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Research Progress on Ionic Erosion of Steel-reinforced Concrete Structures under Marine Environments

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Abstract

As one of the most widely used structural forms in the world, reinforced concrete structures have been widely used in various infrastructure construction. However, the corrosion of steel bars in concrete often leads to durability failure of reinforced concrete structures, leaving the structure unable to meet the requirements of design life. In reinforced concrete structures in marine environments, corrosion and degradation of steel bars caused by chloride ions is one of the important reasons for the durability failure of the structures. In this paper, the chloride ion erosion mechanism of concrete, steel bars and concrete-steel transition zone is introduced, the influence mechanism of different marine environmental factors on chloride ion erosion is clarified.

Keywords: *Steel-Reinforced Concrete, Ionic erosion, Marine Environments, Transition Zone, Durability*

1 Introduction

The ocean is the most extensive area on the earth's surface, with a total area of about 3.6×108 km^2, accounting for about 71% of the earth's surface area, containing rich mineral resources.

Seawater not only contains a variety of inorganic salts mainly NaCl, but also contains dissolved oxygen, particulate organic matter and humic substances including humic acid, etc., and the surface seawater is close to saturation with O_2 and CO_2, and the pH value is about 8.2, which is a corrosive electrolyte solution with a very complex composition. Chloride and sulfate ions in the marine environment infiltrate into the marine engineering from the outside through chemical potential energy and pressure drives, and these corrosive ions are transported to the surface of the steel bar through the pores and cracks in the concrete [1], by destroying the passivation film around the steel bar, the steel bar undergoes a chemical reaction, thereby reducing the service life of the marine project. With the new development period of marine engineering construction, there are more and more marine engineering applications such as cross-sea bridges, port wharves, island construction, submarine tunnels, offshore oil drilling platforms, and offshore floating buildings, and the lack of durability and structural damage caused by concrete cracking and steel corrosion has become an important problem of actual engineering failure.

Due to the increasing cost of repairing and updating offshore concrete structures, the cost of repairing reinforced concrete structures due to steel corrosion worldwide averages more than $100 billion per year [2], the world's loss due to steel corrosion accounts for 1%～2% of GDP [3]. It has accounted for the vast majority of the marine engineering construction budget of all countries in the world, therefore, the corrosion problem of the marine environment in the application of marine engineering, the development of new marine anti-corrosion technologies and new materials such as high-durability marine engineering concrete, high-corrosion resistant reinforcement, and heavy anti-corrosion coating is particularly important.

2 Marine Ion Erosion Mechanism in Concrete

Cl- erosion is often considered to be the main cause of the deterioration of reinforced concrete structures in chloride salt environments [4-5]. When the Cl- concentration is greater than a certain critical value, the reinforced concrete structure is easily damaged due to steel corrosion [6], the durability of the structure is reduced, which in turn leads to a shortened service life of the concrete structure [7-8].

2.1 Ionic erosion process in concrete

In 1997, Hooton [9] et al. pointed out that when concrete is exposed to chloride salts, there are at least six

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transport mechanisms for chloride ions to enter the concrete: diffusion, capillary action, osmosis, adsorption, binding and diffusion, etc.

The erosion process of chloride ions in the marine environment is elaborated, including the permeation mechanism of chloride ions on the surface and inside of different materials (e.g., concrete, steel, alloys, etc.).

2.2 Diffusion

Saturated concrete is composed of liquid and solid phases, and the transmission speed of chloride ions in the liquid phase is much faster than that in the solid phase under the action of the concentration gradient, so the diffusion of chloride ions in the solid phase of concrete is negligible. When the solid phase blocks the transport path of chloride ions, the chloride ions continue to diffuse forward bypassing the solid phase, rather than directly diffusing from the solid phase, so the diffusion rate of chloride ions in saturated concrete is mainly determined by the diffusion rate and pore structure of chloride ions in the pore solution [10].

