

Progress in Corrosion and Protection Research in Offshore Petroleum Engineering

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Abstract: This paper summarizes the latest research progress on the corrosion of concrete structures in marine engineering and its protection technology. The article firstly emphasizes the influence of seawater on the performance of concrete engineering, and then discusses the application of composite corrosion inhibitors in the marine environment. The composite corrosion inhibitor significantly reduces the corrosion rate by simultaneously inhibiting the anodic and cathodic reactions and forming a protective hydrophobic film on the metal surface. The article describes in detail the classification of corrosion inhibitors, including adsorption or film-forming inhibitors with polar hydrophobic groups such as N, S, and -OH, as well as migratory corrosion inhibitors (MCIs) that diffuse through the pores of the concrete to the surface of the reinforcement bar to form a protective film. The article also discusses the performance evaluation criteria of corrosion inhibitors, including the electrochemical performance of saltwater impregnation, the performance of dry-wet cold-heat cycles, and the performance of resistance to Cl⁻ penetration, etc., and lists the relevant national standards and test methods. Through a comprehensive analysis of relevant literature at home and abroad in recent years, the article points out that composite corrosion inhibitors show great potential in improving the durability of marine concrete structures, but the long-term stability and compatibility with different concrete types still need to be further studied. Future research should focus on developing more efficient and environmentally friendly corrosion inhibitors and expanding their application in marine engineering to meet the increasingly severe challenges of marine corrosion. At the same time, a comprehensive evaluation of the longevity, economy and environmental friendliness of corrosion inhibitors is also an important direction for future research.

Keywords: Seawater corrosion; steel reinforcement corrosion; corrosion inhibitor.

1. Introduction

As the cradle of life and the home on which everything depends, the ocean not only has a treasure house of marine life, minerals and space resources, but also is an essential space environment for human survival and development [1]. With the rapid rise of marine economy, coastal countries have made great efforts to develop marine high-tech and formulated deep marine spatial development plans. China is rich in marine resources. There are 11 provinces, cities and autonomous regions in China's coastal areas, which not only have more than 18000 kilometers of coastline, but also have more than 11000 islands and 370000 km² of territorial waters [2]. For the engineering construction in coastal areas, the development of marine economy and marine high-tech has become an essential link in the strategy of "marine power" [3]. With the development of offshore oil and gas wells, the construction of ship ports, and the construction of coastal nuclear power plants and sea crossing bridges, reinforced concrete materials have also become the first choice for marine engineering construction. It is worth noting that corrosion, as the core issue, has become the main threat faced by concrete structures in the process of ensuring the safe service of offshore engineering [4]. In the face of the harsh marine corrosion environment, the reinforced concrete structure without proper protection, its deterioration rate and the corrosion degree of reinforcement are very rapid, and the durability of concrete has also become a major problem to be solved [5]. The research on the corrosion mechanism and protection of reinforced concrete structures in complex

marine environment is particularly important for improving the overall corrosion resistance performance of reinforced concrete structures in complex marine environment, preventing the internal corrosion of reinforcement, and reducing or slowing down the direct economic losses caused by corrosion. It is also of great significance to carry out scientific and systematic research on the corrosion mechanism, protection and repair of concrete structures in complex marine environment, and to explore the evolution law of concrete pouring deterioration and improve the anti-corrosion performance.

2. Corrosion and Protection of Reinforced Concrete in Marine Environment

The corrosion of metals in the marine environment is called seawater corrosion. As a composite material, reinforced concrete is widely used in the construction of buildings, bridges, large offshore oil and gas well platforms, elevated roads and dams. The soluble salt content in seawater is not only as high as 3.5%, but also contains a large amount of dissolved oxygen. It is a natural electrolyte solution in nature and has certain corrosiveness [6]. Concrete is a mixture of calcareous, clayey or other substances containing SiO₂, Al₂O₃ and FeO. It is also a hydraulic cementitious material formed by adding gypsum after calcination at low temperature [7]. Steel reinforcement and concrete complement each other. Therefore, by combining them, a composite material with outstanding tensile strength, shear strength, compressive

strength, durability and fire resistance can be formed [8]. The hydrate of cement is made by mixing hydrated calcium silicate ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})\cdot 4\text{H}_2\text{O}$) and hydrated calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) as binder and adding sand gravel, crushed stone or inert materials in proportion [9]. With the increase of the service life of concrete structures in the marine environment, the external causes of the service life of reinforced concrete structures at present include the corrosion of thick steel reinforcements, the carbonization of concrete structures, freeze-thaw damage, alkali aggregate reaction, chemical erosion, etc., among which the rust of steel reinforcements is the primary factor to accelerate the complete destruction of concrete structures. The steel reinforcement in the concrete will be damaged by the interaction with the surrounding medium [10]. At present, the corrosion and protection of reinforced concrete structures has become one of the issues of universal concern and research in the world.

