

## Review Article

Maohua Zhang\*, Ronghua Xu, Ke Liu, and Shanghui Sun

# Research progress on durability of marine concrete under the combined action of $\text{Cl}^-$ erosion, carbonation, and dry–wet cycles

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**Abstract:** Marine concrete is a kind of construction material which is seeking its growing application in marine engineering. However, the marine concrete structures are exposed to aggressive environment and harmful ions. Therefore, it is crucial to improve the durability of marine concrete. The concrete structure located in the tidal zone is subjected to the dry–wet cycles caused by tidal action, chloride ion ( $\text{Cl}^-$ ) erosion in seawater, and  $\text{CO}_2$  erosion in air. When these factors work together, they cause great damage to the marine concrete structure. In view of the three environmental factors, namely,  $\text{Cl}^-$  erosion, carbonation, and dry–wet cycles, taking fly ash, fibers, and nanomaterials as examples, this article expounds the research status of durability of marine concrete, introduces the latest research progress, the addition of fibers, fly ash, and nanomaterials can improve the  $\text{Cl}^-$  corrosion resistance and dry–wet cycles resistance of marine concrete, while the addition of fly ash is unfavorable for carbonation resistance. And the future development trend of marine concrete is prospected.

**Keywords:**  $\text{Cl}^-$  erosion, carbonation, dry, wet cycles, marine concrete, durability

## 1 Introduction

Marine concrete refers to the concrete used in marine engineering construction. With the development and utilization of marine resources, many countries in the world

are increasing the construction of marine structures, such as cross-sea bridges, undersea tunnels, offshore drilling platforms, ports, and wharves. Concrete is the most common material in marine engineering construction, and it is very important to improve its durability. The marine concrete structures exposed to an aggressive environment, not only suffer from chloride ion ( $\text{Cl}^-$ ) erosion in seawater and carbon dioxide ( $\text{CO}_2$ ) erosion in air but also bear the effects of dry–wet cycles caused by tides action. The combined action of these environmental factors greatly reduces the durability of marine concrete structures and eventually makes them lose their bearing capacity. The investigation shows [1] that more than 80% of seaports and wharves in China have suffered from severe steel corrosion, and some reinforced concrete structures have been corroded within less than 10 years. The annual economic loss caused by corrosion of steel bars is more than 14.3 billion euros.

Scholars at home and abroad have done lots of research on the durability of concrete under the action of a single factor, and fruitful results have been achieved. However, the marine concrete structures in actual engineering do not work under the action of a single factor. When the marine concrete is subjected to the combined action of multi-factors, the damage is not a simple superposition of a single factor, and the interaction between various factors makes the deterioration mechanism of marine concrete more complicated. Therefore, it is very important to explore the deterioration mechanism of marine concrete under the combined action of various factors to improve the durability of marine concrete structures.

With the wide application of concrete, traditional concrete has been unable to meet the needs of engineering. Mixing different admixtures in concrete to prepare high-performance concrete (HPC) can effectively meet the needs of various working conditions. At present, the commonly used admixtures in engineering are fibers, fly ash, nanomaterials, silica fume, slag, etc.

Aiming at three aspects, namely,  $\text{Cl}^-$  erosion, carbonation and dry–wet cycles, and taking fly ash, fiber, and

\* Corresponding author: Maohua Zhang, School of Civil Engineering, Northeast Forestry University, Harbin, 150040, China, e-mail: zmh7716@163.com

Ronghua Xu, Ke Liu, Shanghui Sun: School of Civil Engineering, Northeast Forestry University, Harbin, 150040, China

nanomaterials as examples, this article summarizes the research status of the marine concrete durability under the action of single and multi-factors, and prospects the future research direction of marine concrete.

## 2 Research status of concrete durability

### 2.1 Research status of resistance of concrete to $\text{Cl}^-$ erosion

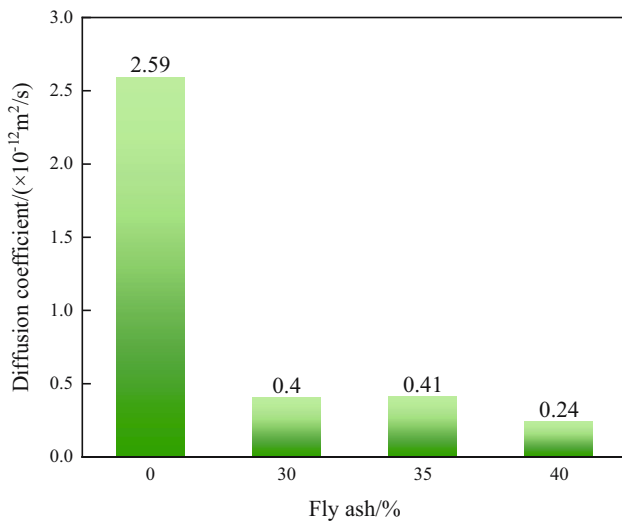
There are a lot of chloride salts such as  $\text{NaCl}$  and  $\text{MgCl}_2$  in seawater, and the biggest hazard to marine concrete is mainly the corrosion of steel bars in concrete caused by  $\text{Cl}^-$ .  $\text{Cl}^-$  can combine with hydration products in concrete to generate Friedel salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ), which causes damage to concrete. Due to the existence of concentration gradient between the surface and inside of concrete,  $\text{Cl}^-$  will diffuse into concrete along the capillary pores and cracks and reach the surface of steel bars. When the  $\text{Cl}^-$  concentration reaches a certain value, it will destroy the passivation film on the surface of steel bar, causing the steel bar to corrode. With volume expansion, the value expansion will cause the concrete to crack, which seriously affects the service life of concrete structures. Over the years, scholars at home and abroad have conducted a large number of  $\text{Cl}^-$  erosion tests on different types of concretes, and analyzed the effects of different admixtures on the  $\text{Cl}^-$  erosion resistance of concrete.

Adding fibers into concrete can effectively improve the  $\text{Cl}^-$  erosion resistance of concrete. Through experimental studies, Berrocal et al. [2] found that the addition of steel fibers and polyethylene fibers changed the corrosion pattern of steel bars in concrete, improved the compactness of concrete, and potentially reduced the depth of  $\text{Cl}^-$  penetration and the extent of local corrosion. Frazao et al. [3] conducted the  $\text{Cl}^-$  penetration resistance test on steel fiber concrete and believed that the incorporation of steel fibers could make the concrete resist  $\text{Cl}^-$  erosion. Yehia et al. [4] studied the effect of steel fibers on the  $\text{Cl}^-$  corrosion resistance of concrete, and the results showed that although the electrical conductivity of steel fiber concrete is lower, it is still improved compared with ordinary concrete, so the addition of steel fibers can improve the  $\text{Cl}^-$  erosion resistance of concrete. Meng [5] studied the influence of steel fiber content on  $\text{Cl}^-$  permeability of HPC, and found that an appropriate amount of

