Int. J. Electrochem. Sci., 14 **(2019)** 8601 – 8610, doi: 10.20964/2019.09.29

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Corrosion-Inhibition Effect of Different Phosphate Compounds for Carbon Steel in Chloride-Contaminated Mortars

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Received: 14 April 2019 / *Accepted:* 24 June 2019 / *Published:* 31 July 2019

The corrosion-inhibition efficiency of four different phosphates, including aluminum tripolyphosphate (ATP), disodium hydrogen phosphate (DHP), sodium pyrophosphate (SPP), and their mixture (COM), were investigated in Cl^--containing mortars. Measurements of the open circuit potential, polarization curve, linear polarization resistance, and electrochemical impedance spectroscopy were performed on carbon steel samples. Furthermore, the morphologies of the corroded rebars were examined after 30 days. The results suggested that corrosion of the rebar in the ATP-containing mortar was suppressed, indicating that the ATP is an efficient corrosion inhibitor.

Keywords: Phosphate corrosion inhibitor; Mortar; Carbon steel; Electrochemical test

1. INTRODUCTION

A reinforcing steel bar is protected by concrete, because a highly alkaline pore solution leads to passivation of the bars [1–3]. After chloride ions penetrate from the environment to the concrete/rebar interface and the ion concentration reaches a critical value, the bars will corrode. In general, the volume of the corrosion products are several times that of the steel substrate, thereby resulting in high stresses at the concrete/rebar interface and, consequently, cracks in the concrete cover layer. Many methods, including cathodic protection, coating, and corrosion inhibition, have been developed with the aim of reducing the corrosion of rebar in marine concrete structures. As an economical and effective method, corrosion inhibition has been widely used in practical engineering [4]. Sodium nitrite has been used as a corrosion inhibitor in concrete structures for several decades [5], but owing to the toxicity of this compound, its use has recently been forbidden in many countries. Therefore, replacement of this compound with environmentally friendly corrosion inhibitors is essential.

Phosphates have attracted significant attention, owing to their low cost and high efficiency of corrosion inhibition [6]. Unfortunately, most of these studies have focused on the effect of phosphates on the corrosion of rebar in simulated pore solutions [7, 8], and only a few have been performed in mortar or concrete [3]. In fact, the mechanism governing the action of phosphates in mortars or concretes is more complex than the mechanism governing the action in pore solutions. Some authors [9] have suggested that the phosphate ion combines with Fe^{3+} and Fe^{2+} to form the insoluble ferric phosphate and soluble ferrous phosphate, respectively. The formation of ferrous phosphate leads to a decrease in the concentration of phosphate ions and an increase in the pH value at the metal/solution interface. Simultaneously, the hydrolysis equilibrium of the phosphate is changed, and the ferrous phosphate gradually becomes the insoluble ferric phosphate, which accelerates the passivation of rebar.

Na_3PO_4 is one of the most common phosphates and its inhibition behavior on carbon steel in a simulated pore solution or in mortar has been extensively investigated [10–12]. Etteyeb and co-authors [13] compared the corrosion resistance of the rebars pretreated with Na_3PO_4 (SP) to that of rebar immersed in a Na_3PO_4-containing pore solution. The results revealed that the corrosion resistance of the former was higher than that of the latter. Yohai and co-authors [3] investigated the corrosion behavior of carbon steel in Cl^--contaminated mortar, where $Na_3PO_4.12H_2O$ was added to the mortar to inhibit corrosion of the steel. The resulting polarization curves indicated that $Na_3PO_4.12H_2O$ is a mixed corrosion inhibitor. In addition, phosphate ions as inhibitors had no effect on the E_{corr} values. However, Shi and co-authors [6] reported that phosphates may be a cathodic inhibitor, based on its lower corrosion rate and more negative E_{corr} at the same dosage as nitrite in mortar specimens. Aluminum tripolyphosphate (ATP) and disodium hydrogen phosphate (DHP), in addition to Na_3PO_4, have also been investigated, and the resutls revealed that the corrosion of rebar in concrete using those compounds was significantly suppressed [14–16]. Bastidas and co-authors [4] assessed the corrosion behavior of rebars in separate mortar mixes containing Na_2PO_3F, Na_2HPO_4, and $Na_3PO_4.H_2O$. The effect of each phosphate on this behavior was evaluated by comparing the linear polarization resistance values and corrosion potentials. The authors reported that these phosphates were anodic corrosion inhibitors and the order of the inhibition efficiency was $Na_2PO_3F > Na_2HPO_4 > Na_3PO_4.H_2O$. Many studies have focused on the corrosion inhibition of phosphates, but owing to contradictory results [3, 6], further studies are required.

