



The inhibition effect of a green inhibitor on steel reinforcement in carbonated concrete

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Received 25 Jan 2015, Revised 12 May 2015, Accepted 12 May 2015

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Abstract

The aim of this study was to evaluate the effectiveness of "tannin" as a green inhibitor against the corrosion of pre-corroded steel initially in a carbonated cement filtrate. Different electrochemical techniques were used as polarization curves and electrochemical impedance spectroscopy. It appears that the pretreatment of pre-corroded steel in an acidic bath containing the green inhibitor provides cathodic protection which restricts corrosion.

Keywords: Corrosion, Carbonation, Steel, Concrete, Tannin.

1. Introduction

Concrete is a material that usually presents high levels of alkalinity, which helps on the formation and protection of passivation film on metal surfaces in reinforced concrete structures (1). After long-term atmospheric exposure, many reinforced concrete structures (2-3) have started to exhibit signs of carbonation-induced reinforcement corrosion and therefore require maintenance to extend their service lives (4).

The process of carbonation causes a pH decrease of the interstitial concrete solution. Under this conditions, rebar passivity and active corrosion can ensue (5). The traditional method repair starts with the removal of deteriorated zones and cleaning of steel surface. This procedure is expensive and may damage the structural integrity when large areas have to be treated (6). The main objective of this study is to evaluate the efficiency of Tannin as a green inhibitor of steel reinforcement corrosion in carbonated concrete. Investigation of natural tannins as acid inhibitors is particularly interesting for two reasons: they are non-expensive and ecologically acceptable (7). Tannins, a class of natural, non-toxic and biodegradable polyphenolic compounds, extracted from plant sources are already in use as corrosion inhibitors in aqueous media, components of rust converters, pigments in paint coatings (8), corrosion inhibitors of reinforcing steel in concrete, chemical cleaning agents (9). A number of tannin-based products found a certain amount of success as pretreatment primers for use on rusted steel without requiring complete removal of the corrosion products (10). The antioxidant capacity of tannins was confirmed by different authors using different analytical techniques such as colorimetry (11) and ESR (Electron Spin Resonance) (12).

2. Materials and methods

2.1. Materials

The working electrode was cut from an ordinary smooth steel rebar ($\varnothing=6\text{mm}$) with chemical composition (wt.%): C 0.22, Mn 0.89, Si 0.24, S 0.016, P 0.046 and Fe balance. For the test in simulation solution, a copper wire was soldered to the rear side of the specimens as an electrical connection. Specimens were mounted in a resin leaving an active surface of 0.2 cm^2 . Then, they were wet ground with abrasive paper from 120 to 1200 grit, rinsed with distilled water and air-dried before being transferred to the experimental media.

2.2. Test cell

The electrochemical investigations were conducted in a three-electrode cell surmounted by a cylindrical cuvercle with the auxiliary electrode made of platinum (surface=1cm²), a saturated (Hg/Hg₂Cl₂/KCl) as reference electrode and the working electrode which is one in ordinary steel.

2.3. Test media

The test media for the steel electrode was a carbonated cement filtrate (pH=8.3±0.2) which simulates the pore solution of the carbonated concrete (noted solution S). This medium was obtained by filtration of a mixture of water and cement in a ratio E/C=2(13), that was previously mixed vigorously. The initial pH of the filtrate was 13±0.2. It reaches about 8.3±0.2 after approximately 12 days of exposure of the filtrate to ambient air. The corrosion test in the filtrate carbonate medium (solution S) has involved both a steel electrode whose surface was perfectly polished and a steel electrode whose surface was completely covered with corrosion products. These products were developed following the carbonation of the electrode. In this case, the electrode undergoes 6 cycles of immersion-drying (IS). Immersion day duration was three days in the filtrate of carbonate cement and drying of same duration was made in the ambient air. At the end of these cycles, the visual observation showed that the electrode surface is completely covered with corrosion products.

