Full Paper

Application of Electrochemical Impedance Spectroscopy as An Alternative Method to Evaluate the Efficiency of Cathodic Protection in Simulated Soil Solution

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Abstract - Buried pipeline steels are exposed to external corrosion due to the aggressive effect of the soil environment. Despite the double protection system consisting of a coating and cathodic protection, the risk of failure is present and can lead to a reduction in the structural integrity of the pipes. Considering the complexity and variability of different soils, a poor estimate of protection conditions can result in either overprotection or underprotection. The current investigation was conducted using a variety of cathodic potentials on X52 carbon steel. The samples were covered by a layer of natural clay and soaked with a simulated soil solution. Chronoamperometry measurements and electrochemical impedance spectroscopy (EIS) technique were used. The analysis of the impedance diagrams revealed significant variations in form and characteristics when the steel was exposed to different cathodic potential degrees. It was also noticed that the charge transfer resistance decreased gradually at lower applied cathodic potentials. On the other hand, it was observed that the passive layer protectiveness could be evaluated by the EIS method. In this study, it was clearly shown that the EIS technique can be used as a method to monitor and control the performance of cathodic protection.

1. INTRODUCTION

Cathodic protection (CP) systems and organic coating are both used to protect underground carbon steel pipes from external corrosion. According to the European Standard [1] cathodic protection reduces the corrosion rate caused by soil below 10 μm/yr, with a minimum potential of -850 mV (CuCuSO$_4$). However, the cathodic protection can be insufficient or excessive, depending on the local soil characteristics.

Several parameters, such as the degree of aeration, pH, soil moisture, ionic species, electrical resistivity, or microbiological activity, can affect the corrosion phenomena in soil. As a result of these physical and chemical variabilities, the corrosion phenomenon in the soil is still unclear. Many investigations focusing on a limited number of predominant factors that affect corrosion in soil have been proposed. While some investigators have evaluated the pipe steels' behavior in soil environments using solutions simulating the soil [2] which gives the possibility to study each parameter separately, others have taken a different approach by focusing on studying the natural soils considering all the characteristics belonging to the environment [3-9].

The application criteria of CP and the evaluation of its effectiveness in the soil environment have been the subject of several studies and discussions showing the limits of these criteria. Barlo et al. [10] found that the critical values of cathodic protection could vary depending on the environment affecting the soil. Gummow [11] in his critical examination of the NACE standards RP-01-69 confirmed that this standard must be revised given that quite a few criteria conflict with other standards. Zdunek et al. [12] evaluated the cathodic polarization for mild steel in soil at different temperatures. The study concluded that more polarization was required to protect the metal at temperatures higher than 30 °C. Schwerdtfeger [13] carried out tests on about 4500 samples to study the relationship between soil resistivity and cathodic protection. It was concluded that the corrosion current densities can be adjusted to approximate current densities necessary for cathodic protection.

An alternative method based on the application of the EIS measurement on cathodically protected steel in concrete was proposed by Martinez et al. [14] to verify the quality of cathodic protection. The results showed that the interpretation of Impedance Spectra can be of significant value in estimating the effectiveness of protection systems.

Barchiche et al. [15] have shown that during the operation of cathodic protection, the surface of the metal was covered progressively by a calcareous deposit, as follows:

Firstly, hydroxyl ions were generated on the metal surface, as described below:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow 4OH^- + H_2 \tag{2}$$

The formation of hydroxyl ions raised the pH near the metal surface, which caused the formation of insoluble salt composed of $CaCO_3$ and $Mg(OH)_2$. The following reactions describe these processes:

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \tag{3}$$
$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3 \tag{4}$$
$$Mg^{+2} + 2OH^- \rightarrow Mg\,(OH)_2 \tag{5}$$

The calcareous deposit contributes to enhancing the efficiency of cathodic protection by protecting against corrosion.

In this work, different levels of cathodic polarization corresponding respectively to protective and overprotective potentials have been applied on a X52 carbon steel in a solution simulating a soil with a layer of clay. Both Chronoamperometry and EIS methods have been used to monitor the evolution of the electric current density when the cathodic polarization either corresponds to an optimal protective potential or when it is excessive. The EIS method was then used to assess the modification of the surface of the metal at the end of each cathodic polarization test.

The aim of our investigation was to use the EIS technique as a tool to evaluate the efficacy of cathodic protection in a soil environment and to provide information on the protective layer which appears and covers the steel surface.

