

CONVENTIONAL DC ELECTROCHEMICAL TECHNIQUES IN CORROSION TESTING

J. Genesca^a, J. Mendoza^b, R. Duran^b and E. Garcia^b

- a. Corrosion Laboratory. Department of Metallurgical Engineering. Faculty of Chemistry. UNAM. City University. 04510 México D.F. e-mail: genesca@servidor.unam.mx
- b. Instituto Mexicano del Petroleo. Eje Central Lazaro Cardenas, 152. 07730 Mexico D.F.

ABSTRACT

Metallic corrosion under wet conditions is generally electrochemical, occurring in corrosion cells at the metal surface. Being corrosion phenomena in aqueous environments generally of electrochemical nature they are dominated by the corrosion potential, E_{corr} , of the metal. The mixed-potential theory was developed by C. Wagner and W. Traud and was published in German in 1938.

Electrochemical methods in corrosion testing have been used ever since the electrochemical nature of corrosion processes was discovered. These methods are used both for corrosion monitoring and as laboratory techniques. One of the most important applications has been the estimation of corrosion rate instantaneously by means of polarization resistance, being of special relevance the relationship between mass loss and polarization resistance, which cannot always be deduced from Tafel parameters, because the constancy of electrochemical parameters with time cannot a priori be assumed. The polarization resistance measurements can also be a very useful technique for the determination of time effect on corrosion. Usually electrochemical techniques have been employed to both speed data development and to better understand corrosion mechanisms.

In this paper, the use of electrochemical methods for corrosion testing will be reviewed, with special attention to conventional dc techniques such as linear polarization and Tafel extrapolation. Other techniques, including corrosion potential measurements, polarization methods such as potentiodynamic polarization (for example, cyclic potentiodynamic polarization, CPP, technique provides a reasonable, rapid method for qualitatively predicting the propensity of an alloy to suffer localized corrosion in the form of pitting and crevice corrosion), and potentiostaircase will be described, reaching conclusions concerning their use, significance and limitations.

Keywords : DC electrochemical techniques, LPR, Polarization Resistance, Tafel.

INTRODUCTION

ASTM defines polarization as: “the change from the open-circuit electrode potential as a result of the passage of current” [1]. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential. Applications of electrochemical techniques to corrosion processes have been made by many researchers during the last 75 years. The fundamental equations for this development can be found in many standard reference texts [2-4]. Polarization measurements pushed the

development in the 1930's of mixed potential theory, in order for the experimental results to be explained [5].

The objectives of corrosion research and testing are to provide information about the reasons for and mechanisms in corrosion processes and the determination of corrosion rates and the efficiency of corrosion protection achieved by the application of appropriate alloys, protective layers, coatings and inhibitors, respectively. Since corrosion processes are mostly of an electrochemical nature, electrochemical methods play an important role in corrosion research and testing.

The polarization resistance method, based on electrochemical concepts, enables determination of instantaneous interfacial reaction rates such as corrosion rates and exchange current densities from a single experiment. The estimation of corrosion rate based on polarization resistance (R_p) measurements has been used more and more extensively. In order to achieve more accurate and reproducible values of the R_p several authors have applied periodic voltage or current waves to the specimen [6]. Under such conditions, in most cases the response of the metal-electrolyte system is far more complicated than that expected for the single equivalent circuit: polarization resistance-double layer capacitance in parallel. Nowadays, the study of corrosion mechanisms and the estimation of the corrosion rate by means of electrochemical techniques tend to be increasingly related to each other.

This paper studies the extent to which the techniques "Linear Polarization Resistance", LPR, and "Tafel Extrapolation Method", can be applied in order to obtain representative values of the corrosion rate in a particular environment. The determination of the corrosion rate at which a metal dissolves in a certain environment and conditions is of primary importance in laboratory and field corrosion studies. Through the years several techniques used to determine such corrosion rate have been developed: weight loss measurements, Linear Polarization Resistance, LPR, Tafel Extrapolation Method, Electrochemical Impedance Spectroscopy, EIS, and more recently Electrochemical Noise. This paper also reports one application of our research group with DC electrochemical techniques for determination of corrosion rate. The example originates from experiments to show the effect of flow conditions on the efficiency of an inhibitor.

The use of different techniques requires different considerations and it is common to obtain results that, at first sight, may not be representative of the system under study. Therefore, it is important to obtain as much information related to the use of different techniques as possible, in order to develop data analysis criteria which lead us to a better understanding of their use, advantages and disadvantages.

LINEAR POLARIZATION RESISTANCE (LPR)

The "Linear Polarization Resistance" technique used for measuring corrosion rates has been extensively used in the past years either in laboratory or field corrosion studies. This measurement technique is based on the "mixed potential" theory proposed by Wagner and Traud [5]. This theory postulates that it is possible to explain the corrosion reactions by assuming that cathodic and anodic partial reactions are occurring at the metal-electrolyte of a corroding electrode interface at a certain "mixed" or "corrosion" potential, E_{corr} .

The E_{corr} depends on a variety of parameters, like alloy composition, activity of oxidizable and reducible species in the environment, its flow rate and the overpotential of relevant

electrochemical reactions at the metal/solution interface. These processes can be influenced strongly by temperature.

The mixed potential theory takes into account two main hypotheses:

- a) Any electrochemical reaction can be divided into two or more partial cathodic and anodic reactions,
- b) There is no net accumulation of electric charge during an electrochemical reaction.

It has been demonstrated that the slope of the potential-current curve (polarization curve) measured near the mixed or corrosion potential E_{corr} of a corroding electrode is inversely proportional to the reaction or corrosion rate of the electrode.

