

Short Communication

Electrochemical Corrosion Behavior of API 5L X60 steel Exposed to Different Concentration of NaCl Solution

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Here, the corrosion behavior of API 5L X60 pipeline steel immersed in different concentrations of NaCl solution as an offshore environment was studied using polarization and electrochemical impedance spectroscopy (EIS) tests. Different parameters were obtained from the fitting EIS data by an equivalent circuit model to indicate the corrosion resistance of carbon pipeline steels in the offshore environment. The polarization results indicate that the performance of corrosion resistant in API 5L X60 pipeline steels considerably improved with formation of a passive layer to restrain both the anodic and the cathodic corrosion reaction. The EIS results indicate that the NaCl concentration in electrochemical solution plays a significant role in the evolution of the charge-transfer processes and film resistance. Furthermore, the resistance of the passive layer is gradually reduced by increasing the chloride content which reveals that porous products and non-protective corrosion have been developed on the surface of the pipeline. Half-cell potential results indicate that the potential values in all NaCl concentrations tend to positive value by increasing immersion time, showing more resistance to corrosion in higher exposure time.

Keywords: API 5L X60 pipeline steels; Electrochemical corrosion; Offshore environment; polarization analysis; Electrochemical impedance spectroscopy

1. INTRODUCTION

Corrosion is an electrochemical process or reaction between steel (metal) and corrosive environment that causes the material to degrade [1, 2]. Pipelines are commonly preserved against

external corrosion by a cathodic protection [3, 4]. The carbon steel behavior in the offshore environment was widely studied and the effect of different parameters such as microbiological activity, ionic species, pH, moisture, electrical resistivity or degree of aeration was already considered [5, 6]. However, ensuring a certain rate of residual corrosion requires a small relationship between the rate of corrosion and the applied potential, but such the relationship is rarely recognized [7, 8]. Many studies have been completed to evaluate the influence of chloride ions on the corrosion behavior of pipeline steels [9]. Electrochemical assessments for example electrochemical impedance spectroscopy (EIS) have been predictably used to consider ionic transport and electrochemical reactions [10, 11]. This technique can be applied to estimate the electrical properties of pipelines during the exposure procedure and help in the evaluation of the corrosion potential and the polarization resistance of the pipeline steel when exposed to the offshore environment. Half-cell potential test for considering corrosion initiation of pipeline steel is convenient and sensitive [12-14].

However, chloride concentration in the offshore environment is extremely believed to be a key factor contributing to pipeline steel corrosion, there is currently no study on electrochemical corrosion behavior of X60 steel to find threshold condition of pipeline corrosion. Therefore, in this work, the corrosion behavior of X60 pipeline steel immersed in different concentrations of NaCl solution as an offshore environment was studied using polarization and electrochemical impedance spectroscopy (EIS) tests.

2. MATERIALS AND METHODS

The API 5L X60 pipeline steels were used in this work as a pipeline with the chemical composition indicated in Table 1.

Table 1. Chemical composition of used pipeline steels (wt%)

C	S	P	Si	Mn	Al	Mo	Ni	Cu	Nb	Fe
0.1	0.014	0.011	0.26	1.3	0.025	0.1	0.11	0.15	0.02	Bal.

The pipeline steel had a cylindrical shape with 8 mm diameter and 5 mm thickness. The pipeline steels were cleaned with silicon carbide and rinsed by water and then quickly dried in the air flow. Evaluations were periodically performed after 1, 2, 3 and 4 months of exposure.