2. EXPERIMENTAL SECTION

2.1. Material and specimen preparation

The carbon steel X52 was used as the working electrode, with a chemical composition (in wt. %) of 0.24 C, 1.4 Mn, 0.45 Si, 0.025 P, 0.015 S, 0.10 V, 0.05 Nb, 0.04 Ti, and Fe balance. The samples used in the electrochemical experiments were machined to a size of $10 \times 10 \times 9$ mm, and then sealed with epoxy. The exposed area was 90 mm^2. Before depositing the clay layer, the exposed surface of the metal was polished with silicon carbide paper (120, 400, and 600). The samples were then cleaned with deionized water and carefully dried.

2.2. Soil and simulated soil solution

The soil sample used in this study was argillite clay soil collected in the western part of Oran (Mediterranean city situated in the northeast part of Algeria). The size of the particle used was less than 50 μm. The powder was compacted on the surface of the electrode in order to obtain a 5 mm layer thickness. For electrochemical measurements, a synthetic electrolytic solution NS4 was used as a soil-simulating solution, where the solution pH is ranged between

8 and 8.5. The chemical composition is described as follows: 0.122 KCL, 0.483 $NaHCO_3$, 0.181 $CaCl_2.2H_2O$, and 0.131 $MgSO_4.7H_2O$ [2].

2.3. Electrochemical measurements

All experiments were conducted in a cell at a constant temperature of 25°C (Fi. 1). A potentiostat Tacussel-Radiometer PGZ 301 was used to conduct the electrochemical tests. Cathodic polarization tests and electrochemical impedance spectroscopy (EIS) were performed on a three-electrode system. The working electrode (WE) was a carbon steel specimen, the counter electrode (CE) was a platinum plate, and the saturated calomel electrode (SCE) was the reference electrode (RE). The electrochemical cell used had a 150 mL total volume. According to the standard En 12954: 2001 the protection potential of steel in anaerobic soil conditions is approximately -950 mV, for more negative values the metal becomes overprotected. Referring to these conditions different protection potentials to reproduce situations where the steel is protected and others where the steel is over-protected were performed, using the potentiostatic technique. For this, different cathodic potentials were used to evaluate the x52 carbon steel behavior. The applied potentials were respectively -950, -1100, and -1200 mV [SCE], with a scan rate of 1mV/s. After each cathodic potential, EIS was measured by applying a sinusoidal signal of 10 mV voltage within a frequency range of 10^{-2} to 10^4 Hz.

2.4. Soil conditions for corrosion testing

First, a 5 mm thick layer of ground clay was manually compacted onto the electrode surface. Due to the specificity of the clay and the compacting operation, the electrodes used were not identical. The active surface of the carbon steel specimen, which was covered with a layer of clay, was set in an upward horizontal position (Figure 1). The simulated soil solution was added slowly in order to avoid removing the clay' layer from the steel electrode. During the experiments, the electrolyte was not desecrated as the clay layer prevented the transport of oxygen to the surface of the metal [16].
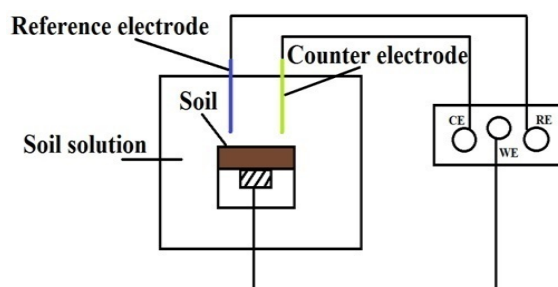

Figure 1. Schematic representation of the experimental setup used for the electrochemical study of a carbon steel electrode covered by a thick clay layer

3. RESULTS AND DISCUSSION

3.1. Potentiostatic polarization

The potentiostatic polarization of the XC 52 carbon steel at three different applied potentials (-950 mV[SCE], -1100 mV[SCE], -1200mV[SCE]) respectively is presented in Figure 2 where the cathodic current density is plotted in positive values. A linear decrease of the current density was observed for all three cathodic potentials. At -950 mV[SCE] applied potential, the current density decreased gradually and a stabilization was observed after 24 hours. It was observed that the current density was stabilized after 60 hours and reached almost null values afterward. These observations suggest the formation of a calcareous deposit on the samples.
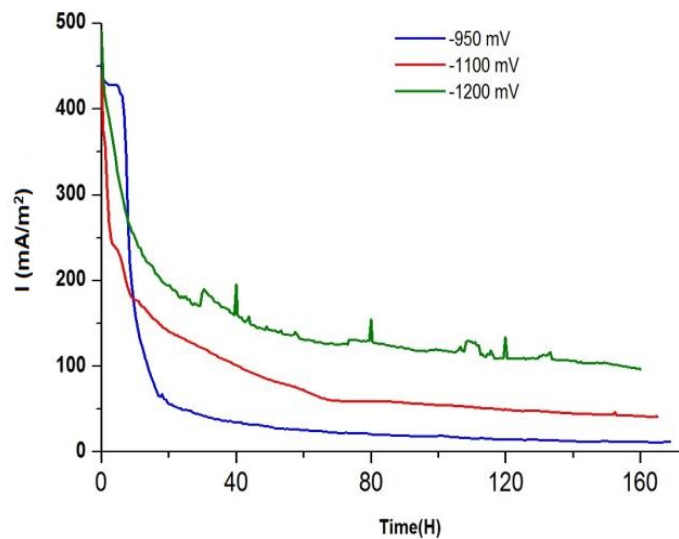