In the present study, ATP, DHP, SPP, and a mixture of all three were employed as corrosion inhibitors in mortars. The inhibition efficiency of each compound was determined via electrochemical tests including measurements of the open circuit potential (OCP), linear polarization resistance (LPR), polarization curves,and electrochemical impedance spectroscopy (EIS). Furthermore, the corrosion status of the rebar in Cl^--contaminated mortar with different inhibitors was evaluated after 30 days. The results suggested that ATP exhibits the highest efficiency for corrosion inhibition of the rebar housed in mortars.

2. EXPERIMENTAL METHODS

2.1. Materials

Carbon steel bars with a diameter of 10 mm were each cut to a length of 50 mm. The samples were polished using grit papers to No. 600, washed with deionized water, degreased with ethanol, and then dried in hot air. In preparation for the electrochemical tests, copper wires were welded at one end of each bar and the welds were coated with silicone.

The cylindrical mortar specimens containing the prepared rebars were used to conduct the experiment. The water-cement ratio (W/C) and cement-sand ratio of the mortar, prepared from Ordinary Portland cement (P.O 42.5) and river sand, are 0.5 and 0.65, respectively. The mortars did not mixed the corrosion inhibitor was used as the control sample. Four types of corrosion inhibitors, aluminum tripolyphosphate (ATP, $AlH_2P_3O_{10}\cdot 2H_2O$), disodium hydrogen phosphate (DHP, $Na_2HPO_4\cdot 12H_2O$), sodium pyrophosphate (SPP, $Na_4P_2O_7\cdot 10H_2O$) and a mixture of the three (COM, consists of 0.1% $AlH_2P_3O_{10}\cdot 2H_2O$, 0.1% $Na_2HPO_4\cdot 12H_2O$, and 0.1% $Na_4P_2O_7\cdot 10H_2O$), were added to the mortars at a ratio of 0.3% (wt.%) of cement. For accelerated corrosion of the rebar, 3.0% (wt.%) NaCl was dissolved in water to prepare the mortar samples. The carbon steel sample was placed in the middle of a $\Phi 20 \times 60$ mm tube mold, and then the stirred mortar was poured into the mold. After curing for 24 h, the mortar samples were removed from the molds and immersed in a 3.5% NaCl solution.

2.2. Experiments

A triple-electrode system was used to conduct the electrochemical tests. The carbon steel sample, a platinum electrode, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. Measurements of the OCP, linear polarization, polarization curve, and electrochemical impedance spectroscopy were performed. Linear polarization was performed at a scan rate of 10 mV/min in the range of open circuit potential of 10 mV. A disturbance signal of 10 mV and a frequency range of 10^5 to 10^{-2} Hz were employed for EIS. The polarization curve was performed at a scan rate of 1 mV/s in the range of -0.3~1.5 V via the open circuit potential. The corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were calculated based on the polarization curves results by using the Cview2 software. All electrochemical tests were repeated five times and a new sample was used each time. Average values in the OCP and LPR results, and the middle curve in the EIS results was accepted and used as the result. In addition, the corrosion status of the rebars was evaluated after a 30-day exposure of the Cl^--contaminated mortars.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential

Open circuit potentials (OCPs) were recorded every 5 days (see Figure 1). As the results show, the OCP values of the carbon steel in the mortar containing inhibitor increased with time in the initial

20 days, indicating the passivation of the carbon steel in the mortars. Similarly, Nahali [17] also noticed that the open circuit potential of carbon steel was improved by the addition of Na_3PO_4 in 0.2% $Ca(OH)_2$ solution. The OCP of the carbon steel sample in the ATP-containing mortar is substantially higher than those of the samples in other mortars. Additionally, the OCP values of the samples in the ATP- and COM-containing mortars are more positive than that of the sample in the blank mortar; however, the corresponding values of the SPP- and DHP-containing mortars are more negative. This indicates that the ATP and COM can efficiently inhibit the corrosion of the carbon steel in the Cl^--contaminated mortars.