When the concrete is saturated, diffusion is the most important way for chloride ions to be transported to the surface of the rebar, and the law of erosion follows Fick's second law approximately [11]. Fick's first and second laws are derived from the Fourier heat conduction equation [12]. In 1970, Collepardi [13] et al. considering the actual situation in the concrete Cl-Fick's second law was first introduced to describe Cl in concrete in the diffusion process:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

Where x is expressed as position. t represents time and D is chloride diffusion coefficient. $C(x,t)$ is the concentration of chloride ions at the x position at the t moment. If the initial conditions $C(0,t)=C_b$, $C(\infty,t)=C_0$ are given, the initial conditions $C(x,0)=C_0$ are set, and if the chloride diffusion coefficient is not a function of time and space, then the solution of the chloride ion transport equation can be written as:

$$C(x,t) = C_0 + (C_b - C_0)[1 - erf(\frac{x}{2\sqrt{Dt}})] \tag{2}$$

where erf is the error function. As can be seen from Equation (2), the concentration of chloride ions at this time is related to the chloride concentration at the initial moment in the concrete.

2.3 Convection

Convection refers to the mass transfer phenomenon caused by the movement of a fluid that drives the molecules or ions dissolved in the fluid. When the reinforced concrete structure is in an unsaturated state, the liquid containing chloride ions from the outside penetrates into the concrete pore structure, and the chloride ions will be convection. The flux of convection can be expressed by the following relation [14]:

$$N_{i,conv} = c_i u \tag{3}$$

Among them, c_i is the concentration of chloride ions. u is the flow velocity of seawater in the reinforced concrete structure, and the flux vector of chloride ion convection is positively correlated with the flow velocity of seawater, so the velocity of chloride ion convection is the same as the flow velocity of seawater. If you need to consider the change in chloride concentration caused by convection at a point on the reinforced concrete structure, you can bring Equation (3) into the mass continuity equation to solve:

$$(\frac{\partial c_i}{\partial t})_{conv} = -\nabla \cdot N_{i,conv} = -c_i \nabla \cdot u - u \cdot \nabla c_i \tag{4}$$

Considering that seawater is an incompressible fluid, the mass of the entire seawater is conserved, so the inclusion term ($\nabla \cdot u$) is zero. Therefore, there is only a difference in the concentration of chloride ions, the concentration of chloride ions in the lining structure is caused by convection change, so Equation (4) can be rewritten as:

$$(\frac{\partial c_i}{\partial t})_{conv} = -u \cdot \nabla c_i \tag{5}$$

The convection zone usually occurs in the area where the reinforced concrete structure meets the external environment, and the thickness of this area is usually 0～20mm. When chloride ions enter the area 20 mm away from the concrete surface, the chloride ion transport mode is mainly diffusion.

2.4 Capillary water absorption

When a liquid comes into contact with a solid, the surface forms an interfacial energy, which is caused by the difference between the attraction of the liquid to the surface molecules and the attraction of the solid to the surface molecules, and this difference can draw the water in the pores to a certain height and form a meniscus in the pores. This transport mechanism mainly occurs in the shallow protective layer, which generally cannot transport chloride ions to the surface of the reinforcement in reinforced concrete, unless the quality of the concrete is very poor and the thickness of the protective layer is very small. However, this mechanism allows for rapid chloride ion transfer to a certain depth of the protective layer, which reduces the diffusion distance of chloride ions to the surface of the rebar [15].

2.5 Thermal migration

Ions or molecules move faster in a hot environment than in a cold environment. If the saturated concrete contains a uniform concentration of chloride ions, and when a part of the concrete is heated, the chloride ions will migrate from the high temperature to the low temperature part, and migrate from the outside to the inside of the concrete under the action of temperature difference.

