Corrosion promotion effect of macrocell current on carbon steel during wet-dry cycles

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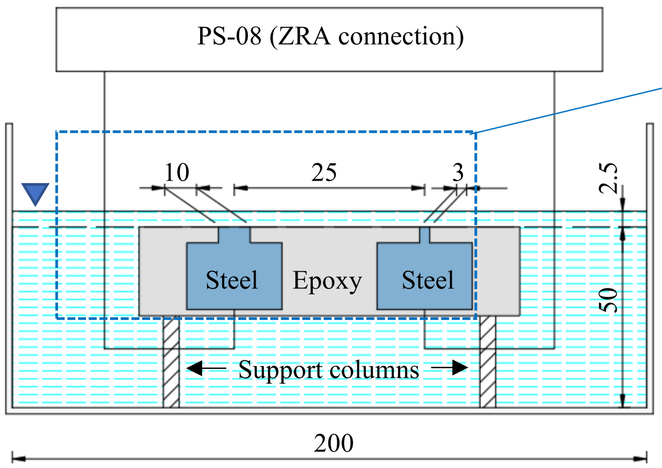
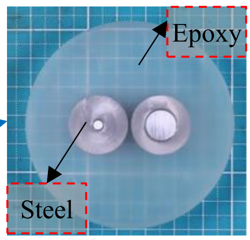
1. Introduction For painted steel structures, the coating can deteriorate due to ultraviolet radiation and environmental water pooling as well as salt, leading to corrosion of steel structures [1]. In this case, the steel structure not only undergoes individual corrosion, but may also generate macrocell current after being connected in the same circuit with adjacent damaged coatings, which could affect the corrosion rate. Our previous research has shown that within a certain distance range, electrode with larger coating defects tend to be fixed as anodes and corrode preferentially [2]. To investigate the promotion effect of macrocell current on corrosion, we measured the macrocell current of two electrodes during immersion and drying stages, and measured the open circuit potential (OCP) of them after the current test. The results showed that macrocell current promoted the corrosion of steel substrates with larger defects. Besides, after promotion, the maximum corrosion rate of the electrode was no more than twice the corrosion rate when steel electrode corroding alone without promotion. The OCP test after five wet-dry cycles further confirmed the trend of electrodes with larger coating defects being fixed as anode.

2. Test method Two circular electrodes made of S45C carbon steel were applied to simulate the defects. The defects were determined as 10mm and 3mm, and circular distance between them was 25mm. 0.1 wt % NaCl aq. was adopted to simulate the rainwater. To minimize the influence of water evaporation on salt solution concentration during the measurement process, the specimen was placed in acrylic box with a cross-sectional size of 20 cm × 20 cm, and the lead wires were drawn out from the electrodes for measurement. The initial electrolyte film thickness on the electrode surface was 2.5 mm, and it was allowed to dry naturally in the room with the temperature controlled at 22°C (40% RH) by air conditioning. After the macrocell current decreased to zero, 100 mL distilled water (corresponding to a 2.5mm thick electrolyte film) was added to the box. The macrocell current and OCP were measured by the Multi Potentio Galvano Stat PS-08. Zero resistance ammeter (ZRA) connection was applied when measuring current, and voltmeter connection was used for OCP measurement. Fig. 1 illustrates the testing setup.

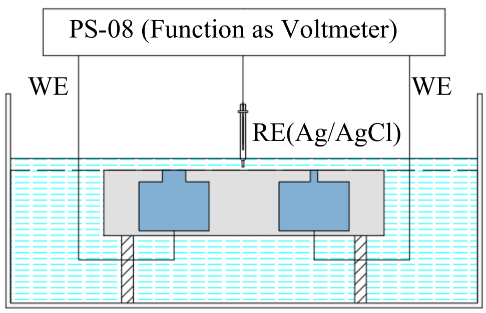
3. Test results Based on our previous research, linear relationship between macrocell current density and the area of the cathode area which could be explained by the catchment principle [3]. Moreover, the proportional coefficient corresponds to the oxygen diffusion current density (i_{O2}), which is also the corrosion current density for steel electrode when corrodes alone. The macrocell current during 5 wet-dry cycles is shown in Fig. 2. The variation of macrocell current over time could be divided into three regions, with region I corresponding to the immersion condition. As the electrolyte film thickness decreased, the corrosion reaction entered region II, where the macrocell current increased and reached a maximum value, followed by a decrease in region III. Our previous research has demonstrated the corrosion rate of carbon steel in atmosphere could be calculated by $I_{macro}=i_{O2}\times S_c$, where S_c is the cathode area. According to Faraday's raw, the corrosion rate (C) of carbon steel could be obtained by C= $i_{O2}\cdot M/(z\rho F)$, where M and F are atomic mass and Faraday constant respectively. ρ is the density of carbon steel and z is determined



a) Elevation of testing set-up for measuring macrocell current. (unit:mm)



b) Steel electrodes fixed by epoxy.



c) Elevation of testing set-up for measuring OCP.

Fig.1 Configuration of testing set-up.

