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Na_2PO_3F as Corrosion Inhibitor in Carbonated Cement Extract Contaminated with Chloride Ions

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In a chloride contaminated carbonated concrete pore solution, the corrosion inhibition behavior of Na_2PO_3F on carbon steel rebar was studied by open circuit potential, linear polarization resistance, electrochemical impedance spectroscopy, respectively. The corrosion state of the rebar was also examined after 30 days immersion in the carbonated pore solution. The results suggest that the open circuit potential, the polarization resistance, the impedance of rebar increased with the concentration of Na_2PO_3F. The viewed corrosion state is consistent with these electrochemical testing results, suggesting that the corrosion inhibition effect of Na_2PO_3F is increased with its concentration. The inhibition effect was especially significant as the concentration of Na_2PO_3F exceeds 0.50%, and no visible corrosion onset was observed on the carbon steel rebar as the concentration of inhibitor further increased to 1.0% after 30 days immersion in the chloride contaminated carbonated pore solution.

Keywords: Concrete, carbon steel, corrosion inhibitor, Na_2PO_3F

1. INTRODUCTION

Corrosion of rebar is one of the main factors to reduce the durability of concrete structures [1-3]. Inhibitor is thought to be one of the most efficient methods to reduce the corrosion of rebar in the aggressive environment [4]. The traditionally corrosion inhibitor $Ca(NO_2)_2$ is gradually forbidden used for its toxicity and the high localized corrosion risk of rebar as insufficient quantity of the inhibitor in concrete [5]. Since Alonso [6] reported that Na_2PO_3F could reduce the corrosion rate of corroding rebar in the carbonated concrete, some researchers studied the corrosion inhibition of Na_2PO_3F on carbon steel rebar in concrete environment. Chaussadent [7] found that PO_3F^- could penetrate into carbonated concrete, while it difficult to penetrate into the non-carbonated concrete. Çopuroğlu [8] also found that the resistance of carbonated blast furnace slag cement concrete against frost salt attack was significantly improved by Na_2PO_3F treatment. In these reports, the Na_2PO_3F were used as migration inhibitor for carbonated concrete structure without deep study the concentration of the inhibitor. In the present study, the corrosion inhibition of Na_2PO_3F on carbon steel rebar was studied in the carbonated cement extract solution. The inhibition effect of Na_2PO_3F was studied and the effective concentration of Na_2PO_3F also was discussed.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Carbon steel rods were cut in 50 mm length after the scale layers were polished. The samples were degreased with acetone, rinsed with alcohol, and dried in hot air. Then, copper wires were welded at one end of the prepared samples. After that, both ends of the samples were coated with epoxy resin. The cement extract solution was prepared by adding 1000 g of ordinary Portland cement (PO 42.5) to 5 L of distilled water. Before being filtered, the mixed solutions were stirred for 30 min. The pH of the filtered solution was adjusted to a value of 9.5 by using a dilute nitric acid solution as the carbonated concrete pore solution. The solution with 0.5 M Cl^- was applied to accelerate the corrosion of the rebar. Different concentrations of Na_2PO_3F, including 0.125%, 0.25%, 0.50%, and 1.0% (wt.%, corresponding to 0.00868M, 0.0174M, 0.0347M, and 0.0694M concentration of the inhibitor) were added in the carbonated pore solution to study the inhibitor behavior of Na_2PO_3F.

2.2 Experiments

After been immersed in the carbonated chloride contaminated pore solution for different time, the open circuit potential (OCP), linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) of the rebars were tested. The electrochemical testing were performed by using a CS350 workstation (Corrtest Instrument, China) in glass cell, at room temperature, with a platinum electrode as a counter electrode and a saturated calomel electrode as a reference electrode. The LPR were test in a scan rate of 10 mV/min at voltages of ±10 mV, with respect to the OCP. The EIS testing was performed at frequencies ranging from 10^5~10^{-2} Hz and an alternating current disturbance signal of 10 mV was applied on the carbon steel electrode at the OCP. After exposed to the aggressive solution for 30 days, the corrosion states of the rebar in solution contained with different concentrations of Na_2PO_3F were examined.