The net current density, j , which circulates through a metal-electrolyte of a corroding electrode interface is given by the equation

$$j = j_{\text{corr}} \left[\exp\left(\frac{\eta}{b_a}\right) - \exp\left(\frac{\eta}{b_b}\right) \right] \quad (1)$$

where: j = net current density across the metal-electrolyte interface, j_{corr} = corrosion current density (A/cm^2), η = overpotential ($E_{\text{measured}} - E_{\text{corr}}$). This relationship is experimentally observed between applied electrochemical current density and potential for a corroding electrode in the absence of competing reduction-oxidation reactions [2,3]. The applicability of this relationship relies on the presence of a single charge transfer controlled cathodic reaction and a single charge transfer controlled anodic reaction. This relationship provides the basis for the electrochemical polarization technique as applied to a corroding electrode at its corrosion potential [7].

β_a and β_c are the anodic and cathodic Tafel constants (parameters) $(\partial E/\partial \log j)$ dependent on the reaction mechanism and are given by:

$$b_a = \frac{RT}{(1-\alpha)nF} \quad (2)$$

$$b_c = -\frac{RT}{\alpha nF} \quad (3)$$

Equation (1) shows that the net current, j , is in exponential relationship with the overpotential, η and assumes that:

- i. The slower step in the electrochemical corrosion process is the charge transfer at the metal-electrolyte interface (the corrosion process is controlled only by charge transfer).
- ii. Ohmic drops in the electrolyte and surface films can be neglected.
- iii. Concentration polarization is absent.
- iv. The corrosion potential, E_{corr} , is far from the reversible potentials of the simultaneous anodic and cathodic reactions occurring.
- v. There are no secondary electrochemical reactions occurring.

The derivation of the polarization resistance

Equation (1) can be mathematically linearized by taking its series expansion and by neglecting higher terms when $\eta/\beta \ll 0.1$. The simplified relationship has the following form:

$$\left(\frac{\partial j}{\partial E}\right)_{E_{corr}} = 2.303 j_{corr} \frac{(b_a + b_c)}{b_a b_c} \quad (4)$$

where b_a and b_c are the Tafel slopes for anodic and cathodic reactions respectively, determined from the $\log j$ vs. E plot and are related to β_a and β_c constants by: $b = 2.303 \beta$.

From equation (4) it can be seen that the variation of the current density across the interface with respect to the potential, near the E_{corr} , is a linear function. The slope R_p of the linear polarization curve is called the polarization resistance. Defining the ‘‘Polarization Resistance’’, R_p , as:

$$R_p (\Omega - cm^2) = \left(\frac{\partial E}{\partial j}\right)_{E_{corr}} \quad (5)$$

and the proportionality constant B as:

$$B = \frac{b_a b_c}{2.303(b_a + b_c)} \quad (6)$$

the corrosion current density is given by:

$$j_{corr} = \frac{b_a b_c}{2.303(b_a + b_c)} \left(\frac{\partial j}{\partial E}\right)_{E_{corr}} = \frac{B}{R_p} \quad (7)$$

which is the well-known Stern-Geary equation [8]. Stern and Geary [8] originally described a region in the vicinity of the corrosion potential where a linear dependence of potential on applied current existed for a corroding electrode. They derived an equation relating the slope of this linear region to the corrosion rate and Tafel slopes and the method became known as Linear Polarization Resistance, LPR. Equation (7) gives a method of measuring corrosion rate as current density, j_{corr} , provided that the parameters R_p and B are known [6-10]. The Stern-Geary mathematical treatment [8] requires that polarization affects only the rates of the anodic and cathodic reactions. It can be noted that the proportionality constant, B , is dominated by the smaller of the two anodic and cathodic Tafel slopes, if unequal.

The fact that the corrosion rate is inversely proportional to the polarization resistance is clearly seen in equation (7). Taking the logarithm of this equation, it is seen that $\log j_{corr}$ vs. $\log R_p$ is linear with a slope of -1 and has the intercept $\log B$ [7]

$$\log R_p = \log B - \log j_{corr} \quad (8)$$

Stern and Wiesert [9] confirmed such relationship over six orders of magnitude change in corrosion rate for corroding systems.

Stern and Geary were able to elaborate their equation based on Kolotyrkin's approach [11] and because advances in electrochemical kinetics had by then produced a detailed two-term expression for the whole Tafel line starting from the reversible potentials [12]. Stern and Geary simplifies the kinetic expression to provide an approximation to the charge transfer controlled reaction kinetics given by equation (1) for the case of small overpotentials with respect to E_{corr} [8,13-14]. By applying the full Tafel expression to the case where the corrosion reaction was balanced by the cathodic reaction (reduction of H^+ for example) and then making some simplifying assumptions, they obtained a convenient and convincing expression for the metallic corrosion current, the equation (7). In many cases j_{corr} is reasonably insensitive to values of b_a and b_c , so that the essence of the method is the measurement of R_p from the linear polarization region close to the corrosion potential, E_{corr} . In one sense, what Stern and Geary accomplished was the quantitative expression of the constant of proportionality between polarization resistance, R_p , and corrosion rate, j_{corr} .

The R_p value

In order to obtain the value of R_p it is necessary to measure the relationship between the potential and the current density which circulates across the metal-electrolyte interface, close to the corrosion potential. This relationship is often approximately linear with potential within $\pm 5\text{-}10$ mV of E_{corr} . This is usually done by polarizing the electrode above and below ± 10 mV [15] its corrosion potential E_{corr} , and measuring the net current, j , circulating between this electrode and an inert or auxiliary electrode. Then the slope of this plot is $\Delta E/\Delta j$. When determined from a tangent to the E-j curve at E_{corr} , it defines the polarization resistance, R_p . Consequently, this method is often called the linear polarization method (LPR). The slope is independent of the degree of linearity [7], although the extent of the approximately linear E-j region can vary considerably amongst corroding systems. [7,16].

