The Anti-Corrosion Techniques and Material Optimization to Enhancing Durability of Concrete in Marine Environments

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Abstract. Concrete is widely used in the construction of marine engineering and has advantages that are difficult to replace. However, the harsh environment of the ocean poses a huge challenge to the durability of concrete. Methods to improve the durability of concrete need to be studied to increase the service life and safety of constructions and reduce maintenance costs. This paper aims to explore the mechanism of chloride ion corrosion and sulfate corrosion, which are common in marine environments. Four existing technologies for improving the durability of concrete are analyzed in detail, including the application of admixtures, surface curing technology, self-healing concrete curing and internal curing, and electrochemical methods. Finally, some future research directions are proposed. Through discussion, it was found that the addition of admixtures reduces erosion by reducing porosity, and its effect is closely related to the dosage. There are cutting-edge ideas for surface and internal maintenance methods by inducing microorganisms and bacteria. In addition, the electrochemical method can simultaneously achieve concrete repair and chloride ion removal, which has the advantages of high efficiency and low cost. This paper can provide a scientific basis and guidance for the design, construction and maintenance of concrete in marine environments, and make suggestions for future research directions.

Keywords: Marine environment, Durability, Concrete, Anti-Corrosion.

1. Introduction

Concrete is widely used in coastal buildings and important infrastructure such as coastal constructions and bridges due to its cost-effectiveness and versatility [1, 2]. However, the salt, humidity, corrosive chemicals, and other adverse factors in marine environment cause decreased durability of concrete structures, which leads to physical and chemical changes inside concrete, such as chloride ion erosion, sulfate erosion and freeze-thaw cycles [3]. These changes not only reduce the serviceability and safety of the structure, but also increase the maintenance cost and inconvenient in construction.

In order to address these challenges, researchers and engineers have been exploring optimization solutions to improve the durability of concrete. Methods include application of admixtures, surface protection, self-healing concrete and internal curing as well as electrochemical methods. In the application of admixtures, admixtures such as fly ash and silica fume will enhance the physical properties of concrete and improves its resistance to chemical attacks, ensuring longer service life in aggressive environments. As for the surface treatments, Dai et al. [4] argued that protective coatings and surface treatment technologies, such as surface preservatives and coating have benefits of economy and are convenient in construction. Other optimization methods such as self-healing concrete methods and electrochemical protection are also the focus of research.

Based on the background mentioned above, the purpose of this review paper is to summarize the current research progress and analyze different anti-corrosion optimization techniques. It aims to discuss their significance in improving the durability of concrete structures in marine environment in order to provide scientific basis and guidance for different stages of concrete construction and future research directions.

2. Factors affecting the durability of concrete

2.1. Corrosion of chloride ions

Due to the particularity of the marine environment, concrete structures face huge physical and chemical challenges [1]. Among them, the corrosion of chloride ions has a particularly great impact on reinforced concrete. Chloride ion corrosion is a complex process. The alkaline environment provided by the concrete material causes a dense passivating film to form on the surface of the steel reinforcement, thereby preventing the steel from being corroded [5]. However, the chloride ions from seawater have strong permeability, they enter the interior of the concrete structure and contact the surface of the steel through diffusion or capillary adsorption [1]. A large amount of chloride ions causes the pH of the steel reinforcement surface to drop, thereby destroying its passivating film and exposing the internal iron [6].

Simultaneously, the internal iron undergoes an oxidation-reduction reaction with the undamaged passivation film in water and oxygen. The passivation film acts as a cathode to obtain electrons and the iron surface can be seen as the anode [5]. The iron reacts to form ferrous ions (Fe^{2+}), and the released electrons migrate to the cathode area, where the oxygen is reduced to hydroxide ions (OH^-) [5].

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

Cathode reaction: $H_2O + 2e^- + \frac{1}{2}O_2 \rightarrow 2OH^-$

Additionally, Pratiwi et al. [1] argued that the soluble ferric chloride complex generated in the subsequent reaction dissolves and detaches from the steel reinforcement surface, further exposing the steel reinforcement. which accelerate the corrosion.