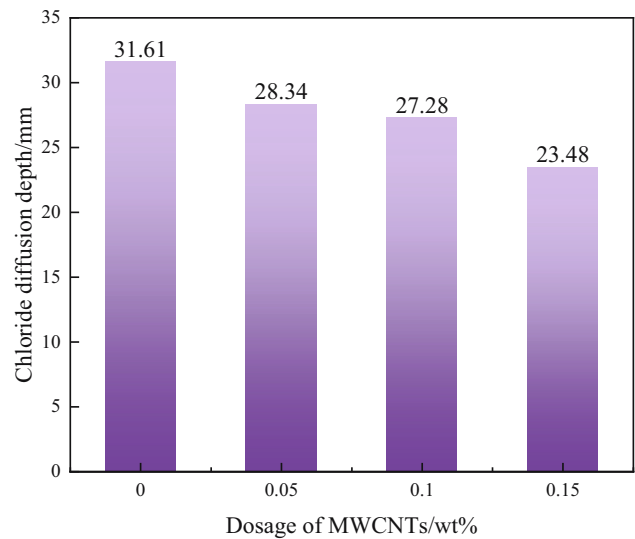
steel fibers (0–2%) can reduce the depth of  $\text{Cl}^-$  erosion in HPC and the  $\text{Cl}^-$  diffusion coefficient of concrete, and improve its ability to resist  $\text{Cl}^-$  erosion. Wang et al. [6] found that basalt fibers effectively inhibit the generation and development of chloride erosion cracks and reduce the  $\text{Cl}^-$  migration rate. Su et al. [7] studied the  $\text{Cl}^-$  diffusion performance of basalt–polypropylene (PP) fibers reinforced concrete, and the results showed that an appropriate amount (0.1%) of hybrid fibers reduces the  $\text{Cl}^-$  concentration in concrete, while excessive hybrid fibers will increase the  $\text{Cl}^-$  concentration at different depths in concrete.

The addition of fly ash can significantly improve the  $\text{Cl}^-$  erosion resistance of concrete. Liu et al. [8] showed that the pozzolanic effect of fly ash leads to the reduction in concrete porosity, which in turn reduces the  $\text{Cl}^-$  permeability of concrete. The research conclusion of Shaikh and Supit [9] showed that the  $\text{Cl}^-$  permeability of concrete at 28 and 90 days of age can be reduced by 18 and 65%, respectively, after the addition of 8% ultrafine fly ash in concrete. Poon et al. [10] concluded that 45% fly ash reduces the  $\text{Cl}^-$  permeability of concrete at 28 and 90 days of age by 62 and 84%, respectively. Fan et al. [11] studied the  $\text{Cl}^-$  permeability resistance of concrete with high dosage fly ash (30–40%) by using 12 year field exposure tests in South China. As shown in Figure 1, the addition of fly ash significantly reduces the  $\text{Cl}^-$  diffusion coefficient of concrete and improves the resistance of concrete to  $\text{Cl}^-$  penetration. For HPC mixed with 30–40% fly ash, its chloride ion diffusion coefficient is reduced by more than 6 times. Yang et al. [12] tested the durability of  $\text{Cl}^-$  diffusion performance and other indicators of typical components of a cross-sea bridge in South China that had been in service for 12 years. The study showed that fly ash could significantly improve the  $\text{Cl}^-$  erosion resistance of concrete, and the  $\text{Cl}^-$  diffusion coefficient of fly ash HPC was about 6 times lower than that of ordinary concrete. Wang et al. [13] and Nath and Sarker [14] found that the  $\text{Cl}^-$  permeability of concrete decreases significantly after fly ash is added, and the optimal dosage of fly ash is 40%.

The addition of nanomaterials can also improve the resistance of concrete to  $\text{Cl}^-$  erosion. Chithra et al. [15] studied the effect of nano- $\text{SiO}_2$  on the  $\text{Cl}^-$  infiltration resistance of concrete, and found that the addition of nano- $\text{SiO}_2$  improved the  $\text{Cl}^-$  infiltration resistance of concrete. Zhang and Hui [16] studied the  $\text{Cl}^-$  permeability resistance of pavement nano-concrete and found that the addition of nano-materials enhanced the  $\text{Cl}^-$  permeability resistance of concrete, and the  $\text{Cl}^-$  permeability resistance of nano- $\text{TiO}_2$  concrete was higher than that of nano- $\text{SiO}_2$  concrete with the same dosage. Lei and Feng [17] found that compared with ordinary concrete,



**Figure 1:** Effect of fly ash on chloride diffusion coefficient of concrete [11].



**Figure 2:** Chloride diffusion depth of concrete with different dosage of MWCNTs [20].

nano-TiO<sub>2</sub> concrete has better resistance to chloride diffusion. Qian et al. [18] found through experiments that the addition of nano-CaCO<sub>3</sub> can effectively fill the pores, make the concrete compact, and significantly improve the Cl<sup>-</sup> infiltration resistance of concrete. Shi et al. [19] studied the Cl<sup>-</sup> permeability resistance of multi-walled carbon nanotubes (MWCNTs) reinforced concrete, and concluded that the free Cl<sup>-</sup> concentration in each depth of concrete decreased, and the Cl<sup>-</sup> diffusion coefficient decreased with the increase in the dosage of MWCNTs, and the addition of MWCNTs improved the Cl<sup>-</sup> permeability resistance of concrete. Figures 2 and 3 show the chloride diffusion depth and unsteady chloride migration coefficient  $D_{\text{RCM}}$  measured in concrete with different MWCNT contents [20]. Compared with the control group (0 wt%), when the content of MWCNTs was 0.05, 0.10, and 0.15 wt%, the 28 days chloride diffusion depth of concrete decreased by 10.3, 13.7, and 25.7%, and the  $D_{\text{RCM}}$  decreased by 11.2, 14.5 and 19.1%, respectively. The incorporation of MWCNTs effectively enhanced the Cl<sup>-</sup> penetration resistance of concrete, and with the increase in MWCNTs' content, the enhancement effect also increased gradually.

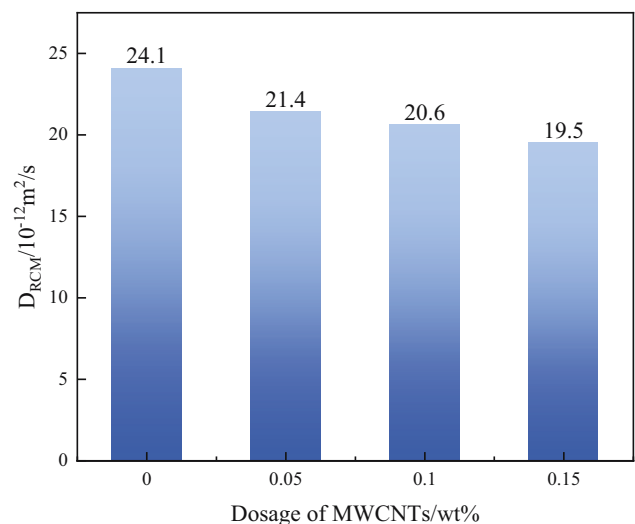
It can be seen that the addition of fibers, fly ash, and nanomaterials can improve the Cl<sup>-</sup> infiltration resistance of concrete, and only the appropriate dosage can have a good effect on the resistance of concrete to Cl<sup>-</sup> erosion.