The constant B can be obtained in several ways:

- Considering a theoretical value of Tafel slopes;
- Obtaining the values of Tafel slopes from separate polarization experiments in identical conditions (potentiodynamic polarization scans or by harmonic distortion analysis);
- Obtaining the Tafel slopes by fitting the same curve used to determine the polarization resistance, R_p ;
- Taken Tafel values from literature for the same or similar corrosion system or by calibrating the B constant using weight loss measurements.

In the case where the reaction mechanism is known in detail, the Tafel slopes may be estimated from the rate-determining step in the mechanism of reaction [16].

Processes Controlled by Mass Transfer (Diffusion)

It is important to note that if the anodic or cathodic processes do not satisfy the assumptions stated before for equation (1), the values of j_{corr} obtained by LPR technique can be erroneous and some corrections must be made. The model which leads to equation (1) can not explain completely the corrosion process if phenomena such as active-passive transitions, reduction of oxide films or diffusion of species to and away from the metal-electrolyte interface occur.

If the cathodic reaction of the corrosion process is controlled by diffusion of reactants from the bulk solution to the metal surface (e.g. reduction of oxygen) the cathodic Tafel constant, b_c , tends to be infinite and equation (6) becomes

$$B = \frac{b_a}{2.303} \quad (9)$$

So equation (7) takes the form:

$$j_{corr} = \frac{b_a}{2.303R_p} \quad (10)$$

Similarly, anodic mass transport control results in [6]

$$B = \frac{b_c}{2.303} \quad (11)$$

Effect of the electrolyte resistance, R_s , on the LPR measurements

In Linear Polarization Resistance measurements it is usually considered that the value of the solution resistance, R_s , surface film resistance and all other electrical resistances between the tip of the Luggin capillary and the test metal surface are smaller than the value of the R_p measured, but this is not the general situation.

Considering that the solution resistance, R_s , is bigger than the surface film resistance and all other electrical resistances between the tip of the Luggin capillary and the test metal surface, the measured polarization resistance, R_{meas} , is given by the following equation:

$$R_{meas} = R_p + AR_s \quad (12)$$

where A = area of the electrode.

Considering equation (7), the true corrosion current density is given by:

$$j_{corr} = \frac{B}{R_p - AR_s} \quad (13)$$

From equation (13) it can be seen that an uncompensated R_p value can lead to smaller values of j_{corr} .

If the error, δ , due to an uncompensated IR drop is defined as [17]:

$$\mathbf{d} = \frac{j_{corr} - j_{corr}^*}{j_{corr}^*} = \frac{j_{corr}}{j_{corr}^*} - 1 \quad (14)$$

where j_{corr} is the true corrosion current density without IR drop effects (given by equation 7) and j_{corr}^* is the corrosion current density with IR drop effects given by:

$$j_{corr}^* = \frac{B}{R_p + AR_s} \quad (15)$$

The error becomes

$$d = \frac{AR_s}{R_p} \quad (16)$$

Equation (16) shows that the error increases with the ratio of ohmic resistance to polarization resistance, R_s/R_p .

It has been stated that an uncompensated solution resistance can lead to a straight line in the LPR measurements and such linear behavior should not be considered as representative of the system.

ASTM standards D2776 [10] and G59 [18] describe standard procedures for conducting polarization resistance measurements. Potentiodynamic [19], potential step, and current-step methods [20,21] have all been described to determine the linear E-j behavior of an electrode near the E_{corr} . The current step method has been cited to be faster than potentiodynamic methods and less susceptible to errors associated with drift in E_{corr} [7]. LPR determined by potentiodynamic sweep is likely the most common method for assessing the corrosion rate.

Electrochemical impedance methods for determination of polarization resistance has been reviewed by Scully [7]. Determination of R_p is attainable in media of high resistivity because R_p can be mathematically separated from R_s by taking the difference between $Z(\omega)$ obtained at low and high ω .

Errors with polarization resistance measurement by LPR method have been collected by Scully in his excellent review about the R_p method for determination of instantaneous corrosion rates [7]. The most common errors involve:

- i. invalidation of the results through oxidation of some other electroactive species besides the corroding metal in question,
- ii. a change in the open-circuit or corrosion potential during the time taken to perform the measurement,
- iii. use of a potential gradient (ΔE) that is too large, invalidating the assumption of a linear relationship between net current density and potential required by equation (7),
- iv. too fast of a voltage scan rate or insufficient potential hold time,
- v. current and potential distributions.

THE TAFEL LINE IN CORROSION SCIENCE

Conversion of polarization resistance to corrosion current requires knowledge of the constant, B, of equation (7). Without knowledge of B, corrosion rates can be estimated to within a factor of two [9], assuming no other error exists. If either b_a and b_c are accurately known, and the other estimated, then corrosion current is relatively insensitive to errors in the estimated Tafel slope value [9]. Tafel slope values can be estimated from high polarization data and this reduces the level of uncertainty in calculating corrosion rates via the polarization resistance method, but the method becomes redundant because corrosion rates can be estimated directly by back extrapolation of high polarization data.

An activation controlled system or process is one where the rates of the electrochemical processes are controlled by the charge transfer across the metal solution interface (hence the alternate term charge transfer control).