2.4. Inhibitor solution

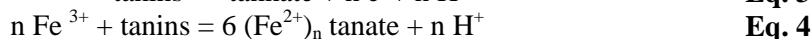
The inhibitor used is a green one named as tannin. It was extracted from a water-methanol mixture (80/20 volume) and heated for 1 hour at 60°C. The tannin powder obtained was dissolved in water H₃PO₄ mixed (70/30 volume) to prepare two inhibitor solutions named S₂ and S₃ containing respectively 3g/l (S₂) and 6g/l (S₃) of tannin. These solutions were used as pretreatment baths of steel electrode and the carbonated concrete specimens.

2.5. Conditions measurements

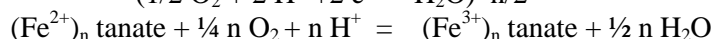
The effectiveness of tannin as green inhibitor for steel electrode was evaluated by means of potentiodynamic curves and electrochemical impedance spectroscopy. The polarization curves were plotted with Potentiostat Galvanostat PGP-201(piloted by "VOLTMASER.4" type software). The scanning was started from -1500 mV/ECS with a scan rate equal to 25 mV/min. However, the impedance spectra were plotted at open potential corrosion using Shlumberger SI 1287.1256 (equipment Led by "Fracom" software "Ariane" for data acquisition and modeling of impedance spectra). The frequency varies from 65KHz to 0.01 Hz with 5 points/decade.

3. Results and discussion

Before carrying out the electrochemical test in the simulated carbonated solution (S), the pre-corroded steel electrodes were pretreated in based tannin inhibitor solutions (S₂ and S₃ solutions) for 1hour. The open circuit potential (OCP) was registered with time (Fig. 1). It appears that the OCP decreased at the beginning of the test to reach approximately -450 mV/ECS. The decrease of the potential may be due to etching of the layer of oxides formed on the metal surface during the process of pre-corrosion. Then, the OCP moves to noble values to reach -400 mV/ECS. After one hour, the surface was completely covered with a dark grey film. The ennoblement of the OCP is probably due to the presence of this surface layer. According to literature (4), this layer is essentially formed of ferric-tanates complexes which protect steel. The mechanism of formation of these complexes is shown in the reaction equation (1) to (6).



consequently:



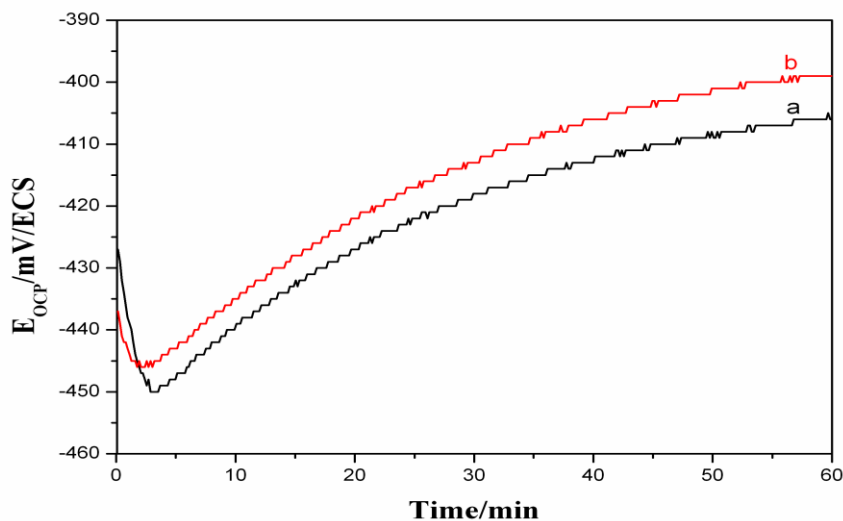


Figure1: Variation of the open circuit potential (OCP) with time for the pre-corroded steel electrode in solution S_2 and S_3 (a) S_2 (70% of tannin solution (3g/l)+30% H_3PO_4); (b) S_3 (70% of tannin solution (6g/l)+30% H_3PO_4)

Fig. 2 shows the variation of the OCP with time in the solution S of the pre-corroded steel electrodes previously pretreated in S_2 and S_3 solutions. The OCP curve of pre-corroded steel is mentioned as reference curve. It appears that all the curves have the same shape characterized by a progressive decrease during time. Hence, the OCP values of the pretreated electrodes are lower than those of the reference electrode.

