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Impact Mechanism of Marine Biofilm on Concrete Durability

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Masses of chlorine salts in the oceans engender a badly electrochemical erosion on the concrete since cross-sea bridge and harbor construction has been intensified in recent years, which has aroused a wide concern. This paper aims to study the corrosion mechanism of seawater chloride ion on the concrete with upper and lower two layers of intertidal zones set up according to different positions. A test is designed to make a comparative analysis on the resistance of marine biofilm to chloride permeability in two cases that the biofilm is active and inactive. The results show that chloride ion takes place electrochemical reaction and plays dual roles of anodic depolarization and conductivity. For its permeability to chloride ions, active biofilm shows stronger, which may be correlated to the halophilic bacteria contained in biofilm and the surface bonding effect of concrete. In relation to the upper intertidal zone, the resistance to chloride penetration in the lower layer of concrete is superior, which reveals that the lower biofilm has a better adhesion effect on the surface and plays a certain role in preventing the erosion of harmful substances.

1. Introduction

In recent years, great efforts have been made in the construction of cross-sea bridges and ports with the development of transportation. There are many traces of chloride salts in the marine environment yet, the concrete is subjected to a quite heavily corrosion of steel bar of chloride salts (Carsten et al., 2008; Fabrega et al, 2011; Leroy et al, 2008; Chen, 2014; Geng et al., 2016; Seddak and Liazid, 2016; Song and Chen, 2015; Sun et al., 2014; Zhang, 2015), so that engineers and scholars show a general concern of this. A new study discovers that the presence of biofilm has a certain impact on the chloride permeability into concrete. It is therefore imperative for us to investigate how the relationship between the two is because it is of great significance for improving concrete durability.

2. Chloride corrosion destruction mechanism

When the concrete is immersed in seawater, the steel bar turns acidic in PH on the surface and is damaged on the passivation film due to infiltration of $C1^-$(Saravanan and Jayachandran, 2008; Gao et al., 2013), more commonly manifested with local corrosion, that is, the iron matrix bares partially due to intrusion of the chloride ions into the passivation film (Pochon et al., 2015; Nandakumar et al., 2002), forming a probit difference from the unexposed part. Iron substrate as an anode and passivation film as a cathode jointly form an electrochemical reaction, as shown below.
Anode:

$$Fe \rightarrow Fe^{2+} + 2e \quad (1)$$

Cathode:

$$O_2 + H_2O + 4e \rightarrow OH^- \quad (2)$$

Secondary chemistry on cathode surface:

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$$Fe^{2+}+2OH^{-} \rightarrow Fe(OH)_2 \quad (3)$$

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

During the electrochemical reaction, chloride ion forms a corrosion cell on the surface of the steel bar and improves the function of cells (Johansson et al, 2014; Faimali et al, 2011; Leary et al, 2014). The $FeCl_2$ generates after Cl^- binds the anodic reaction product Fe^{2+} that is carried away to make the anode process so smooth as to accelerate. In general, that the anodic process is blocked is alluded to as anodic polarization, while that the anodic polarization is accelerated as depolarization. The Cl^- plays anodic depolarization.

The corrosion product of steel bar has a little content due to soluble $FeCl_2$ and binds OH^- to generate sediments $Fe(OH)_2•4H_2O$ when diffusing into the concrete. These precipitates will migrate from the anode of steel bar to the pore of concrete with higher oxygen, decompose into $Fe(OH)_2$ to deposit around the anode, and further be oxidized into $Fe(OH)_3$ while releasing H^+. Cl^- which returns to the anode region. The pore solution in the vicinity of the anode is thus locally acidified, repeat the chemical reaction, as shown in the Eq. (4). It follows that Cl^-plays the transfer effect during the corrosion process only, resulting in a continuous damage to the steel bar (Bergström et al., 2004; Othmani et al., 2016; Srivastava et al., 1990).

Cl^- also has the role of conductivity, which intensifies the ion path, reduces the ohmic resistance between the anode and the cathode, improves the efficiency of corrosion cell and accelerates the electrochemical corrosion process (Mohammed et al., 2004; Hutchinson et al., 2006).

Due to the above electrochemical reaction, the iron on the surface of the steel bar constantly loses electrons and dissolves in water. The rust on the surface promotes its volume increase to the levels that are subjected to the different states of oxidation products, thus causing the concrete cover to expand and crack, further accelerating the corrosion of steel bars.

