STUDY OF CORROSION OF 13 Cr STAINLESS STEEL UNDER ALTERNATING CURRENT IN ARTIFICIAL SEAWATER

by

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ABSTRACT

Corrosion due to alternating current (AC) of the 13 Cr supermartensitic stainless steel has been investigated in the context of the direct electrical heating system (DEH) in artificial seawater, for 40, 240, and 500 A/m² AC densities.

A shift of the DC potential when the AC started passing was confirmed. Pitting was the type of damage observed for the three current densities and it was more intense for increasing current densities. Polarization curves performed while applying AC were successful in showing the passive behavior of the metal. The curves were shifted toward higher current densities and had more negative corrosion potentials. Passivation proved to be less effective. This behavior was evidenced by higher passive current densities and smaller passive ranges with lower pitting potentials when increasing the AC density applied.

Corrosion in the presence of alternating magnetic fields of 49.1 and 56.8 G seemed to be accelerated. Stirring of the electrolyte caused by Lorentz forces was evidenced by changes in the double layer CPE behavior. Corrosion due to AC under magnetic fields formed corrosion products different than those formed in the absence of magnetic fields, the products looked more planar and ordered. Polarization curves performed under AC and magnetic fields showed higher passive current densities, indicating that the modified passive layer formed under the influence of magnetic fields is not necessarily more protective. In general, accelerated reaction rates were observed in the polarization curves performed under magnetic fields, however, the influence seemed stronger for anodic processes than for cathodic processes.

A thermodynamic and kinetic model for corrosion due to AC was presented. The model redefined the Nernst equation for a situation where AC is applied, revisited the concept of overpotential, and finally, solved the Butler-Volmer equation for a poten-
tial with a DC and a sinusoidal alternating components, \( E(t) = E_{bias} + E_V \sin(\omega t) \). The model predicts a deformed sinusoidal current wave strongly influenced by the asymmetry of the Tafel slopes. The model predicts the rectification current (DC component of the resulting current wave) due to the application of the mentioned potential perturbation. The behavior of the rectification current is predicted to be different than a typical Butler-Volmer type of behavior for situations when the sinusoidal part of the potential is dominant. For small potential wave amplitudes, the model predicts a Butler-Volmer type of behavior of the rectification current.
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CHAPTER 1
INTRODUCTION

Corrosion is a destructive attack or degradation of a metal due to its chemical or electrochemical interaction with the surroundings. Other types of degradation, not called corrosion, are erosion and wear which often times occur simultaneously with corrosion. This is the case of corrosion-erosion or stress-corrosion-cracking [1].

The costs of corrosion control, prevention and maintenance of metallic structures have a significant impact on the U.S. economy. Many areas are involved such as:

- Infrastructure, $22.6 billion (16.4%)
- Transportation, $29.7 billion (21.5%)
- Production and manufacturing, $17.6 billion (12.8%)
- Utilities, $47.9 billion (34.7%), and
- Government, $20.1 billion (14.6%) [2, 3].

While the cost of corrosion is one of the most important reasons why corrosion receives so much attention, it is not the only one. Corrosion is important for safety and conservation too. Safety of personnel, public safety, and the integrity of infrastructure are all related in some degree to corrosion determining frequency of inspection, maintenance, replacement, etc.

A broad variety of technologies to minimize corrosion is available such as paints, coatings, cathodic protection, decoupling devices, corrosion inhibitors, and others. However, they are not perfect and corrosion technicians and engineers must monitor the advance of corrosion to make sure that the corrosion rate stays within acceptable limits, and if not, to take the actions to correct the problem.
Although corrosion is considered from the outset of the design of a project, often times certain interactions occur that were not considered in the original design that can result in higher corrosion rates. Such is the case of ground systems of buildings and underground pipelines. These infrastructures can be totally independent, however, over time they can start interacting causing serious damage. The buried pipeline can locally corrode due to AC stray currents from the ground system.

AC corrosion is observed in pipelines parallel to high voltage AC power transmission lines, or to rail systems [4]. It also occurs in marine environments because of improper welding operations, battery charging or even steam generating plants [5, 6]. A substantial amount of work has been done to study AC corrosion from a fundamental and engineering point of view, however, it still remains subject to controversy.