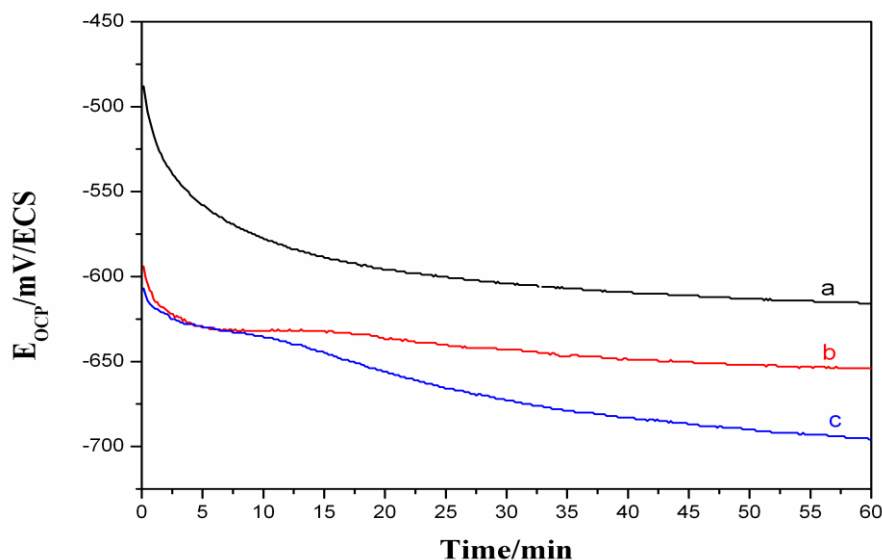


Figure 2: Variation of the open circuit potential (OCP) with time of the pre-corroded steel electrode in the solution S after 1hour of immersion in both pretreatment solutions S_2 and S_3 (a)Pre-corroded steel (b) Pre-corroded steel treated during 1h in S_2 (c) Pre-corroded steel treated during 1h in S_3

Fig. 3 gathers the polarization curves in S solution of the pre-corroded steel without and with the pretreatment. It appears that the curves have the same shape. However, the anodic and the cathodic current densities decrease significantly with the electrode pretreated in S_3 solution.

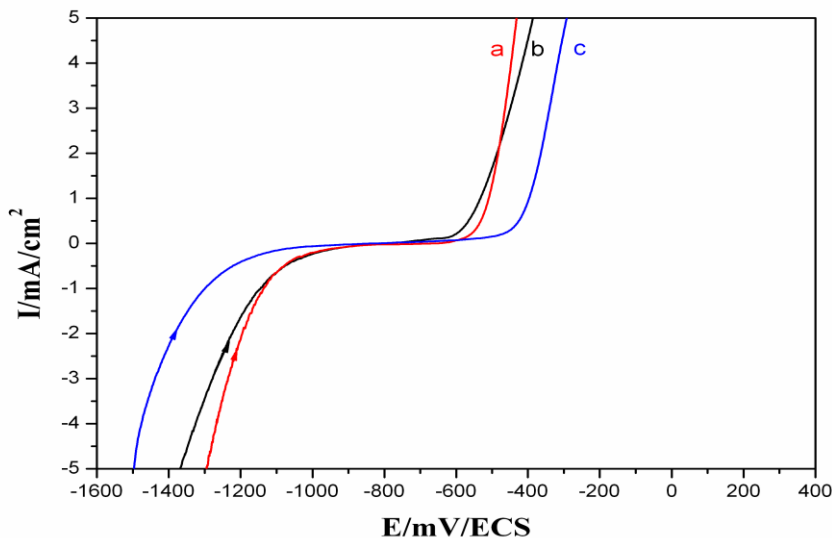


Figure 3: Polarization curves of the pretreated steel electrode in solution S after 1 hour of immersion in S_2 and S_3 (a) Pre-corroded steel (b) Pre-corroded steel treated during 1h in S_2 (c) Pre-corroded steel treated during 1h in S_3

