

MECSOL 2019 - Influence of Mechanical Cyclic Loads on the Corrosion Rate of Grade R4 Steel

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Mooring chains in Floating Production Storage and Offloading (FPSO) units are subjected to severe field conditions, combining fatigue loadings and corrosive marine environment, which result in early failure and safety issues. This study is focused on the effects of the cyclic loads on the corrosion behavior of martensitic steel under marine environment. Offshore Grade R4 steel, commonly employed in mooring chain production, was used in the study. Electrochemical Spectroscopy Impedance (EIS) measurements were carried out to evaluate the corrosion behavior of the material under cyclic load condition in artificial seawater (3.5 wt% NaCl) and stress-controlled $R = -1$ load ratio using a setup developed for the study. EIS tests were also performed in non-loaded samples for comparative purposes. The EIS reveals sensitive to monitor the surface status, showing an increase of modulus with time exposure and a decreasing due to the combined effect of time and damage for the corrosion-fatigue experiments.

Keywords: Corrosion-Fatigue, Grade R4 Steel, Corrosion Rate, EIS.

INTRODUCTION

Corrosion fatigue is considered to be one of the most important factors in determining the life of offshore structures. The fatigue properties of the offshore structural steels are strongly affected by the presence of seawater environment and they become susceptible to premature crack initiation and propagation. Steel chains next to the vessel are under severe field conditions, combining corrosive environment, high pretension and fatigue loads. In this region, known as the splash-zone, corrosion takes place more severely due to high levels of diluted oxygen in the seawater. In a particular case, four offshore mooring lines, designed to last a period that should exceed 20 years, have failed in less than eight months of service time (Melis *et al.*, 2005).

The synergistic nature of corrosion and fatigue is one of the main reasons for the offshore structures under corrosion-fatigue conditions present premature failure (Larrosa *et al.*, 2018). Studies have shown that the marine environment can reduce the fatigue life of the component in more than 95% when compared to the same load condition but in inert environment (Pérez-Mora *et al.*, 2014; Canut *et al.*, 2018). Regarding the corrosion behaviour of offshore steels, the influence of environmental variables (e.g., temperature, salinity, dissolved oxygen) has been systematically studied (Nevshupa *et al.*, 2018). However, the effects of cyclic mechanical load have been often neglected.

In this study, Electrochemical Impedance Spectroscopy (EIS) was used as a non-destructive technique to evaluate the effects of cyclic loading on the corrosion behaviour of the offshore Grade R4 steel using a combined electrochemical-mechanical approach.

METHODOLOGY

Cylindrical samples were machined from offshore Grade R4 martensitic steel round bars, with a gauge section diameter of 6.0 mm and a length of 12.0 mm. This steel meets the requirements imposed by the current Classification Societies. The surfaces were abraded with emery paper up to 1000 mesh and then degreased with alcohol and dried with air jet.

EIS tests were conducted in a three-electrode system configuration (Ag/AgCl reference electrode, platinum counter-electrode and the steel specimen as working-electrode), connected to an Interface 1000 potentiostat (Gamry Instruments, PA, USA) from 1×10^4 Hz to 1×10^{-2} Hz and 7 points per decade. A 3.5 wt% NaCl solution was prepared to simulate

seawater, using Millipore water and pure NaCl (from Sigma-Aldrich). The area used in the EIS simulations was the initial exposed surface.

The equivalent electrical circuit is shown in Fig 1. The electrochemical response is analyzed as the aid of an equivalent electrical circuit, considering the association of resistors and capacitors. The elements represent the physical phenomena of the metallic interface. The measured EIS data were fitted in the equivalent circuit (Figure 1) where R_e and R_p are the electrolyte and the polarization resistances, respectively, and the CPE is a Constant Phase Element. The CPE was used to simulate the non-ideal behaviour of the double layer capacitance formed on the interface between the sample and the electrolyte, having an electrical response as $Z(f)_{CPE} = 1/Q(j2\pi f)^\alpha$, where $j^2 = -1$, f is the frequency, the Q is related with the exposed area and when the exponent $\alpha \neq 1$ it has been attributed heterogeneities on the surface or to distributed time constants of charge-transfer process (Orazem *et al.*, 2008). The fitting was performed using the software ZView[®], version 2.7, from Scribner Associates, Inc.

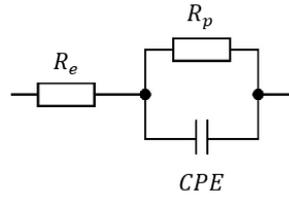


Figure 1. Equivalent electrical circuit used to model the EIS diagrams.