2.6 Electromigration

After chloride ions penetrate into the concrete structure of offshore engineering, it will cause the corrosion of the steel bar and produce galvanic cells. This corrosion phenomenon produces two types of galvanic cells: microcells and galvanic cells [16-17]. A micro-battery is a corroded cell that provides both the anode and the cathode on the same rebar, the area where the anode is not rusted, and the cathode is an oxide of iron on the rebar. Macro-battery refers to a corroded battery with different steel bars providing an anode and a cathode respectively, the anode is the unrusted steel bar, and the cathode is the corroded part of the steel bar that has been corroded. Since both microcells and macro-batteries generate an electric field, the chloride ions in the seawater that invade the concrete under the action of the electric field will move towards the cathode, and the electromigration process can be described by the Nernst-Planck equation [18]:

$$J = D\frac{z_i FE}{RT}C \tag{6}$$

Among them, J is the flow rate of chloride ions in the process of internal electromigration of concrete, D is the diffusion coefficient of chloride ions, F is Faraday's constant 96485.33 C/mol. z_i is the valency of chloride ions, and R is the molar constant of gas 8.314. T represents the internal temperature of concrete. E indicates the electric field strength of the electric current, C is the concentration of chloride ions.

3 Chloride Ion Erosion Process of Steel bars

3.1 Passivation film destruction

Calcium silicate in Portland cement, a concrete component, produces $Ca(OH)_2$ hydration, so that the pore fluid in the concrete presents a high alkalinity, the pH value is between 12.5～13.5, and the OH is in the pore fluid. It is adsorbed on the surface of the steel bar and formed by the reaction with Fe oxide film, which is complete and dense, effectively protects the steel bar from corrosion. The high activity and small ionic radius of Cl^- make it dominant in the competitive adsorption with OH^-, and OH^- preferentially combines with Fe, and Cl^- can penetrate the defects of passive film of steel bar. When the amount is large enough, that is, the pH value of the steel bar surface will drop rapidly at the same time, and the dissolution of the passivation film will be intensified. When a certain critical value is reached, this value is usually Cl^-/OH^-～0.6, the passivation film is activated and begins to dissolve, at which point if there is water and oxygen around the reinforcement, the reinforcement begins to corrode [19]. In this level of erosion mechanism, the effect of Cl^- is mainly manifested in competitive adsorption.

3.2 Formation of corrosive batteries

With the dissolution of the passivation film in some areas of the steel bar surface, the iron matrix is exposed, because the activity of the iron matrix is higher, and the activity of the passivation film coverage area is low, so the surface of the steel bar forms a pattern of large cathode and small anode. The iron matrix is a small anode, the passivation film coverage area is a large cathode, and the concrete pore fluid around the steel bar contains a large number of ions. It can be used as an electrolyte, and because there is an electric potential difference between the large cathode and the small anode, the corrosion battery is formed, accompanied by charge transfer and material transfer, and the corrosion current is generated [20]. The dissolution of the passivation film is often in a small and variable area, so the corrosion of the steel bar caused by the erosion of this layer is often pitting, but the development rate is very fast.

3.3 Chloride ion depolarization

After contributing to the formation of corroded cells, Cl- further accelerates the corroded cell reaction by removing or slowing down anodic polarization. In the corrosion cell reaction, anodizing generates Fe^{2+}, which combines with nearby Cl^- to form $FeCl_2$, which is soluble and spreads outward with the concrete pore liquid, and OH will be encountered in the process-, $FeCl_2$ with OH^-. The reaction produces poorly soluble $Fe(OH)_2$, $Fe(OH)_2$ with H_2O, O_2. Continue the reaction generation of $Fe(OH)_3$, Fe_2O_3 and Fe_3O_4, whereas Cl^- is released and returns to the vicinity of the anode again to combine with Fe^{2+}, and the cycle repeats [21].

In this process, Cl-It plays the role of catalysis and transport, so that the Fe2+ near the anode will not accumulate, resulting in polarization, which will affect the reaction rate of the battery, in fact, only a small amount of Cl- can accelerate the corrosion reaction repeatedly, the following is the main chemical equation of the cathode and anode reaction [22]:

Anode reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic reaction: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Corrosion products: $Fe^{2+} + 2Cl^- + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

$$6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O$$

3.4 Conductivity

Electrochemical reactions are mainly manifested in charge transfer and species transfer, so the ion pathway in the electrolyte is particularly important. The presence of the concrete porosity is able to increase the conductivity of the concrete pore fluid, reduce the ohmic resistance of the electrochemical cathodic and cathodic reactions. In addition, the presence of Ca^{2+}, K^{+}, etc., further increases the material transport rate and accelerates the electrochemical reaction [23].

