J. Mater. Environ. Sci.6 (7) (2015) 1896-1901
ISSN : 1503-1755
CODEN: JMESCN

Localized corrosion study of X60 pipeline steel in soil solution and inhibitive effect by disodic hydrogeno-phosphate

A. Amara Zenati[1], A. Benmoussat[1], A. Bourdim[2]

[1] *Corrosion Equip of LAEPO Research Laboratory - Faculty of technology- Chetouan University Pole Tlemcen University –Algeria*

[2] *Faculty of technology- Chetouan University Pole Tlemcen University –Algeria*

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

Corresponding Author. E-mail: z_amara2000@yahoo.fr ; Tel: (00213 771 752 015)

Abstract

The used X60 pipelines steels for natural gas transmitting are susceptible to failures such as pitting corrosion or cracking in consequence of soil interaction with materials. The corrosion behaviour is simulated by means of electrochemical measurements such as potentiodynamiques polarization and electrochemical impedance spectroscopy (EIS) with and without the corrosion inhibitors containing polyphosphates ions. Appropriate models for corrosion parameters are used to fit the experimental data and extract the parameters that characterize the corrosion process. The corrosion rates were studied in different concentrations of corrosion inhibitors at different near neutral pH values. Results showed the bare steels sensitivity to corrosion and by increasing the temperature, the polarization resistance decreases and the corrosion speed increases as well as the densities of corrosion current I_{Corr}. Corrosion inhibitors tests showed a variation in inhibition performance with varying concentration, temperature and immersion time. Langmuir model have been tested to describe the adsorption behaviour of inhibitor on the steel surface for the temperature range.

Keywords: API 5lX60, localized corrosion, simulation soil solution, electrochemical, Polyphosphate inhibitors.

1. Introduction

X60 pipeline steel is characterized by its good combination of strength and toughness, good weldability, low crack sensitivity coefficient, and low ductile to brittle transition temperature [1-2]. Therefore, several studies [3-4] have been conducted on the corrosion and corrosion protection in different aggressive media. Chemical composition is necessary to examine every particular site to explain the corrosion mechanisms models resulting from the steel interaction with the soil environment that depends of numerous factors such as soil nature, moisture content, soil resistivity soil pH, and oxidation – reduction potential… Appropriate models for corrosion parameters such as corrosion current density (Icorr), corrosion potential (Ecorr), polarization resistance (Rp), soil resistivity are used to fit the experimental data and extract the parameters which characterize the corrosion process. Polyphosphates ions were selected as corrosion inhibitors in consequence of their environmental properties efficacy in soil. Potentiodynamiques polarisation and electrochemical impedance spectroscopy (EIS) were carried out.

2. Materials and methods

Samples were obtained from pipe Sonatrach Algerian gas, specifically they have been chosen of tubes posed on the GZ1 line in 1974 which corrosion pits were detected. There were cut by flame – cut from the pipes walls and the test coupons were then cut from these sections by wet sawing. Pre-treatment of steels samples surfaces was carried out by grinding with emery paper of 600- 1200 grit, rinsing with bid stilled water, and ultrasonic degreasing in ethanol and dried at room temperature.

Microstructure of API 5L X60 pipeline steel is depicted after 30s etch in 2% Nital solution; Micrographic analysis has been done using optical micrograph as shown in Figure 1.It showed a fine pearlitic-ferritic microstructure with a ferritic predominantly.

Chemical composition of the study material shown in table 1

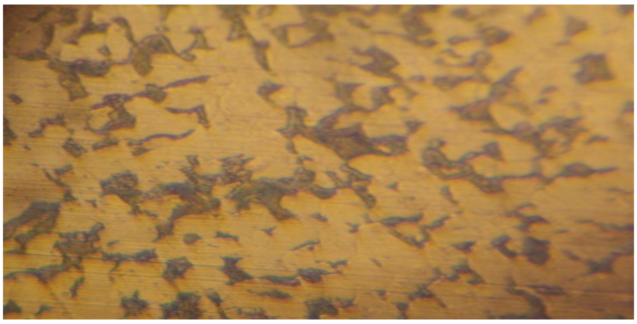

Figure 1 : Microsture of API 5L X60 pipeline steel after 30 s etch in 2% Nital solution