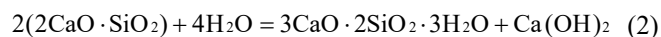
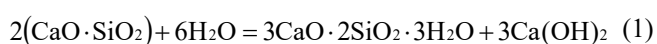
2.1. Causes of steel reinforcement corrosion

The reason for the rapid corrosion of steel reinforcement in concrete is that many micro cells are formed due to the de passivation of the surface passivation film, and electrochemical corrosion is caused by electrochemical reaction [11]. However, the corrosion of steel reinforcement in concrete structure is mainly caused by the damage of passive film on the surface of steel reinforcement, and the damage of passive film is mainly caused by the carbonation of concrete and the invasion of Cl^- . When Cl^- intrudes into concrete pores, the passivation film may damage its protection, thus interfering with the thickness of the film, leading to local erosion and causing corrosion process. When the steel reinforcement and other components in the concrete structure contact with water, the chances of corrosion of the steel reinforcement and other components in the honeycomb structure increase. The corroded steel reinforcement section is damaged, which reduces the mechanical properties of the steel reinforcement itself. At the same time, the volume of the steel reinforcement increases after corrosion, causing cracks on the concrete surface, and ultimately leading to the destruction of the reinforced concrete structure [12]. If steel corrosion occurs in concrete, it will increase the volume of steel perimeter and the volume of corrosion products, resulting in cracks and spalling of concrete due to higher tensile stress [13].

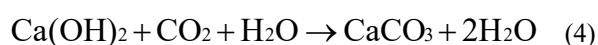
2.1.1. Carbonization of concrete structure

As the adhesive of reinforced concrete structure, the composition of cement is usually expressed by the sum of several oxides such as $2\text{CaO}\cdot\text{SiO}_2(\text{C2S})$, $3\text{CaO}\cdot\text{SiO}_2(\text{C3S})$, $3\text{CaO}\cdot 2\text{Al}_2\text{O}_3(\text{C3A})$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3(\text{C5A3})$, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3(\text{C4AF2})$. Calcium silicate hydrates(C-S-H) is the main chemical component of cement after hydration [14].

The steel reinforcement in concrete is usually in a passive state and is not easy to be corroded. This is because the pores of cement-based concrete are filled with saturated $\text{Ca}(\text{OH})_2$ solution. If some concrete flows out of the pore liquid, calcium hydroxyl cornerstone (Ca-OH) will be deposited on the pores, and some will be automatically supplemented by dissolution, so that the pH of the concrete pore liquid has been kept between 12.5-13.0 [15].



Carbonation of concrete refers to the process in which CO_2 , SO_x and NO_x in the air react with $\text{Ca}(\text{OH})_2$ in concrete to form insoluble calcium salts [16]. When the CO_2 gas dissolved in water reacts with the pore solution $\text{Ca}(\text{OH})_2$ in concrete, the pH of the concrete pore solution will decrease. When the critical pH of the steel reinforcement to maintain the passivation state is less than 11.5, the stability and continuity of the passivation film will be affected. The $\text{Ca}(\text{OH})_2$ (as well as NaOH and KOH) leached from the concrete will reduce the pH of the concrete pore solution to 9-10. At this time, the steel reinforcement passivation film will be completely destroyed and the corrosion rate of the steel reinforcement will be accelerated [17].



The carbonation of concrete is most easily carried out when the relative humidity is 50% -80%. The CO_2 content in the atmosphere is generally 0.03%, and the CO_2 content in the industrial plant is more than ten times or even hundreds of times that in the atmosphere. Therefore, the carbonation of concrete has a particularly serious impact on the buildings and concrete facilities in the industrial zone [18].

2.1.2. Invasion of chloride ion

For the corrosion caused by chloride intrusion, the related corrosion products have different components due to different conditions. In general, the composition is a combination of Fe^{2+} , $\text{Fe}(\text{OH})_2$, hydroxyl/oxide and oxide, and each product has different degrees of hydration. Melchers et al. [19] determined that goethite (α - FeOOH), ferromagnesian (β - FeOOH) and lepidocrocite (γ - FeOOH) are corrosion products in the steel reinforcement contaminated by Cl^- in reinforced concrete structures. According to the ratio of iron ion and chloride ion, ferric chloride and ferric hydroxide show different forms and affect the microstructure of steel/mortar interface. The invasion of Cl^- will reduce the bonding of concrete steel reinforcement and peel off the concrete protective layer. When Cl^- enters the steel reinforcement surface, it will quickly form point corrosion, thus reducing the stiffness, ductility, yield strength and bearing capacity of concrete structure [20]. Therefore, it will lead to the durability reduction or even damage of offshore structures.

