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Testing Method of Ion Corrosion of Reinforced Concrete and its Interface Optimization in the Marine Environment

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Abstract

With the continuous improvement of the strategic position of marine resources in the world, improving the durability of marine engineering and increasing its service life has become an unavoidable topic. In the future, the development of protection optimization methods should be more diversified and integrated. In this paper, the testing method of ion corrosion of reinforced concrete and its interface optimization in the marine environment were investigated. It provides more possibilities for scientific research and technological innovation.

Keywords: *Ionic erosion; Testing method; Marine Environments; interface optimization; Reinforced concrete*

1 Introduction

If the chloride ion content exceeds the standard, the steel bars in concrete will be easily corroded, which will reduce the chemical corrosion resistance, wear resistance and strength of concrete, affect the durability of concrete, and thus lead to the decline of concrete quality. The detection of chloride ion penetration resistance is an important test to evaluate the durability of concrete, which is mainly used to determine the resistance of concrete to chloride ion penetration.

2 Physical Test Research Methods

2.1 Accelerated carbonization method

As carbon dioxide gradually penetrates into the concrete, it reacts chemically with the alkaline substances in it, lowering the pH of the concrete pore fluid, causing the steel passivation film to be destroyed and corroded. We call this process the carbonization of concrete. The accelerated carbonization method is to speed up the carbonization process of concrete, so that the steel bar corrodes quickly and shortens the test time. Alonso et al [1] used the accelerated carbonization method to measure the corrosion process of steel bars in concrete. It was found that there was a strong correlation between the corrosion rate of steel bars and the resistance of concrete. Although the accelerated carbonization method can cause steel corrosion in a short time and effectively shorten the test time, the simulated corrosion process is not consistent with the real situation. This method is more suitable for studying the steel corrosion caused by concrete carbonization, but cannot consider the steel corrosion problem in concrete eroded by chloride ions.

2.2 Chloride ion doping method

The internal chloride method (internal doping) is often used to study the corrosion rate of steel bars in concrete. Yalcyn and Ergun [2] used an internal doping method to study the effects of chloride ions and acetate ions on the corrosion of steel bars in concrete. The results show that chloride ion and acetate ion can significantly increase the initial corrosion rate of steel bars in concrete, and it is found that the corrosion rate of steel bars decreases exponentially with time. Although the internal doping method can effectively shorten the test time, this method is more likely to cause uniform corrosion of steel bars, which is different from the actual local corrosion. In addition, the internal doping method will affect the formation of passivation film on the surface of the steel bar, which will inevitably have a certain impact on the corrosion process of the steel bar. As a result, not many of the more recent studies have adopted this method.

2.3 Galvanostatic method

In order to accelerate the corrosion of steel bars in concrete, the galvanostatic method is also a commonly used test method. This method is to directly connect the steel bar to be corroded in the concrete to the DC power

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supply, so that the steel bar corrodes quickly under the action of electric current. The test results show [3] that the corrosion rate of the steel bar increases with the increase of the crack width of the concrete, and the corrosion rate of the steel bar is inversely proportional to the concrete resistivity regardless of whether there is a crack in the concrete specimen. In addition, a prediction model of steel corrosion rate for reinforced concrete structures with cracks in tidal zone was established, and the effects of crack width, concrete protective layer thickness and concrete performance on steel corrosion rate were revealed [0]. Nossoni et al [0] used galvanostatic method to explore the relationship between the corrosion rate and corrosion products of steel bars and the pressure of reinforced concrete. An electrochemical-mechanical model of concrete protective layer cracking caused by chloride ion erosion was established. It can be seen that the galvanostatic method is mostly used to explore the problem of steel corrosion in cracked concrete.

