



Inhibiting Corrosion of X60 Steel in Natural Seawater by Ascorbic Acid

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Inhibiting corrosion of X60 steel in natural seawater by ascorbic acid

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Abstract : The present work focuses on the study of the inhibitory activity of a natural organic compound (ascorbic acid) on X60 steel (pipeline) in a marine environment by gravimetric and electrochemical methods. The obtained results showed that adding ascorbic acid to the corrosive medium significantly slows down the corrosion process and that the maximum inhibitory efficiency of up to 77% is obtained for a concentration of 0.05 g/L of the inhibitor.

Keywords: Corrosion, X60 pipeline steel, ascorbic acid, seawater.

I. INTRODUCTION

Corrosion is one of the main factors for the degradation of an engineering structure in marine environments, due to the chemical or electrochemical reactions between the marine environment and metals. The presence of microorganism in the corrosive media makes the corrosion more complicated [1-3] For most metallic materials used in the marine environment, their mechanical, physical and chemical properties can be damaged by the activity of the microorganisms that attach on the surfaces of the metallic structures.

Colonization of microorganisms on metallic surface is capable of changing the electrochemical reaction at the biofilm/metal interface, in turn either inhibiting or accelerating the corrosion [4,5] in order to avoid the menace associated with corrosion. There are several methods available for preventing metals from corrosion, the barrier protection, galvanization, and cathodic protection by using antirust solutions and corrosion inhibitors. [6-16] The ascorbic acid is a common monacid that widely exists in animals and plants, which is non-toxic, cheap, and environmentally friendly [17,18]. The structure of ascorbic acid consists of a five-membered lactone ring and four hydroxyl groups, among which one of the hydroxyl groups is prone to dissociation due to the conjugation effect [19]. This makes the ascorbic acid molecule bulky and acidic, with a pKa = 4.25 [20]. However, ascorbic acid is reductive, which could reduce the self-corrosion potential of the substrate, thus reducing the corrosion to the substrate [17, 21]. In this context, the present study evaluated the inhibition efficiency of ascorbic acid for the corrosion of steel x60 in the seawater medium.

II. EXPERIMENTAL

A. MATERIAL

API 5L X60 pipeline steel was used as a working electrode with the following weight percentage chemical composition : C 0.102 max, Mn 1.06 max, Si 0.34 min, P 0.018 max, S 0.17 max, Ni 0.18max, Nb 0.019max, Ti 0.023max. The specimens were cut from petroleum pipeline as cylinders. The cylindrical specimens with diameter 1 cm were used to carry out electrochemical experiments.

The surface of these specimens was mechanically polished with silicon carbide paper of 320 to 2000, rinsed with distilled water and degreased with acetone.

B. MEDIUM

- The corrosive solution is natural seawater.

C. INHIBITOR

- The inhibitory solution is obtained by directly powdering ascorbic acid (AA) in seawater

D. CORROSION TESTING EXPERIMENTS

Mass loss experiments were carried out the following, the initial mass of the completely abraded X60 coupons. The samples completely submerged. Herein, the uninhibited seawater solution is referred to as 'blank' while the corrosive solution containing the inhibitor is referred to as 'inhibited'. Coupons were removed from the test solutions. Thereafter, the mass of the coupons was measured and the mass loss was then calculated using the following equation

$$V_{\text{corr}} = \Delta m / S.t \quad (1)$$

The electrochemical impedance spectroscopy (EIS) experiments, the open circuit potential (OCP) of the corroding system was monitored for 1h to ensure a steady-state condition. The EIS experimental parameters used were: initial frequency = 100 kHz, final frequency = 10mHz, amplitude signal = 10 mV acquiring 10 points/decade at OCP.

The potentiodynamic polarization (PDP) experiments were conducted at a scan rate of 0.5 mV/s from -250 mV

to +250 mV versus open circuit potential. All experiment were carried out , using a potentiostat /Galvano stat with Nova 2.0 software, in a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. In order to minimize ohmic contribution, the Luggin capillary was kept close to working electrode (WE).

