Effects of phosphate on the chloride-induced corrosion behavior of reinforcing steel in mortars

J.J. Shi *, W. Sun

School of Materials Science and Engineering, Jiangsu Key Laboratory of Construction Materials, Southeast University, Nanjing 211189, China

ABSTRACT

The influence of phosphate as a corrosion inhibitor on the corrosion behavior of as-received and pre-rusted reinforcing steels in mortar specimens was investigated after 360 days exposure in 3.5% NaCl solution. This involved the use of electrochemical techniques for studying the steel surface reactions and microscopic observations of the steel–mortar interface. The electrochemical methods, including electrochemical impedance spectroscopy (EIS) and measurements of corrosion potential (E_{corr}) and linear polarization resistance (LPR), were employed to evaluate the corrosion tendency and general corrosion rate of steel. In addition, the pitting corrosion resistance of steel was also determined by cyclic polarization (CP) measurements. The results indicate that different from nitrite, which is generally accepted as an anodic inhibitor, phosphate may be a cathodic inhibitor according to its reduced corrosion rate and more negative E_{corr} at the same dosage as nitrite in mortar specimens. The study also reveals that the inhibiting efficiency of phosphate against general corrosion of both as-received and pre-rusted specimens is lower than 10%, which is inferior to nitrite in some respects. However, as indicated by cyclic polarization measurements, the presence of phosphate provides slightly higher pitting corrosion resistance in comparison to nitrite. Furthermore, it suggests that the corrosion inhibition mechanism of phosphate in mortars mainly depends on a dual effect occurring at the steel–mortar interface. Furthermore, it is confirmed that phosphate has little effect on the long-term mechanical properties of mortars.

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1. Introduction

One of the most important factors governing durability of reinforced concrete structures (RCS) is the chloride-induced corrosion of reinforcing steel, particularly in the coastal marine environment [1]. Numerous protection techniques have been employed to mitigate the corrosion risk, with respect to both the initiation and propagation stages of corrosion. Among them, the use of corrosion inhibitors has been considered as one of the most effective solutions [2–4,7–20].

Corrosion inhibitors are typically introduced either as an admixture during the mixing of fresh concrete [2–5] or as a surface application on the hardened concrete [7,8]. The migrating corrosion inhibitors, used for the latter approach, include sodium mono-fluoro-phosphate [7,8]. However, the efficiency of migrating corrosion inhibitors generally depends on the permeability of concrete [2].

As it has been previously reported, both inorganic and organic chemicals have been considered as corrosion inhibitors to use in RCS. Nitrite-based inhibitors, which are the typical inorganic inhibitor, have been applied effectively in RCS for a long period [2,3]. However, due to the possible toxicity of nitrites, their use for RCS corrosion protection has been forbidden in many countries [2]. Therefore, the investigation of new corrosion inhibitors is an urgent problem. Recently, nitrates (mainly calcium nitrate) have been proven to be a good alternative to nitrites because they are less harmful and more available [4,5]. The development of effective green inhibitors for applications within various severe environments is an important research objective.

At present, phosphate is one of the green inhibitors used for copper and copper alloy [6]. However, phosphate has seldom been studied as the corrosion inhibitor for steel, in particular for reinforcing steel in concrete in previous investigations [7–20]. These phosphate based inhibitors mainly include sodium monofluoro-phosphate (MFP: Na_2PO_3F) [7,8,20], sodium hydrogen phosphate (SHP: Na_2HPO_4) [9–11,20] and sodium phosphate (SP: Na_3PO_4) [12–20]. MFP has been widely investigated as a migrating corrosion inhibitor in chloride contaminated and carbonated concrete [7,8]. It has been reported that MFP may be rendered ineffective during the process of diffusion from the surface of concrete to the steel surface, due to its partial decomposition and precipitation in the cracks and pores of concrete [7]. Abd El Haleem et al. [10] studied the effect of HPO_4^{2-} on the pitting corrosion performance

of reinforcing steel in $Ca(OH)_2$ solution. The results revealed that the efficiency of pitting inhibition of HPO_4^{2-} was lower than NO_2^-. Moreover, in previous research by Jin et al. [11], it was demonstrated that HPO_4^{2-} (PO_4^{3-}) was much less stable than NO_2^- in cement paste according to linear polarization and corrosion potential measurements. Besides, HPO_4^{2-} was also found to inhibit the setting of cement.

Dhouibi et al. [12] compared the inhibiting effect of PO_4^{3-} and NO_2^- in saturated $Ca(OH)_2$ solution. The results from the electrochemical techniques showed that phosphate may be either a cathodic or anodic inhibitor, which normally depended on the concentration of inhibitor. In the later work of Dhouibi et al. [13], it was reported that phosphate can prevent pitting corrosion if its content was equal to chloride concentration. However, the results for the concrete specimens indicated that, after long-term (3 years) exposure in chloride solution, phosphate lost partially the effectiveness of corrosion inhibition. Recently, Etteyeb et al. [14–17] intensively studied the protection against corrosion for steel by pretreatment in phosphate solution before immersion in chloride solution. The results confirmed that the pretreatment contributed to the formation of a passive film on the steel surface, which reduced the corrosion rate of steel in saturated $Ca(OH)_2$ solution effectively. However, with regard to steel embedded in mortar specimens, the pretreatment against corrosion was somehow temporary [17].

