1. Introduction

Corrosion of steel in soil is a complex phenomenon, with a multitude of variables involved. Some variables which affect the corrosion rate of steel in soil are water, degree of aeration, pH, redox potential, resistivity, soluble ionic species, and microbiological activity. Soil is a heterogeneous system of porous material, with the space between particles filled with water or gases [1].

Concerning the environmental aspect, corrosion of steel structures in soil is a relevant problem due to soil contamination caused by failure of pipelines and other structures.

It is well known that the oxidation of the steel is slow when it is buried in aerated soils with a neutral pH and high resistivity, i.e., sand and gravel. Meanwhile, in poorly aerated soils with an acid pH and low resistivity, the oxidation is rapid [2,3].

One of the simplest soil classifications is based on a single parameter, soil resistivity. Sandy soils are high on the resistivity scale and therefore are considered to be the least corrosive. Clay soils, especially those contaminated with saline water, are on the opposite end of the spectrum (<1,000 Ω.cm). Soil resistivity parameters, very widely used in practice, are generally considered to be the dominant variable in the absence of microbial activity [4].

The soil sample studied is a clay soil generated from the itabirite mineral formation. Itabirite, also known as banded-quartz hematite and hematite schist, is a laminat-
ed, metamorphosed oxide-facies iron formation in which the original chert or jasper bands have been recrystallized into grains of quartz and the iron is present as thin layers of hematite and magnetite (iron content is between 50% and 55%). It is composed chemically of silica and iron, with a banded structure of silicates (typically quartz) and iron oxides as hematite and magnetite.

In literature, different experimental approaches have been suggested to study the corrosion process in soils. On one hand, weight-loss measurements with buried coupons immersed at different depths and humidity conditions have been used[24–27]. On the other hand, aqueous solutions and electrochemical techniques have been used to establish its effects[28].

The corrosion resistance of steel in soil environment was studied using the Tafel extrapolation analysis and electrochemical impedance spectroscopy. The electrolytes used were an aqueous extract of soil and a synthetic solution to simulate the soil environment.

2. Methods

The electrolytes used were an aqueous extract of soil and a near-neutral pH environment (synthetic solution), whose chemical composition is given in Table 1[28–30].

The synthetic solution was prepared with analytical grade chemicals and deionised water. The pH was adjusted to 7.7 by adding H_2SO_4, 0.2 N. The pH adjustment was realized in order to maintain the two electrolytes at pH 7.7.

The aqueous extract of the soil was prepared according to the following procedure: a sample of 500 g of wet soil was dried at room temperature for 48 hours, and the residual moisture was measured. A sample of 10 g of soil was weighed and dried in an oven for two hours at 105 °C. After cooling in air, the sample was weighed. The procedure was repeated until constant mass. The moisture content was obtained by the difference between the initial and final mass. The sample was ground, and submitted to screening with sieves of 2.5 mm. Pieces of leaves, roots and branches were removed. A solution of 200 g of dry soil and 1,000 mL of water were prepared in a beaker and agitated after each interval of 30 minutes for 8 hours using a glass stick.

The beaker was coated with a polymeric film, and the mixture remained at rest for 48 hours. After decantation of the soil, the liquid phase (aqueous extract) was obtained.

Carbon and sulphur contents of the steel were analyzed using the combustion technique with detection by infrared, with the LECO 444 LS equipment. Molybdenum, nickel, chromium, aluminum, and vanadium concentrations were evaluated using inductively coupled plasma optical emission spectrometry, ICP-OES, Spectroflame Modula of the Spectra. Manganese, silicon, phosphorus, and niobium were analyzed using the SRS 3000 Sequential X-Ray Spectrometer, Siemens.

The electrochemical tests were performed using Autolab PG 128 N potentiostat, General Purpose Electrochemical System software (GPES), and Frequency Response Analyzer (FRA software) for the electrochemical impedance spectroscopy analysis.

The open circuit potential was measured for 2 hours until stabilization.

