Phosphate ions as effective inhibitors for carbon steel in carbonated solutions contaminated with chloride ions

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ABSTRACT

This investigation focuses on sodium biphosphate (Na_2HPO_4) as corrosion inhibitor for construction steel. All the tests are carried out in a solution that simulates the composition of the pores in chloride-contaminated carbonated concrete. The carbonated solution (CS) contained Na_2CO_3 (0.0015 mol L^{-1}), $NaHCO_3$ (0.03 mol L^{-1}) and NaCl (0.1 mol L^{-1}), resulting in $[Cl^-]/[OH^-]$=10000. Inhibited solutions (IS20, IS60 and IS100) incorporated 20, 60, and 100 mmol L^{-1} Na_2HPO_4 respectively. These were labeled IS20, IS60 and IS100 respectively and result in $[HPO_4^{2-}]/[Cl^-]$ = 0.2, 0.6, and 1. Cyclic voltammograms and anodic polarization curves were complemented with micro-Raman spectroscopy and XPS, to evaluate the surface film composition. The results show that chloride contamination promotes active corrosion. When phosphate ions are incorporated, steel becomes passive with a more positive corrosion potential (Ecorr), and pitting presents as the predominant form of localized corrosion. Raman spectra show a broad band, centred in 982 cm^{-1}, suggesting that phosphates incorporate to the passive film. Phosphates are also present in the corrosion products. The surface film becomes more protective to pitting for the highest biphosphate content. However, after pitting no repassivation was detected. After over one month in immersion, steel remains passive in the condition IS100, with inhibition efficiency higher than 99%. In contrast, in the case of IS60 and IS20, pitting was detected.

It can be concluded that phosphate ions are good candidates to be used as corrosion inhibitors for steel in chloride-contaminated concrete.

1. Introduction

Reinforced concrete is known to have excellent structural and durability properties. However, one of the main pathologies affecting the performance of reinforced concrete structures is the corrosion of the steel reinforcement bars (rebars).

In normal service conditions, the high alkalinity provided by concrete guarantees the presence of an oxide layer that protects steel against active corrosion. However, rebar corrosion may be triggered by external factors such as concrete acidification due to CO_2 diffusion, the presence of aggressive ions (mainly chlorides), or even more by a combination of these factors [1]. In constructions located close to the seashore, chloride ions penetrate the porous structure of concrete and reach the steel. Also, in many coastal cities in Argentina, the use of chloride-contaminated aggregates and water constitutes a recurrent malpractice [2].

The investigation of rebar corrosion is particularly challenging because concrete is a highly resistive and porous material. Frequently, the chemical environment present in the concrete pores is simulated using appropriate solutions [3,4]. Some authors have used highly carbonated solutions to carry out corrosion studies [5,6]. However, the real pore solution presents a low concentration of soluble carbonate and bicarbonate ions [7].

Inhibitors are frequently used to minimize the risk of rebar corrosion [8–10]. The probability of undergoing corrosion at a given chloride content is usually evaluated in terms of the chloride/hydroxyl ratio [11]. Alternatively, in the presence of chloride, inhibiting agents are evaluated as a function of the inhibitor/chloride ratio [12,13].

Several inorganic anions have been successfully used to inhibit the corrosion of steel in concrete, such as chromates, nitrites, tungstates and molybdates [14]. Compared to alternative inhibiting agents, the main advantages of phosphates are low cost and low toxicity. They can be used to pre-treat the rebars or can be admixed into concrete [15–17]. The beneficial effect of phosphate

has been attributed to their absorption onto the passive layer, thus displacing chlorides and hindering the initiation of localized corrosion [6]. Yet, the inhibition mechanism is somewhat controversial. Some authors consider that phosphates are anodic inhibitors, being effective only in the presence of oxygen. Other authors suggest that they act as cathodic inhibitors [16] while they behave as mixed inhibitors for $[PO_4^{3-}]/[Cl^-]$ ratios higher than 0.6 [13].

In this work, the effectiveness of sodium biphosphate as corrosion inhibitor has been tested in low carbonated solutions (pH=9) that simulate concrete pores contaminated with chlorides. The composition of the surface films formed in the presence of the contaminant, with and without the inhibitor will be discussed.

2. Experimental

2.1. Electrodes preparation

Steel electrodes were prepared from reinforcement bars with the following composition: Mn 0.635 wt%, C 0.299 wt%, Si 0.258 wt %, Cu 0.227 wt% and others impurities 0.245 wt%. Discs were cut, flattened and included in fast curing acrylic resin using polyvinyl chloride (PVC) holders. The geometrical area exposed was 0.503 cm^2. Each sample was provided with an appropriate electrical contact. Finally, the samples were abraded up to grade 1000 with emery paper and rinsed gently with distilled water.

2.2. Electrolyte composition

The electrolyte consisted of a carbonated solution (CS) prepared with a low content of carbonate ions to simulate the composition of the acidified solution present in the pores of carbonated concrete. CS contained Na_2CO_3 (0.0015 mol L^{-1}) and $NaHCO_3$ (0.03 mol L^{-1}), so that $[HCO_3^-] + [CO_3^{2-}]$ = 0.0315 mol L^{-1} and pH = 9 [12]. To simulate a carbonated concrete that is also contaminated with chloride ions, CS incorporated 0.1 mol l^{-1} NaCl, resulting in $[Cl^-]/[OH^-]$=10000.