The motivation for studying corrosion due to AC of 13 Cr supermartensitic stainless steel is the necessity of understanding the interaction of the direct electrical system with the pipeline. Although AC corrosion was considered during the design of the direct electrical system, a clearer understanding of the mechanism and severity of AC corrosion in artificial seawater is necessary. For the same reason, the study of possible interactions with the AC magnetic field generated is justified.

The objectives of the present research can be summarized as follows:

- To achieve an accurate and thorough understanding of the mechanisms and severity of applied AC currents on the corrosion of 13 Cr supermartensitic stainless steel in seawater in the context of the direct electrical heating system

- To assess the change in susceptibility to localized corrosion and passivation with and without AC

- To assess the effect of AC magnetic fields on AC corrosion
• To assess the criteria for cathodic protection when in the presence of AC: effectiveness and risk of overprotection

• To understand the fundamentals of thermodynamics and electrode kinetics in the presence of AC
CHAPTER 2
LITERATURE REVIEW

The following sections will cover a description of the alloy under study, a review of basic concepts of electromagnetism, general concepts of corrosion, the analytical techniques used throughout the present study, and finally a description of the direct electrical system (DEH) which sets the parameters to be considered in this research.

2.1 Stainless Steel 13 Cr

Additions of 12 wt. pct. and above of chromium to steel result in alloys with different degrees of corrosion resistance and are better known as stainless steels. There are a number of groups of stainless steel further divided in different types with specific characteristics. The major criterion for classification of stainless steel is its microstructure: ferritic, austenitic, duplex and martensitic [7].

Martensitic grades have a low chromium content (11-13 wt. pct.), are ferromagnetic, and are hardenable by heat treatment. Their high resistance to atmospheric corrosion makes them superior to other steels, but in comparison with other high alloyed grades their use is limited to rather mild environments [7].

The 13 Cr supermartensitic stainless steel was created as an economically viable alternative to higher alloyed stainless steels. It is used in the oil industry because of its high strength and excellent corrosion resistance in CO\textsubscript{2} gas wells [8]. It also exhibits a good corrosion resistance to light sour environments. Besides its relatively low chromium content, it also has relatively low carbon, nickel and molybdenum content. These steels have increased nickel content which expands the austenite loop of the phase diagram, allowing heat treatment to transform the austenite to martensite. The low content of carbon (usually less than 0.10 wt. pct.) in combination with nickel (in the range of about 6 wt. pct.) grants it toughness. Overall, 13 Cr
supermartensitic stainless steel offers an attractive balance of mechanical properties, corrosion resistance and cost [9].

Supermartensitic 13 Cr stainless steel is comparable to types AISI 420 and 410, with lower carbon content and higher content of nickel and molybdenum. Table 2.1 shows the composition of the mentioned alloys. The content of carbon, nickel and molybdenum are the key modifications.

Table 2.1: Chemical composition (wt. pct.) of three types of stainless steel

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<tbody>
<tr>
<td>C</td>
<td>0.15</td>
<td>0.06-0.4</td>
<td>0.03-0.22</td>
<td>0.008</td>
</tr>
<tr>
<td>Mn</td>
<td>1</td>
<td>0.5-1</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>Si</td>
<td>0.65-1.5</td>
<td>1-1.5</td>
<td></td>
<td>0.26</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
<td>0.04-0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.04</td>
<td>0.04-0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>11.5-14</td>
<td>10.5-14</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>1-8</td>
<td>4-5</td>
<td>6.4</td>
</tr>
<tr>
<td>Other elements</td>
<td>0.15-1 Mo</td>
<td>0.5-1</td>
<td>1-2</td>
<td>2.2 Mo, 0.006 Cu, 0.06 N</td>
</tr>
</tbody>
</table>

The addition of nickel, copper, nitrogen and carbon promote the formation of austenite which is the precursor phase of martensite. Nickel usually increases the ductility and toughness of steels. The low carbon content improves the weldability and reduces the risk of formation of chromium carbides.