The previous investigations of phosphate as the corrosion inhibitor of steel were mainly carried out in simulated concrete pore solutions (mainly saturated $Ca(OH)_2$). Therefore, tests for the effectiveness of phosphate used in mortar or concrete are relatively scarce, although the testing in mortar and concrete specimens has generally been considered to be more representative of the real conditions under which steel corrodes. In the present work, various electrochemical methods were performed to evaluate the corrosion behaviors of reinforcing steel in mortar specimens produced with phosphate or nitrite admixtures and exposed to 3.5% NaCl solution for 360 days. Moreover, the inhibiting efficiency of these two inorganic corrosion inhibitors on the corrosion rate of as-received and pre-rusted reinforcing steels was compared. Finally, the mechanism for phosphate in terms of preventing reinforcing steel from corrosion in mortar specimens was analyzed by a combination of electrochemical measurements and characterization of bulk microstructure of the steel–mortar interface.

2. Materials and methods

2.1. Specimen preparation

Small prismatic mortar specimens of 40 mm × 40 mm × 160 mm were cast. The mortar specimens were prepared with ordinary Portland cement (P·I 52.5). The fine aggregate used in this study was river sand with fineness modulus of 2.50. The cement/sand ratio (c/s) of 0.67 and water/cement ratio (w/c) of 0.53 were used for the mortar preparation. Round construction reinforcing steels with the diameter of 8 mm were embedded centrally in mortar specimens with the cover depth of 16 mm. A copper wire was soldered to one end of the reinforcing steel, and both ends were covered with epoxy resin coating, leaving a free exposure surface of approximately 20 cm².

To study the corrosion performance of pre-rusted reinforcing steels which are frequently used under field conditions, two surface conditions of reinforcing steels were investigated in this study: (1) pre-rusted reinforcing steel: the uniform thin corrosion products were formed on the surface of reinforcing steel after placing in humid atmospheric environment for 60 days, and (2) as-received reinforcing steel: without any surface modification.

The corrosion inhibitors, $NaNO_2$ (SN) and $Na_3PO_4·12H_2O$ (SP), were added during mixing both with the content of 0.4 mol per 1 kg cement. The blank mortar specimens without corrosion inhibitor were also prepared for the comparative purpose. After 24 h casting, all specimens were curing (temperature = 20 ± 2 °C, and RH > 95%) for 28 days. Afterwards, the specimens were covered with epoxy resin coating again at both ends to avoid crevice corrosion. All the mortar specimens were exposed to 3.5% NaCl solution to accelerate the corrosion process. The immersion tests lasted for 360 days at room temperature (25 ± 1 °C).

2.2. Electrochemical and analytical methods

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were monitored by means of linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). Cyclic polarization (CP) method was also used to evaluate the resistance to localized corrosion. A classical three-electrode arrangement was used for the electrochemical measurements, namely the reinforcing steel (working electrode), a stainless steel plate electrode (counter electrode) and a saturated calomel reference electrode (SCE), which were all connected to PARSTAT 2273 Potentiostat. In this study, all the potentials were relative to SCE.

In LPR tests, the reinforcing steels were polarized to ±10 mV vs E_{corr} with a scan rate of 0.166 mV/s. The *IR* potential compensation was adopted to eliminate the impact of the high resistivity of mortar matrix. EIS measurement was carried out at the corrosion potential with the scanning frequency ranged from 100 kHz to 10 mHz. The ac signal used in EIS was 10 mV. For CP testing, the potential polarization scanned from 100 mV more negative to E_{corr} of each specimen toward +800 mV and finally the potential was reversed to E_{corr}, with a constant scan rate of 1 mV/s. All the electrochemical tests were carried out at room temperature (25 ± 1 °C).

The photographs of surface topography of reinforcing steels in different conditions were compared after taking from the broken mortar specimens. Quanta 3D FEG environmental scanning electron microscopy (ESEM) was employed to obtain the microstructure variations of steel–mortar interface with and without inhibitors.

2.3. Mechanical properties testing

Flexural strength (three point bending test) and compressive strength of prismatic mortar specimens without reinforcing steels were tested both at early curing stage (28 days) and long-term exposure to atmospheric environment (360 days). The mechanical properties of mortar specimens in the presence of SN or SP were compared to the blank one. The dosages of SN and SP in mortar specimens were the same as in the electrochemical tests.

3. Results and discussion

3.1. Corrosion potential and polarization resistance

Fig. 1 shows the corrosion potential and polarization resistance of reinforcing steel with and without corrosion inhibitors after 360 days exposure in 3.5% NaCl solution. It can be seen from Fig. 1a that the E_{corr} values of all specimens are more negative than −400 mV$_{SCE}$, which is an indication of 90% probability of active corrosion as recommended in ASTM C876. The E_{corr} values of all pre-rusted reinforcing steels are slightly more negative than as-received ones, indicating that the pre-rusted steels exhibit higher probability of corrosion compared with as-received specimens. In addition, the E_{corr} values of blank specimens are much more negative than SN specimens and more noble than those with SP, both