Table 1: Chemical composition of the study material API5L X60, content %

C	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**
0.18	0.036	1.400	0.017	0.013	0.028	0
Ni	**Al**	**Cu**	**Ti**	**V**	**Sn**	**Fe**
0.018	0.049	0.032	0.005	0.0061	0.0031	≈ 97.880

The techniques available to determine the corrosion of the site may include laboratory test based on a soil chemical analysis in a specific location [5]. Several soil samplings have been taken from various sites and the most aggressive soil composition have been chosen for this experiments table 2 [5]. Soil extract was prepared according to AFNOR French norm A–05.250 P.278. A mass of soil is taken then mixed with distilled water and analyzed by spectrophotometer microanalysis. Test solution is obtained by reconstitution of chemical composition of soil in a solution called " soil simulating solution. Shown in table 3 [5]

Table 2: Chemical composition of the soil (mg/L)

Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	$HCO3^-$
37.80	58.08	8.19	137.74	551.04	122

Table3: Chemistry of the simulated soil solution (mg/l)

Components	$CaSO_4$	$MgSO_4$	K_2SO_4	NaCl	Na_2SO_4	$NaHCO_3$
Concentration (mg/L)	2.00	29.04	1.82	22.69	37.48	0.16

Polarisation measurement was performed by Potentiostat equipment using a conventional three electrodes cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode (WE) was in the steel and had the form of a disk with an exposed area of 1,8 cm^2.

The potentiodynamic current-potential curves were recorded by changing the electrode potential from -1400 mV/SCE to 0V/SCE with scanning rate of 1.66 mV/s. The following experimental data have been obtained by electrochemical measurements with polyphosphates ions as corrosion inhibitors such as disodic hydrogeno-phosphate with different concentrations (10^{-3},10^{-2},10^{-1}, 5.10^{-1} M) that have been added to the simulated soil solution. Inhibition efficiencies were determined from corrosion values calculated by Tafel extrapolation method.

3-Results and discussions

3.1 Potentiodynamic polarization

The potentiodynamic polarization tests have been performed in de-areated soil simulating solution at various pH and temperatures simulating the conditions of pipe soil environment. Experiments dealing with the pH effect were however conducted by achieving the desired solution pH through minute adjustments using droplets of HCl or NaOH, respectively.

3.1.1 pH influence

The polarization parameters values of (Icorr), corrosion potential (Ecorr), polarization resistance and cathodic and anodic Tafel slopes (β_c), (β_a) are given in table 4

Table 4: Polarization parameters for the corrosion of X60 steel in Soil simulating solution according to the pH variation in the range 5.0 – 8.5

pH	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	R_p (kΩ.cm^2)	βc (mV/dec)	β_a (mV/dec)
5.0	-740	7.5	6.2	-307	103
6.5	-793	7.4	7.5	-311	220
8.5	-760	4.8	10.6	-323	185

If the pH values decrease toward the neutral or acidic pH in the range studied, steel corrosion increases slightly from 4.8 μA/cm^2 to 7.5 μA/cm^2 and polarization resistance decreases from 10.6 kΩ.cm^2 to 6.2 kΩ.cm^2. The potential corrosion tends towards the anodic values.

3.1.2 Effect of temperature

Polarization curves in the temperature range 25 – 55 °C at pH = 5 are shown in figure 2 and polarization parameters are given in table 5.

Table 5: Polarization parameters for the corrosion of X60 steel in soil simulating solution according to the temperature variation in the range 25 – 55°C (pH = 5)

Temperature (°C)	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2	R_p (kΩ.cm^2	βc (mV/dec	β_a (mV/dec
25	-740	7.5	2.77	-307	103
45	-743	19.8	1.48	-239	125
55	-741	57.8	0.98	-342	213

