The Effect of Nitrite to Anode Reaction Property in Macro-Cell Corrosion

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1 Introduction

Annually, 3% of world GDP is consumed by corrosion, meanwhile concrete construction consumes a large quantity of steel and the corrosion problem is always a heated research field. In macro-cell corrosion status, the distance between cathode and anode is further than micro-cell status which means they are separated and this is tend to occur in chloride induced pitting corrosion (anode is tiny compared to the whole rebar). In Japan, sea sand is wildly used in concrete construction and in order to prevent the corrosion, corrosion inhibitors are commercially utilized in 1970s and nitrite-based corrosion inhibitor is one of the effective anode inhibitors. Many researches concerning nitrite-based corrosion inhibitor have been done, however they are based on micro-cell corrosion mostly and the research concerning the effect of nitrite in macro-cell corrosion is rare and haven’t reached the consensus. In this paper, the research concerning the effect of nitrite was did under the circumstance of macro-cell corrosion by separating cathode and anode artificially.

2 Experiment Design

In order to realize the macro-cell corrosion, cathode and anode are separated. Moreover, according to the experiment did by the author before, the rebar surface area ratio of 16:1 between cathode and anode is enough to realize anode control mode (in this mode, any anode measures will be effective). Thus, the separated cathode and anode specimens are illustrated in Fig.1 and Fig. 2. In the specimens, the diameter of rebar is 13mm and both ends are sealed to control the corrosion area. Moreover, the mixture proportion of mortar specimens is 0.5:1:3(water: cement: sand) and the composition of cathode and anode is demonstrated in Table 1, where NR represents the number of rebar and ELR represents the effect length of rebar. The difference of cathode and anode chloride content is to realize macro-cell corrosion; the enlarging of cathode surface area is to weaken the effect of cathode; the nitrite solution is instilled into the concrete to reach the surface of rebar through the 4 tubes.

There are 2 periods, namely, separated period and connectted period during the experiment and both periods consume one week, which is illustrated in Fig.3. In separated period micro-cell potential($E_{mi,c}$ and $E_{mi,a}$) and crurrent density($i_{mi,c}$ and $i_{mi,a}$) can be obtained and in connectted period, macro-cell potential($E_{ma,c}$ and $E_{ma,a}$) and current density(i_{coor}) can be obtained, which is illustrated in Fig.4, where polarization ratio($\Delta E_i/\Delta E_1$,i=2,3,4) and polarization slope($\beta_c = \frac{E_{mi,c}-E_{ma,c}}{i_{mi,c}-i_{ma,c}}$, $\beta_a = \frac{E_{mi,a}-E_{ma,a}}{i_{mi,a}-i_{ma,a}}$) will be calculated to analysis cathode and anode reaction property. Comparing polarization ratios, the control mode (cathode control, anode control, hybrid control and mortar control) can be understanded and polarization slopes can reflect the polarization resistance of cathode and anode.

During the experiment, the machine CM-SE1 is used to measure corrosion potential, resistance of rebar and resistance of concrete and the measure method refers to standard ASTM C876-91. Moreover, the micro-cell corrosion current density is determined by the polarization resistance of rebar(R_p) and can be calculated by Stern-Geary equation($I_{coor,mi}=\frac{B}{Rp}$, corroded status: B=26mv; passivation status: B=52mv) and macro-cell current is measured by Zero Resistance Ammeters.

Table 1 The Composition of Cathode and Anode

NO.	Cathode (Parallel)			Anode				A_c/A_a
	Cl^- wt%	NR -	ELR mm	Cl^- wt%	NO_2^- mol·L^{-1}	NR -	ELR mm	
1	1.5	4	160	3.0	0	1	40	16:1
2				3.0	3	1	40	
3				3.0	5	1	40	
4				3.0	8	1	40	

