The Analysis of Reinforcement Corrosion in Concrete under the Non-longitudinal Cracks in Marine Environment

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Abstract: Reinforcement corrosion in concrete is an important factor that affects the durability of reinforced concrete structures. In marine environment, especially, non-longitudinal cracks accelerate the intrusion of chloride ions into the concrete structure. Chloride ions destroy the passive film on the surface of the steel, causing steel corrosion and thus deterioration of the durability of reinforced concrete structures. This paper sets forth the impact of non-longitudinal cracks and the marine environment on reinforced concrete structures and analyzes corrosion in non-longitudinal cracks.

Introduction

Reinforcement corrosion in concrete is an important factor that affects the durability of reinforced concrete structures [1]. According to massive research [2-4], concrete structures in marine environment will be influenced both by load and chloride salt, thus producing cracks that help the invasion of carbon dioxide and chloride ions. In this way, it weakens the protection of concrete toward rebar. Furthermore, the corroded rebar accelerates the enlargement of cracks, which is indeed a vicious circle. This paper, under the circumstance of marine environment, illustrates its influence on reinforcement corrosion from the perspective of non-longitudinal cracks and analyzes the corrosion of non-longitudinal cracks from the aspect of corrosion outcome and its effects, so as to provide a reference for the research of the durability of reinforced concrete structures.

The Non-longitudinal Cracks in Reinforced Concrete Structure

The Concept of the Non-longitudinal Cracks. Reinforced concrete structure is composed of concrete and steel. In addition to the rational use of the characteristics of these two materials, reinforced concert structure has the merits of molded with good, good integrality, fire resistance, easy to use local materials and so on, but it also has some weaknesses like poor crack resistance. Due to the low concrete tensile strength, its tensile strain is small. So, in the construction and normal use, the crack is difficult to avoid. Ordinary reinforced concrete structure is often working with cracking. Despite the presence of cracks in the structure does not necessarily mean the destruction occurred, but it affects the durability and aesthetic, and sometimes even a sense of insecurity.

Depending on the relative direction of cracks and main reinforcement, cracks can be divided into the longitudinal cracks and the Non-longitudinal cracks these two categories. The longitudinal cracks are because the reason that the protective layer cracking due to the expansion of steel corrosion in concrete. The rest are the Non-longitudinal cracks, mainly due to the direct or indirect effects, including shrinkage cracks, settlement cracks, transverse cracks, and oblique crack and so on.

The Non-longitudinal Cracks' Effect on the Durability of Concrete Structure. If the width of the Non-longitudinal cracks is less than a limit, generally it will not cause the corrosion of steel, and the influence to its structure bearing capacity and durability are also not large. But when the crack's width is too large, it will accelerate steel corrosion of cracks at seam, reduce capacity and durability of the structure, and even cause a series of damages like concrete cover cracking, spalling, etc., affecting the safety of the structure [5].

The Non-longitudinal cracks' effect on concrete structures can be considered from two perspectives: concrete carbonation and steel corrosion [6].

(1) Accelerate the concrete carbonization

The existence of the Non-longitudinal cracks will accelerate the change of the original alkaline environment of the concrete. Water and carbon dioxide or other acid gas can enter through cracks into the concrete, and then longitudinal diffusion along the crack edge (Fig 1), carrying out neutralization reaction with calcium hydroxide ($Ca(OH)_2$) in concert which results in lower pH values, destructing the steel surface passivation film, In the case of corrosive media intrusion, steel will rust finally.

The mechanism of the reaction can be represented by the following chemical equation [7]:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$Ca\left(OH\right)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 3\ H_2CO_3 \rightarrow 3CaCO_3 + 2SiO_2 + 6H_2O$$

$$2CaO \cdot SiO_2 \cdot 4H_2O + 2H_2CO_3 \rightarrow 2CaCO_3 + SiO_2 + 6H_2O$$

$$\begin{aligned} &3CaO \cdot Al_2O_3 \cdot 3CaO_4 \cdot 32H_2O + 3CO_2 \rightarrow \\ &3CaCO_3 + 3CaSO_4 + Al_2O_3 \cdot xH_2O + (32 - x)H_2O \end{aligned}$$

In addition, concrete carbonation will cause carbonation shrinkage [7], impelling the surface of the concrete easier to produce subtle cracks. And the subtle cracks will also accelerate the concrete carbonation occurs, thus a vicious cycle appeared, further affecting the concrete structure itself and its durability.

