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## Corrosion Science

journal homepage: [www.elsevier.com/locate/corsci](http://www.elsevier.com/locate/corsci)

# Unexpected effect of citrate ions on the corrosion process of carbon steel in alkaline solutions

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## ARTICLE INFO

## Keywords:

- A. Steel reinforced concrete
- B. Cyclic voltammetry
- B. Raman spectroscopy
- B. Weight-loss
- C. Alkaline corrosion
- C. Passive films

## ABSTRACT

The effect of citrate ions on the passive film stability on carbon steel, at pH 13, was evaluated. The study involved cyclic voltammograms, potentiodynamic polarization curves, micro-Raman spectroscopy and weight-loss tests. No beneficial effects on delaying or inhibiting pitting were observed in the presence of citrate ions. Organic compounds with carboxylate groups are promising corrosion inhibitors. However, the incorporation of citrate ions is clearly harmful to carbon steel in alkaline solutions and accelerates the corrosion process. Citrate ions adsorption is not observed on passive steel. Instead, citrate ions can unexpectedly dissolve the passive layer facilitating the corrosion process.

## 1. Introduction

Corrosion inhibitors have been used to prevent reinforcement bar (rebar) corrosion in concrete [1–3]. The stability of the protective passive layer naturally formed on steel can be compromised in aggressive conditions, such as those associated to concrete carbonation or chloride ions contamination. The use of simulated pore solution facilitates the control of the many factors that influence rebar corrosion and this is the approach chosen in the present investigation. The extrapolation to the behaviour of carbon steel in mortar or concrete requires additional investigation.

Organic compounds with carboxylate group have been presented as promising corrosion inhibitors of carbon steel in high alkaline media contaminated with chloride ions [4–7]. Ormellose and col. [6] studied different organic compounds with carboxylate groups using anodic polarization curves. Citrate ions were presented as good pitting inhibitors, as they could adsorb on the bare metal (without a passive layer), avoiding chloride ions adsorption due to a steric effect. However, citrate ions present a chelating effect, forming soluble complexes with Fe(II) and Fe(III) [8]. Nevertheless, other authors proposed that organic compounds with carboxylate groups suppress the formation of a Fe<sub>3</sub>O<sub>4</sub>/γ-Fe<sub>2</sub>O<sub>3</sub> bilayer passive film in borax pH 8.4, by forming a soluble Fe(II)-complex. This avoids oxidation to Fe(III) and subsequently, prevents Fe(III) oxo/hydroxide formation in the passive layer [9]. In particular, citrate ions increase the active dissolution of carbon steel in borax pH 8.4 [10]. In addition, passivated iron weakens the adsorption of carboxylate groups, which is stronger on bare iron

(active) [11]. Citrate ions could adsorb on bare surfaces to prevent chloride ions adsorption but the presence of a passive layer (a more realistic service condition) could interfere in this competition. Furthermore, the protective passive layer could suffer a detrimental effect in the presence of citrate ions. Hence, the effectivity of citrate ions as potential corrosion inhibitors at pH 13 (typical of concrete) needs to be evaluated. The aim of this work is to study the stability of a passive film on carbon steel in a concrete pore simulated solution (pH = 13) contaminated with chloride ions when citrate ions are also present.

## 2. Materials and methods

### 2.1. Electrodes preparation

Reinforcement bars were used to cut disks, embed them in acrylic resin and prepare the electrodes with appropriate back contacts. Average composition is as follows: Mn 0.635 wt%, C 0.299 wt%, Si 0.258 wt%, Cu 0.227 wt% and others impurities 0.245 wt%. The exposed area was 0.503 cm<sup>2</sup>. The surfaces were abraded with 1000 emery paper.

### 2.2. Electrolyte composition

A pH 13 pore simulating solution (PSS) was used as electrolyte, containing KOH 0.08 mol/L, NaOH 0.02 mol/L and Ca(OH)<sub>2</sub> 0.001 mol L<sup>-1</sup> [12]. To evaluate the effect of chloride and citrate ions (cit), NaCl 0.3 mol L<sup>-1</sup> and C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O 0.15 and 0.3 mol L<sup>-1</sup>

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were incorporated. In order to compare to the behaviour of a corrosion inhibitor frequently used in concrete, PSS incorporating  $0.3 \text{ mol L}^{-1}$  nitrite ions were also tested [13–16].

