Influence of Organic Inhibitor on Corrosion Resistance of Steel in Simulated Concrete Pore Solution

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ABSTRACT

Organic corrosion inhibitor is one of lower cost technologies that limit the deterioration of concrete structures. The influence of a newly prepared organic corrosion inhibitor on the corrosion behavior of carbon steel in simulated concrete pore solution was investigated by polarization curves, electrochemical impedance spectroscopy, and so on. The effect of organic corrosion inhibitors on concrete working performance was also studied. The results show that the corrosion rate decreases with the concentration of inhibitor increase; when the content of inhibitor up to 1.5% versus water, the oxide film was completely passive. Organic corrosion inhibitor had no effect on work performance.

1. INTRODUCTION

Steel corrosion is one of the main factors that aggregate the deterioration of reinforce concrete. To minimize reinforcing steel corrosion, cathodic protection, inhibitors dosage or surface coating had been used. Among these, the use of corrosion inhibitors is considered one of the most cost–effective approaches (Valcarce & Vazquez, 2008).

For development of this technique, inorganic corrosion (mainly nitrite) was investigated and applied as early as the 1940s. As a result of possible toxicity, and worse, inhibition effect in case of insufficiency of nitrite, environment-friendly organic corrosion inhibitors have captured attention and have been applied in the market rapidly during the past 20 years (Sawada, Kubo, Page, & Page, 2007). Organic corrosion inhibitors usually promote formation of a chelate on the metal surface, which includes the transfer of electrons from organic compounds to metal, forming a coordinate covalent bond during such a chemical adsorption process. During this process, the metal acts as an electrophile, whereas the nucleophile centers of inhibitor molecules are normally hetero atoms with free electron pairs that are readily available for sharing and to form a bond (Soylev & Richardson, 2008; Zhou, Yang, & Wang, 2012).

Currently, amino alcohols have captured the mark because they present some advantages, such as low effect on concrete performance and increase in the density of the concrete, unlike organic acid or phosphate, which will reduce the compress strength or induce marked concrete setting retarding. However, many conflicting opinions have been reported, and uncertainties related to film formation and deterioration mechanisms still persist (Nmai, 2004; Welle et al., 1997).

In this study, a newly organic corrosion inhibitor was prepared. The electrochemical performance of carbon steel electrode influenced by newly organic inhibitor was investigated by linear polarization resistant (LPR) electrochemical impedance spectroscopy (EIS) in a synthetic medium that simulates the interstitial solution of concrete contaminated with chlorides. The corrosion behavior of steel in simulated concrete pore solution with and without this agent was discussed. The working performance of concrete influenced by this inhibitor was also investigated.

2. EXPERIMENTAL WORK

To obtain the corrosion inhibition efficiency of corrosion inhibitor, the corrosion behavior of carbon steel in simulated concrete pore solution (SCPs) was investigated. Corrosion inhibitor was synthesized by amine, aldehyde, and aromatic ketone, which was marked as ZX. The blank of SCPs is saturated calcium hydroxide with 0.3 mol L^{-1} sodium chloride adding 0.01 mol L^{-1} sodium hydroxide to adjust pH to 12.6, which is considered to simulate the chloride contaminated concrete pore solution. The solutions without ZX would be written as JZ. ZX was added to the solution at the following concentrations: 0.33, 1, and 1.5 wt.% (with respect to the amount of mixing water). The working electrodes were cut from carbon steel bar (Q235), composed of C < 0.22%, Mn < 1.4%, Si < 0.35%, S < 0.05, and P < 0.045, and the rest of Fe, and then connected to a copper wire and embedded in epoxy resin, leaving an exposed working area of 1 cm² for testing in SCPs. Before test, the electrodes were ground gradually with SiC paper (grade 240#, 400#, 1000#, and 2000#) and then degreased and rinsed with ethanol. All the experiments were performed three