2.2. Corrosion of Sulfate

In addition to chloride ion erosion, the negative impact of sulfate on concrete cannot be ignored. The sulfate attack is meanly caused by the sulfate from the environment. Sulfate ions come into contact with cement hydrates and produce chemical reactions to produce components such as ettringite. These components expand in volume after crystallization, causing concrete cracks and causing hazards and dangers [7].

However, there are a large amount of magnesium ions and other metal ions in seawater, and due to the influence of tides, concrete may be in a continuous dry-wet cycle. Therefore, in the marine environment, it is necessary to consider the hazards of magnesium sulfate and dry-wet cycles. On the one hand, magnesium sulfate reacts with calcium silicate hydrate in cement to generate magnesium hydroxide and insoluble gypsum, which causes volume expansion. This reaction can continue until all calcium silicate hydrates have reacted, so the corrosion effect is stronger [8]. On the other hand, concrete in a dry-wet cycle environment is attacked by expansive crystalline substances when it is wet; when it is dry, the evaporation of water causes the concentration of salt solution in the concrete to increase from the outside to the inside, and when it exceeds its saturation state, corresponding salt crystals will be produced [9]. This cycle further exacerbates the erosion of concrete by sulfates.

3. Methods for improving concrete durability

3.1. Application of admixtures

There are many ways to improve the durability of concrete in marine environments from different angles. Among them, the application of mineral admixtures such as fly ash, silica fume and ground-granulated blast-furnace slag to concrete is argued to be effective and practical. Fly ash is formed by the combustion of coal powder. When it is added to concrete, it creates a denser microstructure than the original concrete, therefore reducing its porosity and increasing its durability [10]. Nath & Sarker [10] conducted experiments on concrete specimens with different fly ash ratios and tested the corresponding chloride ion permeability. It was found that replacing 30%-40% of cement with Class

F fly ash can significantly improve the resistance of concrete to chloride ion intrusion through research [10]. Additionally, Islam et al.,[11] concluded that concrete with 30% and 40% fly ash showed better performance under freeze-thaw cycles, including resistance to compressive strength degradation and resistance to chloride ion penetration.

Besides fly ash, silica fume is also a common admixture. Silica fume is a by-product generated during the high-temperature smelting of industrial silicon and ferrosilicon. It reacts with calcium hydroxide in cement to form calcium silicate hydrate (C-S-H), which reduces macropores and improves the concrete's impermeability [12]. Shekarchi et al. [13] explored the effect of silica fume content on concrete properties under different water-cement ratios and evaluated changes in chloride ion diffusion coefficient through field tests. Experiments show that 7.5% silica fume substitution can significantly reduce the chloride ion diffusion coefficient (by about 50%) [13]. However, when the silica fume ratio is between 7.5% and 12%, the effect on permeability is very low, and excessive silica fume may also cause shrinkage cracking of concrete [13]. Therefore, finding the right amount of mixing can maximize its performance.

3.2. Surface treatments

From another perspective, in addition to reducing the porosity of concrete, the method of reducing chloride ion permeability can also use surface coating to prevent chloride ion intrusion. Medeiros & Helene [14] found that polyurethane coating has a great effect on preventing the penetration of chloride ions through experiments, and it can reduce the intrusion of chloride ions by about 86%. Generally, concrete surface protection technologies can be roughly divided into three categories: coatings, pore blocker and pore liner as shown in Fig. 1 respectively [14]. The Fig. 1 (A) shows the principle of coatings, it prevents water from entering by covering the gap surface. The principle of pore blocker is shown in Fig. 1 (B). It reacts with substances in concrete to generate insoluble substances to block gaps and cracks, thereby achieving a waterproof effect. And the Fig. 1 (C) demonstrates the pore liner, it forms a hydrophobic film on the inner wall of the concrete pores instead of completely blocking the pores.

