Comparison of electrochemical techniques during the corrosion of X52 pipeline steel in the presence of sulfate reducing bacteria (SRB)

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This work compares three electrochemical techniques, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN), used in the study of corrosion of X52 steel samples in an environment containing a culture of sulfate reducing bacteria (SRB). The study emphasizes the different electrochemical information obtained when using these techniques in microbiologically influenced corrosion (MIC) studies.

1 Introduction

The use of different electrochemical techniques in the study of the phenomenon of corrosion provides us the necessary parameters to predict the useful life of a metallic structure in relatively short times. One of the types of corrosion that affect the underground pipelines is the corrosion induced by microorganisms (MIC). MIC accelerates corrosion due to the interaction between the microbial activity and the electrochemical corrosion processes [1]. Sulfate reducing bacteria (SRB) are the main microorganisms responsible for the MIC [2–5]. Two main theories try to explain the influence of microorganisms on the corrosion process. The first theory is based on the cathodic depolarisation mechanism proposed by Von Wolzogen Kuhr and Van der Vlught [4, 6–10]. The second theory, proposed by Iverson [11–13], considers the formation of a phosphorous soluble compound. The present work shows the results obtained by electrochemical techniques, during the corrosion of X52 steel in an environment containing a culture of SRB.

2 Experimental

2.1 Materials

A 1-litre glass cell with a three-electrode array was used. All metallic samples used as working electrodes in the experiments were made of API X52 steel [14]. Before each test, all samples were polished up to 600 grit SiC paper, cleaned and degreased with acetone. All electrochemical potentials reported in this work are referred to a saturated calomel electrode (SCE). A sintered graphite rod was used as auxiliary electrode.

2.2 Electrochemical techniques

All the electrochemical experiments were performed with a Solartron SI 1280B potentiostat. These electrochemical measurements were:

a) Corrosion potential (Ecorr) against time.

b) Potentiodynamic Linear Polarization Resistance (Rp). The potential range used was +0.015 V referred to Ecorr and a sweeping rate of 0.1667 mV s\(^{-1}\). In all corrosion rate (Vcorr) calculations a value of 0.026 V for the Stern-Geary constant was considered. Rp measurements were carried out at different exposure times.

c) Electrochemical Impedance Spectroscopy (EIS). A frequency range of 0.01 Hz to 10 KHz and amplitude of 10 mV were used. 5 points per decade of frequency were recorded. EIS data analyses were carried out in the Zview software version 2.1. EIS measurements were carried out at different exposure times.

d) Electrochemical Noise (EN). The sampling frequency used was 1 Hz. Each EN measurement consisted of 1040 data points. The data was analyzed with the ENAnalyse software [15]. EN measurements were carried out at different exposure times.

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10 days. After experimentation the exposed steel samples were prepared [16] for analysis in a scanning electron microscope (SEM).

2.3 Test environment

A pure culture of mesophilic SRB was used in this work. This SRB culture was isolated from a pipeline at the Geothermal Power Plant of “Los Azufres”, located in the Mexican State of Michoacan.

Liquid Postgate C medium [17] was used in all experiments as test environment. The chemical composition of Postgate C medium is shown in Table 1. Before each experiment the medium was purged with nitrogen gas (N₂) in order to remove dissolved oxygen (O₂). After O₂ removal the medium was inoculated with a SRB culture. All the experiments were performed in the glass cell, placed inside an N₂ atmosphere anaerobic chamber, at 25°C and at atmospheric pressure (Mexico City).

The pH experimental results were taken at the beginning and final (10 days) of the experimentation. The pH is 7.5 at the beginning and 6.2 at the final of the experimentation. A little change of the pH was observed, this behavior can be attributed to the secondary metabolite produced by SRB, the hydrogen sulfide (H₂S). The H₂S can dissolve in aqueous solutions turning them in acid corrosive solution.

3 Results and discussion

3.1 Electrochemical Techniques

Corrosion potential (E\text{corr})

Fig. 1 shows the variation of the E\text{corr} with time of the X52 steel sample in the Postgate C medium in presence and absence of SRB. It can be seen that the corrosion process that takes place on the surface of the metal is affected by the presence of SRB.

3.1.2 Linear polarization resistance (R\text{p})

Fig. 2 shows the variation of corrosion rate (V\text{corr}) with time of the X52 steel sample immersed in Postgate C medium, in presence and absence of SRB.