## 2.2 Research status of concrete carbonation

The product formed by cement hydration comes into contact with CO<sub>2</sub> in air, and a chemical reaction occurs to

generate water and carbonate, which reduces the alkalinity of concrete. Such a process is called the carbonation of concrete, also known as the neutralization of concrete. Concrete is eroded by CO<sub>2</sub> in air, so carbonation is an unavoidable process of concrete. Carbonation will increase the shrinkage of concrete, resulting in cracks, thereby greatly reducing the durability of concrete.

The carbonation resistance of concrete can be improved by adding the appropriate amount of steel fibers. Pan [21] conducted an experimental study on the carbonation performance of steel fibers reinforced concrete, and found that



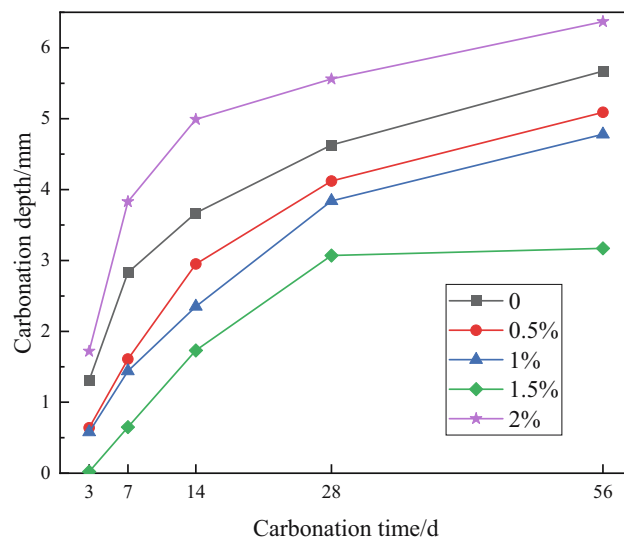
**Figure 3:** Unstable chloride ion diffusion coefficient  $D_{\text{RCM}}$  of concrete with different dosage of MWCNTs [20].

the addition of steel fibers optimizes the pore structure of concrete and improves the carbonation resistance of concrete. Zhang et al. [22] studied the influence of steel fibers dosage on the carbonation performance of HPC through a rapid carbonation test. The results showed that the addition of steel fibers could improve carbonation resistance of concrete and reduce carbonation rate, and the inhibition of carbonation was more obvious when the dosage of steel fibers was 2.0%. Miao [23] carried out the rapid carbonation test of steel fibers concrete, and the results showed that adding steel fibers into concrete improves the micro-pore structure of concrete and makes the internal structure more compact. When the steel fiber content varies from 0 to 2%, the carbonation resistance of concrete is best with a content of 1.5%. Table 1 and Figure 4 show the pore structure parameters and carbonation depth of concrete with different steel fiber contents [24]. When the fiber content is 0–1.5%, with the increase in fiber content, the total porosity, total pore volume, and total pore area decrease, and the pore structure of the concrete matrix develop in a better direction, and the carbonation depth also decreases. When the fiber content is 1.5%, the concrete has the optimal pore structure, the total porosity decreases by 32.13% compared with ordinary concrete, the total pore volume and area decrease by 28.54 and 42.78%, respectively, and the carbonation rate is the lowest. Therefore, it can be seen that the optimal steel fiber content is 1.5%.

The addition of fly ash will reduce the carbonation resistance of concrete. The addition of fly ash reduces the ability of cementation materials to produce  $\text{Ca}(\text{OH})_2$ , and its secondary hydration consumes the generated  $\text{Ca}(\text{OH})_2$ , which reduces the basicity of concrete, and thus weakens the carbonation resistance of concrete [25–28]. For example, the experimental results of Liu et al. [29] showed that with the increase in the amount of fly ash, the carbonation depth of concrete increases gradually, and the growth rate is faster in the early stage (Figure 5). Zhang et al. [30] found that the addition of fly ash has a great influence on the carbonation depth, and the greater the fly ash dosage, the deeper the carbonation depth. Byfors [31] found that the carbonation

**Table 1:** Steel fiber reinforced concrete pore structure parameters [24]

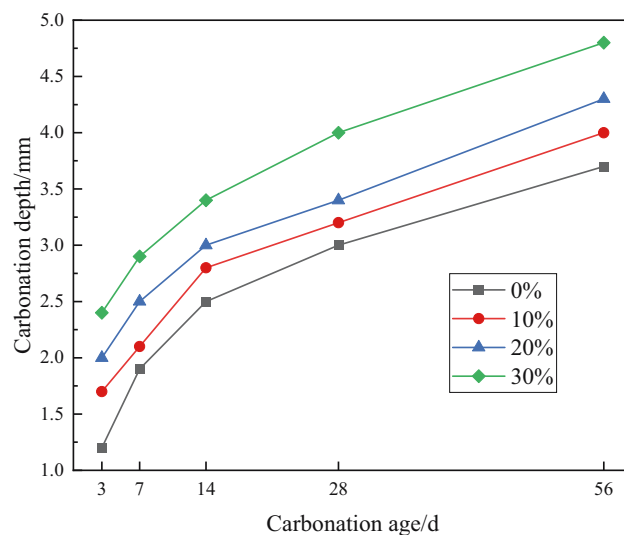
Dosage	0	0.5%	1%	1.5%	2%
Total porosity/%	15.22	14.17	12.69	10.33	14.60
Total pore volume ( $\text{mL}\cdot\text{g}^{-1}$ )	0.0785	0.0664	0.0620	0.0561	0.0681
Total pore area ( $\text{m}^2\cdot\text{g}^{-1}$ )	23.63	19.39	17.04	13.52	18.21



**Figure 4:** Carbonation depth curve of concrete with different steel fiber contents [24].

rate of fly ash concrete is higher than that of ordinary concrete. Liu and Zhu [32] and Zhao et al. [33] found that both the carbonation depth and carbonation rate of concrete increased with the increase in the fly ash content.

The addition of an appropriate amount of nanomaterials is beneficial to improve the carbonation resistance of concrete. Wang [34] and Zhang et al. [35] studied the effect of different dosages of nano- $\text{SiO}_2$  on the carbonation resistance of concrete, and the results showed that nano- $\text{SiO}_2$  with a certain dosage range could improve the carbonation resistance of concrete, but if it is excessive, it will be detrimental to the carbonation resistance of concrete.



