

# Corrosion studies of carbon steel X60 by electrochemical methods

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The paper presents the electrochemical corrosion behavior of carbon steel X60 using the electrochemical impedance spectroscopy and potentiodynamic polarization methods. As test solutions sodium chloride, sodium sulphate and sulphuric acid 0.5M concentration were used in a three electrode open cell. It was observed that the corrosion rate (corrosion current) is higher for carbon steel X60 in 0.5M sulphuric acid and smaller in 0.5M sodium sulphate.

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## 1. Introduction

The carbon steel X60 are used for manufacturing gas and crude oil pipelines, shipbuilding industry, power equipment, in various corrosion environments; it is, therefore, of extreme importance to study their behavior and life service predictability in various systems.

In the literature are studies of carbon steel X60 corrosion behavior in sulfuric acid solution [1]; carbonate and sodium bicarbonate solutions [2], media that are responsible for the occurrence of pitting corrosion initiated by active-passive transition along with fast reactions of hydrogen emission.

A. Benmoussa and others [3] have studied the corrosion resistance of various types of steel using soil as aggressive environment (corrosion are influenced by pH, temperature, humidity and the chemical composition of electrolytes in the soil) and it has been shown that the steel X60 features the highest resistance to soil aggressive action and bacterial activity. Investigations have been carried out using a simulated solution with pH similar to that soil; the method applied was potentiodynamic polarization and electrochemical impedance spectroscopy. It has been found that the corrosion current increases from 20°C to 60°C while the impedance curves indicate that the corrosion resistance increases with immersion time.

The influence of temperature (30°C - 120°C) on the corrosion behavior of low carbon pipeline steels in the CO<sub>2</sub> saturated solutions in the closed autoclave system has been studied by Das and Khanna [4]. At lower temperatures, the surface films have an open porous structure and hence the FeCO<sub>3</sub> film formed dissolved continuously in the CO<sub>2</sub> saturated solution. Between 60°C to 90°C, the FeCO<sub>3</sub> film accumulated more in the outer part, which is more porous, less dense and non-protective

in nature and hence the corrosion rates of samples increase with temperature. In contrast, above 90°C, a dense protective FeCO<sub>3</sub> film is formed and the corrosion rate decreases significantly at 120°C.

The electrochemical impedance spectroscopy (EIS) has been successfully used for thirty years in the study of materials corrosion and proves to be an accurate method to determine the corrosion speed. An important EIS role is that, unlike other laboratory techniques, this makes use of very small amplitude signal which do not significantly alter the stationary state of the surface being investigated. The electrochemical impedance spectroscopy uses polarization frequency values like the linear polarization. To make an EIS measurement, a small amplitude signal, usually a voltage between 5mV to 50mV, is applied to a specimen over a range of frequencies of 100 000Hz to 0.001Hz. Polarization resistance and capacitance are obtained for each frequency and these values can provide information on the corrosion behavior, corrosion speed, diffusion processes and surface properties. By applying a given signal (perturbation) of a system, the transfer function of the system being investigated can be measured and this provides full information on the system dynamic behavior [5 – 7].

Historically, the modern dynamic analysis systems were introduced in electrochemistry by Epelboin and coworkers in 1960, by applying impedance measuring techniques in various fields of electrochemistry (corrosion, corrosion inhibitors, electro-crystallization). The modern equipment for the analysis of a system dynamic behavior consists of a frequency analyzer, spectrum analyzer, combined with an interface analyzer connected to an electrochemical cell and a computerized system for the collection and analysis of experimental data (with a suitable program) [8].

The response  $y(t)$  of a linear system to a perturbation  $x(t)$  is determined by a differential equation of  $n$  order in  $y(t)$ :

$$\begin{aligned} b_0 &= \frac{d^n y(t)}{dt^n} + b_1 \frac{d^{n-1} y(t)}{dt^{n-1}} + \dots + b_n y(t) = \\ &= a_0 \frac{d^m x(t)}{dt^m} + a_1 \frac{d^{m-1} x(t)}{dt^{m-1}} + \dots + a_m x(t) \end{aligned} \quad (1)$$

or a set of first order differential equations.