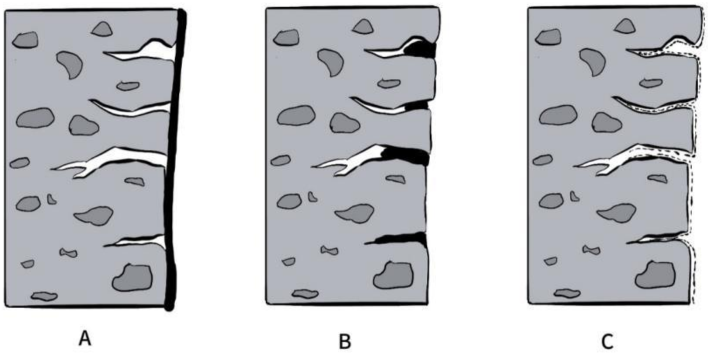

Fig. 1 Schematic diagram of different surface protection technologies [14]

The traditional methods including coatings, pore blocker and pore liner have several limitations. For example; it will cause inconvenience during the secondary construction, and the generated film joints may fall off and hollow. However, inducing microorganisms to achieve surface maintenance and coverage of concrete is considered to be a relatively innovative method. Kim et al. [15] explored the use of microorganisms to induce calcium carbonate deposition to fill cracks and pores in concrete. This method provides a new biotechnology approach to improve the durability of concrete in marine environments.

3.3. Internal maintenance and self-healing technology

The application and research and development of self-healing concrete has made great contributions to improving the durability of concrete. One of the methods to achieve self-healing of concrete is chemical self-healing agents, such as $CaO-NaAlO_2$, which exhibit excellent performance by accelerating crack closure and chemically binding aggressive ions such as chloride ions and sulfate ions. In the experiment, 5% CaO-$NaAlO_2$ was added to the concrete sample, which achieved 80% crack closure within one day [16]. In addition, in the detection of self-healing reaction products, it was found that this process can combine corrosive chemicals such as chloride ions, sulfates and magnesium ion through reactions, thereby reducing their harm [16]. Similar chemical self-healing agents can be used in marine environments, underground projects such as subway tunnels, etc., which can effectively extend the life of concrete and reduce maintenance costs. However, this method is limited in the degree to which it can repair large cracks. In addition, some chemical self-healing agents may pollute the environment, especially the chemicals produced during production and use.

The method of inducing microorganisms has been mentioned in the surface curing method. There are also similar biological methods in the internal curing of concrete. Its curing can reach deep into the cracks and inside the concrete, not just the surface. Khan et al. [17] used Halobacillus halophilus bacteria, embedded in expanded perlite as a bacterial carrier, and calcium lactate as a nutrient. The specimens were placed in fully submerged and tidal conditions. During the self-healing process, bacteria produce aragonite and brucite to fill the cracks. Experimental results found that the healing rate of cracks increased by 16% under complete immersion conditions and by 17% under tidal conditions, and the calcite layer had a higher hardness, which significantly enhanced the durability of the healing product [17]. Compared with chemical self-healing agents, this method is environmentally friendly and does not require human intervention, reducing construction and maintenance costs. This scheme provides a new perspective for improving the durability of concrete.

3.4. Electrochemical protection methods

Electrochemical protection methods such as cathodic protection and electrochemical deposition have been widely used to improve the durability of reinforced concrete structures in marine environments. Under the condition of an applied electric field, the cracks in concrete can be repaired by the insoluble substances such as ZnO and $Mg(OH)_2$ formed by the reaction [18]. In the reaction, the external electrode acts as the anode to attract the hydroxide near the steel bar. At this time, the seawater is regarded as a salt solution electrolyte, and the metal ions in it are attracted by the steel bar as the cathode. The two generate insoluble precipitation during the migration process, and after stabilization, they are deposited in the cracks of the concrete [18].