To experimentally determine kinetic parameters such as j_{corr} , β_a and β_c it is often convenient to produce schematic potential-current density curves for corroding systems, and because of the exponential nature of the relationships these are often drawn as E - log j curves (Tafel diagrams). Then, plotting E against $\log|j|$, activation polarization gives a straight line. For a simple activation controlled metal dissolution (anodic) process, the current density is given by Tafel's Law

$$j = j_a = j_{corr} \exp\left(\frac{h_a}{b_a}\right)$$

The rate of a corrosion reaction depends on potential according to the above equation, being the **region or anodic Tafel domain** (Tafelian zone), the portion of the polarization curve in which potential satisfies the condition that $\eta_a/\beta_a \gg 1$. Taking logarithms:

$$h_a = -b_a \ln j_{corr} + b_a \ln j_a$$

Working with logarithms to base 10 and defining the *anodic Tafel constants*, a_a and b_a , it is possible to get the Tafel equation for an anodic reaction, also known as anodic Tafel line:

$$h_a = a_a + b_a \log j_a$$

where :

$$a_a = -2.303b_a \ln j_0$$

$$b_a = 2.303b_a$$

In the same way, for the **cathodic Tafel domain**, $\eta/\beta_c \ll 1$:

$$j = j_c = -j_{corr} \exp\left(-\frac{h_c}{b_c}\right)$$

$$h_c = b_c \ln j_{corr} - b_c \ln j_c$$

that allows to determine the *cathodic Tafel constants*, a_c and b_c , of the Tafel equation for a cathodic reaction:

$$h = a_c - b_c \log j_c$$

where :

$$a_c = 2.303b_c \ln j_0$$

$$b_c = 2.303b_c$$

POTENTIAL-CURRENT DIAGRAM

It is very useful to know if a metal is immune to corrosion in given circumstances using the potential-pH diagram (Pourbaix diagram), but practical situations most often subject metals to corrosive risks and the rate of corrosion then becomes of great importance. The advent of

polarization curves in corrosion science waited until Evans and Hoar [22] had demonstrated that the current in an ordinary corrosion cell was worth equating to the metal loss. The vogue then started for diagrams with two polarization curves, separate for anodes and cathodes on the corroding metal, each being plotted as a straight line against linear scales of potential and current. The anodic and cathodic lines were seen to approach each other with increasing current were reached, a situation freely identified with the practical corrosion cell where the cathodes and anodes would be virtually short-circuited.

Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential. The proper method for polarization testing of materials is facilitated by the development of standard test methods such as ASTM G5 “Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements” [23].

Several methods may be used in polarization of specimens for corrosion testing [24]. *Potentiostatic polarization* is a technique where the potential of the electrode is changed at a selected rate and involves maintaining a constant potential at the working electrode. *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 used for determining the corrosion current and to identify specific corrosion reactions, such as pitting and crevice corrosion. A variant of potentiodynamic polarization is *cyclic potentiodynamic polarization*, CPP, test technique, described in ASTM Standard Practice G 61 [25] which provides a reasonable, rapid method for qualitatively predicting the propensity of an alloy to suffer localized corrosion in the form of pitting and crevice corrosion. This technique was developed for stainless steels and nickel-base alloys but has been increasingly used for other alloys. This ASTM standard provides details on conducting CPP tests but is very limited with respect to interpretation. Beavers et al [26] have recently published a paper concluding that from the analysis of CPP curves for stainless steel-aqueous chloride system and other alloy-environment systems, both a forward and a reverse scan should be performed in order to maximize the information on localized corrosion obtainable from the test technique. The pitting potential, which is one parameter obtained from a CPP curve, is a non-conservative parameter for assessing susceptibility of a metal to pitting corrosion while the protection potential is a much more conservative parameter. Silverman [27] outlines the features that have been found useful for interpreting the polarization scan, as well as of some of the effects that uncompensated solution resistance, inappropriate scan rate, and improper point of scan reversal can have on the polarization scan features and how these effects might influence the interpretation. Another variant of potentiodynamic polarization is *cyclic voltammetry*, which involves sweeping the potential in a positive direction until a predetermined value of current or potential is reached, then the scan is immediately reversed until the original value of potential is reached. The *potentiostaircase method* is another variation of potentiodynamic polarization. This refers to a technique for polarizing an electrode in a series of potential steps where the time is constant at each potential, and often the current is allowed to stabilize prior to changing the potential to the next step. Another method using polarization methods is *electrochemical potentiodynamic reactivation* (EPR), which measures the degree of sensitization of stainless steels.

EFFECTS OF TURBULENT FLOW ON THE EFFICIENCY OF TRIAZOLE BASED INHIBITORS [28,29]

The effect of moving environments on the efficiency of corrosion inhibitors is a research topic that has been in continuous development over the recent years. The present work explores the

effect of turbulent flow on the efficiency of a triazole-based inhibitor (3-amino-1,2,4, triazole) in a 0.5 M HCl solution, using the rotating cylinder electrode, RCE, as hydrodynamic control system. The influence of turbulent flow on the corrosion rate of X52 pipeline steel was investigated using corrosion potential monitoring (E_{corr}), polarization curves, R_p and electrochemical impedance spectroscopy, EIS. R_p , EIS and E_{corr} monitoring were carried out during a period of 1 day of exposure to the test solution. Anodic and cathodic polarization curves were obtained after the 1 day period. The experimental technique has been described in some detail in recent publications [28,29]. It was found that the inhibiting effect of the triazole is considerably increased by flow.