2.4 Indoor natural diffusion method

In order to more realistically simulate the corrosion process of steel reinforcement in concrete components in the chloride salt environment, scholars have tried to conduct laboratory experiments by exposing reinforced concrete specimens to the simulated environment and waiting for chloride ions to naturally diffuse to the surface of steel bars and induce corrosion. We call this method the natural diffusion method. The effects of the relative humidity, chloride concentration, diameter of the reinforcement, the water-cement ratio of the concrete and the exposure time on the polarization curve of the reinforcement corrosion were discussed[0], and the prediction model of the reinforcement corrosion rate was proposed, and the correctness of the proposed model was verified by comparing and analyzing the measured data of the reinforcement corrosion rate with other studies. The calcium aluminate cement mortar specimens were immersed in NaCl solutions at concentrations of 0.5 mol/L and 1.5 mol/L for up to five years[0]. The effects of environmental factors (temperature and chloride ion concentration) and mortar specimen parameters (water-cement ratio) on the corrosion process of steel bars were studied, and the relationship between the corrosion rate of steel bars and the resistivity of mortar specimens was established. It can be seen that compared with the accelerated test method, the indoor natural diffusion test can simulate the corrosion process of steel bars relatively realistically, but the test time is longer.

2.5 Outdoor exposure test

Scholars have carried out outdoor exposure tests to monitor the corrosion law of reinforced concrete specimens or real structures in outdoor exposure environments. Different concentrations of NaCl solution were mixed into the simulated reinforced concrete bridge slab specimens and exposed to the outdoor environment for 5 years[0]. The corrosion rate of steel bars was monitored, and the effects of chloride ion concentration, ambient temperature, concrete resistance and corrosion time on the corrosion rate of steel bars were explored. Through nonlinear fitting, a long-term prediction model of steel corrosion rate was established. In addition, the exterior walls and terraces of two buildings in an inland and coastal area of Finland were selected as the research objects, and the corrosion rate of steel bars in the structure was continuously monitored within 25 months 22 years after the completion of the two buildings, and the effects of temperature, relative humidity, wind and rain, solar radiation, etc. on the corrosion rate of steel bars were discussed, and a prediction model of steel corrosion rate considering the influence of environmental factors was established[0]. Although outdoor exposure tests are more conducive to monitoring the corrosion of steel bars in concrete in real exposed environments, such tests tend to last for a long time and require a lot of manpower and material resources. At the same time, the outdoor exposure environment is relatively complex, and the test conditions cannot be controlled, so it is impossible to carry out systematic research on a certain influencing factor.

3 Interface Optimization Methods and Strategies

3.1 Concrete protective layer

Many tests have shown that even with the lowest water-cement ratio and high-quality concrete, the chloride ion content in the 12mm depth of the concrete surface is much higher than that in the 25～50mm depth range when exposed to the presence of chloride salts[0]. Therefore, in the project of chloride salt environment, the thickness of the concrete protective layer should not be less than 38mm, and preferably not less than 50mm. Considering the construction deviation, the thickness of the design protective layer should be selected as 65mm.

3.2 Rust inhibitors

The development of rust inhibitors began in the 70s of the 20th century, and has been applied and promoted in Japan, United States, the former Soviet Union and other countries. Rust inhibitor is a mixture or mixtures, generally acting on the metal surface, which can prevent or delay the destruction of chloride ions on the passivation film of steel bars, while maintaining the original properties of metal materials. The use of rust inhibitors should be accompanied by the use of low-permeability concrete to prevent the loss of rust inhibitors, and the addition of rust inhibitors is considered to be a more economical and effective measure. Commonly used rust inhibitors can be divided into inorganic rust inhibitors and organic rust inhibitors.

3.2.1 Inorganic rust inhibitors

Inorganic rust inhibitors are generally nitrite corrosion inhibitors, and NO_2 and Cl have been found. The ratio of the rust inhibitor directly affects the rust inhibition efficiency of the rust inhibitor. When the value is higher than 0.5～0.6, nitrite rust inhibitors have a good rust inhibitor effect[0]. Howl [0] discussed the permeability and corrosion resistance of $Ca(NO_2)_2$ in concrete. It was found that it had good permeability in concrete with high water-cement ratio, and had a good protective effect on steel bars under low chloride salt corrosion, but poor protection against steel bars under high chloride salt environment. The experimental results of Page [0] on sulfite are similar to those of Ngala. It is proposed that a layer of cement mortar mixed with nitrite should be added to the surface of the nitride-coated concrete in the process of use. Thereafter, Na_2PO_3F was developed and came out, which once attracted widespread attention. Alonso [0] studied the corrosion inhibition effect of Na_2PO_3F in reinforced concrete. The results showed that a certain concentration of Na_2PO_3F could significantly change the reinforcement potential in concrete, make it move forward, increase the impedance value, and reduce the electric flux. Hasson [0] confirmed that Na_2PO_3F can increase the compactness of concrete, thereby reducing Cl^- of erosion infiltration. Ngala [0] pointed out that the permeability of Na_2PO_3F in concrete is poor, and it can only penetrate to a depth of 5mm below the concrete surface to effectively protect the steel bar.