4 Reinforcement-concrete Transition Zone

4.1 Formation of a reinforcing steel-concrete transition zone

The structure of the rebar-concrete interface is complex, including the C-S-H gel layer、$Ca(OH)_2$. Deposition layer, corrosion product layer, oxide scale on the surface of steel bar, bubbles and voids in the water secretion area, etc. The bond-concrete interface transition zone can be regarded as the third phase of reinforced concrete materials, and its formation and evolution mechanism is very complex and affected by many factors. YS Ji found [24] that there is a special area of weakness between the steel surface and the cement slurry, that is, the transition zone of the reinforcement-concrete interface. They believe that the "wall effect" is the main reason for the formation of the reinforcement-concrete interface transition zone, that is, a layer of water film will be formed on the surface of the reinforcement, and the cement concentration is close to zero at the surface of the reinforcement and increases with the increase of the distance from the reinforcement surface, so the composition and structure of the hydration products in the reinforcement-concrete interface transition zone are different from the matrix.

In addition, there are studies show that [25-26] the bottom of the horizontally arranged steel bar is prone to form a water-draining area during the concrete pouring process, and after the cement is hydrated, the area may have defects such as holes. During the pouring and vibrating of the new concrete, gravity makes the aggregate sink, and the buoyancy makes the bubbles and slurry move upward, and the horizontal steel bars hinder the movement of the bubbles and the slurry, causing them to gather at the bottom of the steel bar, and eventually form holes and cavities [27-28]. The size of the holes and cavities is related to the height of the concrete under the reinforcement at the time of pouring.

4.2 Structural characteristics of the reinforcing steel-concrete transition zone

The pore structure of the reinforcing steel-concrete interface transition zone is affected by the direction of the reinforcement [29]. The structure of the transition zone between the reinforcement and the upper part of the horizontal reinforcement is dense, but the structure of the interface transition zone at the lower part of the reinforcement is more complex, and the structure is composed of the water drainage zone, the floating bubble hole and the cement slurry porous layer [30].

Kenny et al [31] and Horne et al [32] indicated that the horizontal arrangement of the reinforcement will hinder the floating process of air bubbles in the concrete, and the bubbles will converge at the bottom of the reinforcement, resulting in the formation of a water secretion zone on the lower side of the reinforcement. It makes the porosity in the lower interface of the reinforcement significantly higher than that of the upper interface and the vertical reinforcement interface. Zhang et al [33] through the analysis of backscattered electron images, it is found that the porosity of the area under the reinforcement is obviously higher than that of the concrete matrix, and the area with large porosity is mainly concentrated in the interface transition zone. The area with medium porosity and low porosity mainly appears at the location of mortar and coarse aggregate.

The transport mechanism of chloride ions in concrete is complex, and the capillary pore structure has a significant effect on chloride ion transport in the porous system of hardened concrete [34], of which the pores that have the greatest impact on permeability are concentrated in the 10 nm～10 μm range, but overall, the rate of migration in the concrete matrix is positively correlated with the total porosity of the concrete [35].

5 Factors Influencing Chloride Ion Transport Characteristics

5.1 Temperature

Temperature is one of the important factors affecting the diffusion of chloride ions in the salt spray environment. The increase of ambient temperature will accelerate the thermal movement of chloride ions, cause the acceleration of the chemical reaction rate of cementitious materials, reduce the physical adsorption capacity of hydration products to chloride ions, and improve their chemical binding effect on chloride ions [36-38].

The increase of temperature will accelerate the evaporation of water in concrete, accelerate the crystallization and precipitation of chloride ions in the pore solution, and promote the cracking of concrete. It provides a new channel for chloride ion transport [39].