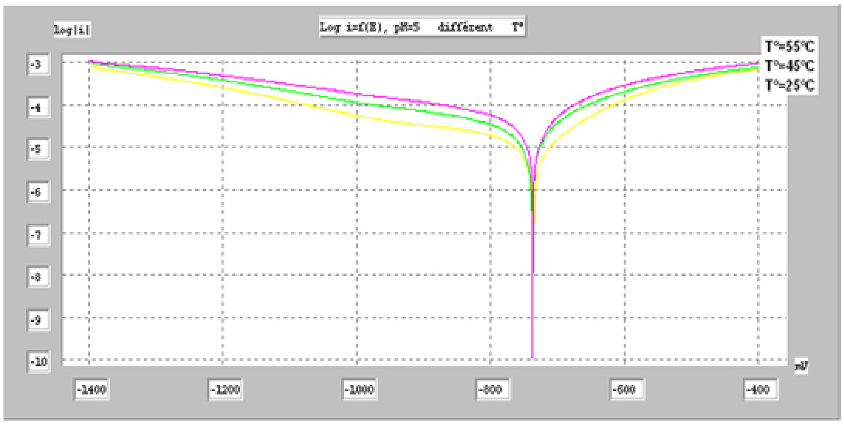

Figure 2: Potentiodynamic polarization curves for X60 steel in soil simulating solution at various temperatures (pH = 5)

In the temperature range studied, the corrosion current density increases with increasing temperature and the steel corrosion potential moves towards the negative values when the temperature increases in the studied solution. The anodic polarization curves present parallel Tafel straight lines indicating that the hydrogen reduction reaction to steel surface is always done according to activation mechanism in all the temperature range studied. In the temperature range at the near neutral pH and alkaline solution, we have also a similar situation of electrochemical parameters variation. Polarization parameters values in the temperature range 25 – 55 °C at pH = 6.5 and 8.5 are given in table 6 and table 7 respectively.

Table 6 Polarization parameters for the corrosion of X60 steel in soil simulating solution according to the temperature variation in The range 25 – 55°C (pH = 6.5)

Temperature (°C)	**E_{corr} (mV/SCE)**	**I_{corr} (µA/cm^2)**	**R_p (kΩ.cm^2)**	***βc* (mV/dec)**	***Ba* (mV/dec)**
25	-793	7.4	7.5	-311	177
45	-757	12	1.97	-331	162
55	-771	14	2.07	-337	195

Table 7 : Polarization parameters for the corrosion of X60 steel in soil simulating solution according to the temperature variation in the range 25 – 55°C (pH = 8.5)

Temperature (°C)	**Ecorr (mV/SCE)**	**Icorr (µA/cm2)**	**Rp (kΩ.cm2)**	**βc (mV/dec`**	**Ba (mV/dec)**
25	-760	4.8	3.74	-323	184
45	-826	17.9	3.20	-285	225
55	-780	50.6	1.33	-160	268

A value of the activation energy E_a = 17.48 kJ.mol^{-1} is obtained from the slopes of Arrhenius plots in the case of solution at pH=6.5. This value is low compared to the value of steels corrosion activation energy in acidic environment [8,9] which to reach a value of 60 kJ mole-1. The activation energies values and delta H for different pH are gathered in table 8. The activation corrosion energy increases with the temperature according to the pH soil environment. These values are close to the literature except for the near neutral pH where the value is different. Figure 3 presents Arrhenius slopes in the pH range 5.0 – 8.5.

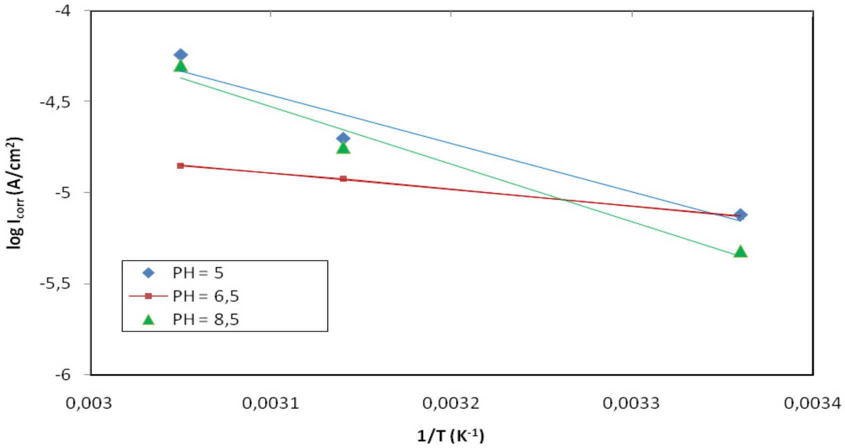

Figure 3: Arrhenius plots calculated from corrosion current density for X60steel in soil simulating solution at different pH values