3. RESULTS AND DISCUSSION

3.1 Open circuit potential

The OCP values of the carbon steels in pore solution with various concentration of Na_2PO_3F are presented in Fig. 1. As the results show, it is easy to notice that the OCP value increased with the increasing concentration of Na_2PO_3F. The increment is especially obvious when the concentration exceeds 0.50%. This situation is consistent with the earlier report which comes from Alonso [6]. Alonso et al [6] also found that the OCP of the rebar was improved by the added Na_2PO_3F in the carbonated saturated calcium hydroxide solution. However, the OCP values (Fig. 1) of samples in the Na_2PO_3F contained solutions in here is much lower than those described by Alonso and Andrade [6]. This difference may have resulted from the different chemical composition of pore solution and the concentration of Na_2PO_3F.

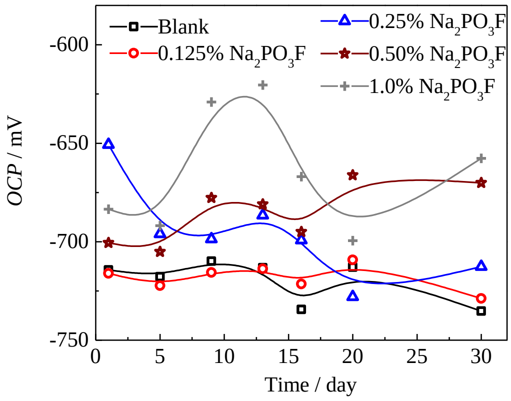

Figure 1. OCP of carbon steel rebar in the carbonated pore solution with various concentrations of Na_2PO_3F.

3.2 Linear polarization resistance

Polarization resistance (R_p) of samples in pore solution with different concentrations of Na_2PO_3F was measured and the corresponding corrosion current density (i_{corr}) was calculated from the resistance as follows:

$$i_{corr} = (\beta_a\beta_c)/[2.303R_p(\beta_a+\beta_c)] = B / R_p \qquad (1)$$

where R_p is the polarization resistance, B is a constant as a function of β_a and β_c, the anodic and cathodic Tafel slopes [9], respectively. For the carbon steel rebar in concrete environment, the B value is normal equal to 26 mV for active state and 52 mV for passive state. In the present study, all the i_{corr} was obtained from Eq.(1) assumed B is 26 mV. As the results in Fig. 2 and Fig. 3 shows, the R_p of samples significantly increased, while the i_{corr} obviously decreased with the concentrations of Na_2PO_3F in the carbonated pore solution. When the concentration exceeds 0.50%, these changing trends are more significantly. In addition, comparing with the samples in the solution without the inhibitor, the i_{corr} of the ones in the solution contained 1.0% Na_2PO_3F is almost lower one order of magnitude (Fig. 3). This concurs with the OCP results, which indicated that the Na_2PO_3F presents effective corrosion inhibition for carbon steel in the carbonated cement extract. On the other hand, the corrosion current density of samples here is much lower than that of carbon steel in the carbonated saturated calcium hydroxide solution [6], even the concentration of Na_2PO_3F in the former is much lower than the later. This situation may be related to the chemical composition of the simulated concrete pore solutions. Similarly, Veleva et al. [10] noticed that an AISI316 stainless steel was better passivated in a cement extract than in a saturated calcium hydroxide solution, and the authors attributed it to the Si and S compositions in the cement extract promote the samples surface formation a more protective film [11]. Thereby, in this study, the carbon steel samples in the cement extract here show the lower current densities than those ones in the saturated calcium hydroxide solution [6].

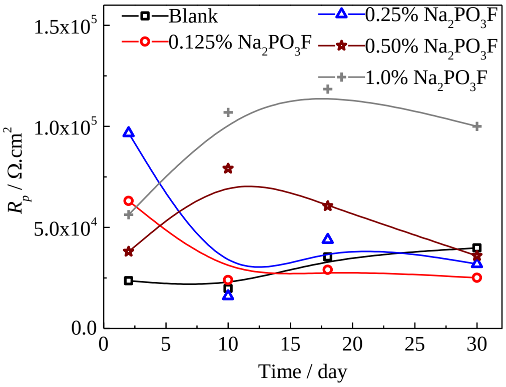

Figure 2. R_p of carbon steel rebar in the carbonated pore solution with various concentrations of Na_2PO_3F.