To evaluate the inhibitor effect, inhibiting solutions (IS) were prepared as described above and incorporated 20, 60, and 100 mmol L^{-1} Na_2HPO_4 [16,18]. These were labeled IS20, IS60 and IS100 respectively and result in $[HPO_4^{2-}]/[Cl^-]$ = 0.2, 0.6, and 1 with pH = 9 in every case.

All the experiments were carried out at room temperature (20 ± 2 °C) without stirring.

2.3. Electrochemical techniques

A conventional three-electrode cell was employed, together with a Voltalab PGZ 100 potentiostat. A Hg/HgO electrode with 1 mol L^{-1} KOH solution (MOE, E = 0.123 V vs. SHE) was used as reference. All the potentials will be referred to this electrode. The counter electrode was a platinum wire of large area. All tests were done without stirring.

Cyclic voltammograms were recorded after having deaerated the electrolyte by bubbling N$_2$ during 15 min. The electrodes were pre-treated in either CS or IS, holding them at –1.1 V$_{MOE}$ for 5 min. Then the potential was scanned at 10 mV s^{-1} starting at –1.1 V$_{MOE}$ and reversing the sweep at convenient values.

The corrosion potential (E$_{corr}$) was found to reach a stable value after 24 h in each condition. Polarization resistance (Rp), polarization curves and electrochemical impedance spectra were recorded after having kept the electrodes for 24 h at E$_{corr}$ without deaereating.

Polarization resistance (R_p) was evaluated as $\Delta V/\Delta i$, from potential sweeps scanning ± 15 mV from the corrosion potential (E$_{corr}$) at a scan rate of 0.1 mV s^{-1}.

Electrochemical impedance spectroscopy (EIS) tests were performed at E$_{corr}$ in each solution. The amplitude of the AC signal was ± 0.01 Vrms while the frequency was varied between 20 kHz and 1 mHz. The results were fitted to two equivalent circuits (see Fig. 1). Circuit **a** is the well-known Randles circuit while circuit **b** is typical of oxidized metals [12,19]. ZView™ [20] was used to fit the experimental data.

To record the anodic and cathodic polarization curves, the potentiodynamic scan was started at the E$_{corr}$, with a sweep rate of 0.1 mV s^{-1}.

2.4. Ex-situ Raman spectra

Raman spectra were recorded using an Invia Reflex confocal Raman microprobe with Ar$^+$ laser of 514 nm in backscattering mode, with a laser spot diameter of 10 μm at a power of 25 mW. A 50 X objective and an exposure time of 50 s (3 accumulations) were used. Raman spectra were collected on spots of interest after having subjected the electrodes to anodic polarization curves and weight loss tests. The samples were withdrawn and dried under N$_2$ atmosphere, and immediately transferred to the Raman chamber. The spectra were observed to be reproducible.

2.5. Weight loss determinations

The weight loss method was applied following the guidelines in ASTM D 2688 Standard Test Methods for Corrosivity of Water in the Absence of Heat Transfer. Disks having 5.67 cm^2 as geometrical area were cut and abraded to grade 120 with emery paper. Three weighted coupons were immersed in each test solutions (CS, IS20, IS60 and IS100) for 42 days. The containers were kept at room temperature in aerated conditions. For surface characterization, one coupon of each condition was conveniently dried to perform ex-situ Raman spectra. Then, the corrosion products were stripped by immersion in HCl 1 mol L^{-1}. Later the coupons were neutralized and rinsed, first with a saturated Na$_2$CO$_3$ solution and then with distilled water, to be finally dried and reweighted.

3. Results and discussion

3.1. Cyclic voltammograms

Fig. 2 shows the first cycle of voltammograms carried out in CS and IS100. A voltammogram recorded in alkaline solution without chloride ions contamination (AS, pH=13) is also included for the sake of comparison. The peaks present in this last voltammogram were discussed in detail elsewhere [13]. In this alkaline electrolyte, the passive region extends up to 0.6 V.

In contrast, in the carbonated solution CS, steel is in active dissolution, as the current increases steadily with the applied potential. The concentration of carbonate and bicarbonate ions is not high enough to develop a passive layer of FeCO$_3$ [1]. Mao and col. [21] reported that the concentration of bicarbonate ions should
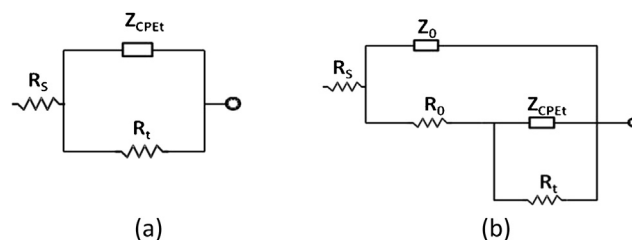

Fig. 1. Equivalent circuits chosen to fit EIS data. Circuit **a** is a typical Randles circuit and **b** is a circuit typically used to fit the behavior of oxide-coated metals.