

INFLUENCE OF TESTING TEMPERATURE ON THE CORROSION BEHAVIOR OF API 5L X70 PIPELINE

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Abstract. Localized corrosion attack is known to take a preponderant role in the onset of stress corrosion cracking of pipeline steels in high pH conditions. Carbonate/bicarbonate solutions can be employed to study the localized corrosion behavior of these materials. In addition to the presence of chloride ions in the electrolyte, the solution temperature is also of prime importance to the onset of pitting corrosion. The aim of this work was to evaluate the influence of the testing temperature on the corrosion behavior of the API 5L X70 pipeline steel which is a standard material for gas pipelines in Brazil. Samples were exposed to a solution consisting of Na2CO3, NaHCO3 and NaCl at three different temperatures: room temperature, 40 °C and 60 °C. The corrosion morphology was observed using scanning electron microscopy. The results showed that pitting corrosion became facilitated when the steel was immersed at higher temperatures.

Keywords: API 5L X70, pipeline steel, corrosion, temperature

1. INTRODUCTION

API 5L X70 is a pipeline steel currently used in Brazil to transportation of natural gas and oil. This type of structure is designed to ensure that failures resulting from high pressure, thermal effects and environmental degradation are prevented (Sánchez et al., 2005). Most part of the oil and gas sources in the world are located in remote areas and demand transportation by pipelines in order to reach their major markets (Hashemi, 2009). The environments where these pipelines are installed are considered aggressive to the API steels due to the presence of species such as Cl, NCO_3 , CO_2 and H_2S (Liu et al., 2008). Stress corrosion cracking (SCC) is a serious threat to the safe operation of pipeline steels (Liu et al., 2009). Several authors studied the SCC mechanisms of pipeline steels in different environments (Eslami et al., 2010; Song, 2009; Zhang et al., 2009a). Most failures due to SCC of API steels are reported to occur under a high pH (approximately 9.5) condition which is associated with a concentrated solution consisting of carbonate/bicarbonate (Li and Cheng, 2008; Tang and Cheng, 2008). A passive oxide layer can develop when the steel is exposed to this condition (Parkins and Zhou, 1997). Chloride ions are reported to lead to the breakdown of the passive layer, forming corrosion pits. Pitting corrosion is considered as the first step of the stress corrosion cracking mechanism of pipeline steels (Van Boven et al., 2007). In this context, it is imperative to investigate the pitting corrosion behavior of pipeline steels in order to guarantee a safer operation. Few works have been devoted to study the effect of temperature on the pitting corrosion resistance of pipeline steels. Nazari et al. (2010) showed that the nature of the oxide layer formed on the surface of the X70 pipeline steel was strongly affected by the testing temperature. The aim of this work was to investigate the effect of the test temperature on the corrosion behavior of the API 5L X70 steel immersed in carbonate/bicarbonate solutions with addition of NaCl. The electrochemical evaluation was performed based on electrochemical impedance spectroscopy measurements and potentiodynamic polarization curves. The onset of pitting corrosion at different testing temperatures was assessed.

2. EXPERIMENTAL DETAILS

2.1. Material

The material used in this work was a hot rolled API 5L X70 steel plate kindly provided by USIMINAS whose chemical composition is shown in Tab. 1.

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	С	Mn	S	Р	V	Nb	Al	Fe
Mass (wt.%)	0.12	1.49	0.006	0.018	0.02	0.017	0.014	Bal.
(WL.%)								

Table 1. Chemical composition of the API 5L X70 steel plate used	sed in this work.
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2.2 Electrochemical tests

The electrochemical tests were performed in an electrolyte which was comprised of 0.05 M Na₂CO₃, 0.1 M NaHCO₃ and 0.1 M NaCl at three different temperatures: 25 °C, 40 °C and 60 °C. The specimens were cut in rectangular dimensions, leaving an approximate area of 1 cm² to be exposed to the electrolyte. All the electrochemical measurements were carried out using a potentiostat/galvanostat Autolab PGSTAT 100 equipped with a FRA module. A three-electrode cell arrangement was used, containing a Pt wire as the auxiliary electrode and a saturated calomel electrode (SCE) as reference; all potentials quoted in this paper are referred to this reference electrode. The specimen acting as working electrode was mounted in epoxy resin. The working electrode was ground with successive grade silicon carbide sandpaper up to 1000 grit, polished with alumina paste (1 m), degreased with ethanol, rinsed with distilled water and dried in air.