**Figure 5:** Relationship between carbonation depth and carbonation age [29].

Gu *et al.* [36] conducted a 180 days carbonation test on nano-TiO<sub>2</sub> concrete and found that no carbonation was detected in any of the specimens. Zhang [37] found through research that the appropriate amount of nano-TiO<sub>2</sub> can reduce the carbonation depth of concrete at each age, and the optimal amount is 1%. At the same time, there is a critical value of nano-TiO<sub>2</sub>, i.e., 3%, when the dosage exceeds the critical value, the carbonation depth of concrete will increase. Li *et al.* [38] carried out a carbonation test on nano-CaCO<sub>3</sub> concrete, and tested the microscopic pore structure of concrete by mercury intrusion porosimetry. It is found that nano-CaCO<sub>3</sub> filled pores and promoted hydration, reduced porosity, and refined micro-pores. And 3% is the best dosage to improve the carbonation resistance of concrete.

It can be seen that the addition of steel fibers, fly ash, and nanomaterials can both improve the pore structure of concrete and make the internal structure of concrete more compact. The active effect of fly ash and nanomaterials can also promote the hydration of cement, thus improving the carbonation resistance of concrete.

### 2.3 Research status of concrete dry-wet cycles

In the dry-wet cycles, the deformation of concrete exhibits the characteristics of dry shrinkage and wet expansion, that is, the concrete shrinks in the dry stage, while it expands in the wet stage [39]. After a complete dry shrinkage and wet expansion process, concrete will produce irreversible deformation, resulting in micro-cracks in concrete. After several dry-wet cycles, micro-cracks continue to expand, forming a continuous reticular hole structure system, resulting in macroscopic cracking of concrete and reducing its long-term performance [40]. Table 2 shows the changes in the percentage of various types of holes in concrete samples with the number of cycles [41]. In the early stage of dry-wet cycles, the cement particles are hydrated, and the hydration products fill the

original large pores, resulting in a decrease in the proportion of harmful pores and multi harmful pores, and an increase in the proportion of innocuous pores and less harmful pores. With the increase in dry-wet cycles, the damage caused by it accumulates, which makes the proportion of harmful holes in concrete to increase and harmless holes to decrease, and finally shows the characteristics of pore coarsening.

Chen *et al.* [42] showed that, after dry-wet cycles, the dynamic elastic modulus of concrete decreases and tends to be stable, and the weight loss rate of concrete increases and gradually slows down. Li *et al.* [43] explored the main mechanism of water migration on the concrete surface under dry-wet cycle conditions through theoretical derivation and numerical analysis. Zhang *et al.* [44,45] conducted experimental studies and numerical simulations on the dry-shrinkage and wet-expansion characteristics and internal moisture distribution of concrete under the action of dry-wet cycles, and concluded that the internal relative humidity of concrete changes periodically during the dry-wet cycles. When the concrete is wet, the internal humidity increases rapidly in a short time, and then the relative humidity reaches a stable level; during the drying process, the internal relative humidity does not drop immediately, but gradually decreases.

In domestic and foreign research works, the study of dry-wet cycles are often accompanied by the study of harmful salts erosion. Concrete is a porous hydrophilic material into which all soluble salts can penetrate and transform into volume-expanding crystals under certain humidity and temperature. When the salt solution is in contact with the surface of concrete, the solution rises to the surface of concrete along the capillary. When water evaporates, salt in the corrosion solution reaches supersaturation and precipitates crystals in the capillary. Because of the precipitation crystallization of salt, the expansion force causes the concrete hole wall to bear great compressive stress, thus accelerating the destruction of concrete. Studies have shown that in the repeated dry-wet cycles of salt solution, concrete will undergo

**Table 2:** Percentage of various types of holes in concrete at different dry-wet cycles [41]

Number of dry-wet cycle	Sample number	Porosity (%)	Innocuous pore (<20 nm) (%)	Less harmful pore (20–50 nm) (%)	Harmful pore (50–200 nm) (%)	Multi harmful pore (>200 nm) (%)
0	1	4.9986	17.35	27.93	36.02	18.70
10	2	2.4948	23.23	33.18	25.66	17.93
20	3	2.8318	20.45	20.70	26.46	32.39
40	4	3.6293	19.32	13.48	27.05	40.15



serious physical corrosion of salt crystallization, as well as chemical corrosion caused by the interaction of various particles, which makes the corrosion process extremely complex [46].

Among the studies on concrete deterioration under the combined action of dry–wet cycles and corrosive medium, sulfate dry–wet cycles are the most widely studied. For example, Cody et al. [47] found that the corrosion rate of sulfate in concrete specimens under dry–wet cycles is much faster than that of solution-soaked concrete, which is because the dry–wet cycles aggravate the crystalline expansion of salt, thereby accelerating the destruction of concrete [48–50]. Yuan et al. [51] believed that the dry–wet cycles changed the migration patterns and erosion process of sulfate in concrete, which aggravated the deterioration of concrete performance. He et al. [52] studied the damage mechanism of concrete under the action of sulfate attack and dry–wet cycles, and found that the dry–wet cycles accelerated the physical crystallization and dissolution of sulfate, and aggravated the damage and deterioration of concrete.

The addition of fibers can improve the resistance to dry–wet cycles of concrete. Fu [53] found that adding PP fibers effectively improved the dry–wet resistance of concrete, and the optimal dosage is 2%. Li and Zhang [54] studied the sulfate erosion resistance of basalt–PP hybrid fibers reinforced concrete under the action of dry–wet cycles. The results showed that fibers blending can improve the balance of three-dimensional distribution of fibers and the coordination between aggregate and fibers from different levels. It makes the concrete denser, and has a significant improvement effect on the concrete's resistance to sulfate dry–wet cycles damage.

Adding fly ash into concrete can improve concrete's resistance to dry–wet cycles. Liu et al. [55] discussed the damage degree of fly ash concrete and found that adding fly ash can improve the dry–wet cycle resistance of concrete, and 20% fly ash has the most significant effect on improving the resistance of the dry–wet cycle. Zhang et al. [56] conducted exposure tests in the natural tidal environment, measured the microstructure parameters of fly ash concrete after different exposure times, and found that fly ash effectively reduced the porosity of concrete and improved its pore size distribution. A denser pore structure is formed, which improves the durability of concrete.

The dry–wet cycling resistance of concrete can be improved by adding nanomaterials. Li and Gao [57] showed that the corrosion resistance of concrete mixed with 1% nano- $\text{CaCO}_3$  was greatly improved after dry–wet cycles in a corrosive salt solution. The addition of nano- $\text{SiO}_2$  reduced

the formation of  $\text{Ca(OH)}_2$  and the alkalinity of cement slurry delayed the crystallization of ettringite and gypsum, and improved the corrosion resistance of concrete. Huo and Ding [58] studied the influence of nano- $\text{CaCO}_3$  on the dry–wet cycles performance of recycled concrete, and the study showed that nano- $\text{CaCO}_3$  improved the compactness of recycled concrete and thus improved its dry–wet cycles resistance. It can be seen that adding nanomaterials into concrete can improve the dry–wet cycles resistance of concrete to a certain extent.

