Efficiency Criterion of Corrosion Inhibitors of Carbon Steel in Seawater

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Abstract
A criterion of the efficiency evaluation of corrosion inhibitors of metallic samples in aqueous solutions was proposed for the first time. The criterion was derived based on calculating the limit of ratio value of the resistivity of carbon steel sample in inhibited seawater ($\rho_{\text{ins}}$) to the resistivity of the carbon steel sample in blank seawater ($\rho_s$). In other words, the criterion; \( \lim (\rho_{\text{ins}}/\rho_s) = 1 \) will determine the efficiency of the corrosion inhibitor in the seawater when $\rho_{\text{ins}}$ becomes equal (decreases) to $\rho_s$ as a function of time of the exposure of the sample to the inhibited seawater. This criterion is not only can be used to determine the efficiency of different corrosion inhibitors, but also, the criterion can be used to determine the efficiency of corrosion inhibitors with a wide range of concentrations in different aqueous solutions. In addition, the criterion can be applied under diverse test conditions with a predetermined period of inhibitor’s dosages.

Key words: Efficiency of corrosion inhibitors; Resistivity; Carbon steel; Seawater

INTRODUCTION
In the oil production, water and acidic gases, i.e., H$_2$S and CO$_2$, are co-produced with the oil. The acidic gases are known to associate with a variety of corrosion damage to the surface facilities leading to costly failures. Also, the acidic gases cause a reduction in the service life of equipment. One of the known method of protection against corrosion damage in oil production is the usage of corrosion inhibitors\[1]. Corrosion inhibitors are organic and inorganic materials that are usually added to a fluid source (liquids or gages) in small amounts on a frequent basis to reduce or to stop corrosion.

The evaluation of corrosion inhibitors of exposed metals has been studied by many investigators\[2-9]. Some studies of the corrosion inhibitors were dependent on electrochemical techniques like linear polarization, polarization resistance, Tafel plot, potential dynamic curve, and electrochemical impedance spectroscopy\[10]. In contrast, other studies were relied on only the weight loss method for evaluation of the corrosion inhibitors\[10].

In the present work, a criterion of the efficiency evaluation of corrosion inhibitors was developed. The criterion was plotted based on obtained resistivity data of the author’s previous works\[11-13]. The resistivity value of the corrosion inhibitor can be measured as the follows\[11-13]:

\[ \rho = \frac{RA}{U_{\text{total}}} \]  

Where,
\( \rho \) is the electrical resistivity of the formed oxide film, Ohm-cm;
\( R \) is the dc resistance of the formed oxide film, Ohm;
\( A \) is the exposed surface area of the sample to solution, 37.5 cm$^2$;
\( U_{\text{total}} \) is the total thickness of the formed oxide film, which can be obtained by holographic interferometry, a noncontact technique, μcm.

\( U_{\text{total}} \) can be determined as the following\[11-13]:

\[ U_{\text{total}} = \frac{N\lambda}{\sin \alpha + \sin \beta} \]  

Where,
\( N \) is the number of fringes;
\( \lambda \) is the wavelength of the laser light used in the experiment, for He–Ne laser light, \( \lambda = 0.6234 \mu m; \)

\( \alpha \) is the illumination angle, \( \alpha = 51.2^\circ; \)

\( \beta \) is the viewing angle, \( \beta = 90^\circ; \) both \( \alpha \) and \( \beta \) can be obtained from the setup of the experiment.