The electrochemical impedance spectroscopy analysis, the potential amplitude was 10 mV(Ag/AgCl), and the frequency range was 100 kHz–1 mHz.

The Tafel analysis was performed with a polarization of ±250 mV(Ag/AgCl) in relation to the corrosion potential at a scan rate of 0.167 mV/s. The electrochemical tests were done in triplicate.

The semi-quantitative chemical analysis of the soil was performed using the Sequential PHILIPS (Panalytical) X-rays fluorescence spectrometer, PW-2400 model.

The conductivity of electrolytes was measured using the HACH Sension 156 equipment.

The steel samples, after Tafel analysis, were analyzed using the scanning electron microscopy, EVO 50 Zeiss equipment, 20 kV of acceleration tension, coupled with the energy dispersive spectrometer, INCA 350 model, and the wave dispersion spectrometer (WDS), model INCA 500i, Oxford Instruments.

3. Results

The chemical composition of steel is shown in Table 2.

The conductivity of the synthetic solution was 1.025 ± 0.6 μS/cm, higher than the conductivity of the aqueous extract of the soil (188 ± 1.7 μS/cm). The resistivity of the aqueous extract of soil is 5.32 μΩ.cm. The pH of both electrolytes was between 7.5 and 8.0.

The semi-quantitative chemical analysis of the soil, obtained using X-ray fluorescence technique (XRF), is shown in Table 3. The chemical composition of synthetic solution is also shown in Table 3.

The extract of soil also contains traces of Sr, P, Ni, Mn, Cr, and Zr. The presence of chloride in the synthetic solution was not identified.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (g/L)</th>
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<tbody>
<tr>
<td>NaHCO₃</td>
<td>0.483</td>
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<tr>
<td>KCl</td>
<td>0.122</td>
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<tr>
<td>CaCl₂·2H₂O</td>
<td>0.181</td>
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<tr>
<td>MgSO₄·7H₂O</td>
<td>0.131</td>
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Table 2

<table>
<thead>
<tr>
<th>Chemical composition (%m/m)</th>
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<tbody>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>API SL X52</td>
</tr>
<tr>
<td>0.26</td>
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</tbody>
</table>
The electrochemical parameters obtained using Tafel analysis and electrochemical impedance spectroscopy are shown in Table 4.

The open circuit potential in function of time of API steel in synthetic solution and in aqueous extract of soil is shown in Fig. 1.

Tafel curves of API steel in synthetic solution and in aqueous extract of soil are shown in Figs. 2 and 3, respectively.

Figs. 4 and 5 show Nyquist and Bode diagrams of API steel in synthetic solution.

The surface of API X52 carbon steel after Tafel analysis in synthetic solution is shown in Fig. 6 and EDS analysis of the API steel surface is shown in Fig. 7.

Region 1 is enriched in iron and oxygen, and region 2 showed a higher content of iron and the presence of calcium, potassium, chlorine, magnesium, carbon, and sodium (Fig. 7).

Figs. 8 and 9 show SEM micrograph and EDS analysis of API steel surface after Tafel analysis in the aqueous extract of soil.

The Nyquist diagram of the API X52 steel in aqueous extract of soil is shown in Fig. 10 and Bode diagram in Fig. 11.

4. Discussions

The higher corrosion resistance of API steel in aqueous extract of the soil was due to the lower conductivity of this electrolyte, the absence of aggressive ions such as chloride and the presence of iron ions, which inhibits the oxidation of steel.

According to the electrochemical parameters obtained, the synthetic solution was more aggressive than the soil extract. The values of corrosion potential and polarization resistance were higher for the API steel in an aqueous extract of soil than in the synthetic solution.