Although a lot of achievements have been made in the research on the dry–wet cycles of concrete, the dry–wet cycle methods involved in these research works are self-developed and there is no unified standard. Due to different test methods, the comparability between these test results is poor. Now some scholars began to explore the dry–wet cycles system. Qiao et al. [59] studied the influence of dry–wet cycles on sulfate erosion of concrete, and the results showed that the shorter the dry–wet cycles period, the faster the concrete deterioration rate. Guo et al. [60] designed four different dry–wet ratios and conducted a study on the dry–wet cycles system of concrete based on sulfate erosion, and found that the wetting process and the drying process affect each other. The increase in wetting time can make the micro-pores and micro-cracks in concrete fill with expansion products earlier, while the increase in drying time can make the crystal growth to generate a greater crystallization pressure, and the interaction between the two will eventually lead to the deterioration of the concrete.

## 2.4 Research status of $\text{Cl}^-$ erosion of concrete under dry–wet cycles condition

Concrete structures in the ocean can be divided into underwater zone, tidal zone, splash zone, and atmospheric zone according to their contact with sea water (Figure 6), and different zones suffer from different degrees of  $\text{Cl}^-$  erosion. The concrete structures in the tidal zone are in a saturated, semi-saturated, and dry state due to the alternation of dry and wet conditions, and at the same time, it is eroded by  $\text{Cl}^-$  in seawater, which greatly accelerates the damage of concrete structures.

Studies have shown that the dry–wet cycles accelerate the  $\text{Cl}^-$  infiltration into concrete structures. Zhang and Yu [61] took salt lake brine as erosion medium and carried out dry–wet cycle tests. The results showed that the diffusion rate of  $\text{Cl}^-$  into concrete is accelerated by the dry–wet cycles. The increase in the number of wet–dry

cycles resulted in the decrease in  $\text{Cl}^-$  diffusion velocity as a power function. Hua *et al.* [62] showed that the increase in the number of dry–wet cycles significantly aggravated the diffusion process of  $\text{Cl}^-$ . When the number of dry–wet cycles reached 300, the erosion of  $\text{Cl}^-$  would lead to rapid and obvious degradation of the performance of concrete beams. Ye *et al.* [63] measured the  $\text{Cl}^-$  invasion in outdoor concrete exposed to the marine environment for a long time, and found that the service life of concrete in the underwater area was longer than that in the splash area. Li and Li [64] conducted a test of  $\text{Cl}^-$  transport in concrete under alternating dry and wet conditions. The study showed that  $\text{Cl}^-$  intrusion in concrete under alternating dry and wet conditions is much more serious than permanently immersed in chloride solution. Lin and Liu [65] carried out a study on  $\text{Cl}^-$  transportation in concrete under alternate wet and dry conditions, and found that the  $\text{Cl}^-$  concentration in the alternating wet and dry environment is much higher than that when the concrete has been in contact with salt water. Hu and Du [66] studied the effect of  $\text{Cl}^-$  infiltration resistance of concrete under the coupled action of chloride salts and dry–wet cycles, and found that the  $\text{Cl}^-$  diffusion rate in concrete under alternating wet and dry environment is much higher than that when the concrete has been in contact with the solution. This further indicates that the dry–wet cycles accelerate the corrosion of concrete by  $\text{Cl}^-$ .

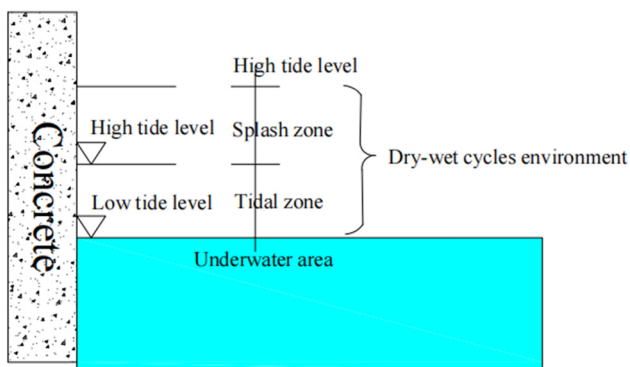
However, some scholars believe that the dry–wet cycles improve the  $\text{Cl}^-$  infiltration resistance of concrete. For example, Wang *et al.* [67] introduced “concrete pore sinuosity” to represent the pore structure characteristics of concrete, which is defined as the ratio of pore specific surface area to pore volume, reflecting the tortuosity of microscopic pores inside the material, as shown in equation (1):

$$\text{PSI} = \frac{\text{SSA}}{\text{VC}}, \quad (1)$$

where PSI is the pore sinuosity ( $10^6 \text{ m}^{-1}$ ); SSA is the specific surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ ); and VC is the void content ( $\text{cm}^3 \cdot \text{g}^{-1}$ ).

For pores of the same volume, a large porosity sinuosity indicates that the pores are long and thin, while small porosity sinuosity indicates that the pores are short and thick. There is a negative correlation between concrete pore sinuosity and concrete  $\text{Cl}^-$  diffusion coefficient, that is, the greater the concrete pore sinuosity of concrete, the better the  $\text{Cl}^-$  permeability resistance. Through experiments, it is found that the dry–wet cycles promote the increase in pore sinuosity, prolong the  $\text{Cl}^-$  permeation path, and improve the  $\text{Cl}^-$  permeation resistance of concrete. Mo and Zhu [68] used the unsteady  $\text{Cl}^-$  migration coefficient to characterize the  $\text{Cl}^-$  infiltration resistance of concrete under dry–wet cycle conditions, and obtained the same results as the literature [67]. At present, due to the differences in test conditions, analysis methods, and test methods, a unified view has not been formed at home and abroad. Besides, the differences in test conclusions are obvious, so the research results have little reference value. Therefore, it is necessary to conduct a standardized study on concrete durability under the joint action of the two, propose a standard test method, provide a basis for future test data sharing, and conduct regular verification of each test result according to the standard.

Adding an appropriate amount of fibers into concrete can improve the  $\text{Cl}^-$  permeability resistance of concrete under wet–dry cycle conditions. Sun *et al.* [69] found in their study that PP fibers can significantly reduce the number of harmful pores in concrete, and its hydrophobicity can inhibit the migration of  $\text{Cl}^-$  with water, so that concrete shows good resistance to dry–wet cycles and  $\text{Cl}^-$  erosion. Wang [70] adopted the dry–wet cycles method to simulate the marine environment and came to the conclusion after analyzing the test results: the addition of PP fibers has a great influence on the pore structure of concrete. Adding 0.1% PP fibers to concrete can greatly improve the concrete’s ability to resist chlorine salt dry–wet cycles damage; however, adding excess PP fibers (with a content of more than 0.3%) will reduce this ability. The results showed that under the same dry–wet cycles, the improvement effect of fibers on the  $\text{Cl}^-$  permeability of concrete increases first and then decreases with the increase in fibers’ dosage. With the increase in dry–wet cycles period, the maximum immersion depth and free  $\text{Cl}^-$  content of concrete with the same fiber content increased. Wei [71] studied the  $\text{Cl}^-$  diffusion properties of fiber-reinforced concrete



**Figure 6:** Schematic diagram of marine concrete service environment.

under the action of alternating dry and wet conditions and found that compared with plain concrete, the addition of steel fibers and imitation steel fibers has an inhibitory effect on the permeability of  $\text{Cl}^-$  in concrete, but excessive fiber content will increase the  $\text{Cl}^-$  diffusion coefficient and reduce the  $\text{Cl}^-$  erosion resistance of concrete.