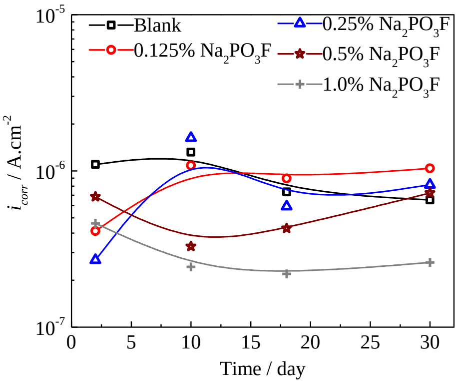

Figure 3. Corrosion current density of carbon steel rebar come from R_p for samples in various concentrations of Na_2PO_3F pore solution.

3.3 Electrochemical impedance spectroscopy

The impedances of carbon steel samples in the carbonated pore solution with different concentration of Na_2PO_3F are presented in Fig. 4 and Fig. 5. As the results show, the radius of the capacitive loop evidently increases with the increasing concentration of Na_2PO_3F (Fig. 4). On the other hand, it is easy to notice than the value of the impedance of samples do not show significantly change since 3 days' immersion (Fig. 5) in the carbonated pore solution with the inhibitor.

To further understand the inhibit character of Na_2PO_3F in the cement extract, the EIS results are fitted to an equivalent circuit (Fig. 6) by using the Zsimpwin software. In the equivalent circuit, R_s represents the solution resistance, R_p is the polarization resistance caused by charge transfer reaction, and Q is a constant phase element (CPE) or a capacitance of the double layer capacitor that characterizes the charge separation between the metal and electrolyte interface [12]. Among that, the protective performance of passive film can thus be described by R_p [13] and the fitting results are presented in Table 1 and Figure 5. Clearly, the polarization resistances come from the EIS results also significantly increase with the concentration of Na_2PO_3F in the carbonated cement extract. As the concentration of Na_2PO_3F higher than 0.50%, the increase rate of R_p is also more obvious. These results are consistent with these results from the OCP and LPR tests, suggesting Na_2PO_3F could offer an effective inhibition on corrosion of carbon steel when the concentration exceeds 0.50% in the carbonated pore solution. Furthermore, it is easy to notice that the fitted polarization resistance (figure 7), together with the OCP (figure 1) and LPR results (figure 2) of rebar do not show significantly change during the whole immersion process. This situation indicated that Na_2PO_3F exhibits the corrosion inhibition effect since the initial immersion.