3. Test introduction

In order to study the relationship between the two, a comparative test is set up. There are two parts covered and uncovered by biofilms respectively. The sample of the drilled core is immersed in seawater for one day and then taken it out. After dry sufficiently, it is fixed in a stationary chamber of a chloride ion permeation tester with a putty and analyzed by the tester. a NaCl 3% is injected into the cathode chamber, after about 10 minutes, it is checked that the NaCl solution in the cathode chamber does not leak into the anode, this shows that the seal between the test piece and the stationary chamber is intact and there is no leakage. Then inject 0.3 mol/L NaOH solution into the anode chamber, the electrode on the tester to the host of the data acquisition system with a wire at 60V, record the current value, stop the data acquisition, and add up the total power for 6 hours. As shown in the formula (5).

$$Q = 900\left(I_0 + 2I_{30} + 2I_{60} + ... + 2I_{300} + 2I_{330} + I_{360}\right) \quad (5)$$

Q represents the total power passed through; I_0 represents the instantaneous current after voltage; I_t represents the current at voltage after minutes *t*.

The concrete core sample to which the marine biofilm is stuck until it gets inactive, and the correlation between biofilm activity and concrete chloride ion permeability is analyzed.

4. Test results

4.1 Contrast test after death of concrete biofilm in lower intertidal zone

In the sublayer of the intertidal zone, a total of 2 sets of test blocks are made for contrast test. Analyze biofilm activity is in the presence or absence, the relationship between the current value and the time is shown in Fig. 1-2, add up the total amount of power over 6 hours, as shown in Table 1.

Table 1: Electric quantity of 6 hours test before and after the death of biofilm on the surface of concrete core sample of intertidal lower layer

Intertidal lower layer	Group 1	Group 2
Non death of biofilm	748.80	501.60
Death of biofilm	922.80	520.80
Ratio of existence and non	81.14	96.31

As can be seen from Figure 1, when the biofilm on the concrete surface loses its activity, the current value passing through the samples increases at the rates basically consistent.

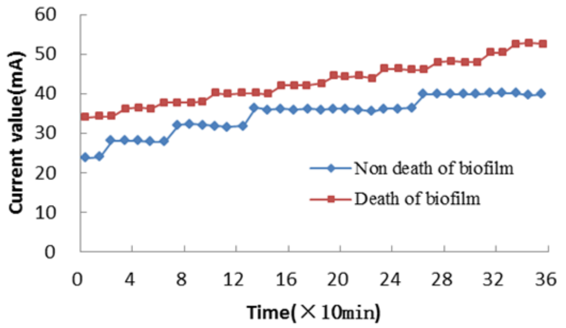

Figure 1: concrete core sample of 1st group of intertidal lower layer before and after the death of biofilm

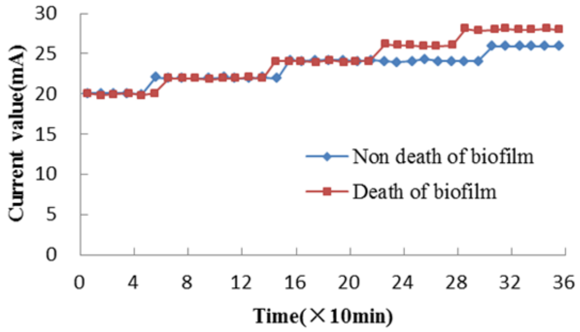

Figure 2: concrete core sample of 2nd group of intertidal lower layer before and after the death of biofilm

As can be seen from Figure 2, when the biofilm on the concrete surface loses its activity, the initial state is roughly similar to that in the presence of biofilm. However, the current value increases obviously over time, and is greater than that in the presence of biofilm after 150min. As can be seen from Table 1, the power value of it in the case of activity is greater than that in the absence. This shows that, if there is a biofilm on the concrete surface, it can resist the chloride ion penetration to a certain extent and play a protective role.

4.2 Contrast test after death of concrete biofilm top layer of intertidal zone

A total of 4 sets of test blocks are made for contrast tests in the upper intertidal zone. Analysis the biofilms in the presence or absence of activity, the relationship between the current value and the time is shown in Figure 3-6, add up the total power over the six hours, as shown in Table 2.

Table 1: Electric quantity of 6 hours test before and after the death of biofilm on the surface of concrete core sample of intertidal upper layer

Intertidal lower layer	Group 1	Group 2	Group 3	Group 4
Non death of biofilm	295.20	350.40	667.20	175.20
Death of biofilm	668.40	346.80	780.00	351.60
Ratio of existence and non	2.26	0.99	1.17	2.01

Analyze it in the case 1 inactive biofilm and case 2 active biofilm. It can be found from the table that for the sets 1 and 4, the total power in the case 1 is significantly greater than that in the case 2, they are 2.26 times and 2.01 times, respectively. The set 3 differs a little, and the total power in the case 1 is 1.17 times that in the case 2. It is found by the analysis that less biofilm adheres to the surface of this sample, and barnacles are dominant. The set 2 seems to differ from other sets, and the total power in the case 2 is basically similar to that in the case 1. Analyze the sample without biofilm in the same coring position, the total power is 1149.60C, which implies that the biofilm activity has a little impact on chloride infiltration, but the presence of bio-film has a greater impact on it. When the second set targets at biofilm itself, oyster shell exists that the infiltration of chloride ions is actively blocked.