The relevant experimental parameters for each electrochemical technique were:

- Linear polarization resistance (R_p): potentiostatic, potential range ± 0.01 V (referred to the E_{corr}), potential sweep rate = 0.017 mV s^{-1} .
- Electrochemical impedance spectroscopy (EIS): frequency range: 20,000 to 0.1 Hz, amplitude = 1×10^{-2} V.
- Polarization curves: At a rotation rate of 0 rpm a cathodic and an anodic polarization curves were measured on different steel samples, after 1 day of exposure to the test solution. These polarization curves were obtained, departing from E_{corr} , at a sweeping rate of 0.001 V s^{-1} , in cathodic or anodic direction, depending on each case. Therefore, two polarization curves were obtained, one cathodic and one anodic. At a rotation rate of 1000 rpm a single polarization curve was obtained after 1 day of exposure time, at each inhibitor concentration. In this particular case, the polarization curves were started at an overpotential of -0.4 V (with respect to E_{corr}) and stopped at an overpotential of $+0.4$ V (referred to E_{corr}).

RESULTS

Polarization Curves.

In the following section the polarization curves, obtained at different rotation rates and inhibitor concentrations, are shown.

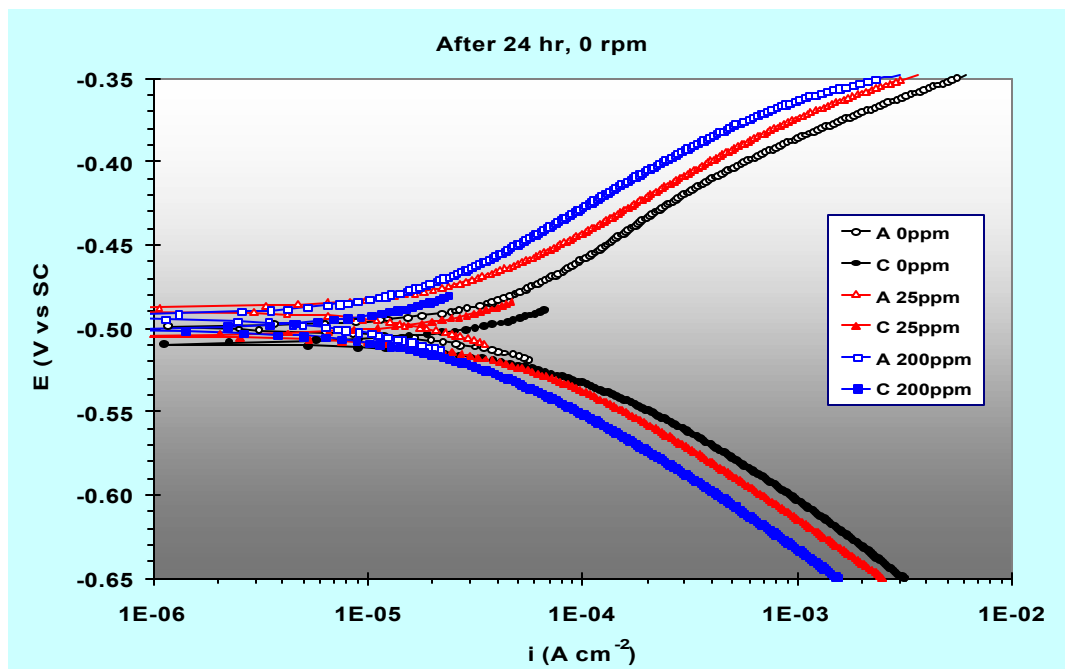


Figure 1.- Anodic and cathodic polarization curves, after 1 day (24 hrs) of exposure. Rotation rate = 0 rpm; inhibitor concentration = 0, 25 and 200 ppm.

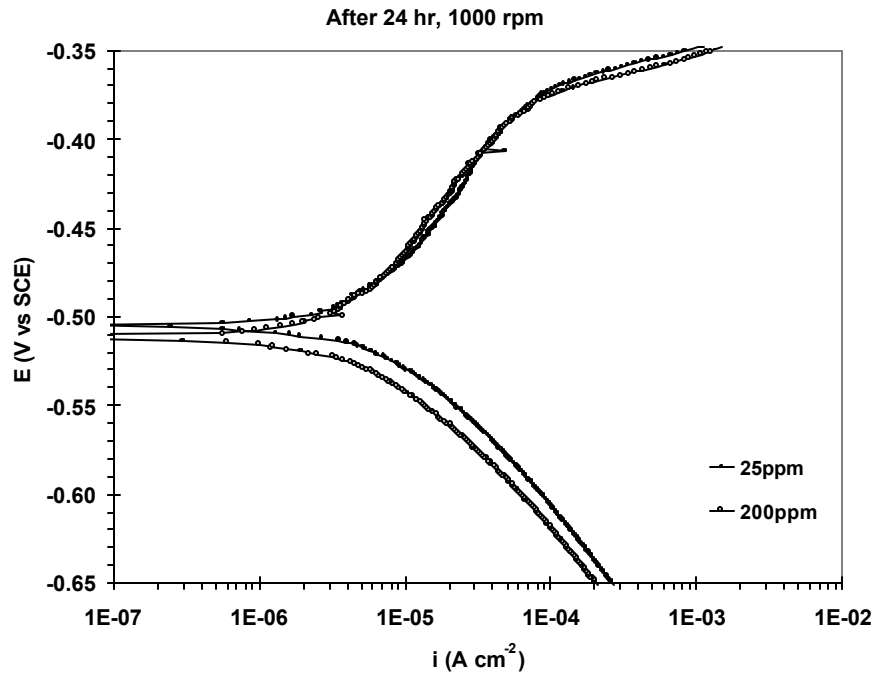


Figure 2.- Anodic and cathodic polarization curves, after 1 day (24 hrs) of exposure. Rotation rate = 1000 rpm; inhibitor concentration = 25 and 200 ppm.