13 Cr alloy is designed for applications where the corrosion resistance requirements are relatively mild, while high strength and toughness are required [12]. Extensive research on weldability, hydrogen permeation, and stress-corrosion-cracking susceptibility of this alloy has been done in recent years. The motivation has been the potential cost saving that would result if 13 Cr alloy could replace other more expen-
2.2 Electromagnetism

Magnetism is the property of materials that occurs in response to a magnetic field. The elementary magnetic element is the magnetic dipole. For example, a magnetic dipole exists whenever a current, \( I \), is conducted in a wire forming a loop on a plane and enclosing an area, \( A \); the magnetic moment is given by Equation 2.1.

The magnetic moment is a vector perpendicular to the plane where the loop exists and its direction is given by the right hand rule.

\[
m = I A
\]  

The torque experienced by the magnetic moment when a magnetic field is applied is given by \( T = \vec{m} \times \vec{H} \). The summation of all the dipole moments give the magnetization, \( M \).

When dealing with the magnetic properties of matter, one must consider what occurs at the atomic level. Here, the two sources of magnetic moment are the orbital angular momentum of the electrons of the atom (analog of a current loop) and the intrinsic electron angular momentum (electron spin). On a microscopic scale, magnetic domains describe regions with uniform magnetization; that is, regions where magnetic moments of the atoms are aligned and pointing in the same direction. Magnetic domains are responsible for the magnetic behavior observed macroscopically.

Ferromagnetic materials like iron, nickel, cobalt and some of their alloys, exhibit a persistent magnetic moment due to spontaneous ordering of moments even in the absence of an external magnetic field. Ferromagnetic materials have unpaired electrons in their outer electron shell (incomplete d or f-shell) which are responsible for the magnetic response to external magnetic fields. The spin of the unpaired electrons is the main source of ferromagnetism. When these small dipoles align in the same direction, they create a macroscopically measurable field. In the case of materials whose
outer shell is filled, no macroscopic field can be measured as the outer electrons are paired and have zero magnetic moment.

At sufficiently high temperatures the ordering of the dipoles is lost, and the material undergoes a transformation from ferromagnetic to paramagnetic. This temperature is known as Curie temperature. The crystal structure also plays a role in the magnetic behavior, which is believed to be the reason why elements like chromium and manganese, with five unpaired electrons, are not ferromagnetic [17].

To understand the behavior of magnetic materials, one must understand the relationship between magnetic flux density \( B \), and magnetic field intensity \( H \) (Equation 2.2).

\[
B = \mu H = \mu_r \mu_0 H
\]  

(2.2)

The factor \( \mu \) is called the magnetic permeability of the material. Often times, it is factored as shown in Equation 2.2 as the product of the free space permeability \( (\mu_0 = 4\pi \times 10^{-7} \text{ H/m}) \) and the relative permeability. For insulators and air, \( \mu_r \) is usually equal to 1 while it can vary from hundreds to thousands for ferromagnetic materials.

Although the magnetic flux density is proportional to magnetic field intensity, their relationship is not always linear. In fact, magnetic permeability changes with magnetic field intensity.

Two regions can be identified in a B-H curve. At low field intensity, a nearly linear region where the slope, \( \mu \), is approximately constant can be observed, and a region at higher intensities where the flux density does not change any further, known as saturation. As the material is magnetized, the magnetic domains align with one another as dictated by the field intensity. When all domains have aligned, further increments of the field intensity will not yield any change in the flux density inside the material and the \( \mu_r \) approaches 1.

It becomes evident that \( \mu_r \) is not a constant value, thus the values found in literature are averaged at low field intensities while saturation occurs at values around a
few Teslas.

2.2.1 B-H Curves

Also known as hysteresis curves and shown in Figure 2.1, they display a rather complex behavior in relation to the magnetic properties of the material. The magnetization curve, when the field intensity increases, and the demagnetization curve do not overlap.