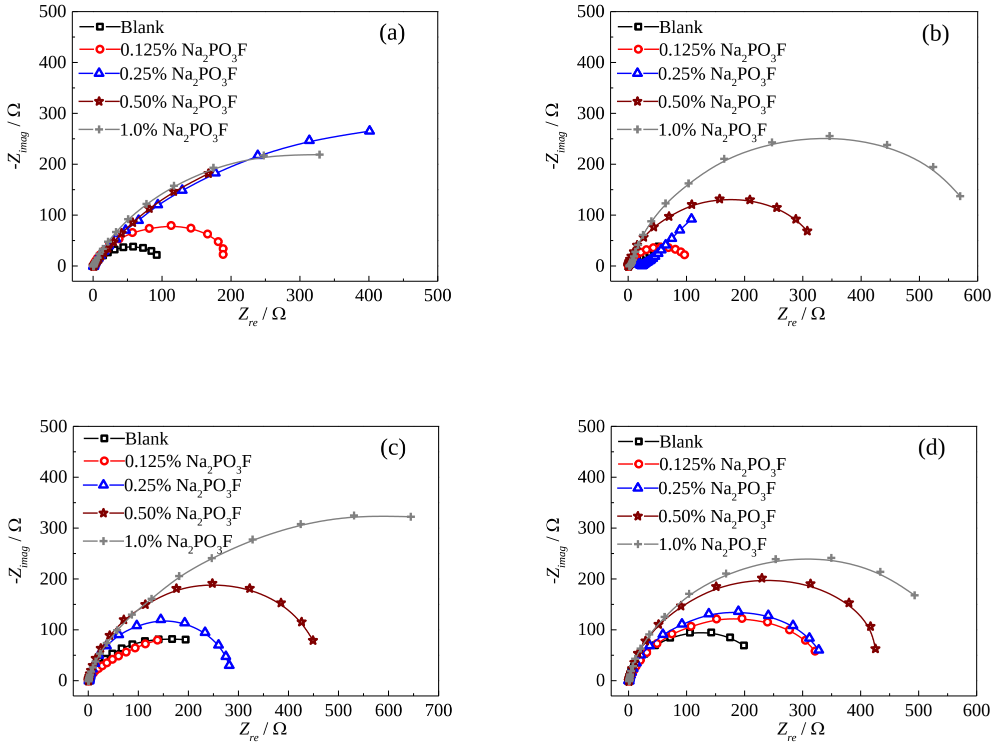

Figure 4. Nyquist plots of carbon steel rebar in the carbonated pore solution with various concentrations of Na_2PO_3F. (a) 4 days, (b) 13 days, (c) 23days; (d) 30 days.

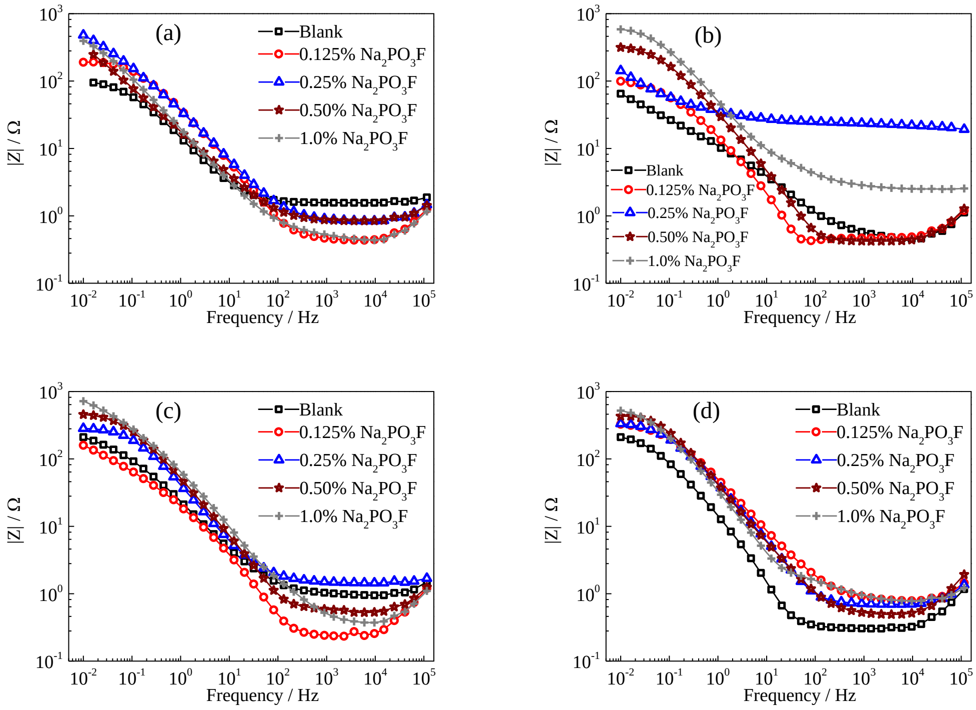

Figure 5. Bode plots of carbon steel rebar in the carbonated pore solution with various concentrations of Na_2PO_3F. (a) 4 days, (b) 13 days, (c) 23days; (d) 30 days.

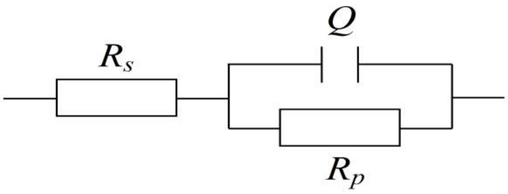

Figure 6. Equivalent electrical circuit for modeling the impedance data.

Table 1. The fitting results of EIS data.