The following tables summarize the electrochemical parameters: anodic and cathodic Tafel slopes (b_a and b_c), corrosion potential (E_{corr}), corrosion current density (j_{corr}) and Stern-Geary constant (B), calculated from the polarization curves shown in Figures 1 and 2.

Table 1. Electrochemical parameters calculated from Figure 1 (0 rpm, 0 ppm).

	b_a V decade ⁻¹	b_c V decade ⁻¹	E_{corr} V vs SCE	j_{corr} A cm ⁻²	B V
Anodic	0.0782	-	-0.5003	2.87×10^{-5}	0.0176
Cathodic	-	0.0843	-0.5083	7.45×10^{-5}	

Table 2. Electrochemical parameters calculated from Figure 1 (0 rpm, 25 ppm).

	b_a V decade ⁻¹	b_c V decade ⁻¹	E_{corr} V vs SCE	j_{corr} A cm ⁻²	B V
Anodic	0.0721	-	-0.4905	2.18×10^{-5}	0.0167
Cathodic	-	0.0821	-0.5037	4.53×10^{-5}	

Table 3. Electrochemical parameters calculated from Figure 1 (0 rpm, 200 ppm).

	b_a V decade ⁻¹	b_c V decade ⁻¹	E_{corr} V vs SCE	j_{corr} A cm ⁻²	B V
Anodic	0.0729	-	-0.4932	1.23×10^{-5}	0.0163
Cathodic	-	0.0776	-0.4997	2.23×10^{-5}	

Table 4. Electrochemical parameters calculated from Figure 1 (1000 rpm, 25 and 200 ppm).

	b_a V decade ⁻¹	b_c V decade ⁻¹	E_{corr} V vs SCE	j_{corr} A cm ⁻²	B V
25 ppm	0.1259	0.1011	-0.5057	9.59×10^{-6}	0.0244
200 ppm	0.1105	0.1046	-0.5125	9.48×10^{-6}	0.0233

Corrosion rate

Using the data obtained from the EIS analyses and the data obtained from the linear polarization resistance (R_p) experiments, the instantaneous corrosion current density values (j_{corr}) can be estimated, using the values of Stern-Geary constants from tables 1 to 4. The variation of j_{corr} with time and inhibitor concentration, at 0 rpm, is shown in Figure 3.

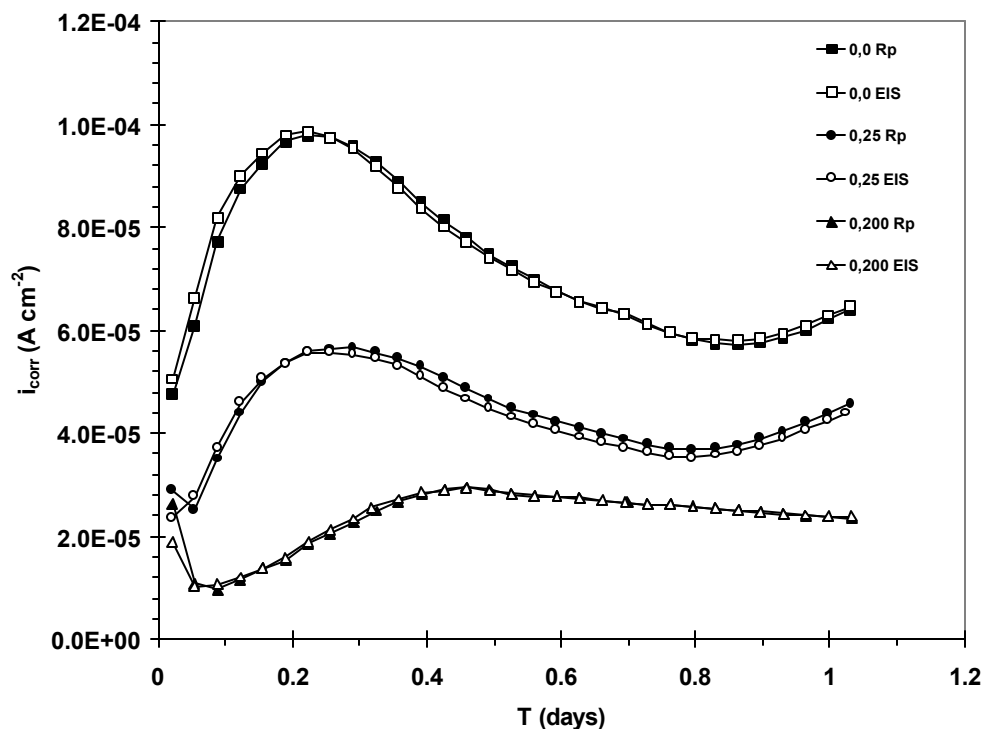


Figure 3.- Values of j_{corr} , estimated by EIS and R_p , as a function of time and inhibitor concentration. Rotation rate = 0 rpm. Legends: the first number indicates rotation rate, the second number indicates inhibitor concentration, the letters indicate the electrochemical technique used.

Figure 3 demonstrates the dependency of the measured j_{corr} with inhibitor concentration. As the inhibitor concentration increases the measured corrosion rate decreases. This is a somehow expected result. It is interesting to note the feature that shows that at the beginning of the experiment j_{corr} increases with time and then decreases to a steady value. This feature can be observed at 0 and 25 ppm. However, at 200 ppm of inhibitor concentration, the tendency of j_{corr} is to decrease at the beginning of the experiment and to increase up to a steady value. This behavior suggests that the surface of the electrode is changing with time and therefore the inhibitor surface concentration is also changing with time.

