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# Review of the Application of Gravimetric and Electrochemical Techniques to Evaluate Corrosion Mechanisms in Metal Materials



**Abstract:** - Corrosion in carbon steels is a phenomenon that causes degradation of mechanical properties; iron alloys are susceptible to corrosion. Factors such as changes in temperature, pH of the medium, and humidity accelerate the corrosion process, and the oxides formed can generate irreversible changes to the material. The evaluation of surface corrosion is necessary to be able to predict in time, to be able to provide good maintenance whether by coatings, inhibitors, or anticorrosive paints, in an opportune way, and to avoid large economic and structural losses. Gravimetric techniques such as mass loss and electrochemical techniques such as Open Circuit Potential-OCP and Electrochemical Impedance Spectroscopy-EIS, help understand the different corrosion mechanisms, simulate real conditions, and generate reproducible studies with efficiency of time and interpretation. This work shows a brief review of gravimetric and electrochemical techniques applied to the evaluation of corrosion of carbon steels.

**Keywords:** corrosion, carbon steel, EIS, Mass loss, OCP

## 1. Introduction

Materials are important for human activities, they allow us to apply them to different industrial sectors, exposed to some factors such as radiation, temperature, humidity, pH changes, among others, they can generate degradation, that is, the loss of their mechanical properties [1-3]. The term corrosion is attributed to the damage caused to metallic materials, which is favored by the wet exposure of the metals [4-7]. Corrosion is a natural phenomenon that can be produced via chemistry or electrochemistry (ion transfer) which results in most cases, the damage occurs at the surface level, where electrons tend to be lost in the presence of oxygen, and oxidation and reduction reactions occur. All metals have an electrochemical potential which will determine their susceptibility to developing corrosion; this value will depend mainly on their chemical composition [1-58]. The nobler materials have the most positive corrosion potential, indicating greater resistance to corrosion. corrosion as is the case of platinum, gold, and silver, on the other hand, the more negative potentials indicate greater ease of developing corrosion as is the case of steel, alloys, and magnesium, zinc [5].

Corrosion is considered a critical problem in the industry, causing direct and indirect damage that is generated, from the change of materials, greater demand for materials, immediate implementation, costs of operators, maintenance, cost of human losses in case of accidents, spills of oil, fires generating environmental and social problems if communities are affected. Corrosion estimates an investment of up to 40% of costs in the United States industry. [4-8]. That is why corrosion studies are important to understand the mechanism, type of corrosion, and causes in order to provide adequate and timely maintenance [3-6].

Corrosion is a spontaneous destruction process that metals experience in contact with the environment, turning into oxides, which produces a gradual deterioration of them. In metals, corrosion is a permanent process; since these are always in contact with water, oxygen in the air, and in recent years, with acid rain, which are the agents that mainly influence the development of corrosion. At the same time, in coastal areas, the problem is intensified due to the saline environment. Cases of deterioration caused by corrosion range from falling bridges, pipe failures, spills, and serious damage to engines, and machines. [5-8].

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Steel is an alloy formed by carbon iron. Being a ferrous alloy, it oxidizes easily in the presence of humidity, in the presence of NaCl. However, steel is an extremely mechanically resistant material, which is why they have a great diversity of applications from components in machines, transportation, bodies, and pipes. The preference is due to the fact that it is a versatile, low-cost material that is easy to cut and weld. [5-6]. Corrosion being one of the main chemical damages in steel, corrosion studies become more than necessary and fundamental for the approval of materials and verification of quality of life. Electrochemical techniques are based on the electrical properties of the analyte in solution when it is part of an electrochemical cell. The physicochemical processes that have a relationship between the chemical reaction and electricity are studied; these occur at the interface between a chemical conductor and an ionic conductor (REDOX). In REDOX reactions (oxidation-reduction) there is a transfer of electrons between a species that undergoes a reduction process and a species that undergoes oxidation. In oxidation, they lose electrons and in reduction, they gain electrons. The advantages of these techniques are: - They allow you to study not only the element but also the oxidation state in which it is found - Many times in this technique, instead of talking about concentration, we talk about activity. This concept is due to the fact that when the amount of fluid increases, the interactions between solute molecules are increasingly important, and therefore not all molecules are available to act in chemical reactions, therefore we cannot speak of total concentration but rather effective concentration or activity. - Simple and cheap instrumentation