3.2.2 Organic rust inhibitors

Organic rust inhibitors have little toxic effect and are more friendly to the environment, so they have been vigorously developed, and organic rust inhibitors migrate to the surface of steel bars through penetration and diffusion to form a dense protective film, because they usually carry hydrophobic groups, which can not only Cl^- and other harmful ions, which also have a shielding effect on H_2O and O_2, thereby slowing down the electrochemical reaction rate of steel corrosion and achieving the purpose of rust inhibition. In the 90s of the 20th centuries, the United States Cortec company developed an organic rust inhibitor whose main component is amino carboxylate, which can change the previous passive penetration, can actively migrate to the surface of the steel bar to form a film, inhibit corrosion, so it is also called migratory rust inhibitor (MCI, Migrating corrosion inhibitor). The corrosion inhibitor with alkylamine ethanol as the main component was studied by Morris et al[0]. It was found that the rust inhibitor also had a certain migration ability, and it was also effective against the low chloride salt environment ($[Cl^-] < 0.2\%$). Jamil et al. [0] studied the alcohol amine organic rust inhibitor, which showed that it would form a protective film on the surface of steel bar after infiltrating into concrete. The electrochemical results show that the film resistance and charge transfer resistance are much higher. In the process of studying amino alcohol rust inhibitors, secondary ion mass spectrometry was used to prove the particles and Cl^- of these rust inhibitors[0]. There is a competitive adsorption situation, which can displace the Cl^- on the surface of the steel bar, and form a dense and stable protective film. The diffusion properties of amino ethanol organic rust inhibitors in concrete were discussed by Tritthart et al [0]. The results showed that the rust inhibitors could not only migrate through the pore fluid in concrete, but also spread in the vapor phase through microcracks in concrete.

3.3 Cathodic protection

The formation of yin and yang on the surface of the steel bar is a prerequisite for the occurrence of electrochemical corrosion, where the cathode is cementite and the anode is ferrite. Anodizing forms an oxide film on the surface of the rebar to prevent the generation of galvanic corrosion. On the basis of electrochemistry, the cathodic protection method has also been developed to keep the steel bar in the cathode state and thus reduce the corrosion of the steel bar. The principle of cathodic protection is that the critical concentration of chloride ions decreases as the electrochemical potential of the steel bar decreases. The penetration of chloride ions in the protective layer is inhibited, thereby reducing the diffusion rate of chloride ions, thus ensuring the durability of the concrete structure [0]. Engineering practice has shown that the use of cathodic protection in concrete structures can effectively prevent chloride ion erosion, thereby preventing corrosion of steel bars. Commonly used cathodic protection methods include impressed current method and sacrificial anode method.

3.3.1 Impressed current method

The impressed current method refers to the cathodic protection effect by providing cathodic protection current through an external constant current power supply or potentiostat, which is released through the auxiliary anode and flows from seawater to the protected structure. The advantages of an impressed current include: (1) the protection effect is better and no pollution; (2) No consumption of non-ferrous metals; (3) The later maintenance cost is low. However, the upfront investment cost is high.

In 2002, Li Yan et al. [22] put forward the related ideas of cathodic protection for offshore platforms, including sacrificial anode cathodic protection method and impressed current emergency protection method. In 2003, Xiong [23] put forward a self-developed cathodic protection monitoring system, which provided valuable experience for the continuous improvement and innovation of the cathodic protection monitoring and detection system. It also proposed a dual-electrode potential detection probe with strong impact and vibration resistance, which was more helpful for measuring the platform potential. In 2006, Wu Lie et al. [24] put forward a new technology of impressed current cathodic protection with central suspension at the 14th Asia-Pacific Corrosion Control Conference. It provided a new idea for cathodic protection design of bridges, docks, platforms and other facilities. Since 2010, impressed current cathodic protection technologies for different types of offshore platforms have been put forward continuously, among which Yin's impressed current cathodic protection technology for jacket platforms in 2012 and Luan's impressed current cathodic protection technology for jack-up platforms in 2015 have both developed a complete set of impressed current cathodic protection technologies from the aspects of impressed current system materials, equipment, design and installation technology [25-26]. In 2017, Huang successfully applied the first self-developed ICCP impressed current cathodic protection life extension system for offshore jacket structures on the platform of CNOOC Lufeng 13-2WHP.