A linear polarization measurement was also performed in a different sample in order to obtain the Tafel slopes and the Stern-Geary “ B ” constant. The potential range was set to -0.1 V to 0.1 V (vs Open Circuit Potential) with a sweep rate of 10 mV/min. From the polarization resistance, the corrosion current density “ I_{corr} ” can be calculated by the Stern-Geary (1957) equation:

$$I_{corr} = \frac{B}{R_p} \quad (1)$$

The value of the Stern-Geary constant is related to the anodic and cathodic Tafel slopes (β_a and β_c) and can be determined under similar experimental conditions using a linear polarization test:

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \quad (2)$$

Considering the Faraday’s law and the material in this study, the corrosion rate “ CR ” can be calculated in terms of I_{corr} as:

$$CR \left(\frac{mm}{yr} \right) = 11.6 I_{corr} \quad (3)$$

Two load cases were analysed: non-loaded and corrosion-fatigue specimens, both immersed in artificial seawater. Corrosion-fatigue tests were performed under load-controlled regime, $R = -1$ ratio and sinusoidal waveform. The stress amplitude was set to 500 MPa, which is 55% of the yield stress. Mechanical loading frequency for the corrosion-fatigue condition was set to 1.0 Hz, which is higher than the typical offshore situation (ordinarily around 0.1 Hz to 0.2 Hz). The EIS measurements were taken at the beginning of the immersion (after one-hour exposure) and after 15 h, for both cases. The non-critical area was isolated with Parafilm[®] M film and beeswax, keeping just the gauge area exposed to the electrolyte. All corrosion-fatigue tests were performed at room temperature using a fatigue test machine (Instron model 8874). Figure 2 illustrates the experimental setup used to perform the corrosion-fatigue tests.



Figure 2. Experimental setup for corrosion-fatigue tests.

RESULTS AND DISCUSSION

The EIS results are shown in Fig. 3 as Nyquist plot.

As expected, the polarization resistances obtained from the EIS measurements for the non-loaded and loaded specimens before the load application were very similar, $2017 \pm 68 \Omega \text{cm}^2$. Starting the cyclic loading, the specimen under corrosion fatigue showed a decreasing corrosion resistance over time, while the non-loaded sample described an opposite trend. In Table 1, the adjusted parameters are depicted. After 15 h of immersion, the non-loaded sample exhibited a 24% increase in polarization resistance, while the specimen under corrosion fatigue exhibited a 33% reduction of polarization resistance. At the last measurement, the loaded specimen had been subjected nearly to 50,000 cycles, close to the final observed life (55,570 cycles). This reduction, in the first moment, can be explained by slip bands emergence due to the cyclic load, which can break the passive layer formed on the surface of the metal. After crack initiation, the crack tip is a region of stress concentration and localized plastic deformation, generating regions of low impedance and contributing to the reduction of the polarization resistance.

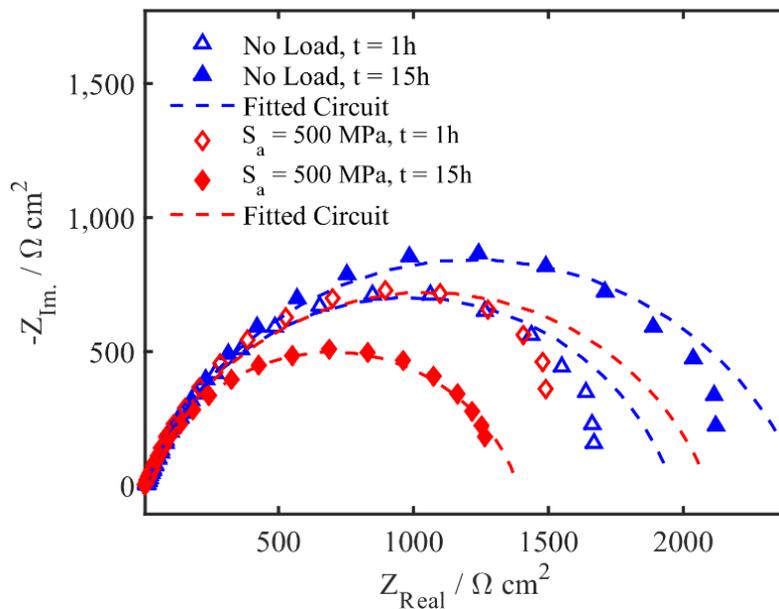


Figure 3. Nyquist plot for the EIS measurements and the fitting.

Table 1 - Parameters fitted from the equivalent electrical circuit.

	$R_e / \Omega cm^2$	$R_p / \Omega cm^2$	$Q / F cm^{-2}$	α
No load, $t = 1$ h	8.619	1950	0.00091336	0.79477
No Load, $t = 15$ h	8.485	2430	0.00079213	0.77283
$S_a = 500$ MPa, $t = 1$ h	6.464	2085	0.00069773	0.77090
$S_a = 500$ MPa, $t = 15$ h	5.496	1382	0.00104560	0.79569

From the linear polarization measurements carried out at the initial condition (1 h of exposure and no load applied) the value of the Stern-Geary constant is $B = 43$ mV. For the purpose of this study, " B " can be considered equal for both load conditions, therefore the evolution of corrosion current density will depend only on the polarization resistance, R_p . For the analysed cases, the I_{corr} of the loaded specimen after 15 h was more than 75% greater when compared to the non-loaded one for the same immersion time, leading to a corrosion rate of 0.67 mm/year against 0.38 mm/year for the non-loaded condition. This behaviour could lead to non-conservative predictions of the corrosion rate if the mechanical effects were not considered.

CONCLUSIONS

The analysis presented in this study revealed that the synergetic effect of marine environment and cyclic mechanic loads must be considered in order to obtain a more realistic corrosion rate prediction for Grade R4 steel under cyclic loading. For exposure of 15 h, the corrosion rate calculated for the sample under cyclic load was more than 75% greater when compared to the non-loaded one.

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