All tests were done in different concentrations of NaCl solution (0.0 wt%, 0.5 wt%, 1.5 wt% and 3.5 wt% NaCl) as an offshore environment. A classic three-electrode electrochemical cell (Solartron 1280C) has been designed for investigation of corrosion protection of API 5L X60 pipeline steels in NaCl solution. The pipeline, saturated copper sulphate and platinum electrodes were a working, reference and counter electrodes, respectively. The surface area was 2.5 cm². EIS measurements were performed in frequency range from 0.1 MHz to 0.01 Hz and 10 mV amplitude. The EIS data attained were simulated by an equivalent circuit. The polarization measurement of API 5L X60 pipeline steels were done at 0.1 mV/s scan rate. The potential of X60 pipeline steels were

measured through open circuit potential (OCP) method by Cu/CuSO₄ reference electrodes. The surface morphologies of the samples were considered with scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

The corrosion resistance of samples can be considered by the polarization analysis. Polarization curves attained with steel X60 pipeline are indicated in Fig. 1. Figure 1 exhibits the polarization curves of the samples in different concentration of NaCl solution. Commonly, all samples indicate no active corrosion and passivation behavior, revealing the anodic current density enhanced continuously by increasing potential. In this study, the corrosion potential was shifted toward more noble direction and current-density at the anode reduced slightly due to the decrease of chloride content, showing the improved corrosion resistance in solution without NaCl. The corrosion rates were calculated by the Tafel extrapolation technique. As stated by Faraday's law, corrosion rate may be determined by the corrosion current-density [15]:

$$\text{Corrosion rate} \left(\frac{\text{mm}}{\text{y}} \right) = \frac{3.16 \times 10^8 i_{\text{corr}} M}{z F \rho} \quad (1)$$

where i_{corr} and M indicate the corrosion current-density and the molar mass, respectively. z and F represent the number of electrons transferred in a metal atom and Faraday's constant, respectively. ρ reveals the metal density (g/cm^3).

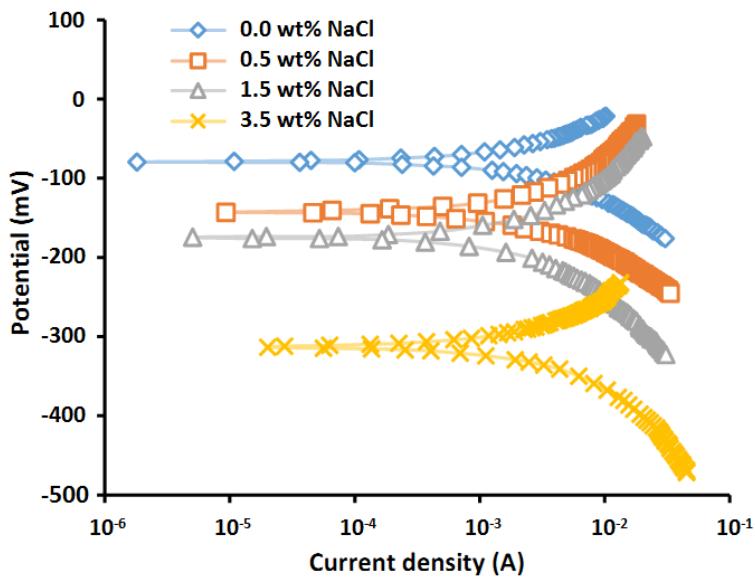


Figure 1. Polarization curves of X60 pipeline steel exposed to different concentration of NaCl solution

The corrosion potential of the samples in low concentration of NaCl were considerably more positive than the high one which indicates that the self-corrosion potential enhanced after reducing

chloride content (table 2). The changes in the corrosion rates may be because of the ohmic drop produced by the resistance of solution, which happened during the polarization assessment [16].

Table 2. Fitting parameters of the specimens achieved from polarization plots

Solution	Corrosion potential (mV)	Corrosion current density (mA cm^{-2})	Corrosion rate (mm/year)
0.0 wt% NaCl	-85	2.75	1.6
0.5 wt% NaCl	-146	3.74	2.1
1.5 wt% NaCl	-172	5.46	2.6
3.5 wt% NaCl	-304	8.57	3.3

The investigation of all the obtained results from polarization tests confirmed the influence and aggressiveness of the offshore environment in comparison to the solution without any addition of NaCl.