times and all the experiments' reproducibility were kept. For electrochemical measurements, a three-electrode cell was used, consisting of a saturated calomel reference electrode (SCE), a platinum foil counter electrode, and the prepared working electrode. All the electrochemical experiments were carried out using 273A (Princeton Applied Research) with a 5210 lock-in amplifier. Linear polarization resistance was conducted at a sweep rate of 0.166 mV s^{-1} from –10 to 10 mV versus the open circuit potential (OCP). EIS was performed at the OCP in the frequency range of 100 kHz—10 mHz with a 10-mV amplitude signal and 10 points of decade after the electrodes were immersed in test solution
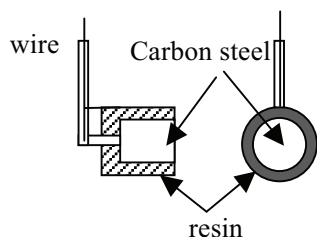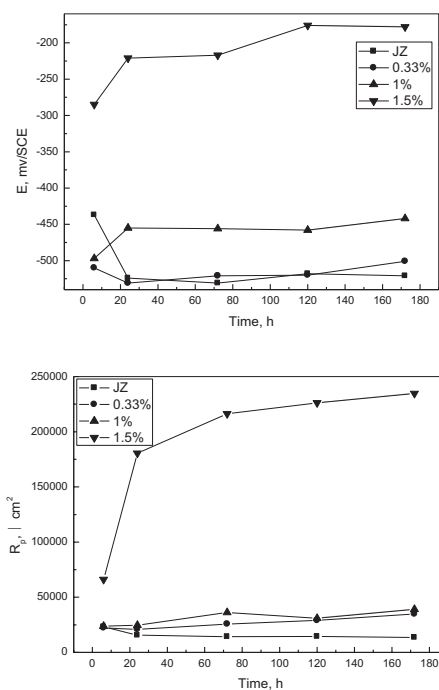

**Figure 1.** The schematic diagram of electrode immersed in simulated concrete pore solution.

Figure 2. Time varied of linear polarization resistant and corrosion potential of carbon steel immersed in SCPs without and with different concentration of ZX.

3. RESULT AND DISCUSSION

3.1 Influence of corrosion inhibitor on linear polarization curve

Linear polarization curve is a simple and fast electrochemical measurement to study the electrochemical behavior of carbon steel influenced by corrosion inhibitor. Two main electrochemical parameters fitted from linear polarization curves are corrosion potential (E) and polarization resistance (R_p); the fitted results were shown in Figure 2.

From the Figure 2, we can see that the corrosion potential carbon steel decrease with immersion time for JZ and with lower concentration of corrosion inhibitor in SCPs. When corrosion inhibitor added up to 1% versus mixture water, the corrosion potential increased with immersion time. When concentration of corrosion inhibitor is 1.5% versus mixture water, the corrosion potential increases to –200 mV (SCE), which means that the carbon steel was passive although the solution with 0.3 mol L^{-1} NaCl. Besides, the polarization resistance of carbon steel immersed in SCPs without and with different content of corrosion inhibitor also showed the same result with corrosion potential. Both the result of the corrosion potential and polarization resistance deformed that the corrosion inhibitor was an effective method to retard the corrosion rate of carbon steel in a chloride-contaminated system, and the ZX can effectively form a passive film when the content of ZX is up to a certain level.

3.2 Influence of corrosion inhibitor on EIS

The carbon steel was also evaluated by EIS in order to gain more insight into its corrosion behavior influenced by inhibitor in Figure 3. Figure 3 (a) and (b) show the Nyquist and Bode plots of carbon steel in JZ solution; the Nyquist plots show the capacitive loop decrease with immersion time, and phase angel in Bode plots also decrease, which means the chloride ions attack the steel surface and aggregate the corrosion rate. When 0.3 wt.% ZX corrosion inhibitor is added, the capacitive, both the loop diameter and phase angle increase with time. When ZX was added to 1.5 wt.%, the capacitive loop diameter and phase angle became very large, and the results show that the ZX can form an adsorption film on the steel surface and effectively retard chloride ions transforming the film layer. Therefore, when the content of ZX corrosion inhibitor was up to 1.5 wt.%, the impedance becomes large and corrosion was inhibited.