Figure 2. Chronoamperometric curves obtained by application of three cathodic potentials (-950 mV, -1100 mV, -1200 mV) in a simulated soil solution

At -1100 mV [SCE] applied potential, the current density decreased again and the stability of the current began after 68 hours of cathodic polarization. However, the current did not tend toward zero as observed in the previous test. This could suggest that a significant part of the surface was not covered.

For the final experiment under cathodic polarization of -1200 mV[SCE] applied potential, some fluctuations including spikes of the current density were observed. Hydrogen evolution greatly contributes to inducing cracks in the deposits and detachment of small fragments which prevents total covering of the surface. As a consequence, the current density tends to increase. Barchiche et al. [15] showed that the presence of Mg^{+2} can inhibit calcite and aragonite deposition and promote the development of brucite. This later compound represents a porous layer and is formed at a more cathodic potential.

3.2. EIS results

Figure 3 shows the Nyquist results of the XC52 carbon steel under the soil layer in a simulated soil solution obtained after potentiostatic tests at various cathodic polarization levels. Firstly, it was observed that the EIS spectra showed different behaviors at each cathodic potential level. The Nyquist plot for an electrode polarized at -950 mV$_{[SCE]}$ showed a large and incomplete semi-circle, as compared to the -1100 mV $_{[SCE]}$ and -1200 mV$_{[SCE]}$ plots. In most cases, the large size of the semi-circle in the measured EIS plot is related to the high charge-transfer resistance, which leads to the formation of a barrier between the sample and the environment. This is confirmed by the polarization results and emphasizes the role of the formation of calcareous deposits in enhancing corrosion resistance.
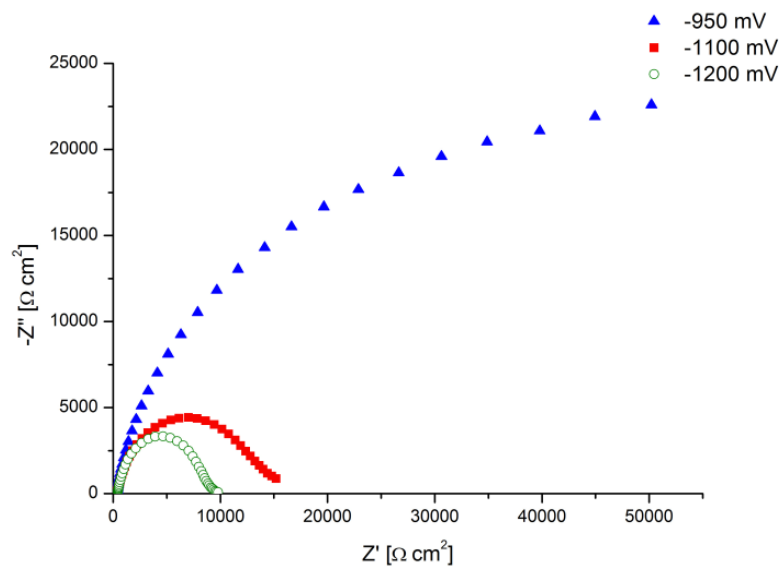

Figure 3. Nyquist impedance diagram after application of cathodic potential on x52 carbon steel in simulated soil solution

On the other hand, the second Nyquist diagram shape obtained at -1100 mV$_{[SCE]}$ polarized potential was characterized by a smaller semi-circle compared to the one obtained at -950 mV $_{[SCE]}$ potential which indicates heterogeneity in the calcareous layer deposed on the carbon steel surface.

Lastly, the spectra obtained at -1200 mV$_{[SCE]}$ showed a slightly positive inflection that can be observed at 100 MHz, which explains the existence of an ancillary electrochemical process at lower frequencies. It is seen that the diameter of the semi-circle is smaller compared to that measured at -950 mV$_{[SCE]}$.