### 2.3. Electrochemical techniques

A conventional three-electrode cell was used. As reference electrode a mercuric oxide Hg/HgO electrode was employed ( $\text{MOE}$ ,  $1 \text{ mol L}^{-1}$  KOH solution,  $E = 0.123 \text{ V}_{\text{NHE}}$ ). All the potential values will be referred to this electrode. The auxiliary electrode was a platinum wire. Electrochemical tests were carried out using a Voltalab PGZ 100 potentiostat in stagnant solutions.

Cyclic voltammograms were recorded at  $10 \text{ mV s}^{-1}$  in deaerated electrolytes after pre-reducing 5 minutes at  $-1.2 \text{ V}_{\text{MOE}}$ .

The corrosion potential ( $E_{\text{CORR}}$ ) was followed during 24 h in each condition investigated. Not less than five individual measurements were registered and averaged.

Polarization resistance ( $R_p$ ) was calculated as  $\Delta V/\Delta i$ , from potential sweeps at  $0.1 \text{ mV s}^{-1}$  scanning  $\pm 0.015 \text{ V}$  from the  $E_{\text{CORR}}$ .

Anodic polarization curves were registered at  $0.1 \text{ mV s}^{-1}$  using two different starting conditions: a) bare metal (electrodes pre-reduced for 5 minutes at  $-1.2 \text{ V}_{\text{MOE}}$ ); b) passivated electrodes (aged for 24 h at  $E_{\text{CORR}}$ ). Each potentiodynamic scan started at the pre-treatment potential. The scan direction was inverted when reaching  $100 \mu\text{A cm}^{-2}$ . The experiments were designed according to the ASTM norms [17]. After these tests, the electrodes were dried under  $\text{N}_2$  to register Raman spectra of the corrosion products.

Tests were performed at ambient temperature ( $20 \pm 2 \text{ }^\circ\text{C}$ ).

### 2.4. Weight loss determinations

Weight-loss tests were performed as recommended in ASTM D 2688 [18]. Disks with  $5.67 \text{ cm}^2$  as geometrical area were cut from the rebars and abraded with grade 120 emery paper. Weighted coupons were immersed for 90 days in PSS, PSS +  $\text{Cl}^-$ , PSS +  $[\text{cit}]/[\text{Cl}^-] = 0.5$  and PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$ . Three coupons were simultaneously immersed at room temperature in each flask. One of them was dried under  $\text{N}_2$  atmosphere to record *ex-situ* Raman spectra on the corroded surface. The other two coupons were cleaned by immersion in  $\text{HCl } 1 \text{ mol L}^{-1}$ , and then neutralized with a  $\text{Na}_2\text{CO}_3$  saturated solution, rinsed with distilled water, dried and weighted.

### 2.5. Ex-situ Raman spectra

The Raman measurements were recorded using a 514 nm laser and an Invia Reflex confocal Raman microprobe. Settings were chosen as reported before [12]. At least five representative spots were evaluated and observed to be reproducible.

## 3. Results

### 3.1. Electrochemical evaluation on bare metal

#### 3.1.1. Cyclic voltammetry

Fig. 1 presents the first cycle of the cyclic voltammograms performed in PSS, PSS +  $\text{Cl}^-$  and PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$ . The curves in PSS and in PSS +  $\text{Cl}^-$  were described in more detail in a previous work [12]. The discussion of those results is summarised here so as to compare with the effect of citrate ions. In PSS, the four anodic peaks have been previously described by different authors [12,19–22]. The first anodic peak at  $-0.92 \text{ V}_{\text{MOE}}$  (Ia) has been associated to the oxidation of hydrogen atoms formed during pre-reduction. Then, peak IIa at  $-0.74 \text{ V}_{\text{MOE}}$  has been attributed to the formation  $\text{Fe}_3\text{O}_4$  together with hydrated Fe(II) and Fe(III) species. Peak IIIa at  $-0.6 \text{ V}_{\text{MOE}}$  corresponds to Fe(OH)<sub>3</sub> and/or  $\alpha$ - or  $\delta$ -FeOOH. Peak IVa at  $-0.30 \text{ V}_{\text{MOE}}$  involves Fe(OH)<sub>2</sub> transforming into Fe(OH)<sub>3</sub> or  $\gamma$ -FeOOH [20]. The two cathodic peaks