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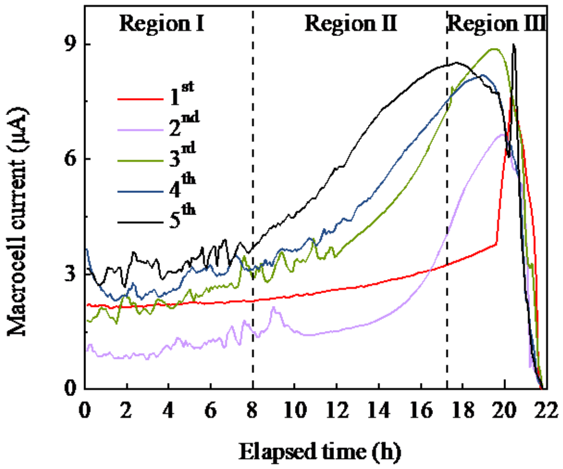

Fig.2 Macrocell current during wet-dry period (5 cycles).

Table 1 Average and maximum corrosion rates of anodes (Φ=10mm) during wet-dry cycles (mm/y).

Cycle number	Ave. (mm/y)	Max. (mm/y)	Max./Ave.
1st	0.36	1.26	3.5
2nd	0.18	1.09	6.0
3rd	0.38	1.46	3.8
4th	0.46	1.34	2.9
5th	0.54	1.48	2.8

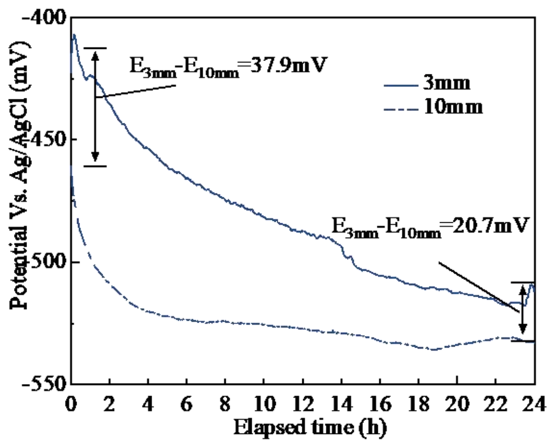

Fig.3 OCP of two electrodes after 5 wet-dry cycles.

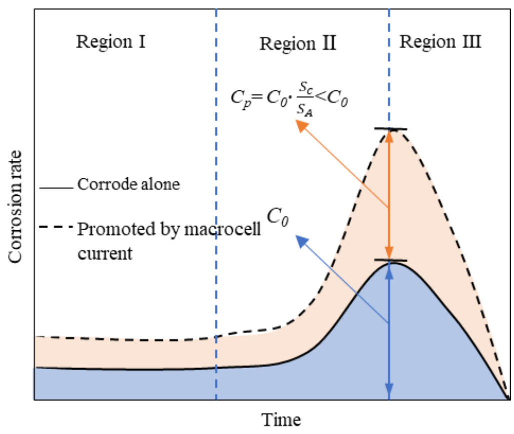

Fig.4 Corrosion promotion effect of macrocell current.

as 2 when Fe^{2+} is produced in the corrosion reaction. The average corrosion rate in region I and the peak corrosion rate during the wet-dry cycle are shown in Table 2. The peak corrosion rate during the electrolyte film drying process was more than 2.8 times the average corrosion rate in the immersion region (Region I).

After 5 wet-dry cycles, the OCP of two electrodes was measured, and the results are shown in Fig. 3. The potential of electrode Φ3mm was consistently higher than that of electrode Φ10mm. The potential difference between the two electrodes decreased from the initial 37.9 mV to 20.7 mV 24 hours later. Although the magnitude of the potential difference does not represent the corrosion rate, it can explain the trend of the reaction through the change of Gibbs free energy: $\Delta G = -nFE$, where E is the potential difference. When $E>0$, we have $\Delta G<0$, which verified the reaction with electrode Φ10mm fixed as an anode could proceed spontaneously.

The promotion effect of macrocell current on corrosion is summarized in Fig. 4, where the three regions correspond to the three regions in Fig. 2. The solid line corresponds to the corrosion rate of a single electrode during drying, and the dashed line represents the corrosion rate of the anode with macrocell promotion. We have observed that the electrode with larger coating defect would be fixed as an anode, therefore $S_C/S_A < 1$. This indicates that after the occurrence of macrocell promotion, the maximum corrosion rate of anode is no more than twice that of steel electrode without macrocell current promotion. However, we can infer that, due to certain environmental factors, such as an electrode with a larger coating defects area being covered by pollutants and becoming the cathode, the corresponding corrosion rate with macrocell current promotion effect may be more than twice that of the individual corrosion, which would be a more dangerous situation.

4 Summary 1) With the drying of the electrolyte film, the corrosion rate of the anode was greatly promoted, and the maximum corrosion rate exceeded 2.8 times the corrosion rate during immersion. 2) After the occurrence of macrocell current, the increase in the corrosion rate of the anode was determined by the ratio of the cathode and anode area, but the maximum corrosion rate does not exceed twice the corrosion rate of individual corrosion.

References 1) M. Yang, S. Kainuma, S. Ishihar, A. Kaneko, T. Yamauchi: Corrosion protection of steel members using an Al-Zn base sacrificial anode and fiber sheet in an atmospheric environment, Construction and Building Materials, 234, 117405, 2020. 2) J. Tang, S. Kainuma & M. Yang: Electrochemical study on the microcell corrosion mechanism between two adjacent iron electrodes in immersion environment. The 201th regular meeting of the Western Japan corrosion prevention research association, 62(3), 20-21, 2022. 3) F. Mansfeld: Area Relationships in Galvanic Corrosion, Corrosion, 27(10), 436-442, 1971.