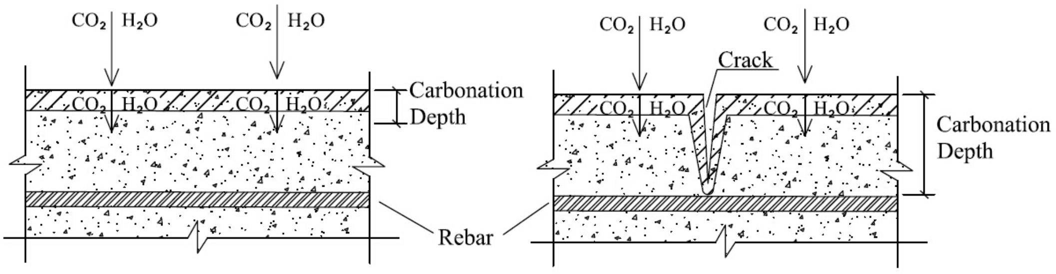

Fig 1 The diagram of cracks or non-cracks' carbonization

(2) Accelerate the erosion of chloride ions

When the concrete cover is complete, erosion of chloride ion diffusion can be viewed as a linear diffusion process, and the chloride ion's regularity of concentration changes inside its concrete can be calculated according to Fick's second law. But for cracked concrete, Fick's second law cannot apply. With the help of the Non-longitudinal cracks, chlorine ions can easily intrude into the interior of concrete and reach to the steel surface. After reaching to a certain concentration, it can damage the passivation film, causing steel corrosion. For the purposes of chloride ions, its intrusive way can be separated into two types: penetration along cracks into the internal structure and intrusion into the interior structure along the crack surface [8].

The Steel Corrosion in Non-longitudinal Cracks in Marine Environment

In the marine environment, the durability of reinforced concrete structures and factors encountered are very different from other environments. A large number of engineering surveys show [9,10] that steel corrosion caused by chloride corrosion is the main reason for the destruction of concrete structures in marine environment. But at the same time concrete carbonation may also lead to chloride ion accumulation, affecting the distribution of chloride ions' concentration and accelerating chlorine ions reach to the steel surface.

Reinforced concrete structure along the longitudinal cracks will affect its structural durability, but its effects on the corrosion of steel in concrete structures and significance on controlling crack width has always been controversial. One view is that: the produce of Non-longitudinal cracks destroys the concrete protective layer and then produces a channel on the concrete structure, making it easier for corrosive substances invade and destroying the steel surface passivation film which plays an important role in accelerating steel corrosion in concrete [11]. Another view is that: the effect of Non-longitudinal cracks to the corrosion of reinforcement in reinforced concrete is not very large. Cracks are only to speed up the depassivation of steel surface passivation film, starting corrosion of steel, and the density of the concrete itself and the protective layer thickness is a key factor in controlling steel corrosion [12].

Table 1 summarizes the given specifications at home and abroad of maximum crack width's limit requirements of ordinary concrete structure under the chloride environment. So, from it we can also see the differences [13].

Table 1 Every country's specification maximum crack width (chloride environment) [mm]

regulation	ACI318	CEB-FIP	BS8110	EN1992-1	GB50010	JTG D62
$w_{\max}$	0.4(0.33)*	0.1~0.3	0.3	0.3	0.2~0.3	0.15

Note: * The values in parentheses are for outdoor situation

Steel Corrosion Mechanism Caused by Carbonized. It is generally accepted that steel corrosion caused by carbonization, its necessary condition is the reinforced concrete carbonizes to the surface and damage the passive film, and its sufficient condition is the oxygen-water intrude to the steel surface, causing steel corrosion occurs [14]. When the surface of the concrete structure has Non-longitudinal cracks, water in the air, carbon dioxide, and oxygen can invade through the cracks into the concrete, greatly reducing the time of carbonation to steel surfaces (Fig 2). After the carbonization of concrete, its pH value is lowered which results in damage to the passivation film, causing reinforcement directly exposed to water, carbon dioxide, oxygen, and formed an electrolyte water film. With the addition of reinforcement, itself contains other metal species and crystal, it constitutes numerous micro batteries, making steel electrochemical reaction happen and steel corrosion occur.

