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## Preparation of phytic acid conversion coating and corrosion protection performances for steel in chlorinated simulated concrete pore solution

Chuansheng Xiong<sup>a,b</sup>, Weihua Li<sup>a,c,\*</sup>, Zuquan Jin<sup>b</sup>, Xiang Gao<sup>a</sup>, Wei Wang<sup>a</sup>, Huiwen Tian<sup>a</sup>, Peng Han<sup>a</sup>, Liying Song<sup>a</sup>, Linhua Jiang<sup>d</sup>

<sup>a</sup> Key Laboratory of Marine Environmental Corrosion and Bio-Fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, 266071, China

<sup>b</sup> College of Civil Engineering, Qingdao Technological University, Qingdao, China

<sup>c</sup> Qingdao National Laboratory for Marine Science and Technology, Qingdao, 266237, China

<sup>d</sup> College of Mechanics and Materials, Hohai University, 1 Xikang Rd., Nanjing, 210098, China

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### ABSTRACT

Phytic acid conversion coating (PACC) for steel was developed by a treatment in a Zn<sup>2+</sup> doped phytic acid (PA-Zn) solution at 20 °C to improve its corrosion resistance in concrete environment. Thickness, morphology, composition and corrosion protection performances of the PACC were investigated via SEM, XRD, FTIR, XPS and Electrochemical measurements. Corrosion rate was decreased by about 50%–80% for the steel with PACC. Zn<sup>2+</sup> could promote the adsorption reaction of PA to form thicker PACC layers on steel surface. A composite structure could form by the combination of PACC and passivation products to restrain chloride attack in alkaline environment.

### 1. Introduction

Reinforced concrete is widely used in infrastructure constructions owing to its good mechanical properties and plasticity. However, due to the porous structures and inevitable defects in concrete, the embedded steel is vulnerable to corrosion, especially when the structures are exposed to environments with chloride ions, e.g., the marine environment, saline-alkali environment, de-icing salt environment and so on [1–6]. In addition, corrosion of the reinforcing steel can also be initiated by the lowering of pH caused by carbonation [7,8]. Globally prevalent corrosion of reinforcement concrete is regarded as the most serious durability problem. The protection of steel is a headache problem for concrete researchers in practical engineering.

In fact, excellent corrosion protection can be provided for the reinforcing steel in concrete attributing to the passivation of steel in alkaline conditions [9–11]. However, the formed passive film can be easily damaged in the presence of chloride ions when the chloride concentration is higher than the threshold value [12,13]. Chloride attack is one of the main reasons that cause the initiation of steel corrosion [2,3]. Thus, the artificial construction of a barrier, that prevents the contact between chloride ions and the steel matrix, is expected to make a breakthrough in the protection of steel bars.

Chemical conversion coating is a very economical and useful protection method for metal because of the shielding functions between

harmful ions and metal matrix [13–17]. The traditional chemical conversion coatings usually include phosphate coating, chromate coating, molybdate coating, etc. However, most of these surface modification techniques lead to environmental problems [18]. Therefore, environmentally friendly pretreatment techniques have been given considerable interests for the development of corrosion protection procedures. In recent years, many researches on organic-inorganic hybrid coatings have been investigated attributing to their excellent corrosion protection performances [12–14,19–21].

Phytic acid (PA, C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>), also known as inositol hexaphosphate with six phosphate carboxyl groups, has a powerful chelating capability with numerous metal ions, such as Co<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup> and so on [20,22]. And, with the presence of P and O in the phosphate carboxyl groups, both PA and its chelates can despite on metal substrates. This can establish a corrosion protective barrier between aggressive ions and the metal matrix [23]. Therefore, it has been widely used for the protection of magnesium alloys [24], aluminium alloys [25] and iron-based metal materials [20,21,26]. So far, most of the investigations on metal protection with phytic acid conversion coatings (PACC) are conducted in acidic or neutral solutions, and few studies have been developed in alkaline solutions, especially, with regards to the concrete corrosive environment.

In this paper, the preparation of PACC and its corrosion protection performances for reinforcing steel in a chlorinated simulated concrete

\* Corresponding author at: Key Laboratory of Marine Environmental Corrosion and Bio-Fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, 266071, China.  
E-mail address: [liweihua@qdio.ac.cn](mailto:liweihua@qdio.ac.cn) (W. Li).

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pore solution (Cl-SCPS) are studied. In view of the good lifting effects of  $Zn^{2+}$  on the corrosion protection performances of PACC [20,22], a certain amount of  $ZnSO_4$  is added in the treating solution for the preparation of PACC. The prepared PACC layer is analyzed using SEM, XRD, FTIR and XPS on the as-fabricated steel surface. The protective mechanisms of PACC for steel in Cl-SCPS are explored and discussed at last.

## 2. Experimental

### 2.1. Raw materials and chemical reagents

The PA (AR > 90%) used was purchased from Shanghai Macklin Biochemical Co., Ltd. 0.5 M  $H_2SO_4$  was prepared by diluting concentrated sulfuric acid (98%  $H_2SO_4$ ) with deionized water. 0.5 M NaOH aqueous solution was prepared by dissolving analytical grade NaOH (AR 99%) in deionized water. The two solutions were used to adjust the pH values of the treating solution. The 6101 epoxy resin and diethylenetriamine (DETA, a kind of low temperature epoxy resin hardener) were used to prepare working electrodes. Analytical grade NaCl (AR > 99.5%), KOH (AR > 99.5%) and  $Ca(OH)_2$  (AR > 99.5%) were used for the preparation of the Cl-SCPS. In the absence of special instructions, all the reagents used in this study were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Preparation of working electrodes

The working electrodes were prepared using carbon steel (Q235, C  $\approx$  0.22%) bars with a diameter of 3 mm. Before starting, the steel bars were deoiled in the 0.5 M NaOH aqueous solution, rinsed with absolute ethyl alcohol (95%) and deionized water. After washing, they were dried off rapidly to avoid corrosion. Then, the steel bars were respectively soldered with a copper line and embedded in a 6101 epoxy resin mold. The liquid epoxy resin was solidified by adding 10 wt.% DETA. When the epoxy resin became hard enough, the working electrode combined with hardened epoxy resin was carefully lifted back from the mold. Finally, the side surface and an end surface of the bars were sealed to prevent corrosion. A bare end surface was reserved for the following tests.