3.3.2 Sacrificial anode method

In 1823, Humphrey Davy[27], an Englishman, found that connecting zinc with the copper skin wrapped on a wooden boat could effectively prevent the copper skin from rusting. In more and more subsequent practical use, people noticed that with the increase of corrosion products attached to the anode surface, the protective ability of the anode was also weakened[28]. Since the 20th century, the cathodic protection of sacrificial anode has been paid more and more attention. In 1913, the Metal Society held in Geneva officially named the cathodic protection of sacrificial anode as "electrochemical protection"[29]. Since then, the research on sacrificial anodes has been carried out all over the world, and the main research directions focus on exploring the protection mechanism of sacrificial anodes, discussing the corrosion behavior of materials protected by sacrificial anodes in different environments, and developing high-efficiency and low-cost anode materials. Beccaria [30-31] et al. put several metals and alloys in the deep-sea environment of the Gulf of Mexico from 1083 to 1945 m, and investigated the performance of materials as protected cathodes. The results showed that the sea area, depth and time in the sea would affect the size of the protection current required by the metal, in general, the deeper the sea, the smaller the protection current required by the material as a cathode. Robin 0 studied the corrosion of low carbon steel and stainless steel protected by sacrificial anode in their own simulated 2500m deep sea environment. On the one hand, in the high-pressure environment, the low carbon steel does not appear "hydrogen embrittlement", but there are a large number of mixtures containing Ca^{2+} and Mg^{2+} deposited on the surface. It requires a large protective current to resist rust. On the other hand, the surface finish of carbon steel has a great impact on the difficulty of corrosion, the smoother the surface, the easier it is to corrode, and the stainless-steel shows "pitting" in the same period. It is analyzed that this is due to the local failure of the surface passivation film, which is independent of the deposit, indicating that the cathodic protection current required by stainless steel at high and atmospheric pressure is similar. Funahashi [33] explored the cathodic protection performance of different sacrificial anode materials. The results show that the protection current provided by the poor anode material is uneven. It will produce acidic substances on the surface of the anode concrete. The research also shows that the anode material coated with titanium metal oxide have better protective effect.

3.4 High-performance concrete

In generally, reinforced concrete structures, chloride ions must penetrate through concrete of different thicknesses to reach the surface of the reinforcement, so improving the durability of reinforced concrete structures can also be achieved by enhancing the erosion resistance of the concrete matrix. There are two main technical ways to improve the resistance of concrete matrix to medium erosion: On the one hand, the incorporation of auxiliary cementitious materials (SCMs) can reduce permeability; On the other hand, the incorporation of erosion inhibition materials inhibits water transport and reduces the chloride permeability of concrete. As technology advances, new erosion inhibition materials are being developed and applied to concrete to improve the durability of reinforced concrete.

Nanotechnology provides new opportunities for mankind to study concrete materials, and concrete research itself is a multidisciplinary system, using nanotechnology to change the structure and properties of C-S-H gels, one of the mechanisms is the lack of tetrahedral grafting polymers on the C-S-H silicon chain [34] or the use of organic matter to form a bond between the C-S-H layers, such as layered di-hydroxides, carbon nanomaterials, nanoparticles, etc., to optimize the properties of concrete.

3.4.1 Graphene nanomaterials

Graphene oxide (GO) contains many oxygen-containing functional groups, including -OH, -COOH, C=O, CH(O)CH-, etc. Graphene and its oxides can not only react with hydration products, affect pore structure, etc., but also change the transport properties of cement-based materials.