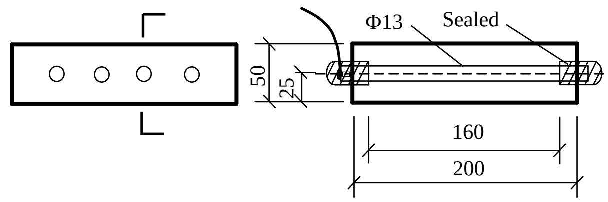

Fig.1 Cathode specimen

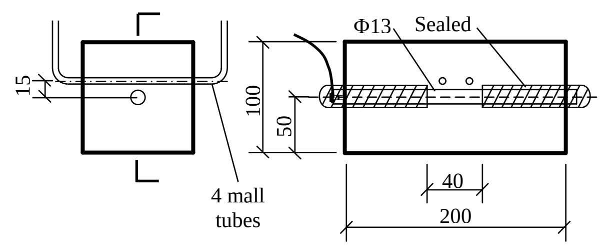

Fig.2 Anode specimen

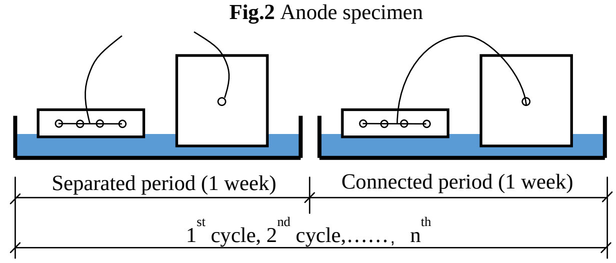

Fig.3 The cycle process of experiment

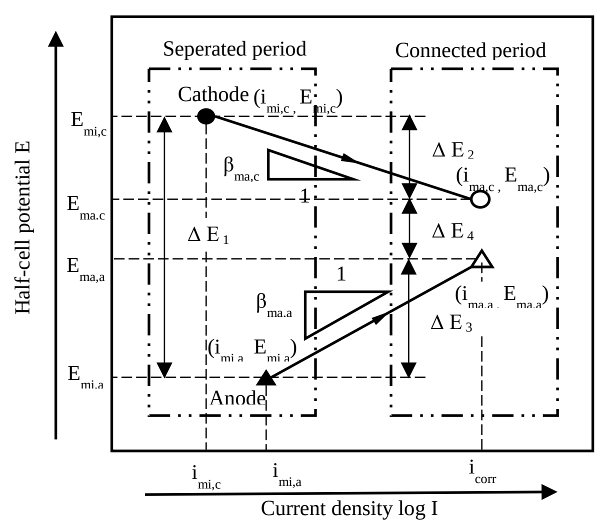

Fig.4 Macro-cell corrosion model

3 Result and Analysis

The author has recorded the date for 5 cycles (70 days), and the calculated result (utilizing the stabilized date of every period) of polarization ratio and polarization slope are illustrated in Fig.5 , Fig.6.

3.1 Polarization Ratio

The polarization ratio can reveal the control mode and in this paper in order to analysis the anode reaction property, realizing anode control mode is necessary. As illustrated in Fig.5, anode polarization ratio is quite higher than cathode and mortar, which means the reaction is controlled by anode dramatically and in this circumstance inhibiting method conducted in anode will be effective but to cathode, the effect is limited.

3.2 Polarization Slope

Polarization slope is a significant parameter which can reveal the polarization ability of cathode and anode, and some papers describe it as polarization resistance. As illustrated in Fig. 6, the cathode polarization slope is quite tiny compared to anode polarization slope and the anode polarization slope keeps soaring from 27.6 to 56.5 mV/dec with the creeping up of nitrite in anode, which means the existence of nitrite in anode cannot affect cathode polarization slope dramatically but can affect anode and make it booming progressively. This is mainly because the nitrite existing in anode escalates the reaction resistance in anode, namely, producing less electron in anode and then decrease the macro-cell current density. Meanwhile, because of the thinner mortar cover and more rebar, which can provide more oxygen, cathode can consume the electron generated by anode immediately, which makes cathode reaction resistance tiny.

3.3 Corrosion Mechanism

What is clearly elaborated in other scholars' papers is that half-cell potential difference (ΔE_1) and polarization slope (β_c and β_a) are the main parameters to influence the corrosion current. β_c can be ignored (anode control mode) and the effect of β_a is already clear, so the effect of ΔE_1 remains to be probed. Thus, the relationship between ΔE_1, I and NO_2^- content is illustrated in Fig.7 and Fig.8 respectively. The average current density ebbs continuously from 2.96 to 1.09 $\mu A/cm^2$ with the increasing of anode nitrite content, but average of ΔE_1 is always in a fluctuation condition around 90mV and the trend of decrease has not appeared, which means in the initial corrosion period the adding of nitrite cannot immediately reduce ΔE_1. Thus, the subsiding of macro-cell corrosion current is mainly due to anode polarization slope, namely, β_a, at least in the initial corrosion period.