The addition of fly ash can improve the  $\text{Cl}^-$  permeability resistance of concrete under dry–wet cycle conditions. Gao et al. [72] studied the effect of fly ash dosage on the  $\text{Cl}^-$  diffusivity of concrete based on the field exposure test in the natural tidal environment, and found that the  $\text{Cl}^-$  apparent diffusion coefficient of concrete and instant diffusion coefficient decreases with the increase in fly ash dosage, which indicates that the  $\text{Cl}^-$  resistance of fly ash concrete is stronger in the early stage, and is gradually weakened in the later stage. Zhang et al. [73] and Petcherdchoo [74] found that the addition of fly ash can effectively reduce the concentration of  $\text{Cl}^-$  in concrete through field exposure tests under the environment of marine tidal. Chen et al. [75] found that the  $\text{Cl}^-$  transport rules of fly ash concrete changed significantly under the action of dry–wet cycles, from the original diffusion-based transport form to the capillary action-based transport form.

An appropriate dosage of nanomaterials can improve the  $\text{Cl}^-$  infiltration resistance of concrete under dry–wet cycle conditions. Zhang and Sun [76] studied the  $\text{Cl}^-$  permeability resistance of nano-concrete under the action of dry–wet cycles, and showed that the dry–wet cycles accelerated the migration of  $\text{Cl}^-$  in marine concrete, and nanomaterials could improve the  $\text{Cl}^-$  resistance of concrete under the action of dry–wet cycles. Han et al. [77] found that the addition of nano-modified mineral admixtures can effectively reduce the porosity of concrete, improve the binding capacity of  $\text{Cl}^-$ , and reduce the influence of dry–wet cycles on concrete. Ji et al. [78] studied the durability of nano- $\text{SiO}_2$  modified concrete under the combined action of dry–wet cycles and salt-bine solution immersion. The results showed that the  $\text{Cl}^-$  permeability coefficient decreases gradually with the increase in nano- $\text{SiO}_2$ . When the nano- $\text{SiO}_2$  dosage is 2%, the  $\text{Cl}^-$  permeability coefficient of concrete is reduced by 55% compared with the reference sample. When the content exceeds 2%, the improvement effect does not change significantly.

The combined action of dry–wet cycles and  $\text{Cl}^-$  erosion accelerates the deterioration of concrete compared to that due to the action of each individually. However, there is still controversy about the effect of dry–wet cycles on the  $\text{Cl}^-$  permeability of concrete. A large number of studies have shown that the appropriate dosage of fibers,

fly ash, and nanomaterials can significantly improve the  $\text{Cl}^-$  erosion resistance of concrete.

## 2.5 Research status of concrete carbonation under dry–wet cycle conditions

Under the influence of ocean tides, concrete is susceptible to damage by dry–wet cycles. Under the condition of dry–wet cycles, due to the capillary siphon effect, the migration of external harmful ions to the interior of the concrete is accelerated, causing damage to concrete, thereby accelerating the carbonation process of concrete. At the same time, under the action of dry–wet cycles, the crystalline stress generated by cement hydration is easy to accumulate in concrete, resulting in the generation of micro-cracks, deteriorating the pore structure, and reducing the carbonation resistance of concrete [79].

Adding an appropriate amount of fly ash into concrete can reduce the effect of dry–wet cycles on carbonation of concrete. Feng et al. [80] found in the study on the durability of fly ash concrete under dry–wet–carbonation coupled damage, adding fly ash would reduce the alkalinity of concrete and change its internal pore structure, and the carbonation resistance of concrete would decrease with the increase in fly ash. The carbonation depth of concrete increases with the number of dry–wet cycles and presents different power function relationships with the number of cycles (Figure 7). Wu [81] conducted a carbonation test of fly ash concrete under the action of

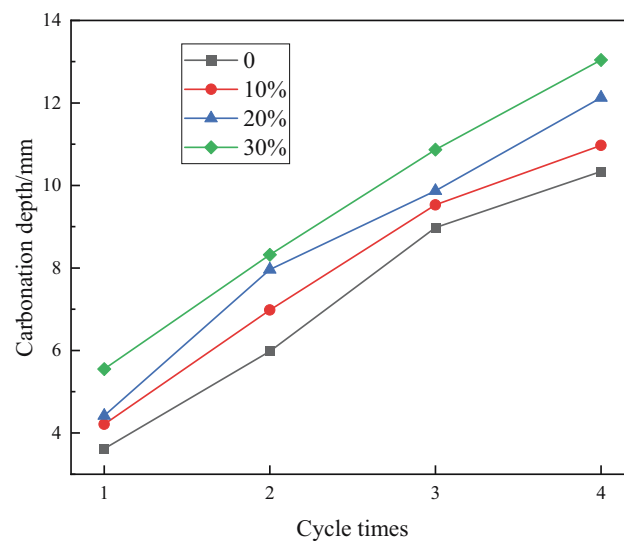


Figure 7: Curve of carbonation depth of fly ash concrete [80].



dry–wet cycles. The results showed that with the increase in the number of dry–wet cycles, the carbonation depth increased in a power function. Zheng *et al.* [82] studied the durability of high-dosage fly ash concrete under the coupled action of dry–wet cycles and carbonation, and the results showed that the coupling effect caused further damage to the concrete, and the addition of a large amount of fly ash would reduce the carbonation resistance of concrete. Xu *et al.* [79] simulated the ocean tidal environment and studied the carbonation behavior of concrete with different mix ratios under dry–wet cycle conditions. The results showed that the dry–wet cycles accelerated the carbonation process of concrete. However, the addition of fly ash can reduce the influence of dry–wet cycles on the carbonation resistance of concrete.

It can be seen that the dry–wet cycles will accelerate the carbonation of concrete and cause further damage to concrete. The addition of fly ash can significantly improve the internal pore structure of concrete and weaken the effect of the dry–wet cycles on the carbonation resistance of concrete. At present, there is no report on fibers and nano-materials to improve the carbonation resistance of concrete under dry–wet cycle conditions. In addition, the current research on concrete under the combined action of dry–wet cycles and carbonation are all laboratory experiments, and some experiments are greatly affected by human factors, and there are many accidental factors, which cannot guarantee the accuracy of the test results. Therefore, it is necessary to carry out finite element simulation research on concrete under the interaction of dry–wet cycles and carbonation, explore the change law of concrete microstructure and internal deterioration mechanism under the coupling of the two, verify the results of simulation test and theoretical analysis, and improve the reliability of the results.

## 2.6 Research status of concrete under the combined action of $\text{Cl}^-$ erosion and carbonation

With the development and construction of coastal areas, the high concentration of  $\text{CO}_2$  in the air and  $\text{Cl}^-$  in seawater make the service environment of concrete structures worse. Many scholars have carried out extensive research on the durability of concrete structures under the combined action of  $\text{Cl}^-$  erosion and carbonation.