For the Postgate C without SRB condition (M \text{Rp}) it is possible to observe that, as the exposure time increases the estimated V\text{corr} decreases from a value of 0.2 mm y\(^{-1}\) to a value of 0.03 mm y\(^{-1}\) approximately. This behavior can be attributed to the fact that at the beginning of the experimentation, the surface of the steel was clean and consequently active. After a period of time, a layer of corrosion products forms on the surface of the working electrode, isolating the metal from the environment and decreasing V\text{corr}. On the other hand, the Postgate C environment inoculated with SRB (M + MO \text{Rp}), shows a different behavior. During the first four days of experimentation, the calculated V\text{corr} was in the order of 0.03 mm y\(^{-1}\). After this V\text{corr} increased up to a value of 0.07 mm y\(^{-1}\) approximately. This behavior can be attributed to the formation of a biofilm on the surface of the working electrode that isolates the steel from the environment and maintains a low value of V\text{corr}. After day 4 the biofilm formed breaks and the measured V\text{corr} increases.

3.1.3 Impedance of X52 steel in Postgate C environment

Fig. 3 and 4 show the Nyquist and Bode representations of the impedance measurements, taken on a X52 steel sample.
immersed in Postgate C environment. These figures show the impedance data obtained at three selected exposure times. Nyquist representation of the impedance in Fig. 3 shows three semicircles. It is possible to observe in this Figure that the diameter of the semicircles increases with time. This trend correlates with the behavior of the measured values of $V_{corr}$ shown in Fig. 2, and can be attributed to formation of a layer of corrosion products on the surface of the working electrode. Fig. 4a and 4b are Bode representations of the data shown in Fig. 3. Fig. 4a and 4b show that the measured EIS data could be analyzed by means of a circuit containing a single time constant element (capacitor).

3.1.4 Impedance of X52 steel in Postgate C environment inoculated with BSR

Fig. 5a is the Nyquist representation of the impedance measured on a X52 sample immersed in Postgate environment inoculated with the SRB culture, at day 1 and 2 of exposure. Fig. 5b is the Nyquist representation of the impedance data measured at days 4 and 10. As it can be seen in these figures, the semicircle detected at the beginning of the experimentation, disappears as the time of exposure increases. Nyquist plots at day 4 and 10 show a straight line at low frequencies which can be related to a diffusion process represented by a Warburg impedance. This feature could be associated to the
diffusion through the biofilm of electroactive species, from the bulk of the solution to the surface of the metal. Fig. 6a and 6b are Bode representations of the modulus of the impedance and the phase angle data for days 1 and 2. These Figures demonstrate the existence of two time constants in the electrochemical process. These two time constants can be the consequence of a charge transfer process and a diffusion process, both occurring at the same time during the total corrosion process.

### 3.1.5 Equivalent circuits analysis

Fig. 7a and 7b show the two electrical equivalent circuits used in this work for the analysis of EIS data. \( R_s \) is the resistance of the solution, \( R_{ct} \) is the charge transfer resistance, \( C_{dl} \) is the capacitance of the electrochemical double layer, \( R_{film} \) is the resistance of the film formed on the surface of the steel and \( C_{film} \) is the capacitance of this same film. In Fig. 7a a short Warburg element was considered (\( W_s \)) in the circuit. Zview software was used in all the numerical analyses.

Tab. 2 shows the best fitting parameters obtained in the numerical analyses. In this table is possible to observe that, in the Postgate C environment without SRB, as the exposure time increases the estimated \( R_{ct} \) also increases, which means that the \( V_{corr} \) decreases as a function of immersion time. The same behavior can be observed in the first two days for the Postgate C inoculated with SRB, but in the day 4 and 10, the corrosion of the X52 steel seems to be dominated by a diffusion process. This behavior could be attributed to the diffusion of electroactive species through the biofilm formed on the surface of the working electrode.

Fig. 8 is an example of the good correlation between the calculated data and the experimental data. It is necessary to mention that in the analyses of EIS data obtained in the Postgate C environment inoculated with SRB, at days 4 and 10, a Warburg element was considered. This was done in order to consider a diffusion process affecting the total corrosion process.

### 3.1.6 Electrochemical Noise (EN)

In order to analyze the measured electrochemical noise data, noise resistance (\( R_n \)) was calculated at selected periods of exposure time. \( R_n \) was estimated from the potential and current time records, as the ratio of the standard deviation of the measured potential to the standard deviation of the measured cur-
rent times the total exposed area of one sample [15, 18–20]. Then, $V_{corr}$ was calculated dividing the Stern–Geary constant (B) by $R_n$. Fig. 2 compares the values of $V_{corr}$ estimated by the EN technique to the values of $V_{corr}$ estimated by the LPR technique, a very good correlation can be observed.