![Figure 2.1: Hysteresis in magnetization curves.](image)

The first magnetization step will ideally go from the origin to the point $m$ in Figure 2.1. Demagnetization will follow the path $m o n$, so at zero field intensity the material exhibits a residual magnetic flux $B_r$ (magnetization). To reduce the magnetization back to zero, the applied field intensity must equal $-H_o$, which is represented by the point $o$ in Figure 2.1. Further decreasing the applied field intensity leads to the point $n$ where saturation is reached again. From the point $n$ increasing the field intensity will follow the magnetization path determined by $n p m$. Although the point
$m$ is reached again, the path followed was different. The area between the curves of magnetization and demagnetization is associated with energy loss which is thought to be the cause of the hysteresis.

The point $o$ defines an important magnetic property of materials known as coercivity. Coercivity, $H_o$ or $H_c$, of ferromagnetic materials is the intensity of the external magnetic field applied that is necessary to reduce the magnetization, $M$, of the material to zero. It is an indicator of how difficult or easy it is to demagnetize a ferromagnetic material [18–20].

Most of martensitic stainless steels are ferromagnetic. Some characteristic values of magnetic permeability and coercivity are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Condition</th>
<th>Maximum Relative Permeability</th>
<th>Coercive Force (Hc), A/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 410</td>
<td>A</td>
<td>750</td>
<td>480</td>
</tr>
<tr>
<td>(Martensitic)</td>
<td>H</td>
<td>95</td>
<td>2900</td>
</tr>
<tr>
<td>Type 416</td>
<td>A</td>
<td>750</td>
<td>480</td>
</tr>
<tr>
<td>(Martensitic)</td>
<td>H</td>
<td>95</td>
<td>2900</td>
</tr>
<tr>
<td>Type 420</td>
<td>A</td>
<td>950</td>
<td>800</td>
</tr>
<tr>
<td>(Martensitic)</td>
<td>H</td>
<td>40</td>
<td>3600</td>
</tr>
<tr>
<td>13 Cr</td>
<td>as received</td>
<td>102</td>
<td>2660</td>
</tr>
</tbody>
</table>

Magnetic properties of alloys become important depending on their application. Resistivity is relevant when conduction is part of the application. Magnetic permeability and resistivity must be considered in applications such as magnetic cores or transformers. These properties are combined in the depth of penetration relationship as shown in Equation 2.3:

$$\delta = \sqrt{\frac{2\rho}{\omega \mu}}$$

(2.3)
where $\delta$ is the skin depth which is defined as the depth below the surface of the conductor at which the current density has dropped to $1/e$ times the current density at the surface, $\rho$ is the resistivity of the metal, $\omega$ is the angular frequency, and $\mu$ is the magnetic permeability of the conductor. Further details of how these properties are of interest will be discussed in Subsection 2.5 when the direct electrical heating system (DEH) will be addressed.

2.3 Corrosion Fundamentals

The concepts presented in this section will be in the context of AC corrosion, electrochemical reactions, thermodynamics and electrode kinetics.

2.3.1 Corrosion Types

The types of corrosion that can be found when in the presence of AC are essentially uniform corrosion, localized corrosion and hydrogen related damage.

Uniform corrosion refers to a type of attack that occurs uniformly throughout the surface, experienced either as metal loss or as the formation of corrosion products like rust for low alloyed ferrous materials. In terms of materials selection and design, this type of corrosion is desirable over the others because the metal loss is uniform.

Localized corrosion, in contrast, occurs when the rate of corrosion is greater in some areas than in others. Pits are the result of this type of attack and they can be shallow or deep depending on how concentrated the attack is in these regions [1]. Because the metal loss is not uniform, this type of corrosion must be avoided. The pits can constitute crack initiation points and lead to failure.

Hydrogen damage is a general term used to refer to a type of environmentally assisted failure. The hydrogen in metals can cause different effects like mechanical properties loss (ductility), cracking, and blistering [10]. In general, if the hydrogen diffuses into the metal, it modifies the mechanical properties of the matrix, usually resulting in embrittlement, which in combination with tensile loads can lead to cracking.
and fracture. The hydrogen can also diffuse into regions where it recombines forming hydrogen gas which can induce blistering or cracking. Regions with high potential for this mechanism of failure are inclusions and dislocations. For more ductile materials, the effect of the diffusion and further recombination of the hydrogen is more often blistering.