Tableau 8: values of Ea and ΔHa° for different pH

pH	**Ea (kJ mole-1)**	**ΔHa° (kJ mole-1)**
5.0	51.01	49.18
6.5	17.48	14.48
8.5	59.22	58.15

3.2 Concentration influence

The electrochemical measurements have been obtained using the polyphosphates ions as corrosion inhibitors such as disodic hydrogeno-phosphate at various pH in range (5.0 - 8.5) and different concentrations which have been added to complete the study solution. For pH = 5.0, the polarization parameters values of (Icorr), corrosion potential (Ecorr), polarization resistance, cathodic and anodic Tafel slopes (βc), (βa) and the inhibition efficiency (E) are given in table 9 and shown in figure 4. Results showed that, according to the concentration of inhibitor and the variation of pH in the range studied, the inhibition efficiency (E) is obtained for low value in acidic medium. We have obtained the similar situation when pH moved to basic near neutral value but decreases for 5.10-1M.

Table 9: Polarization parameters for the corrosion of X60 steel in Soil simulating solution according to the corrosion inhibitors concentration, (pH = 5.0)

Conc. (M)	**E_{corr} (mV/SCE)**	**I_{corr} (µA/cm^2)**	**R_p (kΩ.cm^2)**	***βc* (mV/dec)**	***βa* (mV/dec)**	**E% (I_{corr})**	**E% (R_p)**
Blank	-740	7.5	6.2	-307	165	-----	----
10^{-3}	-725	4.6	11.2	-333	179	38.7	44.9
10^{-2}	-691	2.5	20.7	-373	173	66.7	70.0
10^{-1}	-763	2.1	23.8	-333	173	72.0	73.9
5.10^{-1}	-766	4.2	10.7	-213	204	44.0	42.0

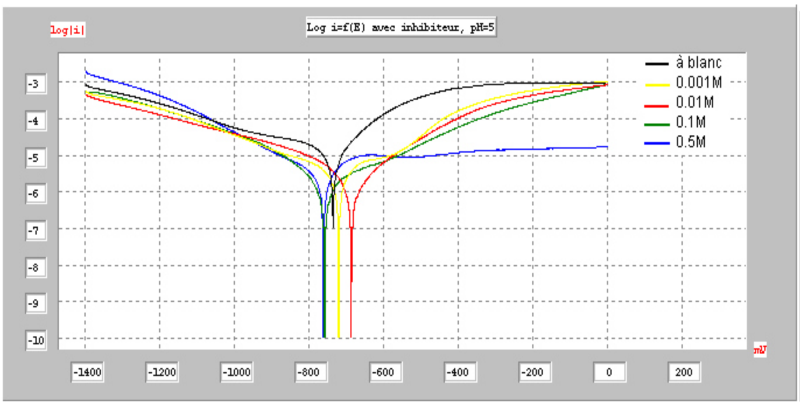

Figure 4 potentiodynamic curves of X60 steel immersed in simulated soil solution at different corrosion inhibitor concentration (pH = 5.0)

3.3 Adsorption consideration

The interaction between the inhibitors and the API steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the fractional coverage value θ as a function of inhibitor concentration must be obtained.

According to this isotherm θ is related to concentration inhibitor C via eq. 5:

$$\frac{C}{\theta}=\frac{1}{K}+C \quad \text{with} \quad K=\frac{1}{55,5}\exp\left(-\frac{\Delta G^{0}_{ads}}{RT}\right) \qquad (5)$$

where K is the adsorptive equilibrium constant and ΔG°ads the free energy of adsorption.