The corrosion possibility of X60 pipeline steel was considered through potential of the X60 steel by open circuit potential (OCP) method. As shown in Fig. 2, there is a high-possibility for corrosion of pipeline because the OCP values are relatively small.

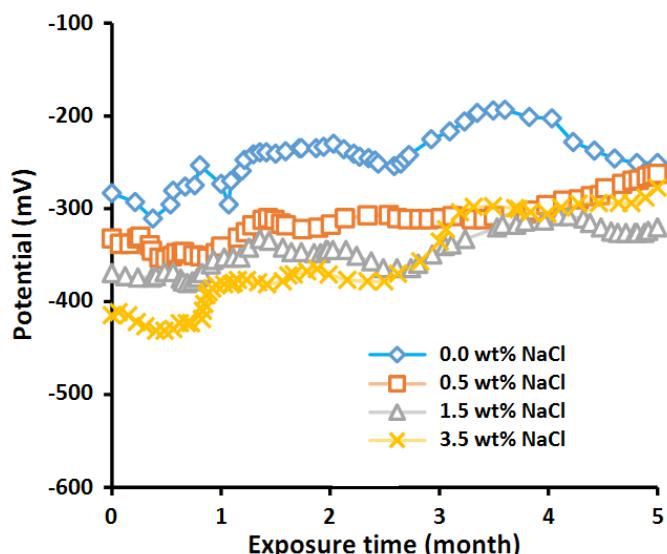


Figure 2. OCP of the sample exposed to different content of NaCl

As revealed in figure 2, for the sample exposed to salt-free solution, the value of potential is reduced by increasing the immersion time. Due to the absence of Cl^- ions in the experiment environment, the increase of potential cannot be related to the passivation film on the pipeline steel. Gradually increasing the potential of steel with increasing exposure time can lead to an increase in the amount of oxygen and thus increase the potential of the pipeline. The oxygen concentration in electrolyte solution usually enhances the potential of steel electrode toward more positive value. The potential of the specimens at the opening of immersion into NaCl solution is lower than -350 mV,

which exhibit a relatively strong corrosion. As stated in ASTM-C876 standard, the value of threshold (-350 mV) for corrosion potential against a Cu/CuSO₄ for electrolyte solution does not apply. It can be attributed to the limitation of oxygen penetration in the solution and thus the inability to create a protective layer. Furthermore, the corrosion phenomena depend on cathodic reaction, and probable cathodic reaction in the electrochemical system needs oxygen, which causes a reduction in the corrosion rate. In addition, the presence of high-strength layers may influence on the potential. This potential difference may occur when layers of corrosion products form on the pipeline steel surface. The difference because of the distance of pipeline steel from the reference-electrode may be reduced through a permanent reference-electrode within solution.

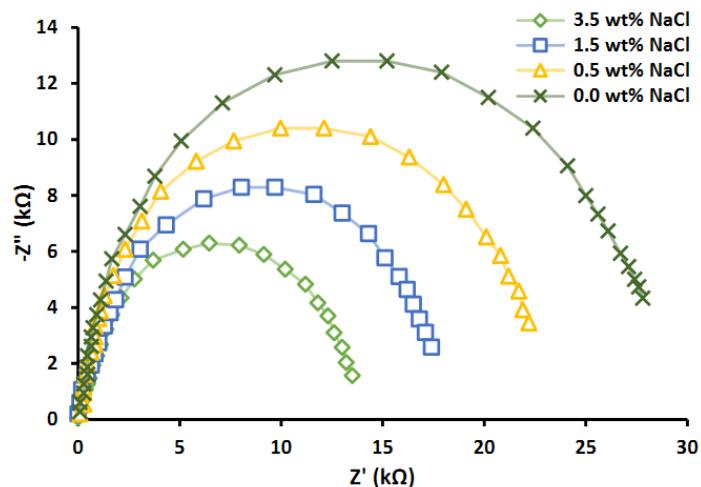


Figure 3. The Nyquist plots obtained from EIS analysis of API 5L X60 pipelines exposed to different concentration of NaCl solution