Time	Concentration of Na_2PO_3F	R_s ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)	Q ($\Omega^{-1}.S^n.cm^{-2}$)	n
4 days	blank	25.2142	1628.09	0.01621	0.7982
	0.125%	11.3526	3041.09	0.004908	0.8634
	0.25%	15.5304	9148.39	0.007120	0.7597
	0.50%	15.2557	9471.81	0.01556	0.7149
	1.0%	10.9869	8782.58	0.01186	0.8063
13 days	blank	10.8660	1147.36	0.02949	0.5887
	0.125%	10.3918	1399.81	0.01245	0.9074
	0.25%	33.8806	2866.82	0.03019	0.647
	0.50%	11.8190	7010.05	0.003593	0.9006
	1.0%	42.6255	12608.67	0.004643	0.7575
	blank	17.0660	3585.88	0.01088	0.7502

22 days	0.125%	10.3918	2969.81	0.01245	0.9074
	0.25%	23.8954	4681.74	0.004966	0.8580
	0.50%	11.8190	7010.05	0.003593	0.9006
	1.0%	10.7435	11076.35	0.003542	0.8239
22 days	blank	9.58010	3141.57	0.01268	0.9568
	0.125%	15.4802	5320.73	0.004432	0.7996
	0.25%	13.5428	5133.90	0.004609	0.8865
	0.50%	16.8618	7336.61	0.004425	0.8949
	1.0%	16.0768	9591.13	0.006395	0.8609

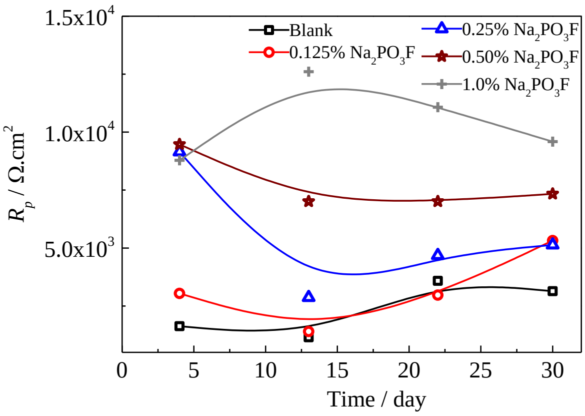

Figure 7. Fitted R_p of the samples as a function of concentration of Na_2PO_3F.

3.4 Corrosion state of rebars

The corrosion state of the carbon steel samples in the carbonated pore solution with various concentrations of Na_2PO_3F was examined after 30 days immersion. As the results in figure 8 show, the rebar in the solution without or a low concentration (0.125% and 0.25%) of Na_2PO_3F was serious corroded, while the ones in the solutions with higher concentration (0.50% and 1.0%) of inhibitor were significantly protection. Especially, the rebar in the solution contained 1.0% Na_2PO_3F do not show any obvious corrosion onset.

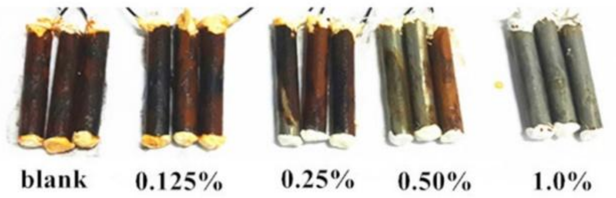

Figure 8. Corrosion state of the rebar in the carbonated pore solution with various concentrations of Na_2PO_3F after 30 days.

The corrosion state situation is consistent with these electrochemical testing results (figure 1, figure 3, and figure 7), further confirmed that the Na_2PO_3F is an efficient corrosion inhibitor for the carbon steel rebar even in the carbonated concrete environment. The inhibition effect of Na_2PO_3F is especially obvious when its concentration exceeds 0.50% in the Cl^- contaminated carbonated pore solution.

4. CONCLUSIONS

(1) In the chloride contaminated carbonated concrete pore solution, the value of OCP, polarization resistance, and impedance of the carbon steel rebar increased; the corrosion of rebar decreased with the concentration of Na_2PO_3F.

(2) The OCP, polarization resistance, and impedance of rebar does not show significantly change as the immersion time prolong. This situation suggests that Na_2PO_3F exhibits the protection effect since the initial immersion.

(3) The corrosion inhibition effect of Na_2PO_3F on the carbon steel rebar increased with the concentration of the inhibitor. After 30 days immersion in the chloride contaminated carbonated pore solution, the corrosion of rebar was obviously reduced as the concentration of Na_2PO_3F exceeds 0.50%, and no visible corrosion onset was observed on the carbon steel rebar as the concentration of inhibitor further increased to 1.0%.

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