2.2. Protection of reinforced concrete structure

For the protection of reinforced concrete structure, the fundamental problem that needs to be solved urgently is the technical problem of corrosion and rust of steel reinforcement. The fundamental protection principle is to greatly improve the anti rust ability of concrete to steel reinforcement. At present, the main methods to control the corrosion of steel reinforcement are: the use of corrosion-resistant steel reinforcement, the coating of protective layer on the surface of steel reinforcement, electrochemical cathodic protection, and the addition of steel reinforcement rust inhibitor [21]. The main methods to protect the concrete structure include: maintaining the high alkalinity of concrete and selecting high-grade and high density concrete materials [22]. The special methods to prevent the corrosion of reinforced concrete

mainly include: galvanized steel reinforcements, copper coated steel reinforcements, alloy steel reinforcements, stainless steel reinforcements, epoxy resin coated steel reinforcements; Spray epoxy powder coating on the surface of steel reinforcement; Cathodic protection is adopted for the overall concrete [23].

The replacement of corrosion-resistant steel reinforcements can effectively avoid corrosion, but it is very expensive for the construction of engineering projects. The external coating protection on the surface of concrete can only play a certain protective role in a short time. With the irradiation of ultraviolet light, the coating on the surface of concrete is prone to cracking and aging, and the coating also fails. The above-mentioned rust prevention and protection methods have their own characteristics and limitations, which should be selected according to the specific situation [24]. Steel reinforcement rust inhibitor is essentially an effective measure to prevent long-term corrosion of steel reinforcements. With the development of offshore industry, the corrosion inhibitor for steel reinforcements has changed significantly, and various efficient corrosion prevention technologies have been developed at home and abroad. It is added to the cement or concrete surface by mixing or coating to prevent steel reinforcement corrosion [25]. From the economic point of view, the cost of steel reinforcement rust inhibitor is low. It is easy to operate for engineering construction, and is more and more widely used. It can protect reinforced concrete structures such as roads, bridges and so on for a long time. Steel reinforcement corrosion inhibitor has become the main protective measure to prevent steel corrosion.

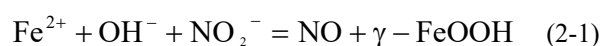
3. Rust Inhibitor of Steel Reinforcement

Steel reinforcement rust inhibitor is a kind of corrosion inhibitor that can effectively inhibit or delay the occurrence of corrosion and reduce the corrosion rate of steel reinforcements by adding a small amount of it into cement or mortar [26]. Generally, the steel reinforcement rust inhibitor can be added together with the fresh concrete mixture or applied externally on the hardened concrete surface. The former can only be used in new concrete structures, while the latter (migration/penetration inhibitors) can be used in the repair of concrete structures because they can diffuse into hardened concrete. Both organic and inorganic corrosion inhibitors have been used in concrete. The use of steel reinforcement rust inhibitor is not only cheap and easy to operate, but also can effectively block or slow down the corrosion of seawater to steel reinforcements. For example, nitrite and sodium fluorophosphate can modify the oxide film on the steel reinforcement to make it more protective. The traditional nitrite rust inhibitor can promote the formation of insoluble and stable passive film on the surface of steel reinforcements through the “anode corrosion inhibition” effect, reduce the corrosion rate of steel reinforcements, and make it have outstanding anti-corrosion performance. However, due to the high toxicity of nitrite, it will cause serious pollution to the marine environment and pose a threat to the lives of marine organisms and gradually fade out of the market [27]. Amino alcohol rust inhibitor is widely used because of its high efficiency, stability, non toxicity and green environmental protection. It can slow down the electrochemical reaction of the anode and cathode of the steel

reinforcement corrosion by forming a dense protective film on the surface of the steel reinforcement. Rust inhibitors can be classified into inorganic, organic and composite types according to their chemical composition; According to different adding methods, it can be divided into migration type and mixing type rust inhibitor [28]. In this paper, according to different mechanism, the corrosion inhibitors are divided into anode type, cathode type and composite type.