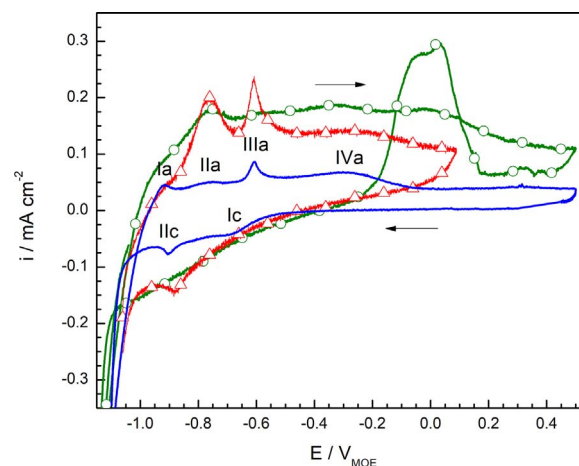


Fig. 1. Cyclic voltammograms for carbon steel (first cycle) in PSS (—), PSS +  $\text{Cl}^-$  (—Δ—); PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$  (—○—). Sweep rate:  $10 \text{ mV s}^{-1}$ .

registered in PSS, Ic at  $-0.69 \text{ V}_{\text{MOE}}$  and Iic at  $-0.89 \text{ V}_{\text{MOE}}$ , are associated to the reduction of Fe(III) and Fe(II) species, respectively. The total reduction charge is lower than the oxidation charge because the inner magnetite layer is quite insoluble and prevents further dissolution of the outer part of the surface film [20,21].

When chloride ions are added (PSS +  $\text{Cl}^-$ ), four oxidation peaks appear at the same potentials observed in PSS (see Fig. 1). Peaks IIa and IIIa are more intense because iron is readily oxidized when chloride ions are present in the electrolyte. Also, as iron oxides and hydroxides are more soluble in PSS +  $\text{Cl}^-$ , there is only one reduction peak [23].

In PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$ , the anodic sweep can extend to potential values higher than those reached in PSS +  $\text{Cl}^-$ . The intensity of peak IIIa decreases compared to that of PSS +  $\text{Cl}^-$  probably due to the lower concentration of Fe(II) species present on the metal surface. Even if it is possible to continue the sweep until  $0.5 \text{ V}_{\text{MOE}}$  without observing localized attack, the current density at potentials higher than  $-0.5 \text{ V}_{\text{MOE}}$  is higher in the presence of citrate ions. This increment in the current could be associated to the formation of an iron-citrate soluble complex resulting from the dissolution of the protective iron oxide [10]. After reversing the scan, one anodic peak at  $0 \text{ V}_{\text{MOE}}$  could be observed. This peak has been observed before in the presence of citrate ions on steel [10,24]. It has been related to Fe(II) species in solution, suggesting that the passive layer is partially soluble in citrate-rich media.

Fig. 2 shows the 10th cycle of the voltammograms recorded in PSS, PSS +  $\text{Cl}^-$  and PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$ . In PSS and PSS +  $\text{Cl}^-$ , one anodic peak (IIIa) at  $-0.6 \text{ V}_{\text{MOE}}$  and one cathodic peak (Ic) can be

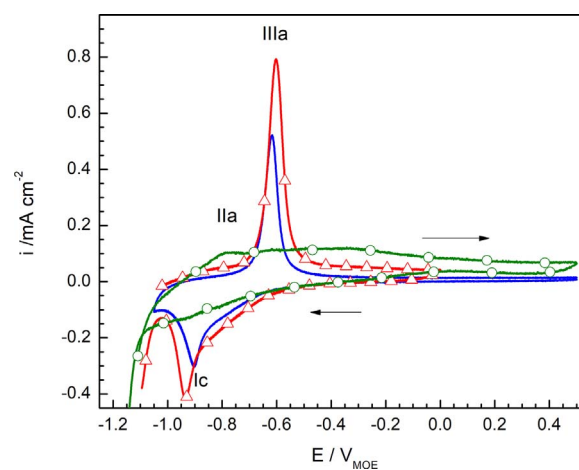


Fig. 2. Cyclic voltammograms for carbon steel (tenth cycle) in PSS (—), PSS +  $\text{Cl}^-$  (—Δ—); PSS +  $[\text{cit}]/[\text{Cl}^-] = 1$  (—○—). Sweep rate:  $10 \text{ mV s}^{-1}$ .

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