In voltammetric analysis, the current intensity that passes through an electrode is measured by applying a potential difference. The different voltammetric techniques are essentially distinguished by the different way of variation of the applied potential. It can be said that the evolution introduced in the type of modulation of the potential shape has resulted from constant research aimed at reaching increasingly lower detection limits, not forgetting that the most advanced voltammetric techniques, with the use of more complex forms of potential modulation, are generally associated with lower detection limits [7-10]. Below, the different pulse voltammetric techniques are summarized with the respective forms of potential modulation and detection limits. The designations of the symbols presented there are the following: time interval referring to the period of a cycle;  $t$ : pulse duration time;  $E_i$ : initial potential;  $\Delta E$ : potential step between each cycle;  $A$ : impulse amplitude;  $t_1$ , and  $t_2$ : times at which the current intensity measurement is carried out. The voltammetric method of chemical analysis is based on the interpretation of the current intensity - potential curves,  $i$  vs.  $E$ , resulting from the electroreduction or electrooxidation of the species in solution [5-12].

To understand electrochemistry the following concepts are of great importance to know:

- Electrolyte. A substance that conducts electrical current in solution.
- Electrode. Conductors, normally metallic, placed in contact with the electrolyte solution.
- Electrochemical tank. Container that contains the solution and the electrodes.
- Battery, cell or electrochemical cell. Set of electrodes, cable, solution and tank.
- Anode. electrode where oxidation of an electrolyte occurs.
- Cathode. electrode where reduction occurs.

Electrochemical cells are devices used for the decomposition of ionized substances by electrical current and are called electrolytes. These cells are also known as galvanic or voltaic cells, in honor of the scientists Luigi Galvani and Alessandro Volta, who manufactured the first of this type in the late 18th century [5-12].

Electrochemical cells have two electrodes, the anode and the cathode. The anode is defined as the electrode where oxidation takes place and the cathode where reduction takes place. The electrodes can be made of any material that is an electrical conductor, such as metals, or semiconductors. Graphite is also widely used due to its conductivity and low cost. To complete the electrical circuit, the solutions are connected through the salt bridge. The dissolved cations move towards the cathode and the anions towards the anode. The electric current flows from the anode to the cathode because there is an electric potential difference between electrolytes. This difference is measured with the help of a voltmeter and is known as the cell voltage. It is also called electromotive force (emf) or as cell potential. In a galvanic cell where the anode is a Zincin bar and the cathode

is a Copper bar, both immersed in solutions of their respective sulfates [6-14].

Currently, the applications of electrochemistry are many. Let's look at some of them: Currently, the applications of electrochemistry are many. Let's look at some of them: Batteries take advantage of the natural tendency of many substances to accept or give up electrons during certain chemical transformations. If a substance with a tendency to give up electrons is combined with another substance eager to capture them, a redox reaction occurs spontaneously. You can find saline, alkaline, lithium-manganese oxide, lead-acid batteries, and many more. Biosensors are analytical devices consisting of a bioreceptor for the detection of biological species (analytes) and a transducer that converts the biological signal into a measurable electrical signal. This signal is proportional to the compound to be detected and can contain quantitative and qualitative information [6-14].

An important industrial application of electrolysis is the electric furnace, which is used to make aluminum, magnesium, and sodium. In this furnace, a charge of metal salts is heated until it melts and ionizes. The metal is then electrolytically deposited. In short, electrochemistry studies the transformation between electrical energy and chemical energy. The field of electrochemistry has been divided into two: The first is related to electrolysis, which refers to the chemical reactions that occur through the action of an electric current. They are also known as oxidation-reduction or 'redox' reactions, and their importance in electrochemistry is vital, since through this type of reaction the processes that generate electricity are carried out or, otherwise, they are produced as a consequence of it. The second field is the galvanic or electrochemical cells that are related to the chemical reactions that generate an electric current. The cells have two electrodes, the anode and the cathode. The anode is the electrode in which oxidation takes place and the cathode where the reduction is carried out. To complete the electrical circuit, the solutions are connected through the salt bridge. The electrodes can be made of any material that is an electrical conductor, such as metals, or semiconductors. Electrochemistry has various uses, among which batteries, biosensors, and alcohol control systems, among others, stand out. [6-14].