If  $x(t)$  is an imposed sinusoidal signal

$$x(t) = A \sin \omega t \quad (2)$$

its response,  $y(t)$  is also sinusoidal:

$$y(t) = B \sin(\omega t + \Phi) \quad (3)$$

and a transfer function can be defined as:

$$H(\omega) = |H(\omega)| e^{j\Phi} \quad (4)$$

$$\text{Where: } |H(\omega)| = \frac{B}{A} \quad (5)$$

$|H|$  and  $\Phi$  are the module and modification of the transfer function phase, respectively.

If  $x(t)$  is the current and  $y(t)$  is the voltage,  $H(\omega)$  is a value of the impedance;

If  $x(t)$  is the voltage and  $y(t)$  is the current,  $H(\omega)$  is the admittance.

Impedance,  $Z(\omega)$  of an electrochemical interfaces is a complex number that can be represented in polar or cartesian coordinates:

$$Z(\omega) = |Z| e^{j\Phi} \quad (6)$$

$$Z(\omega) = \text{Re}Z + j\text{Im}Z \quad (7)$$

where:  $\text{Re}Z$  and  $\text{Im}Z$  represent the real and imaginary, respectively, part of the impedance.

The relations among these quantities are:

$$|Z| = (\text{Re}Z)^2 + (\text{Im}Z)^2 \quad (8)$$

$$\Phi = \text{Arctg} \frac{\text{Im}Z}{\text{Re}Z} \quad (9)$$

$$\text{Re}Z = |Z| \cos \Phi \quad (10)$$

$$\text{Im}Z = |Z| \sin \Phi \quad (11)$$

Impedance can be defined for any physical –chemical system as a stationary current – voltage relationship. Impedance is a function of both frequency and polarization state in a certain point ( $I_0$ ,  $V_0$ ) [9].

The polarization methods, such as potentiodynamic polarization, potentiostatic and cyclic voltammetry are often used in laboratory for corrosion tests. These techniques can provide significant useful information regarding the corrosion mechanism, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current, which is produced as a function of time or potential. Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. It is probably one of the most used polarization test method for measuring corrosion resistance and is used for a wide variety of functions [10, 11].

The paper presents the electrochemical corrosion behavior of carbon steel X60 using the electrochemical impedance spectroscopy and potentiodynamic polarization methods. As test solutions sodium chloride, sodium sulphate and sulphuric acid 0.5M concentrations were used in a three electrode open cell.

## 2. Material and methods

For electrochemical corrosion measurements it was used a potentiostat/galvanostat type SOLARTRON, a three-electrode open cell with carbon steel X60 as working electrode (W.E.), a circular platinum gauze as counter electrode (C.E.) and a saturated Ag/AgCl electrode as reference electrode (R.E.) ( $E_{\text{Ag}/\text{AgCl}} = +200\text{mV/ESH}$ ). The system was connected to a computer program Corware and Zplot and data analysis software. The samples to analyze (working electrode) with a surface area of  $0.5\text{cm}^2$  was inserted into resin. The testing solutions: 0.5M sulfuric acid, 0.5M sodium sulphate and 0.5M sodium chloride were used.

For EIS and PD measurements it was used the following parameters: initial frequency (I.F.) 100 000Hz, final frequency (F.F.) 0.001Hz, amplitude voltage  $U=5\text{mV}$ , sweep rate  $v = 0.2\text{mV/s}$ , initial potential (I.P.) - 1.2V (Ag/AgCl), final potential (F.P.) +1.0V (Ag/AgCl).

Chemical composition and some mechanical properties of carbon steel X60 are presented in Table 1 and Table 2 [12].

Table 1. Chemical composition of carbon steel X60.

Standard	Steel	Chemical composition, %									
		C	Mn	Si	P	S	Cr	Ni	V	Nb	Ti
API-5L	X60	0.2 1	1.52	0.19	0.012	0.003	0.16	0.15	0.05	0.03	0.01

Table 2. Mechanical properties of carbon steel X60 (longitudinal direction).

Standard	Steel	R <sub>p0.2</sub> (MPa)	R <sub>m</sub> (MPa)	A <sub>5</sub> (%)	R <sub>p0.2</sub> /R <sub>m</sub>	HRC
API-5L	X60	733	792	20.5	0.93	21

### 3. Results and discussion

The Nyquist simulated experimental impedance curves with a simple circuit with C<sub>DL</sub> (double layer capacitance) in parallel with polarization resistance is not a very good overlap. So that, for this reason it is necessary to introduce an equivalent circuit with CPE (the capacitance element of the double layer which is dependent of the frequency because the surface is not homogenous).