### 2.3. Preparation of PACC

Prior to treatment, the bare end surface of the working electrodes were polished using a series of emery papers of decreasing particle sizes (400, 800, 1000, 2000 and 3000), then rinsed with absolute ethyl alcohol (95%) and dried off with a dryer. Then, they were immersed in a PA-Zn solution with 1.0 wt.% PA and 0.5 wt.%  $ZnSO_4$  at 20 °C for the preparation of PACC. The pH value of the treating solution was adjusted to 3.5 by adding certain volumes of 0.5 M NaOH aqueous solution. After immersion for 2.5 mins, 5 mins, 7.5 mins, 10 mins, 15 mins and 30 mins, the samples were taken out and rinsed with deionized water for 1 min and dried in room temperature.

### 2.4. Corrosion exposure

To investigate the corrosion protection performances of PACC for steel, the bare steel samples and PACC coated steel samples with treatment of 7.5 mins and 30 mins were exposed to the Cl-SCPS. The Cl-SCPS was prepared with distilled water and analytical pure reagents. The contents of different reagents in the Cl-SCPS were 0.02 M NaOH, 0.06 M KOH, 0.001 M  $Ca(OH)_2$  and 3.5 wt.% NaCl. The pH value of the solution was about 12.6. After a certain age of exposure, electrochemical measurements were performed to evaluate the corrosion protection performances of PACC for steel.

### 2.5. Electrochemical measurements

The electrochemical measurements including open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and polarization measurements were conducted on an Autolab instrument (PGSTAT302N) using a classic electrochemical cell with three-electrode configuration at room temperature (about 20 °C). A platinum grid and a saturated calomel electrode were respectively used as the counter electrode (CE) and reference electrode (RE). Prior to EIS and polarization measurements, the working electrode was left at the open-circuit conditions for 0.5 h to achieve potential stability. EIS was carried out by applying a sinusoidal potential perturbation of 5 mV at the OCP in a frequency range from 100 kHz to 10 mHz with 12 points per decade. Polarization curves were measured by scanning the potential with 0.5 mV/s from  $-250$  mV versus the OCP to the potential slightly positive than the critical pitting potential (at which the current density increased abruptly).

### 2.6. Morphology characterization and composition analyses

Surface and section morphology of PACC on steel surface was observed by a scanning electron microscope (Hitachi S-3400N) at an accelerating voltage of 15 kV. The elemental composition of the PACC was analyzed by the through energy diffraction spectrum (EDS) unit. Samples for the cross-section images of PACC were prepared by embedding coated steels in epoxy resin with a PVC mold and polished perpendicular to the exposed surface with a series of emery papers (particle sizes of 400, 800, 1000, 2000 and 3000). The epoxy resin and mold were used to reduce the modification or damage of PACC on steel during polishing.

The composition of PACC was analyzed by means of XRD, FT-IR and XPS measurements. All the analyses were directly conducted on the as-fabricated steel surface. XRD tests were performed on Ultima IV model X-ray diffraction analyser (Japan) at a voltage of 40 kV and a current of 35 mA. The X-ray source was Cu-K $\alpha$  radiation with a wave length of 1.54 Å. The scanning was in the range of 5–80° with a scanning speed of 2°/min. FTIR measurement was conducted using a Nicolet iS10 infrared spectrophotometer with a resolution of 4  $cm^{-1}$ . The absorbance versus wavenumber was recorded within the spectra region from 4000 to 400  $cm^{-1}$ . The X-ray photoelectron spectroscopy (XPS) measurement was conducted on a Thermo VG Scientific ESCALAB 250 system equipped with a microfocused, monochromatic Mg K $\alpha$  X-ray source. The hemispherical analyser was operated in a fixed analyser transmission (FAT) mode with pass energies of 100 eV for the survey spectra and 20 eV for the high-resolution spectra. The measured binding energies for XPS spectra were calibrated with reference to the C1s (hydrocarbon C–C, C–H) of 285 eV. The peak fitting and quantification of atomic compositions were carried out with a CasaXPS software by using a Gaussian/Lorentzian procedure.

## 3. Results and discussion

### 3.1. Preparation of PACC on steel

#### 3.1.1. The OCP during the formation of PACC

The change of OCP of steel can reflect to some extent the surface change of steel [27]. To characterize the formation process of PACC on steel, the OCP of three parallel steel electrodes was recorded in 1800 s when they were immersed in the treating solution (Fig. 1). As shown in the figure, the OCP of the three electrodes moved to positive direction rapidly from the very beginning of the treatment. Then, after about 450 s–600 s, the OCP reached to a relatively steady value and remained at this level for a period of time. This indicates that the surface of steel electrodes become less active with the development of PACC. The similar results have also been obtained by other researchers [21]. After about 1200 s, the potential gradually started moving to negative

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