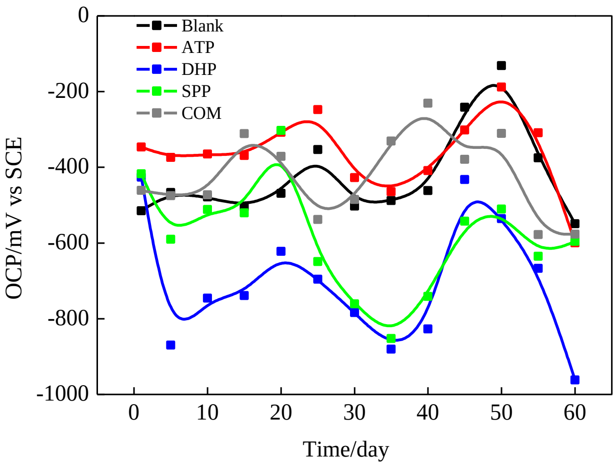

Figure 1. OCP values of the carbon steels in the Cl^-- contaminated mortars containing different 0.3% phosphate inhibitors immersion in a 3.5% NaCl solution.

3.2. Polarization curves

Polarization curves (see Figure 2) of the carbon steel rebars were measured after a 30-day exposure of the Cl^--contaminated mortars with different inhibitors. The corrosion parameters calculated from the polarization curves were listed in table 1, which reflects the effects of the different inhibitors on the values of the associated electrochemical parameters, including the corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), and corrosion rate. As the results show, except for the current density of the rebar in the SPP-containing mortar, the current densities in the anodic zones of the carbon steel samples in other mortars are considerably lower than that of the samples in the blank mortar. This is especially true for the steel in the ATP-containing mortars, which exhibited the lowest current density, and the steel in the COM-containing mortar that exhibited an extremely low current density. The results also show that the rate of corrosion decreased as the corrosion potential (E_{corr}) of the steel in ATP-containing mortars shifted toward increasingly positive values. This finding is consistent with the OCP results (Figure 1), suggesting the the ATP and COM inhibitors can efficiently hinder the corrosion of rebars in the Cl^--contaminated mortar. In contrast, the SPP and DHP yielded only slight reductions in the anodic current densities of the steel in the mortars. However, Yohai [3] investigated the polarization curves of carbon steel in the mortar containing $Na_3PO_4.12H_2O$, and noticed that both the anodic and cathodic current densities of steel were reduced by the addition of $Na_3PO_4.12H_2O$.

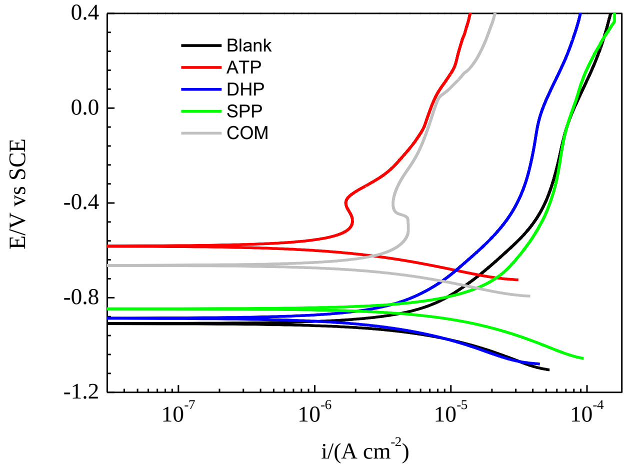

Figure 2. Polarization curves of the carbon steel samples in the Cl^--contaminated mortars containing different 0.3% phosphate inhibitors after 30 days of immersion in a 3.5% NaCl solution.

Table 1. Electrochemical parameters of the carbon steels in the Cl^--contaminated mortars containing different 0.3% phosphate inhibitors after 30 days of immersion in a 3.5% NaCl solution

inhibitor	β_a (mV/dec)	β_c (mV/dec)	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (mm/a)
Blank	333	163	5.259E-6	-0.910	0.061875
ATP	278	85	1.2612E-6	-0.582	0.014834
DHP	504	198	4.6179E-6	-0.887	0.054137
SPP	229	146	7.0743E-6	-0.847	0.083209
COM	285	100	2.7218E-6	-0.664	0.032014

3.3. Linear polarization resistance

The linear polarization resistance (R_p) of the carbon steel sample in each of the mortars with different inhibitors was measured every 5 days (see Figure 3). As the results show, for the steel in the mortar without inhibitor, the R_p is in the magnitude of 10^4 $\Omega.cm^2$, suggesting the carbon steel was in a active state according to an earlier study [18]. For the counterparts in the mortar contained with the phosphates inhibitors, the values of R_p are much higher than that of the control sample, which indicating that the phosphates inhibitors can reduce the corrosion of reinforcement in the Cl^- contaminated mortars. Stable R_p values of the samples were rapidly reached, i.e., after 20 days. Moreover, the lowest and highest R_p values were obtained for the steel in the blank mortars and the steel in the ATP-containing mortars, respectively. This further confirmed that ATP can hinder corrosion of the carbon steel rebar in Cl^--contaminated mortars.