The EIS Bode graphs displayed in Figure 4 show a one-time constant only. The absolute maximum value of the phase angle was about 65° for the -950 mV$_{[SCE]}$ and appeared at around 1 Hz. However, the maximum phase angle value was lower at -1100 mV$_{[SCE]}$ and -1200 mV$_{[SCE]}$

applied potentials. These results indicate that the phase angle is much higher in the protected sample than in the over-protected.
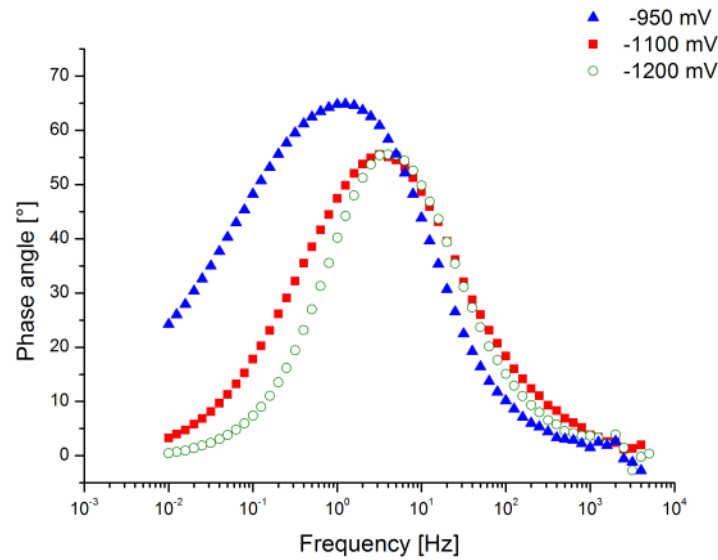

Figure 4. The bode plot of the phase angle *vs.* the frequency profiles for the X52 carbon steel after application of cathodic potential

The impedance modulus decreases with decreasing cathodic protection level as shown in Figure 5. At the beginning, the impedance modulus is higher for the -950 mV [SCE] applied potential and lower for the two other applied potentials (-1100 mV[SCE] and -1200 mV [SCE]). Inversely, the impedance modulus became higher, for the -1100 mV[SCE] and -1200 mV [SCE], and lower for the -950 mV applied potential at 0.1 MHz.
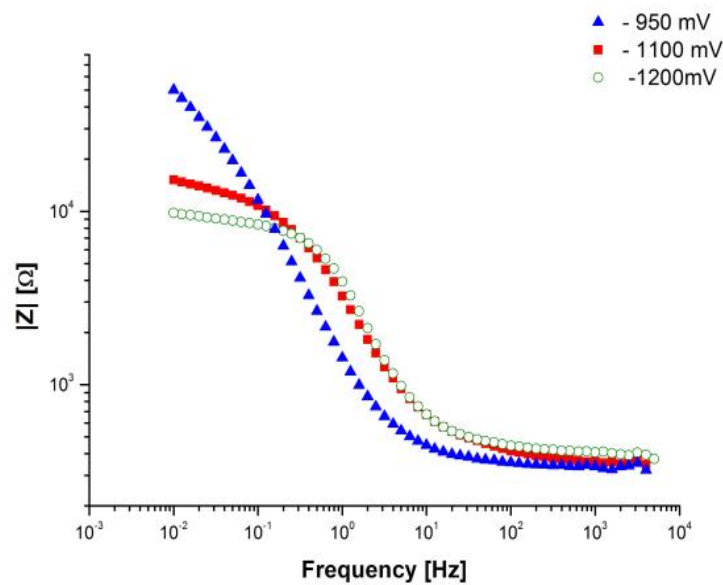
Figure 5. The bode plot of the modulus vs. frequency profiles for the X52 after application of cathodic potential

In Figure 6, two electrical equivalent circuit models with constant phase-resistance elements in a parallel montage were used to simulate the resistance of the carbon steel to corrosion during cathodic protection and in the presence of a calcareous deposition [17]. In Figure 6a, R_s represents the electrolyte resistance, R_{ct} the charge transfer resistance, and $R_{deposit}$ is the resistance of the calcareous deposit. The two constant phases Q_1 and Q_2 respectively are associated with the calcareous deposit and double layer.
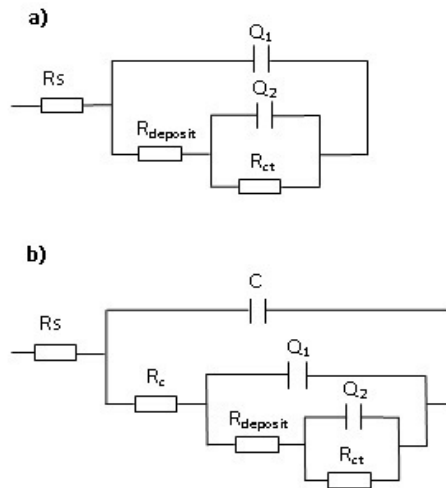
Figure 6. Proposed equivalent circuit for EIS (a) for -950 mV[SCE] and 1100 mV[SCE] (b) for -1200 mV[SCE]