CPE is used like a constant phase element because all capacitive circular curves of the circle are situated under the real part of axis. These characteristics of the capacitive circular curves are presented in all studies about the electrochemical impedance and used for a lot of simulated curves. CPE is not a pure capacitor; he is a component with complex impedance.

The experimental data of electrochemical impedance for carbon steel X60 in different solutions shows that Randles circuit is not a valid model. The most important difference between the experimental impedance of the carbon steel X60 and the points obtained by the Randles model simulation is: the centers of the different circular curves of the impedance are always under the real axis and never on the axis, as derived from the Randles model. An equivalent circuit was proposed to determine the experimental impedance spectra [13]. In most cases, this circuit, represented in Fig. 1 allows for some excellent correlation between experimental and theoretical impedance curves to be obtained.

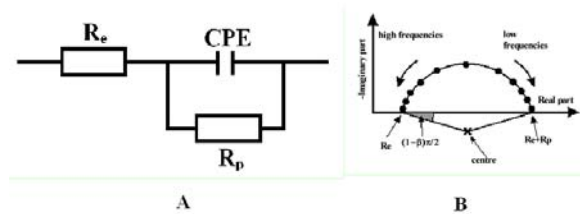


Fig. 1. (A) Equivalent circuit to calculate the polarisation resistance from impedance spectrum with a CPE:  $R_e$  – electrolyte resistance between the reference electrode and the working electrode; CPE – the double layer capacity in parallel with the polarisation resistance  $R_p$ ; (B) Circuit with a parallel combination of a resistance  $R$  and a CPE, and the corresponding Nyquist impedance plot.

Equivalent circuit  $R_e$ -CPE// $R_p$  represented in Fig. 1 gives a single flattened circle arc.

The evolution of the impedance depending on the frequency in this case could be described by the following equation:

$$Z = R_e + \frac{R}{1 + (j\omega\tau)^\beta} \quad (0 < \beta \leq 1) \quad (12)$$

In this expression the value of the parameter  $\beta$  (always smaller than 1) indicates the smoothing of the circular curves from Randles models and the experimental circuit with CPE: the line corresponding to the Randles model was found only in the value  $\beta = 1$ . In this case, the CPE is a pure capacitor.

The Nyquist plot representation of impedance spectra performed in 0.5M sodium chloride and 0.5M potassium sulphate solutions at time of immersion and at the different times of immersion are shown in Figs. 2 – 4.

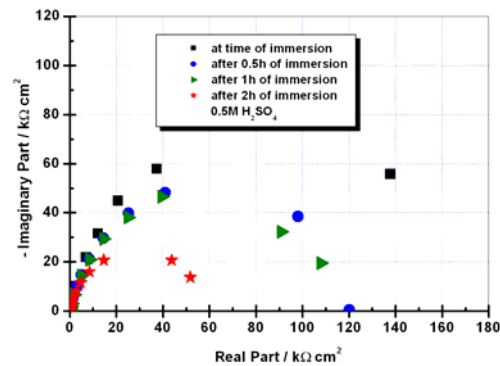


Fig. 2. Nyquist diagrams of impedance spectrum for carbon steel X60 in 0.5M sulfuric acid

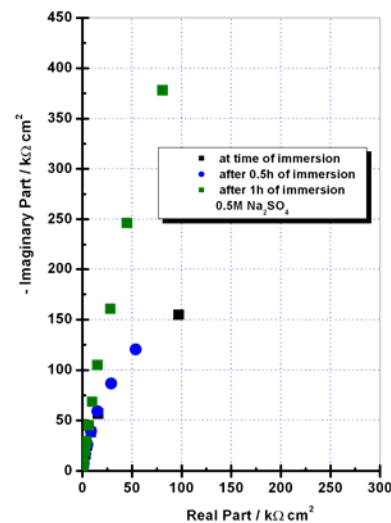


Fig. 3. Nyquist diagrams of impedance spectrum for carbon steel X60 in 0.5M sodium sulfate