Steel corrosion Mechanism Caused by Chloride Ions. With respect to the carbonation, in the marine environment, the impact of the erosion of chloride ions on the durability of concrete structures is not only more rapid but also more serious.

In the reinforced concrete structure, steel corrosion belongs to the electrochemical corrosion, and it is generally believed that the occurrence of electrochemical corrosion requires four necessary conditions:

(1) Steel surface has potential difference.
(2) There is an electrolyte link between the cathode and the anode.
(3) The steel surface of the anode region is in depassivation activated state.

(4) The surface of the cathode region has sufficient oxygen and moisture to make reaction smoothly.

Under normal circumstances, because the chemical composition of steel bars are very different, and the distribution of carbon and alloy elements inside it is uneven, , there is always a lower potential of the anode region and a higher potential of the cathode region on the steel surface, that is so called the presence of the steel surface potential difference. And at the same time, the steel surface and concrete interface are always presenting pore solution, which means the electrolyte contact between the cathode and the anode. The presence of Non-longitudinal cracks makes chlorine ions and other corrosive substances invade the concrete and rebar in a shorter time, and can easy to reach to the concentration that can damage the steel surface passivation film. Subsequently, the reinforcement which has damaged the passive film along with other steel rebar which has intact passive film in and around cracks form an "active - passive" macro cell. The activated steel rebar around crack lost electrons and become anode of electrochemical reaction, the passivated steel rebar got electrons and become cathode of electrochemical reaction that meets the conditions of the steel surface of the anode region is in the state of depassivation activation. When the oxygen and moisture in the external environment get to the surface of rebar through concert cover, passivation film still exists in the cathode region, so this region has sufficient oxygen and moisture to make electrochemical reaction proceed smoothly. If it also meets the need of condition four, the reinforcement in reinforced concrete structure will occur electrochemical corrosion (Fig 3).

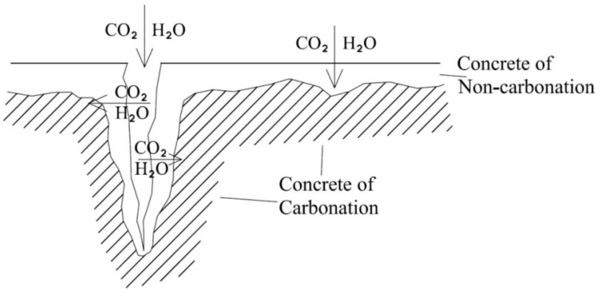

Fig 2 The diagram of carbonation of concrete in cracks

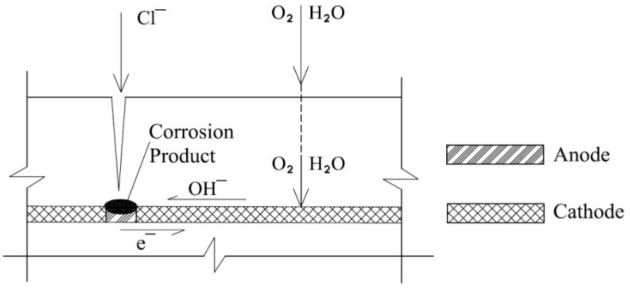

Fig 3 Electrochemical reaction of reinforcement in Non-longitudinal cracks' section

Corrosion electrochemical reaction equations are as follows:

(1) Destroyed passivation film in anode region of reinforcement surface loses electrons, forming a ferrous ion and two free electrons, then electrons will be transported to the cathode region where passivation film has not been destroyed, that is

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-}$$

(2) Ferrous ions occur oxidation reactions, reacting with chloride ions which intrude into the concrete, producing water-soluble ferrous chloride, that is:

$$\mathrm{Fe}^{2+} + 2\mathrm{Cl}^{-} + 4\mathrm{H_2O} \rightarrow \mathrm{FeCl_2} \cdot 4\mathrm{H_2O}$$

(3) Oxygen and moisture in the external environment by means of absorption, permeability, diffusion and other ways to reach the cathode in the steel surface through the concrete pores, and dissolved in the pore fluid, absorbing the electron came from anode region, occurring reduction reaction, that is:

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^{-} \rightarrow 4\mathrm{OH}^{-}$$

(4) Hydroxide ions migrate to the anode through steel and concrete interface, taking the pore liquid as the carrier. In the anode region, $\mathrm{FeCl_2 \cdot 4H_2O}$ move to a higher oxygen area, broken down into ferrous hydroxide, that is:

$$\mathrm{FeCl_2} \cdot 4\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_2} \downarrow + 2\mathrm{Cl}^{-} + 2\mathrm{H}^{+} + 2\mathrm{H_2O}$$