The shape of Bode plots and Nyquist plots let assume two times constant to fit the experimental data and it can be interpreted in terms of the equivalent circuit (Ormellese, Lazzari, Goidanich, Fumaglli, & Brenna, 2009). The appearance of two times constant can be attributed to the resistance and capacitance of passive film at low frequency and resistance of charge transfer and capacitance of electric double layer at higher frequency. The corresponding equivalent circuit is shown in Figure 4.
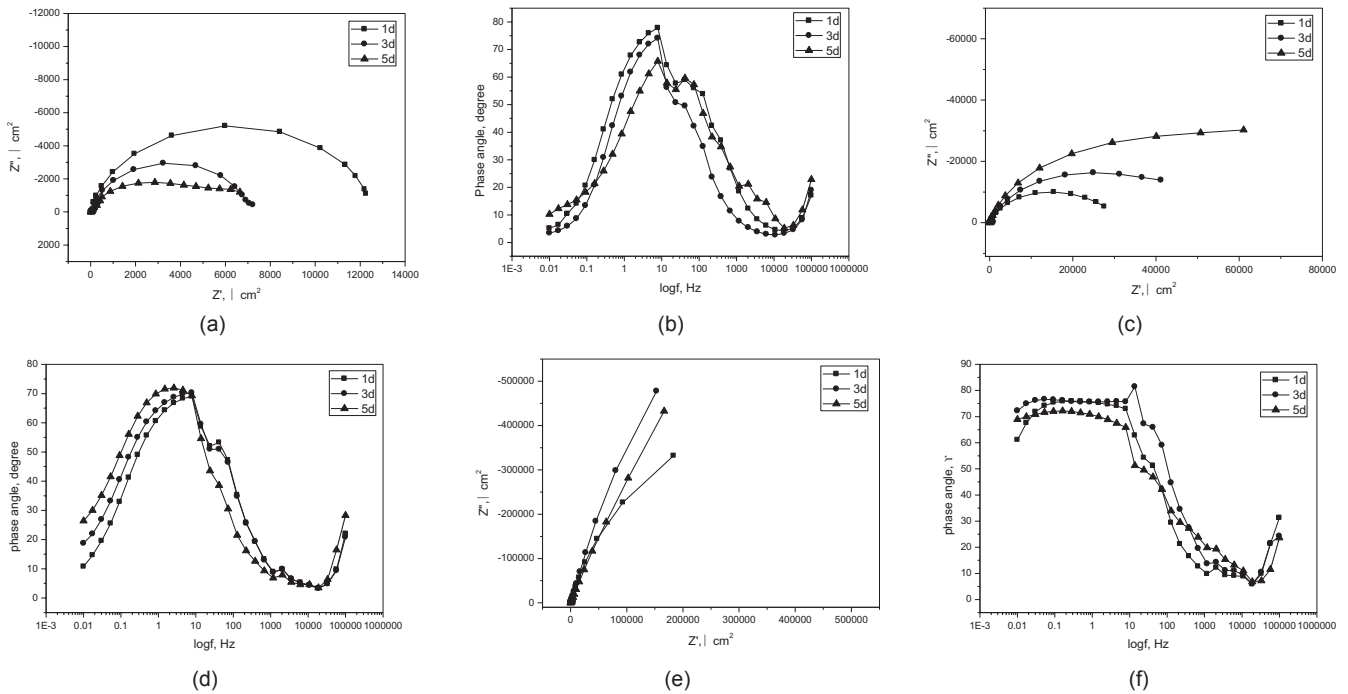
Figure 3. Nyquist plots and Bode plots of carbon steel in SCPs with different content of corrosion inhibitor (a) and (b) 0%, (c) and (d) 0.33%, (e), and (f) 1.5% during first, third, and fifth day.
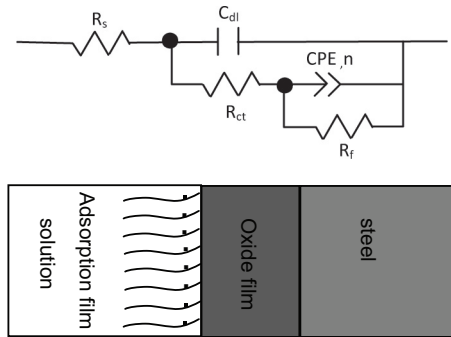
Figure 4. Electrochemical equivalent circuit.