Du et al. [35-36] improved the chloride ion permeability resistance of cement-based materials through graphene nanosheets. When adding 1.5% graphene nanosheets, the water penetration depth, chloride ion diffusion coefficient and chloride ion migration coefficient decreased by 80%, 80% and 37% respectively. The result showed that more than 50% of the reduction effect was achieved by increasing the tortuosity of the cement slurry, and the other effect was to improve the pore structure of the cement slurry. Graphene nanosheets are well distributed in cement matrix and can improve the performance of cement-based materials. After adding 2.5% graphene nanosheets, the most acceptable pore size of cement-based materials is reduced by 30%, and the effect of graphene nanosheets will not be further improved if the graphene nanosheets are further increased, and the effect of reducing water transport by more than 20% is contributed by the increase of the tortuosity of the transmission path, and the decrease of chloride diffusion coefficient is almost all caused by the change of tortuosity. After the content of graphene nanosheets exceeded 7.5%, the inhibitory ion transport effect of the nanomaterials began to weaken due to the agglomeration of the nanomaterials. The graphene oxide nanomaterials were prepared by in-situ polymerization by Gao Ruijun [37]. It is found that the graphene oxide nanomaterials had good dispersion in the aqueous solution and the centrifugal solution of the cement slurry. The graphene oxide nanomaterials formed graphene oxide end-caps on the surface of the hydration products, which improved the compactness of the matrix, could block chloride ion transport and improve the chloride ion permeability of concrete, and the electric flux of concrete mixed with 0.15% graphene oxide decreased by 40%.

3.4.2 Nano-silica

Said et al. [38] found that the strength of concrete mixed with nano silica was improved, and the total porosity, maximum pore size and electric flux of 2% nano silica 0.4 were reduced by 33%, 40% and 49% respectively compared with the benchmark group, and the nano silica could improve the chloride ion permeability of concrete, mainly due to the reaction of nano silica with calcium hydroxide to generate more C-S-H and the filler effect of nano silica. Feng et al. [39] added pre-dispersed silica into cement-based materials, which can greatly improve their properties. The addition of 6% silica and 0.2% ball mill pre-dispersed silica can significantly reduce the chloride content in the 0-4mm surface of concrete, which is only 60% of the benchmark group, thanks to the formation of a denser structure and more gel. Chen et al. [40] added hydrophobic modified nano-silica into cement paste, which can react with calcium hydroxide generated by cement hydration to form substances containing hydrophobic groups, and finally can reduce the most probable pore size and water absorption. Wang et al. [41] hydrolyzed ultrafine silica oligomer and then used it to treat the surface of cement-based materials. It was found that the water absorption could be reduced by 46.4%, but the silica oligomer needed to be hydrolyzed under the condition of pH 4.0, and acidic conditions would destroy cement-based materials to some extent. Li [42] used nano-SiO_2 to improve the performance of concrete. Adding 1% nano-SiO_2 can effectively improve the anti-corrosion ability of concrete, but it will affect the workability of concrete, and the water demand will increase sharply and the slump will decrease. Gu [43] modified nano- SiO_2 particles by polycarboxylic acid to solve the problem of dispersion and penetration, and then coated on the surface of cement-based materials can reduce the water absorption of cement-based materials.

3.4.3 Fatty acid materials

Hydrophobic materials with fatty acid salts can also be used to improve the properties of concrete substrates, and their calcium salts, ammonium salts, and butyl stearate are the most common types.

Calcium stearate is a hydrophobic compound of fatty acids and calcium ions, which can reduce the water absorption rate and chloride penetration depth of concrete, and improve the durability of concrete [44-45]. Calcium stearate is a component of petrolatum corrosion pastes and can be used to protect steel structures in coastal environments [0]. Maryoto [0] added calcium stearate to concrete with water cement ratio of 0.44, and added 1 kg calcium stearate per cubic meter of concrete. Compared with the reference group, the water absorption decreased from 2.00% to 0.94%, while the corrosion quality loss of steel bars decreased from 11.79% to 4.18%, indicating that calcium stearate can improve the chloride ion corrosion resistance of concrete, and the compressive strength of concrete has little change. Maryoto et al [0] Added 0.4% calcium stearate to the cement-based material can reduce the water absorption rate of concrete by 53%, and at the same time, it has little effect on strength, chloride ion corrosion can be reduced by 28.5%, and the chloride penetration depth can be reduced by 15%. The addition of 4 kg of calcium stearate per cubic concrete can increase the permeability of concrete by 50% while guaranteeing minimal change in concrete strength. Wu et al. [0] used calcium stearate to change the hydrophilicity of the mortar, and the contact angle of the mortar could reach 130° , and calcium stearate could reduce the water absorption rate of the mortar and improve the chloride ion permeability of the mortar, but the treatment steps of calcium stearate were more complicated.