3.1. Anodic corrosion inhibitors of steel reinforcement

The anodic corrosion inhibitor can effectively prevent and slow down the corrosion of steel reinforcements by inhibiting the electrochemical anodic reaction, increasing the anodic polarization and making the corrosion potential move forward. Typical anode rust inhibitors include $\text{Na}(\text{NO}_3)_2$, Na_2CrO_4 , $\text{Ca}(\text{NO}_3)_2$, $\text{Na}_2\text{B}_4\text{O}_7$, etc., which generally have oxidation [29]. Among them, $\text{Ca}(\text{NO}_3)_2$ is the most widely used corrosion inhibitor in the world, and its mechanism of action is as follows:



NO_2^- promotes Fe^{2+} to form a protective passive film $\gamma - \text{FeOOH}$. When the steel reinforcement is eroded by Cl^- , the destructive effect of Cl^- will compete with the film-forming repair effect of. When the “repair” effect is greater than the “damage” effect, the corrosion of steel reinforcement will stop [30]. Therefore, the amount of nitrite must be sufficient, otherwise the steel reinforcement is prone to local corrosion (deep hole corrosion), which will seriously affect the mechanical properties of the steel reinforcement. Therefore, anode type rust inhibitor is also called “dangerous” rust inhibitor. Especially in the marine environment, the amount of rust inhibitor must be ensured, otherwise it may cause accelerated corrosion [31]. The simple use of nitrite can easily lead to the above problems. At the same time, the carcinogenicity of nitrite will also pollute the marine environment and cause certain harm to marine organisms. The United States and other countries have listed nitrite type rust inhibitors in the list of prohibited [32].

3.2. Cathodic corrosion inhibitors of steel reinforcement

The cathodic rust inhibitor can reduce the cathodic reaction rate in the corrosion process by inhibiting the cathodic reaction of electrochemistry. This kind of rust inhibitor can form a film in the cathode area or adsorb on the cathode surface, so as to prevent or slow down the cathode process of electrochemical reaction. It is sometimes called precipitation type rebar inhibitor [33]. Zinc salt and magnesium salt are cathodic inhibitors, which can form $\text{Zn}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates at the cathode. Compared with anode corrosion inhibitor, cathode corrosion inhibitor can hardly cause pitting corrosion, but its effectiveness is low and the price is relatively high [34]. Typical cathodic rust inhibitors also include phosphates, which rely on the precipitation of zinc (or metal) hydroxide at the cathode. At this time, the pH increases, making the cathodic reaction more difficult. Phosphate is precipitated and adsorbed on the steel surface in the form of ferrous and ferric phosphate [35]. In addition, phosphates such as $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$ and sodium hexametaphosphate can form a protective film on the metal surface as cathodic

inhibitors [36]. In recent years, rare earth organophosphorus compounds have been reported as a potential cathodic rust inhibitor. Rare earth organophosphorus compounds can be partially dissociated into polynuclear species or cluster complexes in solution, not just single ionic species. These species initially form a local surface film, which may limit the cathodic process of electrochemical corrosion reaction, resulting in local pH rise at the cathode [37]. This phenomenon may lead to the hydrolysis of rare earth ions, resulting in the deposited film completely covering the metal surface, thus inhibiting the electrochemical corrosion of the metal surface.

3.3. Composite steel reinforcement rust inhibitor

The main application method of the composite rust inhibitor is to add it to the fresh concrete as an admixture, apply it to the hardened concrete and damaged structure, and add it to the repair mortar for the steel reinforcement surface treatment before concrete pouring. In recent years, countries have been committed to developing efficient new rust inhibitors. The composite rust inhibitors simultaneously inhibit the reaction between anode and cathode, and form a thin protective hydrophobic film on the entire metal surface through the adsorption mechanism, thus reducing the corrosion rate [38]. Rust inhibitors with polar hydrophobic groups such as N, S and -OH are called adsorption or film-forming inhibition rust inhibitors. The effectiveness of the film depends on its chemical composition, molecular structure and affinity with the metal surface [39]. Migration corrosion inhibitor (MCI), as a composite rust inhibitor, diffuses to the steel reinforcement surface through the gas and liquid phases of the concrete pores to form a protective film to prevent rust [40]. The MCI studied by malik[41] and others is a mixture of surfactant and amine salt in water, which can be used not only on the surface of concrete, but also as a rust inhibitor for steel reinforcement. Saxena[42] pointed out that MCI based on amino carboxylate salt chemistry is the most effective in the simultaneous interaction between anode and cathode. Pandian[43] reviewed the types of rust inhibitors that may play a role in concrete and the corrosion mechanism of Cl⁻ on concrete, and summarized that amines, alkylamines, amino acids, monocarboxylates, polycarboxylates, amino

alcohols, organic heterocyclic compounds and green products can be successfully used as effective rust inhibitors for concrete protection.