III. RESULTS AND DISCUSSION

1 . GRAVIMETRIC METHODS:

Gravimetric is one of the oldest methods used for determining the corrosion rate and inhibitory efficiency in the case of using an inhibitor.

The corrosion rate is calculated by the following equation:

$$V_{\text{corr}} = \Delta m / S.t \text{ (mg / j.cm}^2\text{)}. \quad (2)$$

the value of the inhibitory efficiency is given by the following equation :

$$E (\%) = (V_{\text{corr}} - V_{\text{inh}} / V_{\text{corr}}) \times 100. \quad (3)$$

V_{corr} and $V_{\text{(inh)}}$ represent respectively, the corrosion rates without inhibitor and in the presence of inhibitor .

The experiments are conducted in seawater, containing different concentrations of inhibitor, at room temperature ($25 \pm 1^\circ\text{C}$).

We prepare five samples of the piece of steel. Each sample has a dimension $5 \times 4 \text{ cm}^2$ to be ready to immerse in a solution as shown in Figures 1:



Figure 1: The test pieces after immersion

(a) Variation of the inhibitory efficiency with concentration

At a fixed time (48 h), experiments was carry out in differents concentration of the Inhibitor. The results obtained are summarized in the table below.

Table 1 : Variation of the inhibitory efficiency of carbon steel the concentration of Ascorbic Acid.

[AA] (g/L)	V_{corr} (g/cm ² .h)	E (%)
0,00	$8,368 \cdot 10^{-6}$	—
0,03	$3,311 \cdot 10^{-5}$	45,48
0,05	$2,516 \cdot 10^{-5}$	77,01
0,5	$3,650 \cdot 10^{-5}$	50,09
1	$2,190 \cdot 10^{-5}$	74,16

The results of Table 1 are shown in the following figure.

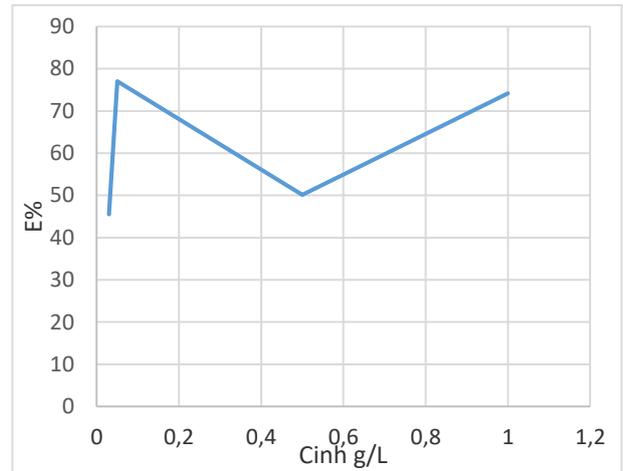


Figure 2: Evolution of inhibitory efficiency with concentration of AA in seawater.

According to the results grouped in Table 1, there is a clear decrease in the corrosion rate of the steel in seawater after the addition of the inhibitor AA and that a better inhibitory efficiency is obtained for a concentration of 0.05 g / L inhibitor.

(b) Evolution of inhibitory efficiency with immersion time

The results of the study of the variation in the inhibitory efficiency of ascorbic acid as a function of immersion time are collected in Table 2. These results show that the inhibitory efficiency of AA is increasing over time by reaching a maximum of 77% after 48 hours, and then it decreases slightly to a value of 60%. After an immersion time of 168 hours, inhibition efficiency increases again to reach a value of 65%. This can be explained by the presence of a fairly stable inhibitory film covering the surface of the steel.

Table 2: Inhibition efficiencies for corrosion of X60 steel in seawater by AA as a function of immersion time.