Some scholars believe that carbonation of concrete hinders the diffusion of  $\text{Cl}^-$ . Tumidajski and Chan [83] found that the presence of  $\text{CO}_2$  reduced the diffusion performance of  $\text{Cl}^-$  in ordinary concrete by immersing

concrete in a sulfate–chloride composite solution flushed with  $\text{CO}_2$  gas. Puatatsananon and Saouma [84] used the method of alternating chloride salt solution immersion and carbonation test to simulate the marine environment, and studied the effect of carbonation on  $\text{Cl}^-$  erosion. It is believed that carbonation generates calcium carbonate, which reduces the pores of concrete, thereby hindering  $\text{Cl}^-$  diffusion in concrete. Zheng *et al.* [85] obtained the same result through research: carbonation reduces the internal porosity of concrete, improves the compactness of concrete, and reduces the  $\text{Cl}^-$  diffusion coefficient. Chindaprasirt *et al.* [86] studied the effect of  $\text{CO}_2$  on the  $\text{Cl}^-$  permeability coefficient and  $\text{Cl}^-$  diffusion coefficient of cement mortar, and found that carbonation slowed down the diffusion of  $\text{Cl}^-$ . Goñi and Guerrero [87] conducted an accelerated carbonation test on Friedel salt in cement slurry containing 3% NaCl, and found that although carbonation decomposed Friedel salt, the free  $\text{Cl}^-$  content did not increase significantly, indicating that carbonation hinders the diffusion of  $\text{Cl}^-$ . Hassnan [88] carbonated the cement paste first and then immersed it in chloride salt solution, and found that the ability of the test block after carbonation to combine with  $\text{Cl}^-$  was almost zero, which further demonstrated that carbonation hindered the diffusion of  $\text{Cl}^-$  in concrete.

Other scholars believe that carbonation of concrete promotes the diffusion of  $\text{Cl}^-$ . Papadakis *et al.* [89] showed through the carbonation experiment of concrete mixed with a certain amount of chloride salt that carbonation promotes the decomposition of Friedel salt and accelerates the penetration of  $\text{Cl}^-$  in concrete. Suryavanshi and Narayan [90] found that under carbonation, chlorides in Friedel salts are released into the pore solution, so steel bars have a higher risk of corrosion in chloride-contaminated concrete structures. Niu and Sun [91] conducted an alternate test between salt solution immersion and carbonation of concrete, and studied the influence of carbonation on  $\text{Cl}^-$  diffusion in concrete. The results showed that carbonation accelerates the diffusion rate of  $\text{Cl}^-$  in concrete and increases the content of  $\text{Cl}^-$  in concrete. Although carbonation will release free  $\text{Cl}^-$  from partially bound  $\text{Cl}^-$  and increase the free  $\text{Cl}^-$  content in concrete, the results show that the increase in  $\text{Cl}^-$  is mainly due to the redistribution of concrete microstructure caused by carbonation. This has also been confirmed by some scholars. Su [92] tested the pore structure of carbonated and uncarbonated concrete at 28 days and found that the porosity of concrete decreased after carbonation, from 6.8628% before carbonation to 6.8107%. However, the average pore size and the most probable pore size of concrete after carbonation increased from 38.68 and 20.05 nm before carbonation

to 45.71 and 33.52 nm, respectively. The diffusion rate of  $\text{Cl}^-$  in concrete is proportional to the square of concrete pore size [93], so carbonation accelerates the diffusion rate of  $\text{Cl}^-$ , thereby increasing the  $\text{Cl}^-$  content in concrete. Jin [93] immersed the carbonated concrete in a corrosive solution and found that carbonation increases the  $\text{Cl}^-$  content in concrete and the concrete  $\text{Cl}^-$  apparent diffusion coefficient, and the change range becomes larger with the increase in carbonation time. Sun [94] studied the degradation mechanism of concrete under the alternating action of carbonation and  $\text{Cl}^-$  erosion, and confirmed that carbonation accelerates the diffusion of  $\text{Cl}^-$  in concrete. Wang et al. [67] discussed the relationship between carbonation resistance and  $\text{Cl}^-$  permeability resistance of concrete, and analyzed it by using the concept of “concrete pore tortuosity.” The results showed that the increase in carbonation depth would reduce the  $\text{Cl}^-$  diffusion coefficient and enhance the  $\text{Cl}^-$  permeability resistance of concrete. Wan [95] believed that the main reason for the influence of carbonation on  $\text{Cl}^-$  erosion was the change in the concrete pore structure. The test showed that carbonation increases the  $\text{Cl}^-$  diffusion coefficients of both concrete and mortar. Since the hardened cement paste in mortar is more concentrated, the increase in the proportion of macropores caused by carbonation of mortar is more obvious, and the  $\text{Cl}^-$  permeability is greatly improved. Recent studies have shown [96–98] that although the total porosity of the carbonated concrete decreases, the most probable pore diameter increases, which improves the connectivity of the internal pores and makes  $\text{Cl}^-$  more permeable.

At present, there is no unified conclusion on the effect of concrete carbonation on  $\text{Cl}^-$  diffusion, and the research on the coupling of the two is still insufficient and needs to be further improved. Most of the experimental studies mainly focus on the effect of concrete carbonation on chloride ion erosion, while the research on the effect of chloride ion erosion on carbonation is lacking. However, for the marine environment, chloride ion erosion is the main cause of concrete durability problems. Therefore, it is very necessary to study the influence of chloride ion erosion on carbonation, and it is suggested that simulation tests and theoretical analysis should be carried out in the future.

## 2.7 Research status of concrete durability under the combined action of dry–wet cycles, $\text{Cl}^-$ erosion, and carbonation

In practical engineering, the service environment of marine concrete is complex, and it is not affected by a single factor.

The marine concrete located in the tidal area is most commonly affected by dry–wet cycles,  $\text{Cl}^-$  erosion, and carbonation. The durability research under the combined action of dry–wet cycles,  $\text{Cl}^-$  erosion, and carbonation is rarely reported.

The combined action of the three factors makes the deterioration law of marine concrete more complicated. Qian et al. [99] carried out a carbonation and chlorine salt dry–wet cycles test on HPC specimens of marine concrete structures, and the test results showed that under the carbonation and chlorination dry–wet cycles, the compressive strength of concrete increases first and then decreases, and long-term carbonation would cause the decrease in the compressive strength. There is a critical carbonation depth which is related to the compressive strength, carbonation will increase the compressive strength before reaching the critical carbonation depth, and decrease the compressive strength after reaching the critical carbonation depth. Fan [100] conducted a study on the mechanical properties and microstructure of concrete under the coupled action of chloride salt dry–wet cycles and carbonation. The cured specimens were subjected to chloride salt dry–wet cycles first, and then the specimens were taken out and placed in a carbonation box for carbonation. The research results showed that after the coupling effect of dry–wet cycles and carbonation, the elastic modulus of concrete decreases, and the pore size distribution curve of concrete deviates to the direction of large pore size, which is mainly caused by the influence of the dry–wet cycles of chloride salt. Yuan et al. [101] carried out the  $\text{Cl}^-$  erosion test of carbonated concrete under the mechanism of the dry–wet cycle, and the results showed that carbonation increased the content of free  $\text{Cl}^-$  in concrete, slowed down the decay of  $\text{Cl}^-$  concentration, and adversely affected the  $\text{Cl}^-$  erosion resistance of concrete. Through SEM analysis, it is found that carbonation reaction has a certain deterioration effect on the microstructure of concrete, which will accelerate the invasion of harmful media. Reducing the water–binder ratio can significantly improve the compactness of concrete, enhance the resistance to  $\text{Cl}^-$  erosion of concrete, and reduce the aggravation of  $\text{Cl}^-$  erosion caused by carbonation reaction.