The Arrhenius formula was used to analyze the effect of temperature on the chloride diffusion coefficient in concrete, and it was found that the apparent chloride diffusion coefficient increased significantly with the increase of temperature [40]. The effect of increasing temperature on chloride ion transport has a dual effect: first, high temperature will reduce the pore water saturation and accelerate the hydration of cement, reduce the porosity of the matrix, thereby slowing down the erosion of chloride ions; The second is the decomposition of Friedel's salt will release the adsorbed bound chloride ions, increase the concentration of free chloride ions, change its activation energy. The increase of the temperature will accelerate the water transport in the concrete, thereby accelerating the convection rate of chloride ions [41-43].

5.2 Wind speed

The effect of wind speed on chloride ion transport is mainly reflected in the first stage of erosion, where ocean aerosols in the atmosphere are transported inland by the sea breeze and settle at a certain distance [44-45]. Wind speed can affect the concentration of chloride ions in the atmosphere by affecting the distance and amount of ocean aerosols transported [46]. The increase in the concentration of chloride ions in the atmosphere will accelerate the deposition of chloride ions on the surface of concrete, creating more favorable conditions for the transport of chloride ions to the interior of concrete. Some scholars believe that when the wind speed exceeds 3 m/s, the concentration of chloride ions in the air will rise rapidly [47-48]. Secondly, wind speed increases the humidity gradient inside the concrete [49], increases the water migration rate, and accelerates the convection of chloride ions. Gustafsson et al [50] found that the chloride ion deposition rate under different wind speed conditions was measured by chloride ion detector, and it was found that the chloride ion deposition rate had a good correlation with the exponential wind speed, and the correlation coefficient at each position was above 0.99. In general, the increase of wind speed will accelerate the deposition of chloride ions on the surface of concrete, intensify the capillary adsorption of the matrix, increase the transmission rate of chloride ions, and adversely affect the chloride ion erosion resistance of concrete.

5.3 Distance from shore

Chloride ions in the atmosphere settle due to gravity and the blocking of trees and mountains as they move inland, causing chloride concentrations to decrease farther away from the coastline [51]. The transport process of chloride ions inside the concrete is closely related to the amount of chloride ions deposited. Meira et al [52] found that the quantitative relationship between chloride ion deposition and chloride ion content in concrete at different distances from the coast was established, and a nonlinear relationship between the two was determined. The Civil Engineering Society of Japan has established the value of chloride ion concentration on the surface of concrete in coastal atmospheric areas [53]. The chloride ion concentration on the concrete surface in the coastal atmosphere is shown in Table 1.

Table 1 Concentration of chloride ion on concrete surface in coastal atmospheric area [53]

Distance from coast line/km	Chloride ion concentration(mass friction)/%
Near the coast line	0.450
0.10	0.225
0.25	0.150
0.50	0.100
1.00	0.075

In general, the amount of salt spray in the atmosphere is closely related to the distance from the coastline, and the reduction of the salt spray content weakens the erosive effect of chloride ions, that is, the farther away from the coastline, the less susceptible the reinforced concrete structure is to the erosion of chloride ions.

5.4 Exposure time

In general, the erosive effect of chloride ions on concrete increases with the increase of exposure time. With the increase of exposure time, the amount of chloride ions deposited on the surface of the concrete gradually increases, and the chloride ions transported to the concrete through capillary adsorption and diffusion also increase until the dynamic equilibrium is reached. The study shows that with the increase of the service life of reinforced concrete structures, the chloride ion erosion depth of reinforced concrete structures also increases, and the chloride ion erosion depth of concrete structures in 60 years of service is 1.5 times that of 10 years of service [54]. In order to explore the time-varying characteristics of chloride ion transport in self-compacting concrete, a five-month real-sea exposure test was carried out. The results show [55] that the longer the exposure time, the higher the concentration of chloride ions within a certain erosion depth, and the chloride concentration tends to be consistent beyond this depth. The diffusion coefficient of chloride ions is negatively correlated with time.