## 2. ELECTROCHEMICAL TECHNIQUES

### 2.1 POLARIZATION POTENCIODINAMIC

Potentiodynamic polarization techniques are an electrochemical technique that allows controlling the potential and current in a system composed of a working electrode, an auxiliary electrode and a reference electrode. Through the application of a variable voltage, it is possible to generate a current that is recorded and analysed to obtain information about the electrochemical reactions that occur in the sample [6-10].

- **Benefits of potentiodynamic**

The potentiodynamic offers a series of benefits that make it attractive for use in different applications. Some of the main benefits are:

- ❖ **Precise voltage control:** allows the voltage applied to the electrochemical system to be precisely established and controlled, which facilitates the study of different phenomena and reactions.
- ❖ **Wide current range:** The potentiodynamic can work with currents ranging from microampere to ampere, allowing it to adapt to a wide range of samples and experiments.
- ❖ **Adjustable scan speed:** It is possible to adjust the speed at which the potential is varied, allowing the study of electrochemical reactions that occur on different time scales.

- **Potentiodynamic characteristics**

- ❖ **Voltage control:** One of the key features of potentiodynamics is the ability to control the voltage applied to the electrochemical system. This is achieved through a potentiostat, which is responsible for maintaining the potential of the reference electrode constant and applying variable potentials to the working electrode. This precise voltage control is essential for studying and analyzing electrochemical reactions.

- ❖ **Current range:** Another important characteristic of the potentiodynamic is its ability to work with a wide range of currents. This allows it to be adapted to different types of samples, from small quantities to

highly concentrated solutions. This flexibility in the current range makes it versatile and applicable in various areas of research and development.

- ❖ **Sweep speed:** The scan rate refers to the speed with which the potential applied to the electrochemical system is varied. The potentiodynamic allows this speed to be adjusted according to the needs of the experiment. For example, in electrochemical reactions that occur rapidly, a high scan rate can be used to capture changes in current more accurately [6-14].

- **Potentiodynamic applications**

- ❖ **Electrochemistry:** Potentiodynamics is widely used in the field of electrochemistry to study and understand electrochemical reactions. It is used to investigate reaction kinetics, determine reaction mechanisms, and analyze the stability of materials and compounds, among others. In addition, it is a useful tool in electrochemical synthesis, allowing the formation of desired products to be controlled and optimized.

- ❖ **Scientific investigation:** In scientific research, potentiodynamics is used in a variety of disciplines, such as chemistry, physics, biology, and materials science. It allows you to study and characterize electrochemical materials and systems, perform electrochemical impedance analysis, analyze the corrosion of materials and develop new methods and techniques of electrochemical analysis [6-8].

- ❖ **Pharmaceutical industry:** In the pharmaceutical industry, potentiodynamics is used to research and develop new drugs. It allows evaluating the stability and electrochemical behaviour of active compounds, as well as studying the release of drugs in controlled release systems. It is also used in the manufacture of medical devices and electrochemical sensors [6-8].

- **How potentiodynamic works**

- ❖ **electrode system:** The electrode system in the potentiodynamic consists of three electrodes: the working electrode, the auxiliary electrode, and the reference electrode. The working electrode is the one that is in direct contact with the sample and where the electrochemical reactions of interest occur. The auxiliary electrode is responsible for allowing current flow to the working electrode, while the reference electrode is used to establish a constant reference potential.

- ❖ **Control software:** The potentiodynamic is associated with control software that allows you to configure and control the measurement parameters, as well as analyze the data obtained. Through this software, it is possible to set the voltage range, sweep speed, and other parameters relevant to the experiment. Additionally, the software provides the ability to view and analyze data in real-time, as well as perform calculations and graphs to interpret the results [9].