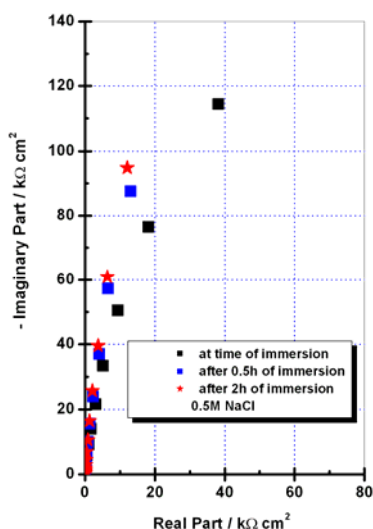


Fig. 4. Nyquist diagrams of impedance spectrum of carbon steel X60 in 0.5M sodium chloride.

On the Fig. 5 it was represented one experimental diagram together with the simulation curve described by the equivalent circuit from Fig. 1. It could be observe that the experimental impedance data fit very well with the equivalent circuit proposed.

From impedance experimental data for the samples of carbon steel X60, the value of  $\beta$  is 0.82 (sulfuric acid), 0.92 (sodium sulphate) and 0.94 (sodium chloride).

From the value of electrolyte resistance and used the equivalent circuit presented in Fig. 1 it was possible to calculate the polarization resistance for the sample in those three testing solutions. The results are presented in Table 3.

It can be noted that the polarization resistance of carbon steel X60 in 0.5M sulfuric acid solution decreases in time. After two hours from immersion in the solution of sulfuric acid, the steel was destabilized due to the potential

general corrosion with the dissolution of corrosion products.

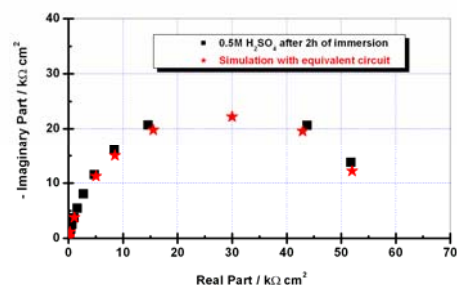


Fig. 5. Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (triangle points) for carbon steel X60 in 0.5M sulfuric acid solution after 2h of immersion

In 0.5M sodium sulphate solution the carbon steel X60 was stabilized within two hours from immersion while the polarization resistance increased in time. This means that on the sample surface protective film of corrosion products was formed.

In 0.5M sodium chloride solution, the polarization resistance values of carbon steel X60 have a tendency to increase in time. The impedance diagrams also indicate strong low -frequency oscillations which can be caused by the localized corrosion on the steel surface.

The values of polarization resistance in the three solutions testing can also be accounted by the anion effect:  $\text{Cl}^-$  anion is a simple anion while  $\text{SO}_4^{2-}$  has a complex structure; the diffusion coefficient of  $\text{Cl}^-$  is  $2.302 \times 10^{-9}$  and  $1.065 \times 10^{-9}$  for  $\text{SO}_4^{2-}$  [14].

Thus the different diffusion speed and of the two anions can cause lower corrosion resistance in sulfuric acid as compared with sodium chloride and sodium sulfate.

Table 3. The values of polarization resistance of carbon steel X60 in testing solutions at different time from immersion

Solution	$R_p$ ( $\text{k}\Omega \text{ cm}^2$ )		
	At time of immersion	After 0.5h from immersion	After 2h from immersion
0.5M sulfuric acid	138	117	56
0.5M sodium sulphate	521	533	1400
0.5M sodium chloride	503	1090	1600

The corrosion current values at different time from immersion into three testing solutions using the

polarization resistance and the corrosion potential are presented in Table 4.

Table 4. Corrosion current values of carbon steel X60 at different time from immersion in 0.5M sulfuric acid, 0.5M sodium sulphate and 0.5M sodium chloride solutions

Solution	$i_{\text{corr}}$ , nA/cm <sup>2</sup>		
	At time of immersion	After 0.5h from immersion	After 2h from immersion
0.5M sulfuric acid	116.10	185.56	387.69
0.5M sodium sulphate	41.67	40.73	15.50
0.5M sodium chloride	84.84	17.64	12.01

The performed potentiodynamic diagrams for steel carbon X60 in testing solutions after 30min from immersion are shown in Fig. 6 and the corresponding values of the corrosion current, polarization resistance and calculated Tafel constants are presented in Table 5.