Time (h)	Δm (g)	V_{corr} (g/cm ² .h)	E (%)
24	0,0047	$8,368 \cdot 10^{-6}$	59,61
48	0,0372	$3,311 \cdot 10^{-5}$	77,01
72	0,0424	$2,516 \cdot 10^{-5}$	74
96	0,082	$3,650 \cdot 10^{-5}$	60,15
168	0,0424	$2,190 \cdot 10^{-5}$	64,43

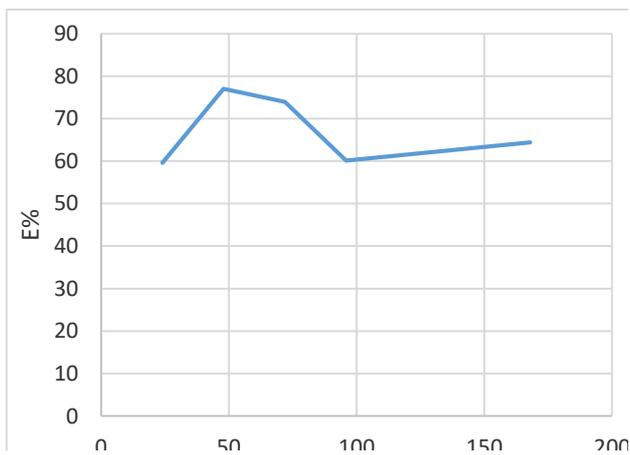


Figure 3: Evolution of the inhibitory efficiency of AA in function of immersion time in seawater

2. ELECTROCHEMICAL TECHNIQUES:

(a) Open circuit potential (OCP) curves

The variation of the open circuit potential (OCP) versus time was observed in Figure 4,

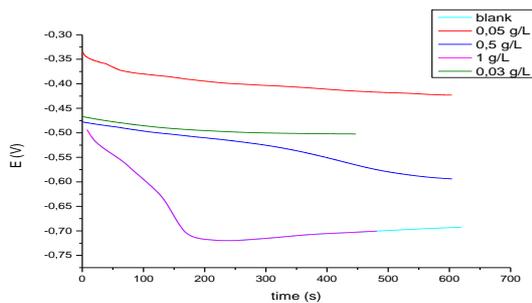


Figure 4: Variation of OCP versus immersion time for the systems with and without inhibitor.

It can be observed that the medium containing AA showed a regular increase in the potential which corresponds to a regular decrease in the rate of corrosion of the metal during the same period. We also note from the plot of this curve that the inhibitor AA has an anodic behavior, which indicates that the potential of inhibited system more positive to the corrosive system.

(b) Polarization analysis

The examination of the polarization curves in Fig 5,

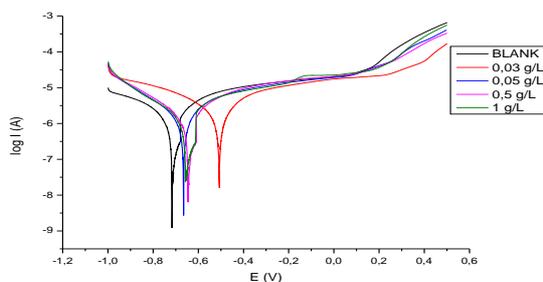


Figure 5: polarization curve of steel in seawater without and with the addition of different Concentrations of (AA).

shows that the addition of the AA inhibitor shifts the corrosion potential to more positive values, we also note a decrease in the anode partial currents on the anode branches. Elsewhere, we observe a slight increase in the current on the cathode branches. This increase in current is related to the reduction reaction. Indeed, according to the literature [22], anodic inhibitors increase the density of the cathodic partial current so as to allow spontaneous passivation of the metal, the corrosion potential then shifts in the active domain to the passive domain.

Table 3: Polarization parameters for X60 steel in seawater with various concentrations of AA inhibitor.