Although the above research carried out the concrete durability test under the combined action of three factors, the number of test cycles was small and the period was short, which could not effectively simulate the real marine atmospheric environment. It is recommended to carry out a long-term indoor simulation test and seaside exposure test, and compare the indoor test data with the test data of the real environment, to improve the indoor accelerated test and simulate the real environment to the

maximum extent. At the same time, it is also proposed to carry out a correlation study between the deterioration of concrete caused by artificial accelerated tests and natural environment, to lay a foundation for improving the effectiveness of the accelerated test results in the evaluation of concrete durability in the marine environment in the future.

In summary, the effects of various admixtures on the durability of concrete are summarized in Table 3.

### 3 Measures to enhance durability of marine concrete

The durability of concrete structures is the result of a combination of internal and external factors. In addition to adding admixtures, the following measures can also be adopted to improve the durability of concrete:

- (1) Control the water–cement ratio. Generally speaking, the smaller the water–cement ratio of concrete, the better its mechanical properties and durability. This is because the water consumption required for cement hydration is far less than the actual mixing water consumption, and the excess water will form capillary channels after the cement hardens. And the larger the water–cement ratio, the denser the capillary channels and the larger the average pore size, which in turn affects the strength, permeability, and later drying shrinkage of concrete. At present, the method of reducing the water–cement ratio is generally used in engineering to improve the durability of marine concrete. However, if the water–cement ratio is too low, the workability of the concrete will be deteriorated, and the cohesion will be too large, making it difficult to remove air bubbles in the concrete, which will reduce

the durability of the concrete and significantly increase the project cost.

- (2) Appropriately increasing the thickness of the concrete protective layer can effectively limit the carbonation of concrete and control the corrosion of chloride salts. Generally, the penetration depth of  $\text{Cl}^-$  and the depth of carbonation are proportional to the square root of time. Therefore, increasing the thickness of the protective layer can prolong the penetration time of  $\text{Cl}^-$  into the steel surface.
- (3) The use of resin, paint, asphalt tar, and other coatings can improve the compactness of the concrete surface, isolate the direct contact between the concrete and the outside world, and have a significant effect on preventing the carbonation of the concrete or the corrosion of  $\text{Cl}^-$ .

### 4 Conclusion and prospects

In conclusion, the durability of concrete has attracted extensive attention from scholars at home and abroad. A lot of research has been done on  $\text{Cl}^-$  erosion, carbonation, dry–wet cycles, and fruitful research results have been achieved. Compared with the action of a single factor, the deterioration of concrete under the action of multi-factors is more serious. Adding admixtures to concrete can improve the durability of concrete to a certain extent. For example, the addition of fly ash can improve the resistance of concrete to  $\text{Cl}^-$  corrosion, but it is not good for the ability to resist carbonation; the addition of fibers can improve the ability of concrete to resist  $\text{Cl}^-$  corrosion and carbonation; the addition of nanomaterials can enhance the resistance of concrete to  $\text{Cl}^-$  corrosion, carbonation, and dry–wet cycles. However, due to the different test conditions and systems, there is no

**Table 3:** Influence of admixture types on concrete properties

Admixture		Resistance to $\text{Cl}^-$ erosion	Resistance to carbonation	Resistance to dry–wet cycles
Fly ash		↑	↓	↑
Fiber	Steel fiber	↑	↑	↑
	Polyethylene fiber			
	Basalt fiber			
	Basalt–PP fiber			
Nanomaterial	Nano- $\text{SiO}_2$	↑	↑	↑
	Nano- $\text{TiO}_2$			
	Nano- $\text{CaCO}_3$			
	MWCNT			

Note: “↑” means “improve,” “↓” means “reduce.”

unified conclusion about the optimal dosage of various admixtures.

It is vital to improve the durability of marine concrete. In order to make the research results more effective to guide the design and construction of practical projects, there are still many key problems that need to be solved urgently:

- (1) At present, a large number of research works are still at the stage based on the action of a single environmental factor or two factors, and the research on the durability of concrete under the combined action of multi-factors is still relatively lacking. It is suggested that the deterioration law of concrete can be studied from the perspective of combined action of multi-factors in the future, so as to provide a reliable basis for improving the durability of concrete in practical applications.
- (2) At present, there have been a lot of achievements in macroscopic phenomenon research on concrete durability, but the hidden microscopic mechanism still remains to be further explored. It is suggested that the degradation law of concrete microstructure can be studied at the micro scale to provide a reliable basis for the degradation mechanism of concrete.
- (3) With the consumption of natural aggregates, especially the increasing shortage of freshwater and fine sand, the raw materials for cement-based materials need to have more choices and sources. For coastal and offshore buildings, the cost and difficulty of transporting fresh water and ordinary fine aggregates are very high, but these areas are rich in seawater and sea sand resources. If these raw materials can be effectively used to prepare seawater sea sand concrete, it can not only reduce construction costs, but also protect the ecological environment. However, the large amount of chloride salts contained in seawater and sea sand will affect the mechanical properties and durability of concrete, resulting in the development and utilization of seawater and sea sand is still in its infancy. In the future, the research on endogenous  $\text{Cl}^-$  in seawater sea sand concrete should be strengthened, so as to promote the use of seawater sea sand concrete, alleviate the problem of insufficient resources of water and river sand in inland rivers, and truly take it from the sea and use it in the sea.
- (4) Concrete will be damaged by physical, chemical, and biological actions during its service, which will eventually lead to its deterioration. The mechanism of concrete deterioration caused by physical and chemical action has been widely studied; however, the

deterioration of concrete durability caused by biological effects in marine environment is rarely explored by researchers. The macroscopic effects of algae and animals are more significant in the destruction of marine life. They can not only penetrate deep into the concrete and grow freely between cement and aggregate, causing the concrete to crack, but also produce biological acids, metabolites, and humic organic matter, which can also lead to the gradual deterioration of concrete durability, spalling of concrete, and corrosion of steel reinforcement. It will cause huge damage to the social economy and environment. Therefore, more attention should be paid to the destruction of marine organisms, and more reasonable, efficient, economical, and environmentally friendly anticorrosion control measures for marine concrete should be sought.

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