EIS technique has been used for considering anticorrosion of API 5L X60 pipelines exposed to different concentrations of NaCl solution. The Nyquist plots obtained from EIS analysis were shown in Figure 3. As shown, the Nyquist diagram contains two sections. The first one has high-frequency parts which have slightly changed. The second one has low-frequency parts which have remarkably changed. The phenomena indicates that the corrosion products slightly change and the charge-transfer resistance (R_{ct}) changes regularly with the change in NaCl concentration [17]. R_{ct} can show the corrosion rate of specimens where low-frequency impedance spectra revealed that the resistance obtains into a greatest value with the reduction of chloride content.

An equivalent circuit based on the EIS results is indicated in Figure 4. R_s show inductive reactance and soil resistance. During the passivity procedure, the parameters of second-time constant found at the low-frequencies such as C_{dl} and R_{ct} were attributed to the non-ideal interfacial capacitance and charge-transfer resistance of the API 5L X60 steel surface. It revealed that the corrosion resistance of the pipeline steel was controlled through the properties of passive layer [18, 19]. The parameters of

first-time constant found at the low-frequencies such as C_f and R_f and were recognized to the redox-transformation in corrosion products which occurred on the surface of oxide film [20].

Zsimpwin software was used to analyze the EIS results of X60 pipeline steels consistent with the equivalent circuit. The results obtained from various soils are indicated in table 3.

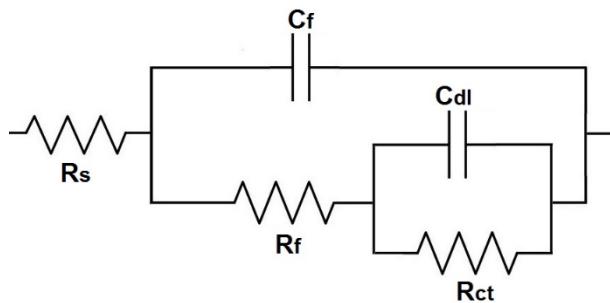


Figure 4. An equivalent circuit used

Polarization resistance (R_p) is an assessable indicator to study the resistance of steel corrosion into the corrosive environment. The higher value of R_p reveals higher corrosion resistance of pipeline steels.

As shown in table 3, by increasing NaCl content into the electrolyte solution, the R_p was enhanced. Moreover, the decrease of corrosion rate was exhibited due to absorption of chloride ions onto the surface of X60 steel. Hence, corrosion rate decreased by increasing the salinity value which was in accordance with polarization results.

Table 3. Electrochemical parameters obtained from the EIS analysis

Solution	R_s ($\Omega \text{ cm}^2$)	R_f ($k\Omega \text{ cm}^2$)	C_f ($\mu\text{F cm}^{-2}$)	R_{ct} ($k\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	R_p ($k\Omega \text{ cm}^2$)
0 wt% NaCl	48.5	19.8	0.9	28.6	1.4	48.4
0.5 wt% NaCl	37.7	16.7	1.2	23.8	1.7	40.5
1.5 wt% NaCl	42.4	12.9	1.8	18.2	2.5	31.1
3.5 wt% NaCl	43.6	9.5	2.3	14.1	3.3	23.6

The thickness of the passive layer can be measured with the following equation [21]:

$$D = \frac{\varepsilon \varepsilon_0 A}{C_{dl}} \quad (1)$$

Where D is the passive film thickness, ε_0 ($8.85 \times 10^{-12} \text{ F m}^{-1}$) and ε (12 for Fe oxides) are the vacuum permittivity and dielectric constant, respectively. A is an effective area and capacitance.