[AA] (g/L)	E_{corr} (V)	$I_{corr} \cdot 10^{-3}$ (mA/cm ²)	β_a (V/dec)	$-\beta_c$ (V/dec)	E (%)
0	-0,71	8,97	0.13	0.14	/
0.03	-0,50	5,70	0.10	0.07	36
0.05	-0,66	3,94	0.09	0.06	56
0.5	-0,64	5,79	0.11	0.11	35
1	-0,65	4,34	0.20	0.14	45

The electrochemical parameters, extracted from polarization curves (Fig .5) are summarized in Table 3. Show that , there is a shift in corrosion potential upon introduction of AA into the corrosive medium towards more noble values compared to the uninhibited medium ,whereby the E_{corr} is changed from $-0.71V/(ESC)$ to $-0.66 V/(ESC)$. This behavior is indicative of AA behaving as an anodic-type corrosion inhibitor. Compared to the blank, there is a significant decrease in i_{corr} of the AA inhibited corrosive medium. The i_{corr} value diminished from $8,97A \cdot cm^{-2}$ recorded in the unprotected medium to $3.94 A \cdot cm^{-2}$ in the system inhibited with $0.05 g/L$ AA . This translated to a corrosion inhibition of 56%.

Finally, there is a good agreement with the results obtained by the gravimetric method.

(c) Electrochemical Impedance Spectroscopy (EIS):

Electrochemical impedance is a powerful tool in the study of corrosion and adsorption phenomena [23, 24]. It has been studied in order to complete the understanding of the corrosion and inhibition mechanisms of steel X60 in seawater in the absence and presence of inhibitor (AA), electrochemical impedance measurements are carried out at the abandonment potential in the corrosive medium.

The diagrams obtained (Fig. 6), show a single capacitive loop in the high frequency ranges . This indicates that the corrosion reaction is controlled by a charge transfer process. The capacitive loop is not really a perfect semicircle, and this is attributed to the dispersion of the frequency of the inter-facial impedance [25], generally due to the heterogeneity of the surface of the electrode . This heterogeneity can result from roughness, impurities,

dislocations, adsorption of the inhibitor and the formation of porous layers [26, 27]. This type of diagram is generally interpreted as a charge transfer mechanism on a heterogeneous and irregular surface [28,29]. The size of the loop visibly increases with the addition of inhibitor, in particular for the 0.05 g / L concentration. This once again reflects a better inhibitory efficiency of this concentration

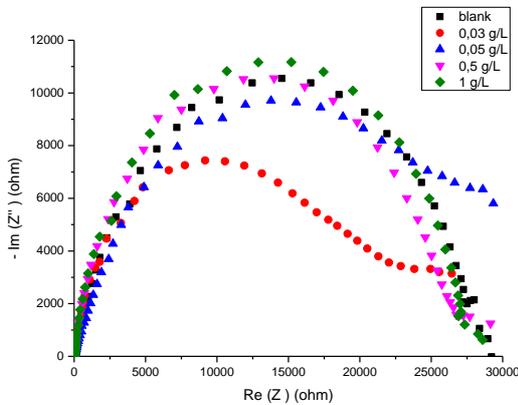


Figure 6: Electrochemical impedance diagram of X60 steel in seawater, in the absence and in the presence of AA at different concentrations

The values of the electrochemical parameters and the inhibition efficiency E (%) for different concentrations of AA obtained by electrochemical impedance spectroscopy are given in Table 4.

Table 4: ESI parameters of steel X60 in seawater without and with different concentrations of AA.

AA (g/L)	R_t (Ω)	C_{dl} (μF)	E (%)
0	21	12,0	/
0.03	34	8,75	34
0.05	87	6,72	75
0.5	50	7,92	57
1	80	7,85	73

By the Table 4, it can be observed that the values of R_t increase while the values of C_{dl} decrease with increase in concentration of AA, this is the result of the formation of a protective film on the surface of the metal [30]. This can be related to the adsorption of the inhibitor molecules to the surface thus forming a protective film at the interface

3. CONCLUION

In summary, the following conclusion can be drawn:

- Ascorbic acid (AA) has a strong inhibitory power from low concentrations.
- The product tested, has been identified as an anodic inhibitor and shows better efficacy for the concentration of 0.05 g/L.

- The inhibitory efficiency of AA in seawater reaches a value of 77%.
- the agreement between the impedance results and those obtained by gravimetry is perfect.

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