Huang et al. [19] pointed out that the electrochemical method using an applied electric field can also be used to extract chloride ions that penetrate into concrete. This process uses oxidation reaction to pull chloride ions to the external anode: at the steel bar, water gets electrons to generate hydroxide and hydrogen, and at the external anode, hydrogen ions and oxygen are generated [19]. In addition, when the pH value of the electrolyte is not high enough, chloride ions will also generate chlorine gas and be discharged from the pores of the concrete [19]. This method will not damage the concrete and has the advantages of low cost and high efficiency, especially when dealing with chloride ion corrosion.

4. Discussion

The development of methods to improve the durability of concrete in the ocean has been going on for a long time, and the technology has been iterating step by step. However, there are still some technical difficulties and application limitations at the current stage. In terms of the application of admixtures, the amount of admixtures will affect the mechanical properties of concrete and the initial construction cost. For example, if fly ash is added in large quantities due to its low reactivity, it will lead to a decrease in the compressive strength of concrete [1]. Therefore, further research is needed to determine the optimal amount of admixture for different components and different environments. For concrete self-healing and internal maintenance technology, the degree of crack recovery is limited, and it only treats the symptoms but not the root cause. Moreover, there are few cases of its application in actual engineering and it is still in the development stage. Its effect and performance still need further research.

Based on existing research and technology, the following possible research directions and development prospects are summarized:

(1) In terms of admixture materials, more new materials need to be tested. For existing materials such as fly ash, silica fume, etc., their usability in dealing with different marine environments such as dry-wet cycles and freeze-thaw cycles needs to be discussed. The appropriate amount of different admixture in different environments also needs to be summarized through more research.

(2) Among the concrete surface maintenance and self-repair measures mentioned above, biological technologies such as microbial and bacterial induction have been proposed as a cutting-edge method. This method is green and environmentally friendly, has a novel perspective, and has great potential in future applications.

(3) The post-inspection and repair process of concrete structures consumes a lot of costs. The combined application of smart sensors and electrochemical methods can provide a possibility of real-time detection of concrete corrosion and cracking and active repair, which can significantly reduce maintenance costs and extend the service life of concrete.

5. Conclusion

This article discusses the erosion mechanisms of common types of concrete corrosion in marine environments, summarizes and provides some methods to improve the durability of concrete in the ocean, and finally discusses the current limitations and future development prospects. In the analysis of corrosion mechanism, chloride ions enter the interior of reinforced concrete through penetration and capillary action, destroying the passivation film on the surface of the steel bar, exposing the internal iron and causing redox reactions, thus causing corrosion. Sulfate reacts with concrete materials to produce precipitate crystals that crack the concrete. This effect is more harmful when magnesium ions in seawater and dry-wet cycles are present.

Additionally, four methods to improve the durability of concrete are proposed, which are the application of admixtures, surface treatments, internal maintenance and self-healing technology, and electrochemical protection methods:

(1) By adding admixtures such as fly ash and silica fume, the resistance to chloride ion permeability of concrete is significantly improved. However, the amount of blends added will affect its cost and physical properties and needs to be further determined based on specific circumstances.

(2) Among the surface maintenance methods, coatings, pore blockers and pore liners are traditional methods that improve the anti-permeability of concrete, but may cause inconvenience during secondary construction. Additionally, chemical self-healing agents are used in self-healing concrete, which can effectively repair concrete cracks, but it is difficult to repair large cracks, and some self-healing agents may harm the environment. However, inducing bacteria and microorganism to fill internal and surface cracks is mentioned as a new technology. It has the advantages of being environmentally friendly and not requiring human intervention.

(3) The electrochemical method can simultaneously repair concrete cracks and remove chloride ions in concrete by applying an external electric field, and has high resistance to chloride ion corrosion.

In future research directions, the appropriate materials and dosage of the blend need to be further discussed, and the application of microorganisms and bacteria as a new perspective has great room for development. In addition, the combination of smart sensors and electrochemical methods may achieve real-time monitoring and autonomous repair, which has great potential.

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