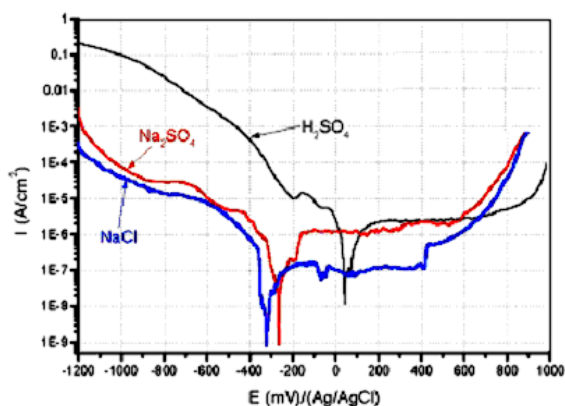


Fig. 6. Comparative polarization potentiodynamic curves for carbon steel X60 in: 0.5M sulfuric acid; 0.5M sodium sulphate and 0.5M sodium chloride solutions obtained after 30 min from immersion time (log scale).

The corrosion current of the potentiodynamic diagrams was calculated with Stern - Geary formula expressing the dependence of corrosion resistance on corrosion current [15]:

$$i_{\text{corr}} = \frac{1}{2.303R_p} \left( \frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c} \right) \quad (13)$$

- $i_{\text{corr}}$  – corrosion current density, Amps/cm<sup>2</sup>;
- $R_p$  – corrosion resistance, ohm cm<sup>2</sup>;
- $\beta_a$  – anodic Tafel slope in V/decade or mV/decade of the current density;
- $\beta_c$  – cathodic Tafel slope in V/decade or mV/decade of the current density;
- the quantity  $(\beta_a \cdot \beta_c)/(\beta_a + \beta_c)$  is referred to as the Tafel constant.

In general, it may be considered a good correlation between the polarization resistances values calculated from potentiodynamic diagrams with those obtained from the impedance diagrams using the equivalent circuit shown in Fig. 1. The largest anodic Tafel slope is registered in 0.5M sodium chloride and may be associated with diffusion and pitting corrosion.

Table 5. Polarization resistance values of carbon steel X60 calculated from polarization potentiodynamic curves obtained after 30 min from immersion in solutions.

Solution	$i_{\text{corr}}$ (nA/cm <sup>2</sup> )	$E_{\text{corr}}$ (mV/Ag/AgCl)	$\beta_a$ (V/decadă)	$\beta_c$ (V/decadă)	$R_p$ (kΩcm <sup>2</sup> )
0.5M sulfuric acid	775.6	47	$100 \cdot 10^{-3}$	$100 \cdot 10^{-3}$	78.0
0.5M sodium sulphate	83.0	-267	$100 \cdot 10^{-3}$	$100 \cdot 10^{-3}$	606.4
0.5M sodium chloride	15.7	-324	$246 \cdot 10^{-3}$	$54 \cdot 10^{-3}$	2720.0

#### 4. Conclusions

The electrochemical impedance technique is a useful method to investigate the corrosion behavior of carbon steel X60. Three different solutions: sulfuric acid, sodium chloride and sodium sulfate of 0.5M concentrations were used.

The polarization resistance values from the impedance spectrum could not be simulated with the circuit Randles and it was needed an equivalent circuit with CPE. The values of  $\beta$  are different: 0.82 in 0.5M sulfuric acid; 0.92 in 0.5M sodium sulphate and 0.94 in 0.5M sodium chloride.

The polarization resistance of carbon steel X60 in 0.5M sulfuric acid decreases in time and after two hours from immersion the steel surface is destabilized because of the possibility of general corrosion with the dissolution of corrosion products.

In 0.5M sodium sulphate and 0.5M sodium chloride solutions the polarization resistance of carbon steel X60 increases in time, therefore the corrosion resistance is higher than in 0.5M sulphuric acid solution.

The polarization resistance values obtained in 0.5M sodium chloride are highest than those obtained in 0.5M sodium sulphate and 0.5M sulfuric acid, but it can be noted that this type of steel is sensitive to localized corrosion caused by chlorine ions.

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