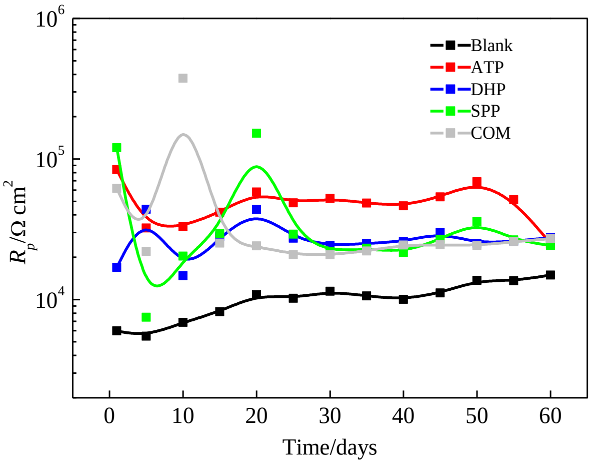

Figure 3. Time dependence of R_p characterizing the carbon steels in the Cl$^-$-contaminated mortars containing different 0.3% phosphate inhibitors inmmersion in a 3.5% NaCl solution.

3.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is commonly employed for corrosion studies of the rebar in concrete [1, 19, 20]. In the present study, mortars with various inhibitors were immersed in a 3.5% solution and the impedances of carbon steel samples in these mortars were measured at 40 days. As the results in Figure 4 show, the impedances of the samples in the inhibitor-containing mortars were significantly higher than that of the sample in the blank mortar. The highest impedance was obtained for the rebar in the ATP-containing mortar. This is consistent with the polarization curves and the liner polarization resistance results, which indicated that ATP added to the Cl$^-$-contaminated mortars is the most effective inhibitor for the carbon steel rebar.

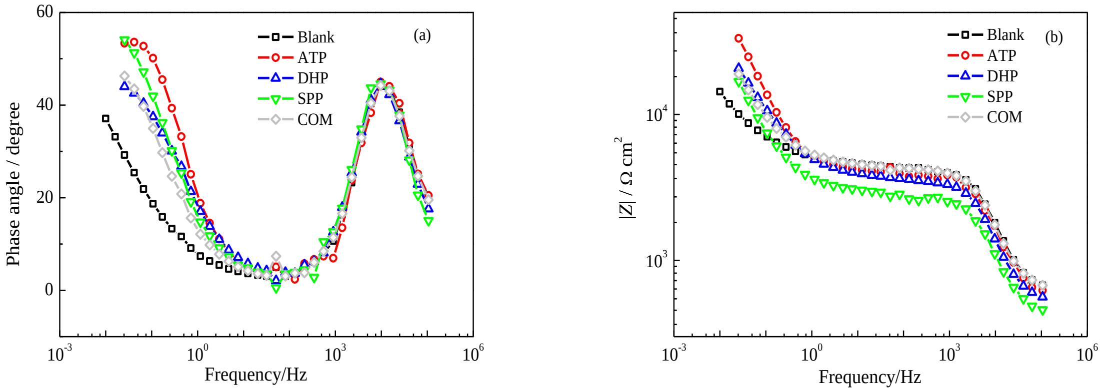

Figure 4. Impedances of the carbon steels at 40 days in the Cl$^-$-contaminated mortars containing different 0.3% phosphate inhibitors immersion in a 3.5% NaCl solution, (a) phase-frequency plots and (b) Bode plots.

In addtion, an equivalent circuit (see Figure 5) was used to fit the EIS results. R_s represents the solution resistance, R_{con} and C_{con} are the resistance and capacitance, respectively, of the concrete cover layer. Similarly, R_{ct} is the polarization resistance, and Q_{ct} is the the constant phase element, which is used in place of the pure capacitance characterizing the double layer capacitance [21, 22].