Fig. 4 shows the impedance diagrams after 1 hour of immersion in solution S of the pre-corroded steel (reference) and pre-corroded steel electrodes previously treated in S_2 and S_3 solutions. All the diagrams have two time constants. The first one in high frequency region is very little. It was associated to the surface film. However, the second time situated in low frequency region has a large diameter and was attributed to the corrosion process. We note that the size of the impedance diagrams of the pretreated steel is larger than that of the non-treated steel.

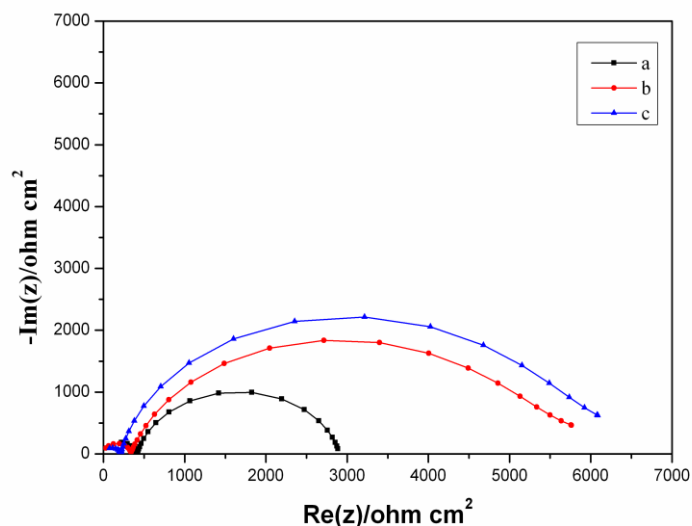


Figure 4: Nyquist plots for the pre-corroded electrode in solutions (a) Pre-corroded steel (reference); (b) Pre-corroded steel electrode previously treated during 1h in S_2 ; (c) Pre-corroded steel electrode previously treated during 1h in S_3

Modeling of the spectra was carried out by the circuit indicated in Fig. 5. It gives the values of R_p (polarization resistance) and R_f (ionic resistance of a surface layer) determined from of the adjustment of the impedance spectra by the simplex method (Table 1). It is noted that the resistance R_p increases significantly when the pre-corroded electrode is treated in S_2 and S_3 solutions. The resistance of the film increases slightly. Over all, these

results show that pretreatment of the steel in an acidic solution based on tannin is capable of forming an effective film against corrosion. The protective power seems better when the bath contains 6 g / l of tannin solution (S_3).

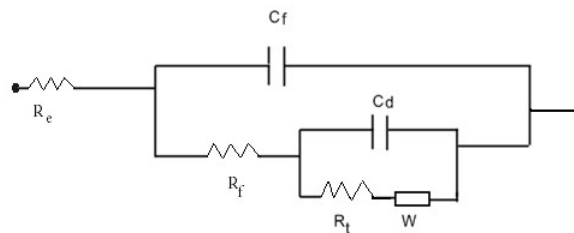


Figure 5: Equivalent electrical circuit used to model the impedance diagrams shown in Fig.4

Table 1: R_f and R_p Values determined from the adjustment of impedance diagrams of Fig.4

Electrode	$R_f \pm 0.1$ ($k\Omega \cdot cm^2$)	$R_p \pm 0.2$ ($k\Omega \cdot cm^2$)
Pre-corroded steel electrode	0.4	3
Pre-corroded steel electrode treated in S_2	0.5	6
Pre-corroded steel electrode treated in S_3	0.6	7

Conclusion

From this study, the following conclusion can be drawn: The efficiency of tannin as a green inhibitor of steel corrosion was proved. Indeed, the surface film formed on the metal surface after the pretreatment of the pre-corroded steel in an acidic bath based on tannin provides cathodic protection which restricts corrosion.

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