5.5 Cement composition

5.5.1 C3A and C4AF

In the case of internal chloride ions, Racheeduzzafar et al [56] found that the water-soluble chloride ion decreased significantly with the increase of C_3A content. In addition, they soaked concrete, a cement formulation containing 9% and 14% C_3A, in a chloride salt solution, which was confirmed by X-ray diffraction analysis Formation of salts. Blunk et al [57] found that the pure C_3A-gypsum mixture and ordinary cement and C_3S slurry were soaked in chloride salt solutions of different concentrations, and it was found that the amount of chloride ions adsorbed by the C_3A-gypsum mixture was greater than that of the other two slurries. By soaking ordinary cement slurry and sulfate-resistant cement slurry in a 20g/l NaCl solution, Arya et al [58] found that the amount of chloride adsorbed by sulfate-resistant cement was much lower than that of ordinary cement slurry because of the C_3A of sulfate-resistant cement. Some of the results of studies on the internal chloride ions on the surface [59-60], The higher the C_3A content, the greater the chloride ion adsorption.

Chloride ions and C_3A and C_4AF can undergo chemical reactions to form Friedel's salts and their analogues. Therefore, the content of C_3A and C_4AF in cement determines the chemical adsorption of chloride ions. Friedel's salts may be produced by the direct reaction of C_3A and $CaCl_2$. When chloride salts taste sodium chloride, the reaction equation is as follows [61]:

$$Ca(OH)_2 + 2NaCl = CaCl_2 + 2Na^+ + 2OH^- \tag{7}$$

$$C_3A + CaCl_2 + 10H_2O \rightarrow C_3A \cdot CaCl_2 \tag{8}$$

According to Suryavanshi et al [62] study, Friedel's salts and their analogues can be formed by two different mechanisms: the adsorption mechanism and the ion exchange mechanism. In the adsorption mechanism, the formation of Friedel's salt is to adsorb chloride ions in pore solution through the interlayer ($[Ca_2Al(OH)_6 \cdot 2H_2O]^+$) of AFm phase to achieve electrical neutrality. The mechanism of ion exchange is that chloride ions replace hydroxyl ions between the layers of AFm hydration phase (C_4AH_{13}) to form Friedel's salt, which can be expressed by the following formula: $R-OH^- + Na^+ + Cl^- \rightarrow R-Cl^- + Na^+ + OH^-$. Where R is $[Ca_2Al(OH)_6 \cdot nH_2O]^+$.

When Friedel's salt is formed by adsorption mechanism, sodium ions equivalent to chloride ions are also adsorbed from the pore solution to maintain the electrical neutrality of the pore solution. When Friedel's salt is formed by ion exchange mechanism, some hydroxyl ions are released into the pore solution, which increases the PH value of the pore solution. It is generally believed that the adsorption of chloride ions increases with the increase of the aluminum phase, and in the case of carbonization or sulfate ion intrusion, the chemisorption is reversible[63].

5.5.2 C3S and C2S

C-S-H gel is the main hydration product of cement, which determines the physical adsorption of chloride ions. Physical adsorption is due to the adsorption of chloride ions by C-S-H gels.

Ramachandran et al considered [64] that chloride ions in C-S-H are classified into three categories: chemical adsorption on the surface of hydrated calcium silicate; adsorption in the interlayer of C-S-H; It is tightly adsorbed in the molecules of C-S-H. The higher the content of C_3S and C_2S, the higher the content of C-S-H, and the higher the content of chloride ions in physical adsorption. Tang et al [65] found that the chloride ion adsorption capacity of ordinary Portland cement concrete depends entirely on the content of C-S-H, and has no relationship with the water-cement ratio and aggregate content. Beaudoin et al [66] believed that the chloride adsorption capacity of C-S-H depends on its calcium-silicon ratio C/S, and that a low calcium-silicon ratio may lead to a low adsorption capacity. However, by incorporating chloride ions in the Alite phase, Lambert et al [67] found the C-S-H phase is thought to adsorb only a very small amount of chloride ions.