Therefore, it is of great significance to study the composition, structure and performance of composite rust inhibitor and design and prepare efficient and reliable composite rust inhibitor for prolonging the service life of concrete structures.

4. Evaluation Method of Rust Inhibitor Performance

In the early 1950s, due to the corrosion of rebar by deicing salt, the Soviet Union, the United States and Japan took the lead in using rebar rust inhibitor in concrete, and proposed the application requirements of rebar rust inhibitor and standard specifications [44]. In recent years, China has formulated a series of evaluation procedures and specifications for steel reinforcement rust inhibitor, and further strengthened and improved the experimental indicators and technical specifications of steel reinforcement rust inhibitor [45]. At present, the general evaluation standard for rust inhibitors is GBT 33803-2017 technical specification for corrosion resistance application of rust inhibitors for reinforced concrete. The commonly used evaluation methods mainly include: salt water immersion method, electrochemical comprehensive rust prevention performance evaluation, dry and wet cold and heat cycle test, anti chloride ion penetration test, etc. [46]. The salt water immersion test is to immerse the steel reinforcement in saturated Ca(OH)₂ solution containing NaCl for 7 days, and observe whether there is rust on the surface of the steel reinforcement, and measure the natural corrosion potential [47]. The electrochemical comprehensive evaluation method is to obtain the corrosion current of steel reinforcements by measuring the polarization curve under different concentrations of rust inhibitor, and the electrochemical impedance spectroscopy (EIS) method is to obtain the solution resistance and transfer resistance through analog circuit fitting, and calculate the corrosion inhibition efficiency [48]. The chloride salt dry wet cold heat cycle test is a simulation test method closer to the real corrosion environment, but the standards at home and abroad are not unified, and the test cycle is long, so the determination of

Table 1. Relevant technical indexes and evaluation methods of corrosion inhibitor

Standard Name	Performance evaluation criteria			
	Brine immersion	electrochemical performance	Dry-wet cold-heat cycle	Cl ⁻ penetration resistance
GB/T33803-2017	No rust on steel, no rust in glass bottles	Corrosion current <150 μA	Percentage of corroded area of steel reinforcement < 5%	—
YBT9232009	No rust on steel, no rust in glass bottles	Corrosion current <150 μA	—	—
JGJ/T192-2009	No corrosion of steel reinforcement	Corrosion current <150 μA	Percentage of corroded area of steel reinforcement < 5%	—
JT/T537-2018	No rust on steel, no rust in glass bottles	—	Percentage of corroded area of steel reinforcement < 5%	Cl ⁻ migration coefficient ratio ≤ 100%
GB31296-2014	No rust on steel, no rust in glass bottles	Corrosion power ratio ≤ 80% or 50%	Percentage of corroded area of steel reinforcement < 5%	Cl ⁻ migration coefficient ratio ≤100% or 85%

corrosion indicators is also different [49]. The rapid chloride migration method (RCM method) can accurately reflect the

permeability of Cl⁻ in concrete. This method mainly migrates Cl⁻ from the outside of the sample to the inside of the sample

under the action of external electric field. After a period of time, the sample splits along the axis and sprays AgNO₃ solution on the section. According to the generated AgCl precipitation, the chloride ion permeability is measured and the Cl⁻ diffusion coefficient of concrete is further calculated^[50]. See table 1^[51] for relevant technical indicators and corresponding evaluation methods of rust inhibitor.

5. Summary and Outlook

Corrosion and protection in marine engineering has been an important topic in the field of materials science and engineering technology. This paper systematically reviews the latest research progress of corrosion protection technology for reinforced concrete in marine environment, especially the application of anodic, cathodic and composite rust inhibitors and their mechanisms are deeply analyzed. The study shows that composite rust inhibitors exhibit superior corrosion protection performance due to their ability to inhibit both anodic and cathodic reactions and form a protective hydrophobic film on the surface of steel reinforcement. However, the longevity, economy and potential impact on concrete properties of rust inhibitors in practical applications still need to be further evaluated and optimized. Looking ahead, with the increasing requirements for the durability of marine engineering structures, the development of more efficient and environmentally friendly anticorrosion technologies will be the future direction of development. This includes, but is not limited to, the development of new green rust inhibitors, the application of intelligent protection systems, and the innovation of corrosion monitoring and assessment technologies. At the same time, it will be of great significance to strengthen multidisciplinary cross-fertilization and transform the research results in the fields of material science, chemical engineering and computer science into practical applications to enhance the corrosion prevention capability of marine engineering structures. Through continuous technological innovation and accumulation, we are expected to provide a more solid guarantee for the safe and stable operation of marine engineering structures.

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