Tafel extrapolation shows that the corrosion current density of the API steel in a synthetic solution was an order of magnitude higher than in the soil solution. The corrosion
Fig. 4  Nyquist diagram of API steel in synthetic solution

Fig. 5  Bode diagram of API steel in synthetic solution

Fig. 6  SEM micrograph of surface of API SL X52 steel after Tafel analysis in synthetic solution

Fig. 7  EDS analysis of API SL X52 steel surface after Tafel analysis in synthetic solution (region 2)
Fig. 8  SEM micrograph of surface of API SL X52 steel after Tafel analysis in the aqueous extract of soil

Fig. 9  EDS analysis of surface of API SL X52 steel after Tafel analysis in the aqueous extract of soil

Fig. 10  Nyquist diagram of API SL X52 steel in aqueous extract of soil

Fig. 11  Bode diagram of API steel in aqueous extract of soil
rate of steel in both media was calculated using Faraday's law. Concentration polarization occurred as a secondary effect at the tail end of the Tafel region as shown in Fig. 2 for the API steel in synthetic solution. On the anodic side of the curve, increased metal dissolution at large anodic over voltages may lead to the accumulation of dissolved cations near the electrode surface. However, the cathodic curve for oxygen reduction (Figs. 2 and 3) flattens out. For electrode potentials more negative than ~800 mV vs. Ag/AgCl, the current density essentially becomes independent of the electrode potential as shown in Figs. 2 and 3. This is a typical polarization curve under concentration control and is a characteristic curve for the diffusion-limited reduction of oxygen.

The anodic and cathodic reactions of the corrosion of API steel in aerated neutral electrolytes are:

$$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e^-$$
$$2\text{H}_2\text{O} + \text{O}_2 + 4e^- \leftrightarrow 4\text{OH}^-$$

The equivalent circuit for API steel in synthetic solution and in aqueous extract of soil consists of an electrolyte resistance in series with a constant phase element in parallel with a charge transfer resistance in series with a constant phase element in parallel with a polarization resistance. The formation of two capacitive arcs is supported by the presence of two maxima in the Bode diagram of the phase angle versus frequency and two inflections in the Bode plot of impedance modulus versus frequency. The presence of a corrosion product layer on the steel surface after Tafel analysis in both electrolytes also corroborates the appearance of two capacitive arcs.

The surface of API SL X52 steel after Tafel analysis in the synthetic solution shows localized corrosion with pits containing chlorides (Figs. 6 and 7). The anodic reaction generates iron cations that attract chloride ions. Literature reports the occurrence of localized corrosion of API steel in sulphate solutions with additions of humus substances of a surface soil, and in aqueous extracts of several soils[8]. This corrosion of API steel occurs with pits associated to complex inclusions containing sulphides[8,11]. API steel contains 1.28% m/m of manganese, and the occurrence of manganese sulphide inclusions is possible. Both media contained sulphur.

Cosmes López et al. also identified a localized corrosion of API X52 carbon steel immersed in an aqueous solution simulating a clay soil[15]. They observed that molecular oxygen, chloride, and sulphate ions induce the nucleation and growth of the pitting damage in a corrosion product layer consisting of magnetite, maghemite, lepidocrocite, and goethite[11]. According to literature[2], a corrosion product layer of iron oxide/hydroxides was identified on the surface of steel as shown in Fig. 6.

The surface of API X52 steel after Tafel analysis in the aqueous extract of soil, a medium without chloride ions, shows generalized corrosion. The corrosion product of iron oxide/hydroxides shows morphology with circular nodules.

5. Conclusions

According to the electrochemical parameters obtained, the synthetic solution was more aggressive than the soil extract. The values of corrosion potential and polarization resistance were higher for the API steel in an aqueous extract of soil than in the synthetic solution. The corrosion current density of the API steel in a synthetic solution was an order of magnitude higher than in the soil solution.

The surface of API SL X52 steel after Tafel analysis in both electrolytes showed a corrosion product layer, which presents a high content of iron and oxygen. The corrosion product of iron oxide/hydroxides formed on the surface of API steel after Tafel analysis in aqueous extract of soil shows morphology with circular nodules. A localized corrosion with pits containing chlorides was observed on the API surface after Tafel analysis in the synthetic solution.

The Nyquist diagram of API steel in synthetic solution and in aqueous extract of soil showed two capacitive arcs, with two time constants.

Acknowledgments

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References