Linear plots were obtained for inhibitor. These results suggest that the adsorption phenomenon obeys a modified Langmuir isotherm proposed by Villamil et al. [10], which is given by the corrected equation:

$$\frac{C}{\theta}=\frac{n}{K}+nC \qquad \textbf{(6)}$$

The obtained values of K, n and ΔG°ads are summarized in table 10.

Table 10: The thermodynamic parameters for of API steel in simulated soil solution in the absence and presence of different concentrations of the inhibitor.

pH	**K (L/mol)**	**n**	**-ΔG°ads (kJ/ mol)**
5	512.11	1.48	25.41
6.5	1131.15	1.38	27.37
8.5	1574.8	1.40	28.19

Conclusion

The main objective of the present investigation was to study the susceptibility interactions of steel with the soil environment. Corrosion phenomena was simulated in laboratory while approaching the industrial context and chosen a most corrosive composition of soil simulating solution. Results showed that if pH decreases in the pH range 5.0 – 8.5, steel corrosion increases and polarization resistance decreases. In the studied temperature range 25 – 55 °C the corrosion current density increases with increasing temperature and the steel corrosion potential moves toward the negatives values when the temperature increases. The activation corrosion energy increases with the temperature according to the pH soil environment. These values are close to the literature except for the near neutral pH where the value is different. Potentiodynamic polarization with addition of the polyphosphates ions as corrosion inhibitors at various pH in range (5.0 -8.5) in different low concentration from 10^{-3} to 10^{-1} showed that the inhibition efficiency is obtained for low value in acidic medium. We have obtained the similar situation when pH moved to basic near neutral value but decreases for the concentration of 5 10^{-1} M. The maximum inhibition efficiency was 72%. These results suggest that the adsorption phenomenon obeys a modified Langmuir isotherm

References

1. Benmoussat A., Hadjel M., *Eurasian Chem. Tech. Journal*, 7 (2) (2005) 147.
2. Benmoussat A., Hadjel M., M. Traisnel, *Materials and Corrosion*, 57 (10) (2006) 771.
3. Benmoussat A., Traisnel M., Integrity of Pipelines Transporting Hydrocarbons, NATO Science for Peace and Security Series C*: Environmental Security*, (2011) 67.
4. API specification 5L (SPEC 5L), specification for line pipe, 14th edition, November 1, 1992, American petroleum institute 1220 L street, northwest Washington, DC 20005
5. Belmokre K., Azzouz N., Kermiche F., Wery M., Pagetti J., *Materials and Corrosion*, 49 (1998) 108.
6. Landolt D, *Corrosion Metals Surface Chemistry*, Alden Press, Oxford, (1993) 495.
7. El Ouali I., Hammouti B., Aouniti A., Ramli Y., Azougagh M., Essassi E.M., Bouachrine M., *J. Mater. Environ. Sci*. 1 (2010) 1.
8. Larabi L., Harek.Y, Benali.O., Ghalem S., *Progress in Organic Coatings*, 54 (2005) 256.
9. Selles C., Benali O., Tabti B., Larabi L., Harek Y., *J. Mater. Environ. Sci*., 3 (1) (2012) 206.
10. Villamil R.F.V., Corio P., Rubin J.C., S.M.L. Agostinho, *J. Electroanal. Chem*, 535 (2002) 75.
11. Fouda A.E., Mostafa H.A., Abu-Elnader H.M., *Monatshefte fur Chem*-104 (1989) 501.
12. Donahue F.M., Nobe K., *J. Electrochem. Soc*. 112 (9) (1965) 886.
13. Khamis E., Bellucci F., Latanision R.M., E.S.H. El-Ashry *Corrosion* 47 (1991) 677.
14. Metikoš-Hukovič M., Babić R., Grubač Z., Brinić S., *J. Appl. Electrochem*. 26 (1996) 443.
15. Benali O., Larabi L., Traisnel M., Gengembre L., Harek Y., *Appl. Surf. Sci.,* 253 (2007) 6130.
16. Ismail A.I.M., El-Shamy, *Appl. Clay Sci* 42, (2009) 356.

(2015) ; http://www.jmaterenvironsci.com