A detailed derivation of Equations (1) and (2) is given elsewhere in literature\(^{[11-13]}\). Equation (1) can be used to determine the resistivity of carbon steel samples in aqueous solution by the substitution of the value of alternating current impedance \(|Z|\) (Ohm) in the place of the value of R. This is valid when the \(|Z|\) value was measured by the technique of electrochemical impedance spectroscopy (EIS) at very low frequency, at room temperature\(^{[11-13]}\). In other words, Equation (1) can be rewritten to a modified version of the following form:

\[
\rho = |Z|A/U_{\text{total}} \tag{3}
\]

Therefore, the model of the efficiency evaluation of the corrosion inhibitors can be derived from Equation 3 as follows:

\[
\lim (\rho_{\text{ins}}/\rho_s) = 1 \tag{4}
\]

Where,

\( \rho_s \) is the resistivity of carbon steel sample in blank seawater, Ohm-cm

\( \rho_{\text{ins}} \) is the resistivity of carbon steel sample in inhibited seawater, Ohm-cm

Equation (4) states that when \( \rho_{\text{ins}} \) becomes equal (decreases) to \( \rho_s \) as a function of time of the exposure of the sample to the inhibited seawater, the sample is no longer protected by the corrosion inhibitor.

### Table 1
Calculated Parameters of Carbon Steel Samples in 5-20 ppm TROS C-70 in Inhibited Seawater

| RA-41 inhibitor concentration (ppm) | Ac impedance \(|Z|\) (Ohm) | Total displacement \((U_{\text{total}})\) (\(\mu\text{m}\)) | Resistivity by Ohm (pins) \((\text{Ohm-cm})\) | Ratio of \((\rho_{\text{ins}}/\rho_s)\) |
|-----------------------------------|---------------------------|-------------------------------------------|-----------------------------------|-----------------|
| 0.0                               | 3.6×10^7                  | 3.525×10^3                               | 1.0×10^5                          | 1.0             |
| 5                                 | 1.72×10^7                 | 3.5×10^3                                  | 1.85×10^7                         | 1.85×10^12      |
| 10                                | 2.4×10^7                  | 2.7×10^3                                  | 3.35×10^7                         | 3.35×10^12      |
| 20                                | 980.4                     | 2.2×10^3                                  | 1.7×10^3                          | 1.7×10^12       |

### 2. RESULTS AND DISCUSSION

It is obvious from Table 1 that the carbon steel sample in 10 ppm TROS C-7 inhibited seawater has the highest efficiency among the rest of the samples in the TROS C-7 inhibited seawater with respect to the carbon steel sample in blank seawater. The ratio of \((\rho_{\text{ins}}/\rho_s)\) of the carbon steel sample in 10 ppm TROS C-7 inhibited seawater is the highest \((\rho_{\text{ins}}/\rho_s = 3.35×10^{12})\) compared to the carbon steel sample in 5 ppm TROS C-7 \((\rho_{\text{ins}}/\rho_s = 1.855×10^{12})\) and 20 ppm TROS C-7 \((\rho_{\text{ins}}/\rho_s = 1.7×10^{12})\) inhibited seawater, respectively. Plots of the limit \((\rho_{\text{ins}}/\rho_s)\) versus Time of exposure (a predetermined time of a 12 months of inhibitor’s dosage) are illustrated in Figures 1, 2,3 for efficiency evaluation of the carbon steel samples in 5,10, 20 ppm TROS C-7 inhibited seawater solutions, respectively. Figures 1, 2, and 3 were plotted at time of exposure = 0, \((\rho_{\text{ins}}/\rho_s) = 1.85×10^{12}, 3.35×10^{12},\) and \(1.7×10^{12}\) for carbon steel sample in 5, 10, and 20 ppm TROS C-7 inhibited seawater, respectively. Furthermore, at time of exposure = 12 mons, Figures 1, 2, and 3 were plotted; \((\rho_{\text{ins}}/\rho_s) = 1, 1, \) and 1 for carbon steel sample in 5, 10, and 20 ppm TROS C-7 inhibited seawater, respectively.