- **How to use the potentiodynamic**

- ❖ **Step 1: Sample Preparation**

Before starting the experiment, it is important to properly prepare the sample. This may involve preparing solutions, conditioning solid samples, or cleaning electrodes. It is essential to follow recommended procedures to ensure reliable results.

- ❖ **Step 2: Computer Setup**

Once the sample is prepared, the potentiodynamic equipment must be configured. This involves setting measurement parameters such as voltage range, scan speed, and measurement duration. You must also ensure that the electrodes are correctly connected and that the software is configured according to the needs of the experiment.

- ❖ **Step 3: Taking the measurement**

Once the equipment is configured, you can proceed to perform the measurement. This involves applying the programmed voltage to the working electrode and recording the current generated. It is important to take into

account the measurement time and take the necessary readings to obtain accurate results. During measurement, adjustments can be made in real time through the control software [9].

#### ❖ Step 4: Analysis of results

Once the measurement is completed, the results obtained are analysed. This involves using control software to analyze the recorded data, perform calculations and generate representative graphs. The analysis of results allows us to interpret the electrochemical reactions that occurred in the sample and obtain relevant conclusions for the experiment.

#### • Considerations when using the potentiodynamic

#### ❖ Security measures

When using the potentiodynamic, it is important to follow the recommended safety measures. This involves working in an appropriate environment, using personal protective equipment, and following guidelines for handling chemicals and hazardous materials. Likewise, specific precautions for the use of electrical equipment and the handling of potentially hazardous samples must be considered [10-16].

#### ❖ Equipment maintenance

The potentiodynamic requires regular maintenance to ensure its correct operation and prolong its useful life. This involves cleaning the electrodes regularly, calibrating the equipment according to the manufacturer's instructions, and performing periodic inspections to detect possible failures or wear. In addition, it is important to follow the recommendations for storage and handling of the equipment when it is not in use. In figure 1 a model diagram of the polarization curves with their main components and their respective units is shown. This is a graphic representation of the results obtained by applying this technique[10-16].

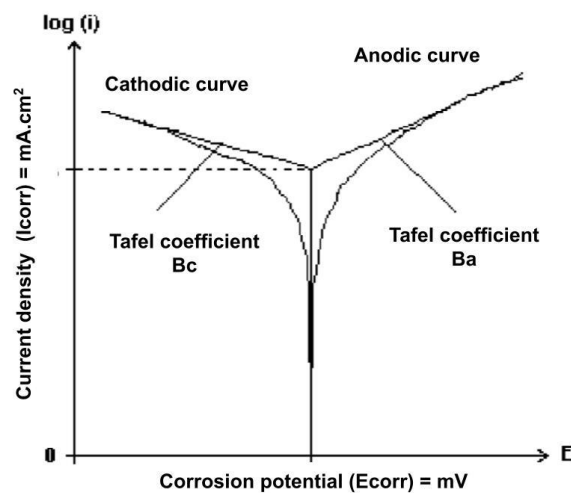


Figure 1. Graphics of powerful dynamic measurements by polarization curves and their components.

## 2.2ESPECTROSCOPY IMPEDANCE-EIS

During the last three decades, the EIS technique has proven to be advantageous for the characterization of oxide layers on the surface of metals. This technique requires minimally invasive procedures and from the data obtained in the electrochemical tests, it is possible to obtain information on the dissolution of the passive layer (in terms of speed and type of control) and the characteristics of the passive layer (thickness, dielectric constant of the passive layer, diffusion coefficient of the diffused species, etc.). An impedance spectrum obtained in response to the small amplitude excitation signal is frequently interpreted in terms of an equivalent electrical circuit, which is based on a possible physical model whose elements represent and characterize the electrochemical properties of the oxide layers. and its structural characteristics or the physical-chemical process

that takes place in the study system. Depending on whether the oxide layer has a monolayer or multilayer structure, if it is porous or if the charge transfer process is affected by diffusive limitations, the spectrum over a wide range of frequencies could present one, two or more-time constants at the cause of the previous characteristics and processes [14-18].