Figure 4 shows the measured dependency of j_{corr} with time and inhibitor concentration, at a rotation rate of 1000 rpm. The axis limits in Figure 3 are maintained in Figure 4, in order to facilitate comparison.

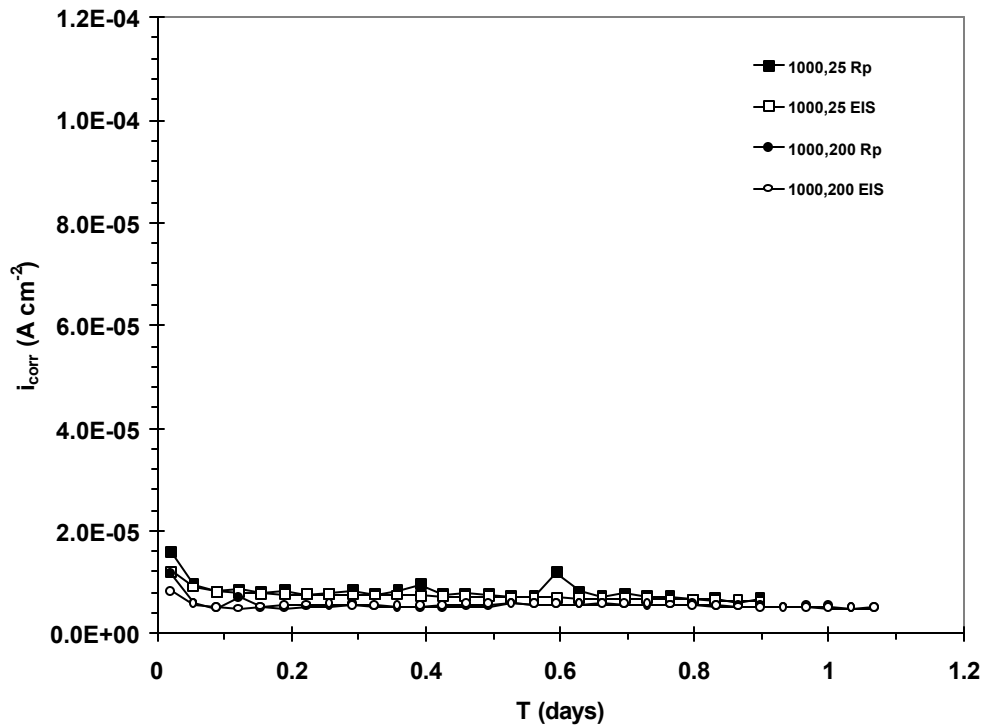


Figure 4.- Values of j_{corr} , estimated by EIS and R_p , as a function of time and inhibitor concentration. Rotation rate = 1000 rpm. Legends: the first number indicates rotation rate, the second number indicates inhibitor concentration, the letters indicate the electrochemical technique used.

Figure 4 demonstrates that, at 1000rpm, j_{corr} is independent of the inhibitor concentration. The calculated values of j_{corr} are practically the same, at bulk concentrations of inhibitor of 25 and 200 ppm of inhibitor. These results indicate that, the controlled hydrodynamics favours inhibitor migration from the bulk of the solution towards the surface of the electrode. This increased migration rise inhibitor concentration and coverage at the surface of the electrode, decreasing j_{corr} .

It is also interesting to note the excellent correlation between the j_{corr} values calculated by EIS and R_p .

Figure 5 shows the calculated instantaneous efficiency of the inhibitor, referred to the values of j_{corr} at 0 rpm and 0 ppm of inhibitor bulk concentration. This Figure demonstrates that the calculated efficiency of the inhibitor reaches a maximum value of about 94% at a concentration of 200 ppm and 0 rpm, and then decreases with time to values of about 60%.

At a rotation rate of 1000 rpm and 25 ppm bulk concentration of inhibitor, a maximum value of efficiency of about 92% is reached and then decreased to a value of 90% approximately. This value of efficiency is practically constant during all the testing time.

At a rotation rate of 1000 rpm and a 200 ppm bulk concentration of inhibitor, a maximum value of efficiency of about 95% is reached and then decreased to a value of 92% approximately. This value of efficiency is practically constant during all the testing time.

It is clear that the efficiency of the tested inhibitor is strongly dependent on the flow conditions of the system.