With the analysis above, the corrosion mechanism can be demonstrated in Fig.8. In the typical macro-cell corrosion circumstance (large cathode and small anode), the corrosion is mainly depended on the anode polarization slope and nitrite ion as one of the corrosion inhibitors can repair corrosion with escalating anode polarization slope in the initial corrosion period but ΔE_1 remains stable.

4 Conclusion

Through the 5-cycles-experiment of macro-cell corrosion, the effect of nitrite to the initial corrosion period of macro-cell can be concluded as follows:

(1) In the typical macro-cell corrosion of large cathode and small anode, the corrosion is mainly controlled by anode and the influence of cathode is tiny.

(2) The existence of nitrite in anode under chloride-induced macrocell corrosion can dramically escalate the anode polarization slope, but to cathode polarization slope the influence is limited.

(3) The nitrite can reduce the corrosion current dramatically although in the initial corrosion period, which is mainly due to the booming of anode polarization slope. However, the nitrite cannot decrease the potential difference between cathode and anode in the initial corrosion period.

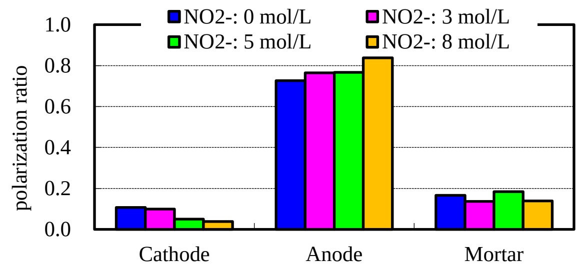

Fig. 5 Polarization Ratio

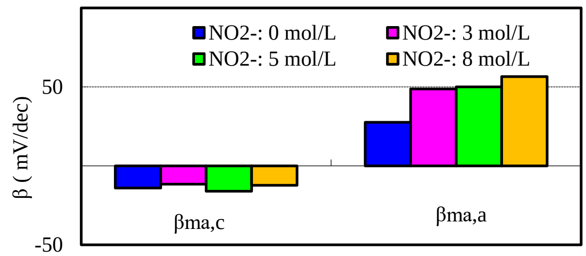

Fig. 6 Polarization Slope

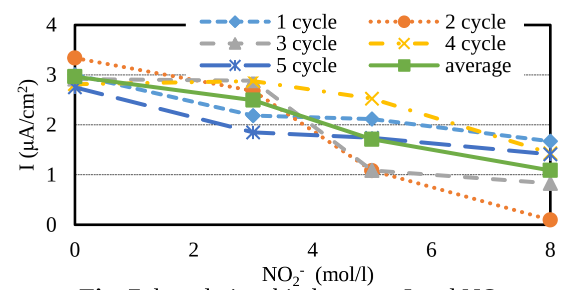

Fig. 7 the relationship between I and NO_2^-

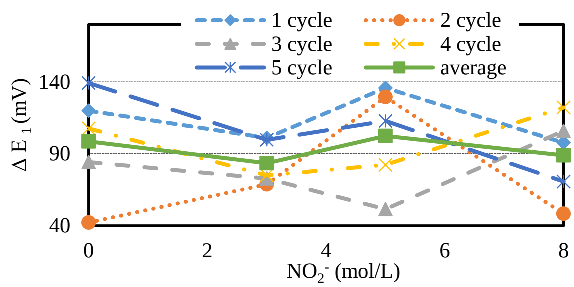

Fig. 8 the relationship between ΔE_1 and NO_2^-

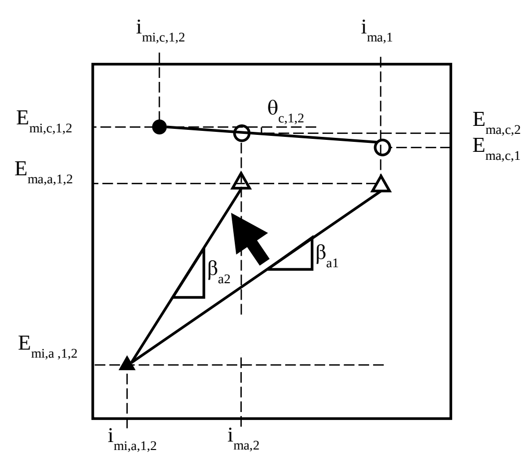

Fig.9 Mechanism of nitrite inhibitor