In Figure 6b, R_c and C represent respectively the resistance and capacitance caused by the passage of the particles onto the surface of the metal through the defects of calcareous deposits [18]. Due to surface heterogeneities, Constant Phase Elements (CPE) are used instead of ideal capacitor elements. Brug et al. [19] suggested that the capacitive idealness of the CPE is determined by the exponent (n) ratio in the CPE impedance relationship (6).

$$Z_{CPE} = [Q(jw)^n]^{-1} \qquad (6)$$

To convert CPE amplitudes to equivalent capacitances, the Westing-Martens method (7) was used where $w\Theta$ is the frequency of inflection at which the absolute value of the phase angle is higher [20,21].

$$C_i = \frac{Q_i \omega_{\theta,1}^{n_i-1}}{\sin(\pi n_i/2)} \qquad (7)$$

Table 1 presents the EIS parameters obtained by fitting the results of the X52 carbon steel after exposure in a simulated soil solution for different cathodic polarization potentials.

It is worth mentioning that the resistance ($R_{deposit}$) value obtained at -950 mV [SCE] cathodic potential was relatively high. This is most likely explained by the deposited layer which has a protective effect.

The resistance decreases when applied cathodic potentials were decreased to -1100 mV [SCE] and -1200 mV [SCE] respectively. At these potentials the calcareous deposit begins to crack, becomes less compact, and as a result, $R_{deposit}$ begins to fall dramatically. These data reveals that both the resistance and the integrity of the calcareous deposit decrease with decreasing cathodic potential.

The results obtained for the charge transfer resistance R_{ct} showed a significant decrease at lower applied potentials, as can highlighted in Table 1. R_{ct} value was very low at -1200 mV [SCE] cathodic potential. This is due to the calcareous film detachment as a result of the hydrogen evolution.

It was confirmed that $R_{deposit}$ and R_{ct} values were associated with the effectiveness of the cathodic protection. Indeed, below optimal cathodic potential, a decrease of $R_{deposit}$ and R_{ct} can be induced.

Table 1. EIS component values obtained from the fitting to circuits of Figure 6

Components	Cathodic polarization -950 mV[SCE]	Cathodic polarization -1100 mV[SCE]	Cathodic polarization -1200 mV[SCE]
R_S [Ohm.cm^2]	338.5	359.4	398.7
C [F.cm^{-2}]	-	-	6.08×10^{-6}
R_C [Ohm.cm^2]	-	-	107.7
C_1 [F.cm^{-2}]	7.1×10^{-5}	3.57×10^{-5}	1.7×10^{-5}
Q-n[0<n<1]	0.85	0.79	0.85
$R_{deposit}$ [Ohm.cm^2]	35320	12790	8232
C_2 [F.cm^{-2}]	2.4×10^{-4}	1.8×10^{-3}	5×10^{-3}
Q-n[0<n<1]	1	1	1
R_{Ct} [Ohm.cm^2]	22640	1384	492

4. CONCLUSION

Based on the data and discussion of the electrochemical results obtained by the application of cathodic potential on a carbon steel pipeline exposed to a simulated soil solution, conclusions can be drawn as follows:

The steady-state current decreased as the applied potential became more negative, and it was observed that the cathodic potential had an impact on the calcareous scale deposition.

When lowering the potential below -1100 mV [SCE], the calcareous deposits are not formed completely.

From the EIS experiments performed at the end of the potentiostatic tests, one can distinguish the cathodically protected steel from the unprotected one. The decrease of both the charge transfer resistance (R_{ct}) and resistance of calcareous deposit ($R_{deposit}$) to lower values when decreasing the applied potential level, showed good compatibility with potentiostatic results. In conclusion, this work shows clearly that the EIS technique seems to be useful in estimating the efficiency of cathodic protection and may be used as a diagnostic tool for CP systems in the underground pipeline. Moreover, the EIS technique can be useful for evaluating the passive layer protectiveness. However, obtained data could be difficult to use in the field for instant analysis and interpretation.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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