2.3.2 Electrochemical Reactions and Thermodynamics

An electrochemical reaction is one in which electrons are transferred from one specie to another, as in iron dissolving in an acidic solution. The overall reaction can be separated into at least one cathodic reaction (reduction) in which electrons are received, and at least one anodic reaction (oxidation) in which electrons are given out. In the following example, metal oxidation is the anodic reaction and hydrogen reduction is the cathodic reaction. To preserve electron neutrality, both reactions involve the same number of electrons.

\[
Fe \rightarrow Fe^{2+} + 2e^-
\]

\[
2H^+ + 2e^- \rightarrow H_2
\]

Corrosion occurs either by dissolution or metal loss as in the previous example or by formation of corrosion products like rust as in, the formation of iron oxide in the presence of dissolved oxygen in water as in the reaction below.

\[
2Fe + 1.5O_2 \rightarrow Fe_2O_3
\]

Electrochemical reactions occur with a change of Gibbs free energy. The change of Gibbs free energy is given by Equation 2.4.

\[
dG = -dW_{ext} + VdP - SdT + d \sum \mu_i n_i \tag{2.4}
\]

The first term refers to the external work caused by the displacement of the charge; the second term corresponds to the energy associated to pressure change; the
third term represents the contribution of temperature variation; and the last term, chemical potential, accounts for the activities (concentration) of the species involved in the reaction. Thus, in a closed system where the external work is zero, the change of Gibbs free energy equals the change of chemical potential.

Usually the second and third term can be ignored as the reactions occur under constant temperature and pressure. Thus, the change of Gibbs free energy is generally given by the external work and the chemical potential change of the species involved, as shown in Equation 2.5.

\[
dG = -dW_{ext} + d \sum \mu_i n_i
\]  

(2.5)

Because the external work in a electrochemical cell is not zero, the change of Gibbs free energy is defined as the deviation from a standard state, and this deviation is given by the chemical potential of the species involved in the electrochemical reaction, as in Equation

\[
\Delta G = \Delta G^o + RT \ln \left( \frac{\Pi \alpha_{\text{prod}}^{\nu}}{\Pi \alpha_{\text{react}}^{\nu}} \right)
\]  

(2.6)

The change of Gibbs free energy at standard state of the electrochemical reaction is defined in terms of the number of electrons exchanged in the reaction. The Gibbs free energy change at standard state is given by the chemical potential at standard temperature and pressure,

\[
\Delta G^o = RT \ln \left( \frac{\Pi \alpha_{\text{prod}}^{\nu}}{\Pi \alpha_{\text{react}}^{\nu}} \right)
\]  

(2.7)

In addition, electrochemical reactions where \( n \) electrons are transferred, will develop a potential, \( E^o \) at standard state which is given by Equation 2.8.

\[
\Delta G^o = -nFE^o
\]  

(2.8)

An important difference between chemical and electrochemical reactions is that, at equilibrium, the change of Gibbs free energy does not equal zero. The work required
to move the charge and have it exchanged during the electrochemical reactions is equal to the Gibbs free energy.

Further combining Equations 2.5 and 2.8, yields Equation 2.9, better known as the Nernst equation.

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \frac{\Pi a_{\text{prod}}^e}{\Pi a_{\text{react}}^e} \right) \tag{2.9}
\]

The Nernst equation predicts the potential generated due to an electrochemical reaction at conditions different than the standard state of temperature and composition.

It has been postulated in previous works that the changes that magnetic fields induce in the metal should be accounted with a different operator, such as the Helmholtz free energy, \( A \) [22, 23]. This operator includes all the work, external and internal. By definition,

\[
A = U - TS \tag{2.10}
\]

\[
G = U + PV - TS \tag{2.11}
\]

and combining Equations 2.10 and 2.11 yields, \( A = G + PV \) which can further be expanded as \( A = G + PV + w_{\text{internal}} \). Because the in the system of interest, \( PV \) is constant, it follows that,

\[
\Delta A = \Delta G + w_{\text{internal}} \tag{2.12}
\]