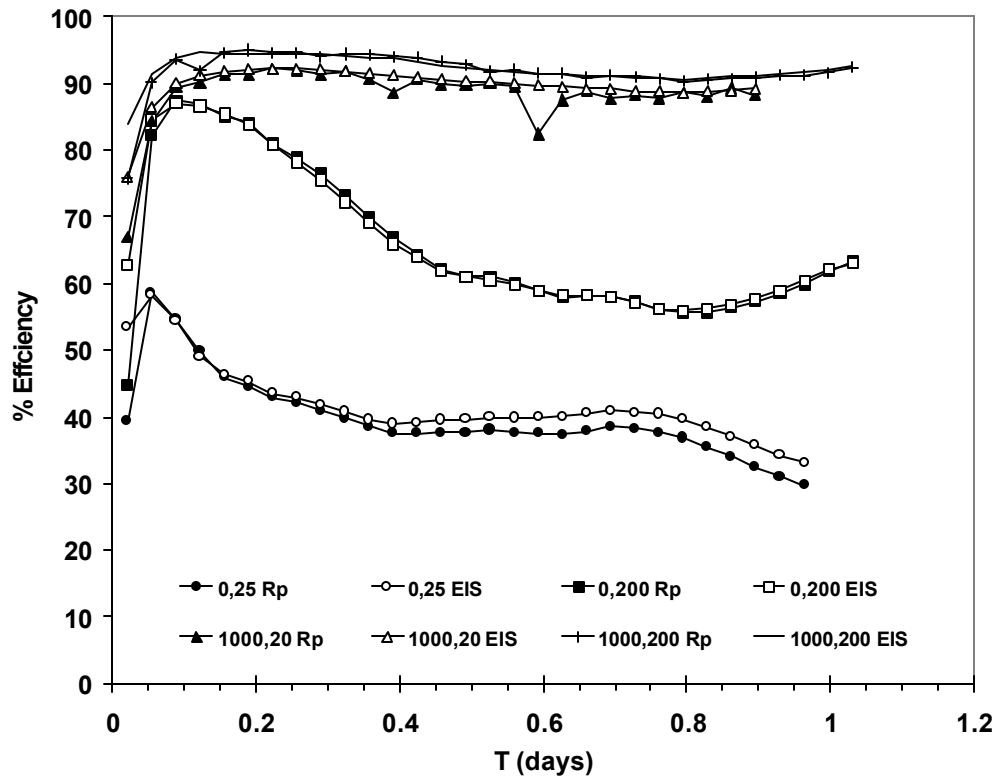


Figure 5.- Estimated values of efficiency of the inhibitor calculated by EIS and R_p , as a function of time, inhibitor concentration and rotation rate. Legends: the first number indicates rotation rate, the second number indicates inhibitor concentration, the letters indicate the electrochemical technique used.

Corrosion potential (E_{corr}).

Figure 6 shows the variation of the measured corrosion potential (E_{corr}) with time, rotation rate and inhibitor concentration. In general, at a rotation rate of 0 rpm E_{corr} increases as the concentration of the inhibitor increases. However at a rotation rate of 1000rpm E_{corr} decreases dramatically in comparison with the values measured at 0 rpm. This behavior is consistent with the previous observations.

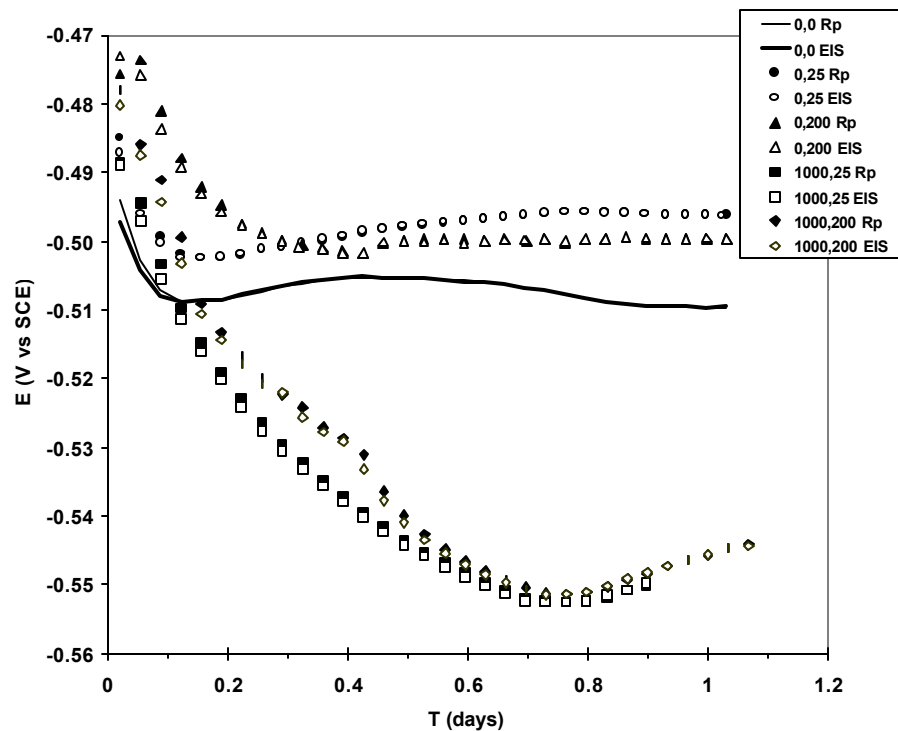


Figure 6.- Measured values of E_{corr} as a function of time, inhibitor concentration and rotation rate. Legends: the first number indicates rotation rate, the second number indicates inhibitor concentration, the letters indicate the electrochemical technique in which the E_{corr} was measured.

CONCLUSIONS

DC electrochemical techniques and their applications in the corrosion study of materials have been demonstrated. These techniques provide a powerful tool for corrosion and electrochemical kinetics study.

The extent to which the techniques “Linear Polarization Resistance”, LPR, and “Tafel Extrapolation Method”, can be applied in order to obtain reliable determinations of instantaneous corrosion rates in a particular environment has been studied.

Regarding the behavior of the 3-amino-1,2,4, triazole, as a corrosion inhibitor, the results obtained in this work support the following conclusions:

- The inhibiting effect of the tested substance is strongly dependent on the hydrodynamic conditions of the environment. As the turbulence of the environment increases, the efficiency of the inhibitor also increases. This increment is associated to an increased migration of the inhibitor, from the bulk of the solution towards the surface of the corroding electrode. This increased migration can generate a better coverage of the surface of the corroding electrode and therefore a decrement of j_{corr} .
- When the efficiency of this inhibitor is estimated, controlled hydrodynamic conditions must be taken into account. Otherwise the value of efficiency can be underestimated.

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