Electrochemical impedance spectroscopy (EIS) measurements were used to monitor the electrochemical behavior of the specimens during 7 days of immersion. The data were collected under the open circuit potential (OCP) over a frequency range from 100 kHz to 10 mHz with an acquisition of 10 points/decade. The amplitude of the perturbation signal was \pm 10 mV. Potentiodynamic polarization curves were obtained after 7 days of immersion using a scan rate of 1 mV.s-1 in the potential range from -300 mV vs. the OCP up to 1 V.

2.3 Corrosion morphology

The corrosion morphology of the tested specimens, emphasizing the presence of pits, was assessed using scanning electron microscopy (Hitachi TM3000 tabletop).

3. RESULTS AND DISCUSSION

3.1 EIS measurements

EIS results are represented as Nyquist plots as shown in Fig. 1. The plots are referred to 7 days of immersion in the electrolyte at different testing temperatures.

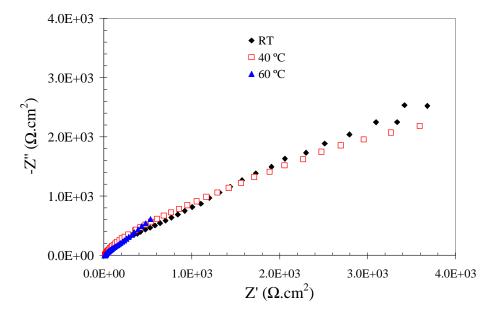


Figure 1. Nyquist plots of the API 51 X70 steel immersion for 7 days at different testing temperatures.

Electrochemical AC techniques such as EIS have a low amplitude perturbation signal, making it attractive to study the corrosion processes of electrical conductors in aqueous electrolytes (Jüttner, 1990). EIS is a powerful tool for investigating the mechanisms of electrochemical reactions. The Nyquist plots are characterized by a depressed semicircle spanning throughout the whole frequency range independently of the testing temperature. The highest frequencies are on the left whereas the lowest frequencies are on the right of the plots shown in Fig.1. At a first glance, this indicates that the corrosion mechanism should be the same for the three different temperature conditions. In fact, Zhang et al. (2009b) stated that the capacitive semicircle which characterizes the Nyquist plots shown in Fig. 1 is typical of activation-controlled interfacial reactions. In this regard, diffusion-controlled processes throughout the oxide layer formed on the surface of the specimen during immersion can be neglected. In spite of the similarity akin to the corrosion mechanisms suggested by the Nyquist plots, it is important to observe the relative impedance values obtained at each condition and, most importantly, the radius of the capacitive loops. It is well-known from the literature, that this radius is closely related to the corrosion resistance of the electrode surface (Antunes et al., 2010). Thus, the results suggest that the corrosion resistance was little affected when the testing temperature was raised from the room temperature (RT) to 40 °C. However, by further increasing the temperature to 60 °C the radius of the semicircle was greatly depressed, indicating a significant loss of corrosion resistance. Recent studies by Tang et al. (2013) and Xiang et al. (2013) confirm that temperature seriously affects the corrosion rate of pipeline steels. The electrochemical reactions leading to reaction are favored at temperatures up to 70 °C or 90 °C, accelerating corrosion. For higher temperatures, the corrosion rate can be depressed due to the formation of more protective oxide films. The results shown in Fig. 1 confirm the trend of increased corrosion kinetics for the temperatures evaluated in this work.

3.2 Potentiodynamic polarization curves

Potentiodynamic polarization curves of the API 5L X70 steel immersed for 7 days at different temperatures in the electrolyte solution described in section 2.2 are shown in Fig. 2. The electrochemical parameters determined from these curves are presented in Tab. 2. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and breakdown potential (E_b) are reported.

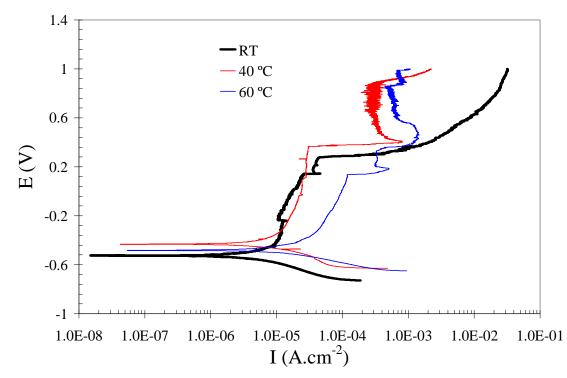


Figure 2. Potentiodynamic polarization curves of the API 5L X70 steel immersed for 7 days at different temperatures in the electrolyte solution described in section 2.2.