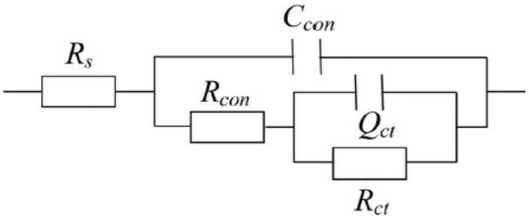

Figure 5. Equivalent circuit used to fit the EIS data.

The fitting results are shown in Figures 6 and 7, respectively. As the figures show, the resistance of the concrete cover layer (R_{con}) increased with time, whereas the capacitance of the layers (C_{con}) decreased. Actually, this situation is related to the hydration reaction of cement in the concrete cover layers.. In fact, according to a previous study [23], the impedance and the angle at low frequency values (<10 Hz) increase with increasing cement content of the mortar. The authors attribuated this increase to the C-S-H and C-A-H hydration products in the mortars, which increased with increasing cement content, thereby leading to enhanced compactness of the mortar. In the present study, the C-S-H and C-A-H content also increased as the hydration reaction of the cement progressed, thereby leading to increased compactness of the mortars. Thus, the impedances of the concrete cover layer increased with time, whereas the capacitance decreased, as shown in Figure 6(a) and 6(b), respectively. The impedances characterizing the concrete cover layer of the ATP- and SPP-containing mortar were slightly lower than that of the blank mortars, whereas the impedances of the DHP- and COM-containing mortars were slightly higher. This suggests that ATP and SPP have a negative effect on the hydration reaction of cement in the mortars, whereas DHP and COM have a positive effect.

The fitting results of Q_{ct} and R_{ct} are presented in Figure 7. As the figure shows, with the addition of inhibitors to the mortars the polarization resistance (R_{ct}) of the carbon steel rebars increased significantly, compared with that of the blank mortar. In contrast, the value of the constant phase element Q_{ct} decreased considerably. This may have resulted from protection films formed on the carbon steel surface in the inhibitor-containing mortars. Moreover, the highest R_{ct} was obtained for the sample in the ATP-containing mortars, consistent with the polarization curves (Figure 2) and the linear polarization resistance (Figure 3) results. This indicates that the ATP is the most effective inhibitor among the four types of phosphates.

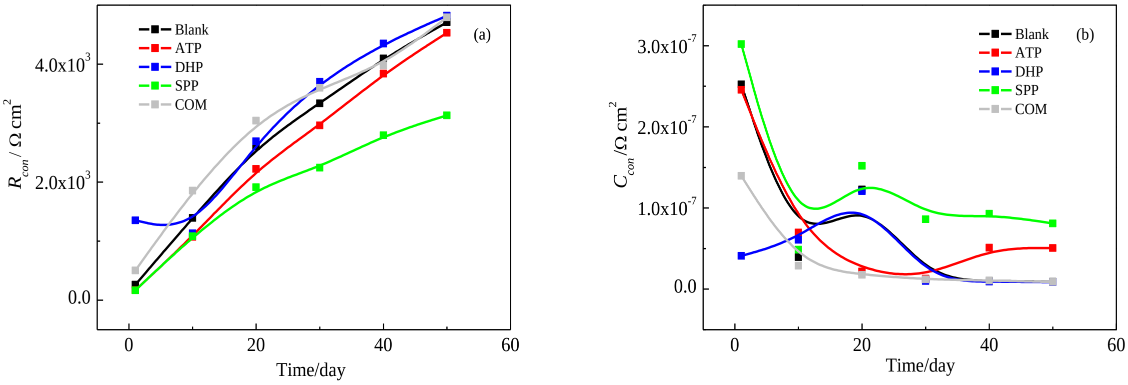

Figure 6. Fitting results (a) R_{con} and (b) C_{con} of the Cl^--contaminated mortars at 40 days containing different 0.3% phosphate inhibitors immersion in a 3.5% NaCl solution.