The meaning of the symbols shown in Figure 4 and in Table 1 is as follows: R_s, solution resistance; R_{ct}, the charge transfer resistance; C_{dl}, double layer capacitance; R_f, film resistance; CPE, constant phase elements to replace the film capacitance (C_f); n, the CPE exponent. $Z(CPE) = [Q(j\omega)^n]^{-1}$, where Q is the constant, ω is the angular frequency, and n is the CPE power, which is an adjustable parameter that usually lies between 0.5 and 1, when $n = 0.5$, it is the Warburg resistance, $n = 1$, is the ideal capacity. The presence of the CPE is due to the distributed surface heterogeneity, roughness, fractal geometry, electrode porosity, and due to current and potential distributions related with electrode geometry (Cao, 2004; Zhou, Yang, & Wang, 2011). The fitted results of the experiment data by the proposed equivalent circuit are also shown in Table1. The R_{ct} and R_f decrease with immersion time. The results indicate that the values of R_{ct} and R_f increase with content of inhibitor. That is due to the growing adsorption film. The remarkable increase in R_{ct} suggests that the amount of inhibitor molecules adsorbed on the carbon steel surface

Table 1. The electrochemical parameters obtained from electrochemical impedance spectroscopy presented in Figure 3.

Sample	Time (day)	R_s	C_{dl}	R_{ct}	C_f	n	R_f
		$\Omega \cdot cm^2$	$\mu F \cdot cm^{-2}$	$k\Omega \cdot cm^2$	$\mu F \cdot cm^{-2}$		$k\Omega \cdot cm^2$
JZ	1	16.3	11.9	4.5	53.4	0.79	11.6
	3	18.9	12.8	3.8	54.1	0.72	9.2
	5	17.3	14.3	3.1	55.4	0.72	8.4
0.33% ZX	1	28.6	7.8	16.4	33.1	0.72	28.3
	3	26.7	7.7	17.5	26.5	0.79	32.0
	5	25.4	7.3	19.3	24.6	0.84	78.5
1.5% ZX	1	12.2	7.2	19.5	16.1	0.92	113.8
	3	22.5	7.0	20.7	15.5	0.93	257.9
	5	23.6	6.9	22.4	14.9	0.93	425.1

Table 2. Effect of corrosion inhibitor on concrete working performance.

Sample	Slump (mm)	Expansion (mm)	Air containing (%)	Setting time	
				Initial setting	Final setting
JZ	197	425	2.6	10:05	12:57
ZX	181	395	2.5	10:15	13:10

increases and consequently results in the decreasing of active sites where dissolution of iron is easy.

3.3 Influence of corrosion inhibitor on mortar performance

The corrosion inhibitor is as admixture, which will be added during concrete cast. Therefore, the effect of corrosion inhibitor on concrete working performance was investigated. All projects were tested by GB8076, which is a Chinese standard. The slump, expansion, air containing and setting was shown in Table 2. From Table 2, it can be seen that the corrosion inhibitor had less effect on the concrete working performance.

4. CONCLUSION

The electrochemical tests show that the corrosion of reinforcing steel in chloride contaminated SCPs was significantly reduced after adding a certain content of corrosion inhibitor, and the inhibition efficiency of ZX increase with the content of inhibitor. When the content of ZX added up to 1.5% versus mixture water, the steel surface was covered by corrosion inhibitor completely and corrosion rate became very low. Moreover, the ZX corrosion inhibitor had less effect on the concrete working performance, which can be used as admixture organic corrosion inhibitor.

ACKNOWLEDGMENT

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