Techniques based on the concept of impedance. Fundamentals. Faradaic impedance. ac circuit Concept of impedance. Nyquist and Bode representations. Equivalent circuit of an electrochemical cell: Randles circuit, components. Interpretation of faradaic impedance. Characteristics of the equivalent circuit. Properties of the chemical system. Kinetic parameters from impedance measurements. Electrochemical impedance spectroscopy. Variation of the total impedance of the cell. Limit for high and low frequencies. Analysis of EIS data is commonly carried out by fitting it to an equivalent electrical circuit model. An equivalent circuit model is a combination of resistances, capacitances and/or inductances, as well as some specialized electrochemical elements in the model, each component of the circuit comes from a physical process in the electrochemical cell and has a characteristic impedance behavior. The shape of the impedance spectrum of the model is controlled by the style of the electrical elements in the model and the interconnections between them. The equivalent circuit should be as simple as possible to represent the electrochemical system and should provide the best possible match between the model impedance and the measured impedance of the system [14-18].

Bode and Nyquist curves. The impedance spectrum of an electrochemical system can be presented in Nyquist and bode graphs, which are representations of impedance as a function of frequency. Given the support for graphs measured in KHz, alternating current signals applied to an electrode are normally used. The bode diagram represents the steady state of a linear system invariant in time; it is varied on a synodal scale when the value of the varies frequency until the range to be handled is covered. The representation of the frequency response of the open loop system is done through two graphs for magnitude (logarithmic scale “ $\log |Z| - \log w$ ”) and for phase (linear scale “ $\emptyset - \log w$ ”). Both graphs generally start at a high frequency and end at a low frequency, allowing initial resistance to be found more quickly. The Nyquist diagram in signal processing to evaluate the stability of a feedback system, represented by a graph in polar coordinates. for the experimental data set  $Z$  ( $Z_{re} j$ ,  $Z_{im} j$ ,  $w_i$ ), ( $i=1, 2, ,n$ ) of  $n$  points measured at different frequencies, where each point represents the real and the imaginary [9-10]. Figure 2 presents the Nyquist diagram of electrochemical test results by EIS, showing a comparison of some materials such as the highest resistance to carbon steel, followed by ASTM A36 steel, AISI 1020 and finally cast irons. These diagrams show the maximum resistance to charge transfer in 3.5 M NaCl medium[14-20].

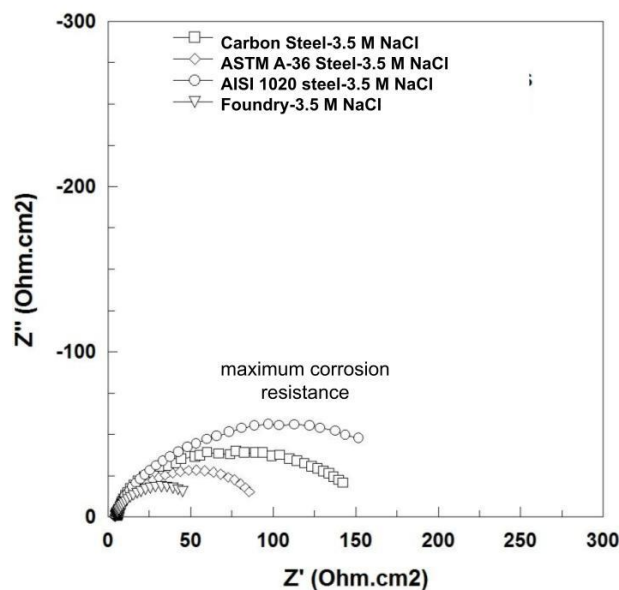


Figure 2. Comparative Nyquist diagram for metallic materials in 3.M NaCl medium

### 3. Conclusions

- Electrochemical EIS techniques facilitate the study of metallic materials, are reliable, reproducible, and reduce analysis time.
- Polarization techniques are recommended for studies to determine mass loss and as a complementary stage to corrosion studies where there is time since, despite being reliable, the execution time takes longer.

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