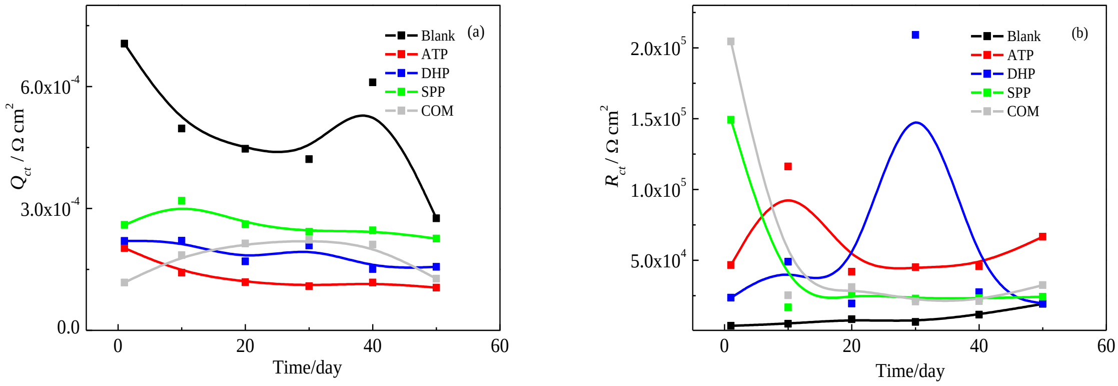

Figure 7. Fitting results (a) Q_{ct} and (b) R_{ct} of the Cl^--contaminated mortars at 40 days containing different 0.3% phosphate inhibitors immersion in a 3.5% NaCl solution.

3.5. Corrosion morphology

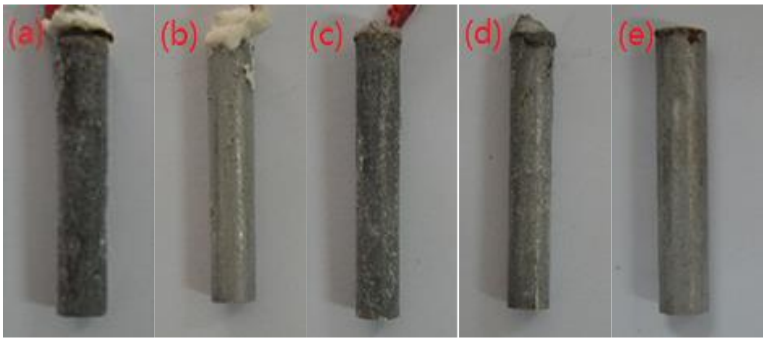

Figure 8. Images of carbon steels in the Cl^--contaminated mortars containing different 0.3% phosphate inhibitors, after 30 days of exposure to a 3.5% NaCl solution, (a) blank mortar and mortar containing (b) ATP, (c) DHP, (d) SPP, (e) COM.

The corrosion degree of the carbon steel rebars in the Cl^--contaminated mortars was evaluated after 30 days (see Figure 8). As the results show, the carbon steel rebars in the blank mortar (Figure 8(a)) and the DHP-containing mortar (Figure 8(c)) underwent severe corrosion. However, the samples in the SPP-containing (Figure 8(d)) and COM-containing mortars (Figure 8(e)) were only slightly corroded, and the ATP-containing mortar seemed to be corrosion free. In summary, the corrosion status results (Figure 8), together with the electrochemical results (Figures 2–4), comfirmed that the ATP can effectively inhibit corrosion of carbon steel in the Cl^--containing concrete.

4. CONCLUSIONS

The same amounts of ATP, DHP, SPP, as well as compounds of these three phosphates were added to Cl^--contaminated mortars to investigate the corrosion-inhibition effect on the carbon steel. Electrochemical tests, including measurements of the OCP, polarization curves, linear polarization resistance, and electrochemical impedance spectroscopy were performed. Furthermore, the corrosion status of the rebar was evaluated. The major findings of this work are summarized as follows:

(1) The addition of the phosphate inhibitors yielded a significant increase in the polarization resistances of the carbon steel in the Cl^--containing mortars.

(2) The phosphate inhibitors resulted in increased polarization resistance of the rebar, and affected the quality of the concrete cover layer. The ATP and SPP had a negative effect on the hydration reaction in the mortars, whereas the DHP and compounds had a positive effect.

(3) Among the four corrosion inhibitors, the ATP exhibited the highest efficiency for suppressing corrosion of the carbon steel rebar in the Cl^--contaminated mortar.

ACKNOWLEDGMENTS
This research was supported by the National Natural Science Foundation of China (51601074), the Fundamental Research Funds for the Central Universities (2018B07214, 2019B62014), the Opening Fund of State Key Laboratory of Geohazard Prevention and Geoenvironment Protection (Chengdu University of Technology) (Grant SKLGP2018K014), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJKY19-0505).

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