A second approach to EN data analysis was the calculation of the noise Impedance spectra ($Z_n$). $Z_n$ was calculated dividing, at each analysed frequency, the power spectral density (PSD) of the potential by the PSD of the current. PSD was obtained using the Maximum Entropy Method (MEM) [15]. Fig. 9 compares, in a Bode plot, the impedance data obtained by the EIS technique and the equivalent $Z_n$ results obtained in the EN analysis. The information in this figure corresponds to day 1 of exposure in Postgate C environment, inoculated with SRB. Good correlation of the information at low frequencies can be observed.

### Table 2. Parameters obtained in the equivalent circuit analyses

<table>
<thead>
<tr>
<th>EIS data</th>
<th>$R_s$ ($\cdot \text{cm}^2$)</th>
<th>$R_{ct}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{dl}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
<th>$R_{film}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{film}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
</tr>
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<tbody>
<tr>
<td>Postgate C environment inoculated with SRB, days 1 and 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>20.09</td>
<td>5615</td>
<td>429.68</td>
<td>298.6</td>
<td>91.7</td>
</tr>
<tr>
<td>Day 2</td>
<td>21.55</td>
<td>9468</td>
<td>2621.5</td>
<td>125.1</td>
<td>592.1</td>
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</table>

Postgate C environment inoculated with SRB, days 4 and 10

<table>
<thead>
<tr>
<th>EIS data</th>
<th>$R_s$ ($\cdot \text{cm}^2$)</th>
<th>$R_{ct}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{dl}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
<th>$R_{film}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{film}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
<th>Warburg Resistance ($\cdot \text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 4</td>
<td>23.3</td>
<td>187.3</td>
<td>819.67</td>
<td>45.29</td>
<td>579.08</td>
<td>5632</td>
</tr>
<tr>
<td>Day 10</td>
<td>22.46</td>
<td>194.3</td>
<td>876.35</td>
<td>69.75</td>
<td>1039.2</td>
<td>1391</td>
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</tbody>
</table>

Postgate C environment

<table>
<thead>
<tr>
<th>EIS data</th>
<th>$R_s$ ($\cdot \text{cm}^2$)</th>
<th>$R_{ct}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{dl}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
<th>$R_{film}$ ($\cdot \text{cm}^2$)</th>
<th>$C_{film}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>15.48</td>
<td>608.6</td>
<td>456.1</td>
<td>429.9</td>
<td>174.87</td>
</tr>
<tr>
<td>Day 4</td>
<td>18.33</td>
<td>6730</td>
<td>883.12</td>
<td>6510</td>
<td>451.53</td>
</tr>
<tr>
<td>Day 10</td>
<td>17.95</td>
<td>11100</td>
<td>684.4</td>
<td>8970</td>
<td>416.67</td>
</tr>
</tbody>
</table>

Fig. 8. Example of EIS data fitting (Nyquist and Bode) using the equivalent circuit in Fig. 7a. Dots = measured data, continuous line = fitting results.
3.2 Scanning electron microscope (SEM)

Fig. 10 shows that the SRB used in this experiment do not have locomotion apparatus, their morphology is curved rod and have a length of 4 \( \mu \text{m} \) approximately. These are general characteristics of SRB [21]. Fig. 11 is a microphotograph of the biofilm formed on the surface of the steel, SRB can be observed suspended in the biofilm.

4 Conclusions

1. The highest corrosion rates \( V_{\text{corr}} \) were recorded in the Postage C environment and the decrement of the measured \( V_{\text{corr}} \) is associated to the formation of a film of corrosion products on the metal surface.
2. When SRB is present in the Postage C environment, the formation of a compact biofilm on the surface of the metal originates clear differences on the recorded electrochemical behavior. These differences can be attributed to the influence of the microbial activity on the corrosion processes.
3. It is demonstrated that data obtained with the electrochemical noise (EN) technique has a good correlation to the data obtained by EIS and LPR techniques.
4. It was demonstrated the usefulness of using three electrochemical techniques in the study of the electrochemical processes taking place during the corrosion of X52 steel, in an environment containing SRB. The comparison of the results, obtained from the same corroding system by three different electrochemical techniques, provides a useful tool for the judgement of the validity of the measured data. It also helps in the full understanding of the charge transfer processes taking place on the surface of the metal. These two advantages are not easily addressed by a single electrochemical technique.
5. EIS data analysis shows that the corrosion phenomenon taking place on the surface of the steel immersed in Postgate C environment inoculated with SRB, is affected by the formation of a biofilm that affects the diffusion of electroactive species form the bulk of the environment towards the metal surface.
6. A MIC phenomenon can be regarded mainly as a pitting corrosion process. However, the electrochemical data obtained in the LPR, EIS and EN tests, do not give clear indication of localized attack. This observation can be related to the fact that the corrosion process taking place on the surface of the steel is a combination of localized and uniform corrosion.

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6 References


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