K30        | 60–90    | 14             | 2.2         | 4.07       | 0.27                                         | 0.21  | 1.06 | 1.4  | 2.35|

### Figure 18: Prediction results with various concrete cover thickness.

### Table 4: Cost and CO₂ emission of raw materials of concrete production.

| Materials          | Cement (RMB/ton) | GGBS (RMB/ton) | Fly ash (RMB/ton) | Aggregate (RMB/ton) | Sand (RMB/ton) | Water (RMB/ton) | Superplasticizer (RMB/ton) | CO₂ emission (ton/ton) |
|--------------------|------------------|----------------|-------------------|---------------------|---------------|----------------|---------------------------|------------------------|
| Cost               | 623              | 396            | 265               | 75                  | 102           | 1.9            | 9800                      | 0.85                   |
| CO₂ emission       | 0.85             | 0.13           | N/A               | 0.003               | 0.003         | N/A            | 0.028                      |                        |

### Table 5: Average cost and CO₂ emission per year.

| Concrete | OPC | HPC | F30 | K30 |
|----------|-----|-----|-----|-----|
| Service life (years) | 61 | 132 | 104 | 212 |
| Cost (KRM/ton/year) | 1651.4 | 667.7 | 870.9 | 444.7 |
| CO₂ emission (ton/ton) | 1328.5 | 347.4 | 548.7 | 286.5 |
4. Conclusions

The chloride ion concentration of concrete mixed with 0–50% fly ash and 0–65% GGBS exposed to marine submerged zones was tested, and OPC and HPC with fly ash and GGBS were also investigated by marine exposure and WBE, respectively. The main conclusions are as follows:

(1) Admixtures of fly ash and GGBS replacing cement will significantly improve the chloride ions binding ability by 10% and 21%, respectively, and the chloride migration coefficient of concrete with fly ash and GGBS are 93% and 83% of ordinary Portland concrete.

(2) Fabrication procedures of wire beam electrode (WBE) have been introduced in detail, which have been proved as a novel and reliable test method against corrosion. And also, it has agreement with the test result of electrochemical device.

(3) The average cost and CO₂ emission per year will be reduced by 59.6% and 73.8%, respectively, when taking consideration of using high-performance concrete with mineral admixtures. Moreover, if 30% cement was replaced by fly ash, the average cost and CO₂ emission per year will be reduced by 52.7% and 58.7%, respectively, and that of 73.1% and 78.4% would be saved, respectively, if 30% cement was substituted by GGBS.

Data Availability

All the data used to support the findings of this study are available within this manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest in this work.

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