(5) Ferrous hydroxide can easily further oxidized to ferric hydroxide; however, iron hydroxide is very unstable and will easily dehydrate and then decomposed into loose and porous red rust ferric oxide; when oxygen is insufficient, oxidation of ferrous hydroxide is not very full, partial formation of black rust ferroferric oxide, that is:

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

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

$$6Fe(OH)_3 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O$$

Therefore, many experts and scholars believe that a very important means to prevent corrosion of steel in Non-longitudinal cracks region is to increase the density of concrete protection layer and to improve the quality of concrete. Under the circumstances, moisture and oxygen in the external environment will be more difficult to diffuse into the steel surface through protective layer of concert.

The Products of Corrosion of Reinforcement in Non-longitudinal Cracks Region

The Products of Corrosion of Reinforcement. The corrosion layer of reinforcement corrosion in concrete under the Non-longitudinal cracks is mixture of rust and cement gel [15], reinforcement corrosion product is consists of β-FeO(OH), γ-FeO(OH), α-Fe_2O_3,γ-Fe_2O_3, Fe_3O_4, and FeO.

The figure below shows the various corrosion products and the transformation among them in the process of corrosion (Fig 4).

The Influence of the Products of Reinforcement Corrosion to Concrete Cover. The influence of the products of reinforcement corrosion in concrete to concrete cover can be illustrated from three aspects or four processes. The three aspects are as follows: corrosion products reduce the bond force between reinforcement and concrete; corrosion products exacerbate the Non-longitudinal cracks' development and corrosion products make the concrete cover cracking. The four processes are as follows: reinforcement depassivation stage; free expansion stage; stress stage and protective layer cracking and cracks' development stage [16].

Since the Non-longitudinal cracks happened on the surface of reinforced concrete structures, corrosive medium such as chlorideion can accelerate the invasion to the inside of the concrete from cracks, gathering on the steel surface. After reaching critical chloride ion concentration, the passivation coating will be destroyed, and it will enter into the depassivation stage. After reinforcement started rusting, corrosion products generated, and the corrosion product volume increases 2~4 times than rusted steel volume, and its expansion part will enter the space of the reinforced concrete, forming a short transition period, this is so called the free expansion stage. With corrosion products increasing, it will produce the ring to the tensile stress. When the linear strain from the stress produced is greater than the ultimate strain of concrete, the interface of reinforcement and concrete will appear inside the radial cracks [17], and increasing with the development of corrosion (Fig 5). At the same time, because of the steel corrosion products is mainly about Fe_2O_3 and Fe_3O_4, they are loose and multiaperture, thus they can seriously affect the sticky relay between steel and concrete.

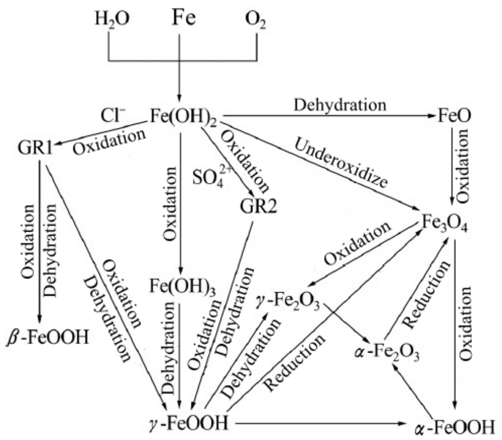

Fig 4 The products of reinforcement corrosion and its transformation[15]

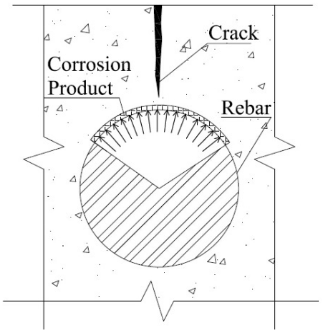

Fig 5 The stresses model of reinforcement corrosion

Corrosion products exacerbate the Non-longitudinal cracks' development and make the concrete cover cracking in the fourth stage - the cracking of protective layer and cracks' development stage. On the one hand, it can be counterproductive to the Non-longitudinal cracks and exacerbate micro cracks' development, turning into vicious spiral; on the other hand, after corrosion continues to develop, concrete cover will produce the longitudinal cracks along with reinforcement, affecting the durability of the concrete structure seriously.