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Temperature	$E_{corr}(V)$	I _{corr}	$E_{b}(V)$	Passive	
		$(A.cm^{-2})$		range (V)	
RT	-0.53	2.18	0.27	0.80	
40 °C	-0.43	4.17	0.38	0.81	
60 °C	-0.51	11.7	0.11	0.62	

Table 2. Electrochemical parameters determined from the potentiodynamic polarization curves shown in Fig. 2.

The curves shown in Fig. 2 present a well-defined passive region independently of the testing temperature. The onset of pitting corrosion is evident from the sharp increase of the current density at the breakdown potentials (E_b). In spite of the similarities between the curves especially in respect to the presence of a passive region, remarkable differences can be observed depending on the testing temperature. The passive currents for the room temperature condition are slightly lower than at 40 °C up to the breakdown potential as well as the I_{corr} value, suggesting that the corrosion resistance of the API steel is higher at the lowest testing temperature. Nevertheless, the passive range is very similar for these conditions and the current densities associated with the specimens tested at 40 °C are also small, indicating that the corrosion properties of the API 5L X70 steel was little affected when the temperature was raised up to this level. This is in agreement with the EIS measurements as inferred from the Nyquist plots shown in Fig. 1.

For the tests performed at 60 °C, though, there was an evident reduction of the corrosion resistance. The onset of pitting corrosion occurred at a breakdown potential of only 0.11 V and the passive range was shortened to 0.62 V. Thus, it is possible to affirm that the API 5L X70 steel became more prone to localized corrosion attack when the temperature reached 60 °C. Furthermore the corrosion current density was almost three times higher at 60 °C when compared to that determined at 40 °C and more than five times higher than that obtained at the room temperature. This result points to an overall higher corrosion rate of the specimens tested at 60 °C.

3.3 Corrosion morphology

According to Van Boven et al. (2007) stress corrosion cracking of pipeline steels can be initiated in the bottom of a pit. The initial pitting mechanism is related to corrosion at metallurgical heterogeneities such as grain boundaries, non-metallic inclusions and interfaces between different phases. As observed in the potentiodynamic polarization curves shown in Fig. 3, the onset of pitting corrosion has been observed for the API 5L X70 steel independently of the testing temperature. Moreover, the resistance to pitting corrosion was found to decrease at 60 °C. Hence, the propensity to stress corrosion cracking should accompany this temperature dependence. In order to share more light on this subject, the corrosion morphology of the steels was evaluated using SEM. The micrograph shown in Fig. 3a corresponds to the surface of a specimen tested at room temperature after potentiodynamic polarization. Figure 3b shows the same region at a higher magnification. The specimens tested at higher temperatures presented similar corrosion morphology but with increasing number of pits, especially those tested at 60 °C. Shallow pits were observed. Van Boven et al. (2007) showed that cracks originate from shallow pits during stress corrosion cracking of the X65 pipeline steel in simulated soil solution. In this regard, the results obtained in the present work point toward a dangerous corrosion activity of the X70 pipeline steel at 60 °C. Even at room temperature the presence of shallow pits is also observed.

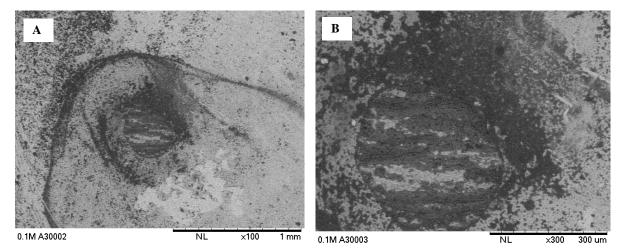


Figure 3. SEM micrograph showing the presence of one sharrow pit after potentiodynamic polarization of the API 5L X70 steel at room temperature. The micrograph on the right is referred to the same region on the left at a higher magnification.

4. CONCLUSIONS

The influence of the testing temperature on the corrosion behavior of the API 5L X70 pipeline steel in 0.05 M Na_2CO_3 , 0.1 M $NaHCO_3$ and 0.1 M NaCl solution has been evaluated. The results showed that the steel was prone to pitting corrosion even at room temperature. When the temperature was raised to 40 °C the corrosion properties were little affected. Nevertheless, for the tests performed at 60 °C there was a marked decrease of the corrosion resistance, in respect to either the overall corrosion rate expressed as the corrosion current density or the pitting corrosion resistance. In this context, based on the well-established relationship between the formation of pits and stress corrosion cracking of pipeline steels, the results point to a more dangerous situation for the initiation of stress corrosion cracking at 60 °C, even though pits have also been observed at lower temperatures

5. ACKNOWLEDGEMENTS

Usiminas is acknowledged for kindly providing the API 5L X70 steel plate used in this work.

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7. RESPONSIBILITY NOTICE

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