As indicated in table 3, the value of C_{dl} increases as the concentration of Cl⁻ ions increases, which reveals that the passive film thickness was reduced and the resulting protective capacity was enhanced when the Cl⁻ content of solution was decreased. It can be related to the broken passive layer

on the steel surface, when the Cl⁻ concentration was in the threshold value [22, 23]. Moreover, table 3 shows that R_f gradually reduced by increasing the concentration of Cl⁻ ions which reveals that porous and non-protective products have been developed on the steel surface[24]. These findings are consistent with the best-fit results for C_{dl} which were gradually increased over $3.3 \mu\text{Fcm}^{-2}$ in 3.5 wt% NaCl, indicating that produced corrosion can happen on the steel surface [25, 26].

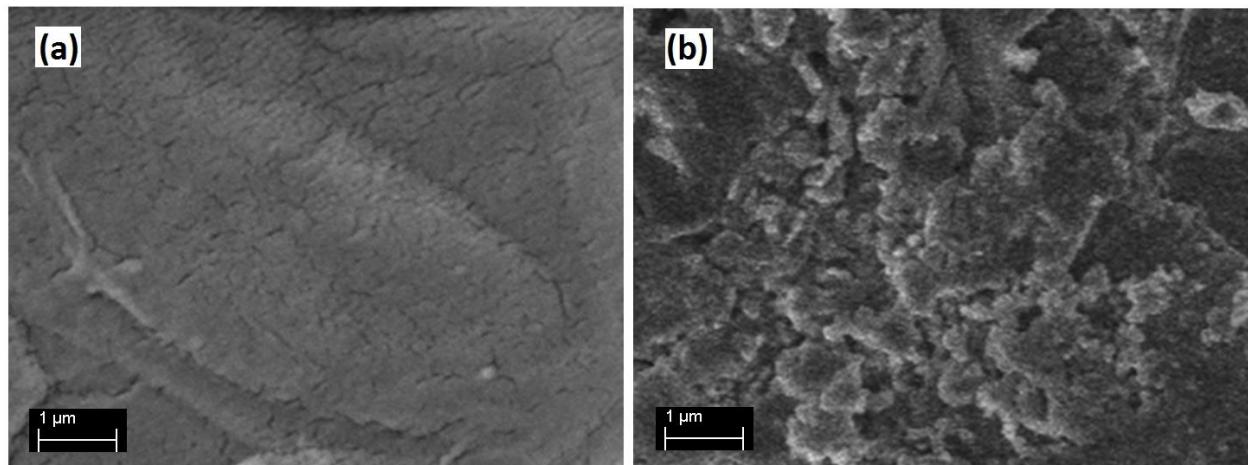


Figure 5. SEM images of the steel surface after (a) 1 day and (b) 2 month exposure time in the 3.5 wt% NaCl solution

Figure 5 reveals typical morphologies of corrosion attack of the steel surface after 2 month exposure time. After 2 month exposed in the 3.5 wt% NaCl solution, a corrosion layer was formed by the composition of soil and rusted particles, indicating the surface of steel is under intense corrosion attack over the whole surface. While low pit corrosion appeared on the steel surface at the initial exposure time and most of the X60 steel surface remained intact.

4. CONCLUSIONS

Corrosion is an electrochemical process or reaction between steel (metal) and corrosive environment that causes the material to degrade. In this work, the corrosion behavior of X60 pipeline steel immersed in different concentrations of NaCl solution as the offshore environment was studied using polarization and EIS tests. Different parameters were obtained from the fitting EIS data by an equivalent circuit model to indicate the corrosion resistance of carbon pipeline steels in the offshore environment. The polarization results indicate that the performance of corrosion resistant in API 5L X60 pipeline steels considerably improved with formation of a passive layer to restrain both the anodic and the cathodic corrosion reaction. The EIS results indicate that the NaCl concentration in electrochemical solution plays a significant role in the evolution of the charge-transfer processes and film resistance. Furthermore, the resistance of the passive layer is gradually reduced by increasing the

chloride content which reveals that porous products and non-protective corrosion have been developed on the surface of the pipeline. Open circuit potential results indicate that the potential value in all solution concentrations tends to positive value by increasing immersion time, showing more resistance to corrosion in higher exposure time.

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