3.4.4 Silanes, siloxanes and their derivatives

As an important chemical functional material, silane, siloxane and its derivatives are stably dispersed in the aqueous phase with nanometer or micron size particles, which have many advantages such as improving the toughness of hardened cement slurry and enhancing the anti-cracking and impermeability of cement slurry. However, the addition of silanes, siloxanes and their derivatives will significantly affect the cement hydration process, which is mainly manifested in delaying cement hydration, and then affecting the hardening and strength growth of cement-based materials.

He et al. [0] used 66% octyl triethoxysilane, 2% sodium dodecyl sulfonate and 32% water to prepare silane emulsion. When the silane content is 1%, the strength of the mortar decreases significantly, and the water absorption rate also decreases, but the water absorption rate changes little if the silane content continues to increase. The addition of silane can effectively improve the erosion resistance of the mortar to sulfuric acid solution. Vivian et al [0] used polymethylsiloxane to modify kaolin and silica fume, and then used it to change the surface structure of concrete. The Different series of tests have shown that super-hydrophobicity can be achieved by adding 0.5% kaolin or 5% silica fume. Zhang et al [0] used polydimethylsiloxane and silane coupling agent to modify micro-silica powder, which can improve the contact angle of cement-based materials and reduce the porosity.

3.5 High-performance steel bars

In 1933, United States scholars added a small amount of copper, nickel and other corrosion-resistant elements to carbon steel for the first time to develop weathering steel, that is, atmospheric corrosion-resistant steel. In 1951, United States scholars developed seawater-resistant steel for the first time. Subsequently, various countries gradually carried out research on corrosion-resistant steel bars. Some researchers [0] added corrosion-resistant elements such as Cr and Ni to carbon steel to improve the corrosion resistance of steel bars. The results show that the corrosion resistance of steel bars containing 0.40%～0.70% Cr and 0.30%～0.50% Ni is better. At the same time, the content of Cr and Ni in the reinforcement is directly proportional to the critical pitting potential. Some researchers [54-55] added corrosion-resistant elements such as Cu and Mo to carbon steel to improve the corrosion resistance of steel bars. The addition of Mo to stainless steel can promote the increase of Cr content in the passivation film, and improve the stability and pitting resistance of the passivation film. Halada et al. [56] studied the influence of Mo and N elements on the corrosion resistance of steel bars. The results showed that the addition of Ni and Mo elements would form $MONi_4$ films, which would improve the stability of the passivation films. Hermas et al.[0] studied the influence of Si element on the corrosion resistance of steel bars, and showed that Si element can form a silicon-rich film on the surface of steel bars, thus improving the pitting corrosion resistance of stainless steel. Yoshioka et al.[0] found that the stability elements Nb and Ti can slow down the occurrence of pitting corrosion of steel bars and reduce the corrosion rate of steel bars.

Corrosion-resistant steel bars are an important means to prevent rust damage of steel bars in concrete. Although stainless steel can directly avoid the occurrence of steel corrosion, the price of stainless steel is about 7 times that of general carbon steel, and the high cost directly hinders the use of stainless-steel bars. Chromium has significant corrosion resistance, and adding a small amount of chromium to ordinary carbon steel can form a dense protective layer on the surface of the steel bar and improve the corrosion resistance of the steel bar. On the basis of alloying, chromium is added to the steel bar to form a corrosion-resistant low-alloy steel, which not only has an advantage in price, but also can prolong the service life of the steel bar in terms of performance.

6 Conclusion and prospect

At present, the research on improving the durability of reinforced concrete in marine engineering mainly focuses on concrete and steel bars, and there are few studies on the lifting methods of the steel-concrete transition zone. It is one of the key issues in the development of marine engineering to combine multiple interface optimization methods to achieve the highest protection effect under economic conditions.

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