Conclusion

(1) Comparatively speaking, the corrosion of non-longitudinal cracks has a more obvious tendency toward macro cell corrosion. Therefore, the problems, such as, local pit corrosion, stress corrosion, and reinforced brittle fracture, have become more severe.

(2) Compared to longitudinal cracks, concrete, at the very beginning of non-longitudinal cracks, its physical and mechanical properties of structures and carrying capacity haven't changed dramatically. Moreover, there is no significant decline of bond force between concrete and rebar.

(3) As for relatively wider non-longitudinal cracks, the corrosion product, on the one hand, can intensify the cracks, on the other hand, the further corrosion can lead to the longitudinal cracks along concrete protective layer, thus greatly influencing the durability of reinforced concrete structures.

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References

[1] Weiliang Jin, Xiyu Zhao. Durability of Reinforced Concrete Structure. Beijing: Science Press, 2002: 1-10. (In Chinese)

[2] Li Yin. Analysis of Corrosion Fatigue of Reinforced Concrete Structures under Marine Environment [J].Shanxi Architecture, 2012, 38(21): 51-53. (In Chinese)

[3] Licheng. Wang The Research Progress of Service Life Evaluation of Reinforced Concrete Structure sunder the Chloride Environment [J].Journal of Hydraulic Engineering, 2004, 4: 54-60. (In Chinese)

[4] Lingbo Meng. The Research of Durability of Reinforced Concrete Structure under the Mechanical Loading and the Chloride Environment [D]. Shandong: Qingdao Technological University, 2012. (In Chinese)

[5] Hongyu. Nie Study on the Effect of Cracking on the Durability of Concrete Structure in Chloride Environment [D]

[6] Li Yao. Cracks Influence on Reinforcing Steel Rust of the Bridge and It’s Prevention and Cure [J]. Liaoning Province Traffic College Journals.2006, 8(1): 7-9. (In Chinese)

[7] Wen Yin, Wangjun Wei, Xuyan Wang, et al. The Analysis of Concrete Carbonated Shrinkage and Mechanism [J].Research and Explore, 2014, 32(8): 31-35. (In Chinese)

[8] Weiliang Jin, Yongdon Yan g, Hailong Wang, et al. Simplified Analusis of Chloride Diffusion into Saturated and Cracked Concrete [J]. Journal of Transport Science and Engineering,2010, 26(1): 1362-1369. (In Chinese)

[9] Dinghai Hong. Corrosion and protection for reinforcing steel bar in concrete [M].Beijing: China Railroad Press,1998. (In Chinese)

[10] Yingshuo Yi. The Research of Thickness of Concrete Cover with Prevent Reinforcement Corrosion in Concrete [J]. Express Water Resources Hydropower Information, 2013, 34(7):30-36. (In South Korea)

[11] P SCHIEBL, M RAUPACH. Laboratory Studies and Calculations on the Influence of Crack Width on Steel in Concrete [J]. ACI Materials Journal, 1997.

[12] Xide Zhang, Zhitao Lv. The Influence of Concrete Crack on the Durability of Prestressed Concrete Structures [J]. Industrial Construction, 2003, 30(11): 12-14. (In Chinese)

[13] Shaofeng Zhang. The Research of The Chloride ion Erosion in Curved cracked concrete member [D]. Jiangsu: Jiangsu University, 2012. (In Chinese)

[14] Wenjuan Zhao. Experimental study of reinforcement corrosion induced by carbonization of concrete [J]. Shanxi Architecture, 2010, 36(16):53-54. (In Chinese)

[15] Yongsheng Ji, Linglei Zhang, Huirong Ma, et al. Analysis on rusts of steel bar in concrete exposed tochloride-containing environment [J]. Journal of Central South University (Science and Technology), 2012, 43(11): 4484-4490. (In Chinese)

[16] Yu Zhang, Lixue Jiang, Weiping Zhang, et al. Introduction to the durability of concrete structure [M]. Shanghai: Science Technology Press, 2003: 190-192. (In Chinese)

[17] Yu Liu. The Research of Steel Corrosion Mechanism and the Chlorine Ion Influence Mechanism [D]. Xiamen: Xiamen University, 2007. (In Chinese)