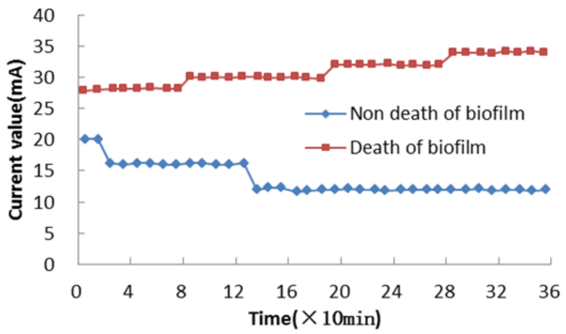

Figure 3: Concrete core sample of 1st group of intertidal upper layer before and after the death of biofilm

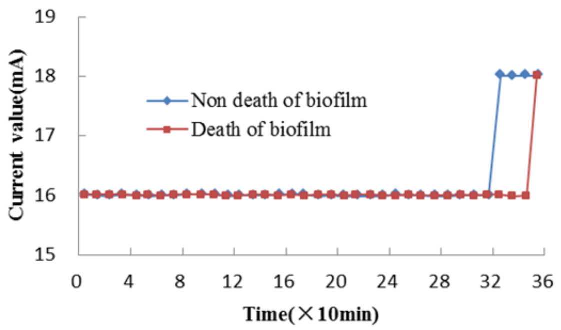

Figure 4: Concrete core sample of 2nd group of intertidal upper layer before and after the death of biofilm

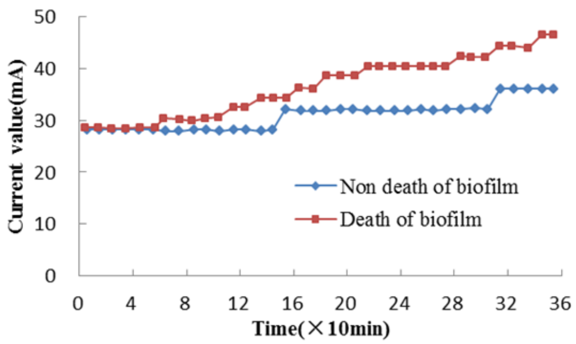

Figure 5: Concrete core sample of 3rd group of intertidal upper layer before and after the death of biofilm

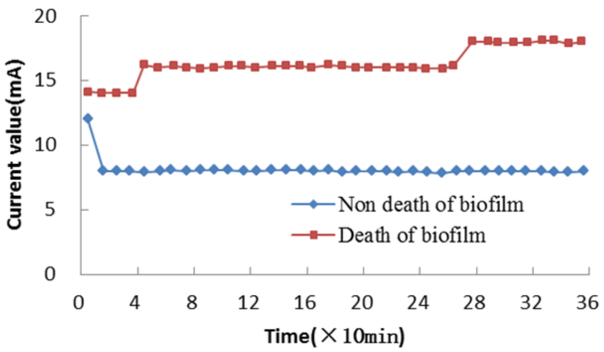

Figure 6: Concrete core sample of 4th group of intertidal upper layer before and after the death of biofilm

When the biofilm of intertidal zone concrete loses its activity, the resistance to the infiltration of chloride ions weakens mostly because it is vulnerable to the biofilm characteristics. Biofilms adhered to the surface of concrete contain diversified substances, including barnacles, oyster shells, and various metabolites whose mucosa can effectively fill the remaining voids in the biological shells, thereby forming an organic integrity. The survival of halophilic bacteria in the biofilm can hold back the infiltration of chloride ions to some extent. When the biofilm loses its activity, the adhesion between the biofilm and the concrete surface is impacted so that the effect of halophilic bacteria is weakened. As a result, the biofilm activity is positively correlated to the resistance of the concrete to chloride penetration.

5. Conclusions

This paper investigates the corrosion mechanism of seawater chloride ions to the concrete. Upper and lower two layers of intertidal zones are set up according to the different positions. A test is also devised to make a comparative analysis on the resistance of marine biofilm to chloride permeability in two cases that it is active and inactive.

(1) Concrete in seawater, due to the infiltration of chloride ions, the iron matrix forms an anode and the passivation film area forms a cathode, resulting in an electrochemical reaction. While chloride ion plays the roles of anode depolarization and conductivity. The iron on the surface of steel bars continuously loses electrons and dissolves in water. The rust on the surface causes the volume to increase so that the concrete cover swells and cracks, further accelerating the corrosion of steel.

(2) If the biofilm does not lose its activity, its resistance to chloride penetration is superior to that in the case of inactivity. This may be correlated to the halophilic bacteria contained in the biofilm and the bonding effect on the concrete surface, but the biofilm has a hard biological shell on the surface, both seem to differ a little.

(3) Compared with the concrete in the upper intertidal zone, the resistance to permeability of lower concrete is superior, which shows that the lower biofilm has better adhesion and plays a certain role in preventing the erosion of harmful substances.

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