In this investigation, Equation (4) was used for the first time to determine the efficiency of corrosion inhibitors of the carbon steel samples in blank seawater and in seawater with a concentration range of 5-20 ppm of TROS C-7 corrosion inhibitor, at room temperature. The \(pH\) of the blank seawater, seawater with 5 ppm TROS C-70, seawater with 10 ppm TROS C-70, and seawater with 20 ppm TROS C-7 is 8.24, 8.23, 8.23, and 8.22, respectively. The chemical composition of the carbon steel is 0.18–0.23%C, 0.3–0.6%Mn, and balanced Fe. The TROS C-70 corrosion inhibitor has been commonly used in the petroleum industries.

In addition, Equation (4) was used with the assumption that \(U_{\text{total}}\) is the total thickness of the formed oxide layer of carbon steel samples in inhibited seawater or \(U_{\text{total}}\) is the total thickness of the anodic dissolved layer of carbon steel samples in blank seawater. So, one can measure the total thickness of the formed oxide layer, \(U_{\text{total}}\), of carbon steel samples in 5-20 ppm TROS C-70 inhibited seawater solutions or the thickness of the anodic dissolved layer of carbon steel samples in blank seawater.

### 1. CALCULATION OF THE EFFICIENCY OF THE CORROSION INHIBITOR

From Equation (4), the ratios of \((\rho_{\text{ins}}/\rho_s)\) were calculated based on the obtained data of carbon steel samples in 5-20 ppm TROS C-70 inhibited seawater solutions\(^{[11]}\). The data of the values of the \((\rho_{\text{ins}}/\rho_s)\) are given in Table 1. The values of \(|Z|\), \((U_{\text{total}})\), \(\rho_s\), \(\rho_{\text{ins}}\) were taken from the literature elsewhere\(^{[11]}\).
Figures 1, 2, 3 show two regions. One region is above the line in the Figures, in which the corrosion inhibitor is efficient enough with respect to the proposed criterion of Equation (4). The other region is below the line in the Figures, in which the inhibitor is not efficient with respect to the proposed criterion of Equation (4). In this case, an addition of inhibitor’s dosage is essential. The efficiency of inhibitor can be actually determined by measuring $\rho_{\text{ins}}$, $\rho_s$, and then $\lim (\rho_{\text{ins}}/\rho_s)$ on a frequent basis during the predetermined of exposure time of the carbon steel sample in the inhibited seawater. Then, the obtained value of $\lim (\rho_{\text{ins}}/\rho_s)$ can be compared with a standard plot of $\lim (\rho_{\text{ins}}/\rho_s)$ like those in Figures 1, 2, 3 with a specific time of exposure. So, Figures 1, 2, 3 can be standard efficiency plots for different kinds of corrosion inhibitors.
CONCLUSION REMARKS

A criterion of the efficiency evaluation of corrosion inhibitors was developed for carbon steel sample in seawater. The criterion was derived based on the ratio value of the resistivity of carbon steel sample in inhibited seawater \( (\rho_{\text{ins}}) \) to the resistivity of the carbon steel sample in blank seawater \( (\rho_s) \) according to \( \lim(\rho_{\text{ins}}/\rho_s) = 1 \), when \( \rho_{\text{ins}} \) comes equal (decreases) to \( \rho_s \) as a function of time of the exposure of the sample in the inhibited seawater. The ratio of \( (\rho_{\text{ins}}/\rho_s) \) of the carbon steel sample in 10ppm TROS C-7 inhibited seawater was found the highest \( (\rho_{\text{ins}}/\rho_s = 3.35 \times 10^{12}) \) compared to the carbon steel sample in 5ppm TROS C-7 \( (\rho_{\text{ins}}/\rho_s = 1.855 \times 10^{12}) \) and 20 ppm TROS C-7 \( (\rho_{\text{ins}}/\rho_s = 1.7 \times 10^{12}) \) inhibited seawater, respectively. Plots of the \( \lim(\rho_{\text{ins}}/\rho_s) \) versus Time of exposure like those of Figures 1, 2, 3 can be standard efficiency plots for different kinds of corrosion inhibitors.

REFERENCES