C_3A and C_4AF controlled the chemisorption of chloride ions, while C_3S and C_2S determined the physical adsorption of chloride ions. By soaking the pure monomer compounds C_3A, C_4AF, C_3S and C_2S in chloride ion solution, Zibara [61] found that C_3A is an important influencing factor for chloride ion adsorption: in the high concentration range (1.0-3.0 mol/l), C_3A content is a good indicator of the chloride ion adsorption capacity of cement; In the low concentration range (0.1 mol/l), the C_3A content is no longer a good adsorption capacity of cement, but only an indicator. The adsorption capacity of C_4AF for chloride ions is about one-third of that of C_3A, and the contribution of C_3S to chloride adsorption is between 25% and 50%.

5.6 Marine conditions

In the marine environment, according to the location of the concrete structure, the concrete structure can be divided into underwater zone, tidal range zone, splash zone and atmospheric zone. The chloride ion transport mechanism in concrete in different areas is different [68].

(1) The underwater zone refers to the substructure completely submerged in seawater, the concrete in this area is in a saturated state. There is no humidity gradient, and the chloride ion transport mechanism is mainly diffusion caused by the difference of chloride ion concentration inside and outside the concrete [69].

(2) The tidal range zone refers to the structural part within the range of the elevation of the tide water level, which is subjected to the alternating dry and wet environment, and there is chloride ion concentration gradient, humidity gradient, concrete pore surface tension, etc. inside the concrete, so its chloride ion transport mechanism is the coupling of various mechanisms such as diffusion, unsaturated seepage and capillary absorption [69].

(3) The splash zone refers to the structural part near the high tide level that is impacted by the splash of waves, and this area is also affected by the alternating dry and wet environment, and the chloride ion transport mechanism is similar to that of the tidal range zone.

(4) The atmospheric zone refers to the superstructure that does not come into contact with seawater, and this area is mainly through the accumulation of chloride ions in the air on the surface of concrete, and then transport inward under the concentration gradient, and its main transport mechanism is diffusion. Among them, the tidal range area and splash chloride ion in the alternating dry and wet environment have the fastest transmission rate and the most serious corrosion.

5.7 PH value of concrete porosity

Back in the 60s of the 20th century, Venu, etc [70] proposed that hydroxide ion is one of the important factors to inhibit the corrosion of steel bars caused by chloride ions. Ghods [71], Li and Sagues [72] proposed that the higher the pH value of the concrete pore fluid, the greater the critical chloride ion concentration. Tan et al. [73] studied the inhibition of carbonate and bicarbonate on the corrosion of steel bars by using the simulated solution of concrete pore fluid. Figueira et al [74] proposed that when the pore fluid pH decreases from 13.5 to 11.6, the corrosion resistance of the steel bar will gradually decrease. The effect of pH on the critical chloride concentration was analyzed by concrete pore fluid simulant by Figueira [75].

6 Conclusion and Prospect

The deterioration mechanism of reinforced concrete structures in the marine environment and the analysis of their time-varying reliability are one of the important topics to be solved in engineering. In this paper, we introduce the mainstream physical experimental research methods in the academic circles based on the chloride ion transport mechanism, and comprehensively evaluate the advantages and disadvantages of each interface optimization method based on the influence of various factors on ion erosion in the marine environment. Therefore, future research can seek breakthroughs in the following several areas to advance the service life of marine engineering.

The simulation method of steel corrosion process in concrete still needs to be further explored and improved. In all physical experiments, the use of reasonable test methods is an important prerequisite to ensure the correctness of the research results. Because chloride ions enter the concrete slowly, it takes years or decades to reach the surface of the rebar and accumulate to a certain point where the rebar begins to corrode. Therefore, scholars often use accelerated test methods to simulate the corrosion process of steel bars, and accelerated tests are often different from the actual situation. It is still worth exploring the relationship between the results of laboratory tests and the results of field tests.

In actual marine engineering, reinforced concrete structures mostly work under certain loads, and at present, a series of durability studies of concrete are mostly carried out on the basis of the non-load state, which has certain limitations and has a certain gap with the actual concrete engineering. In the future, the research on the durability of concrete under various environmental factors under stress should be strengthened and expanded, so that the research results are closer to engineering practice.

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