Several effects, which are beyond the scope of this research, have been attributed to the magnetic fields. Magnetostriction is the isotropic (volume) or anisotropic (shape) deformation suffered by a magnetic material when it becomes magnetized [24]. Magnetization is the spin change produced in response to the magnetic field. The angular frequency of the electrons is modified as work is by the magnetic force (Larmor angular frequency) [19]. The preceding are just three examples of effects of the magnetic field on materials; however, there could be more.
Equation 2.12 in combination with Equation 2.5, becomes,

\[ \Delta A = -\sum w_{\text{external}} + \sum \Delta \mu_i n_i + \sum w_{\text{internal}} \]  

(2.13)

\[ \Delta A = -nFE^o + RT \ln \left( \frac{\Pi \alpha_{\text{prod}}^v}{\Pi \alpha_{\text{react}}^v} \right) + \sum \delta w_{\text{internal}} \]  

(2.14)

In an electrochemical cell, the electrode potential is the measurable quantity that reveals the state of energy of the electrode. If the definition \( \Delta A = -nFE \) is applied, and Equation 2.9 is substituted,

\[ E = E^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) + \sum \frac{other \ w_{\text{external}}}{nF} - \sum \frac{\delta w_{\text{internal}}}{nF} \]  

(2.15)

Further developments will be presented in Chapter 6.

### 2.3.3 Pourbaix Diagrams

Thermodynamic data relating potential and pH was compiled by Marcel Pourbaix in a fundamentally derived form, known as Pourbaix Diagrams. Corrosion behavior can be predicted knowing potential, pH, and at least an estimate of the concentration of metal ions in solution. Regions where the metal does not react (immune zone), or where it can react and form oxides (passive zone) or complex ions, can be identified at a glance. This knowledge is very relevant to corrosion engineers because potential or pH can be modified to take the metal structure to the domain of interest, mainly: immunity or passivation. The Pourbaix diagram of iron is presented in Figure 2.2 as an example.

The lines of the Pourbaix diagram correspond to chemical or electrochemical reactions of the metal with its environment. The lines define the regions of stability of metal compounds, such as metal, oxides, hydroxides, and ionic species.

The lines of the Pourbaix diagram are calculated using the Nernst equation at room temperature and, for corrosion related applications, activities of \( 10^{-6} \) molar. Chemical reactions do not involve changes in oxidation state; in consequence, they appear as vertical lines independent of potential. Electrochemical reactions involving
Figure 2.2: Pourbaix diagram of iron at 25°C [25].

water produce lines of finite slope (but different than zero) indicating their dependance on pH; while electrochemical reactions, in which water does not participate, produce horizontal lines.

Pourbaix diagrams are used for the design of cathodic protection systems. The idea of the cathodic protection is that when the potential is reduced, the solid metal is the thermodynamically favorable phase and the corrosion rate is expected to be reduced. Other tests are necessary, however, to determine the corrosion rate since Pourbaix diagrams only provide thermodynamic data [1, 26, 27].

2.3.4 Electrical Double Layer

When a metal is immersed in an electrolyte, depending on the Fermi energy levels of the solid electrode and the chemical potential of the electrolyte and electrode, a small charge is transferred either to the metal or to the electrolyte and an electrical
field is formed on the electrolyte side of the interface. Ions are mobile charges capable of distributing themselves in response to this electrical field.

Figure 2.3: Electrical double layer depicting the inner Helmhotz plane formed by a layer of solvent and the outer Helmhotz plane determined by the alignment of hydrated cations.

The simplest model of the interface is presented in Figure 2.3. It consists of a line of ions at a fixed distance from the surface of the electrode, which was first proposed by Helmholtz in 1879. The two layers of charge are considered to be the double layer, i.e. negative charges aligned on the metal surface and cations aligned in front of it, in the electrolyte side [27]. More complex models were proposed later on. Gouy and Chapman, in 1910, proposed their model of the interface which is the analog of the Debye-Hückel theory applied to a planar geometry. The thickness of the layer
is determined by a balance between electrical forces bringing the charges toward the surface in an ordered region, while thermal-convective forces tend to disperse the charges.

The relationship of the potential created on the surface with the position is described with the Poisson equation (Equation 2.16) [27, 28],

$$\frac{d^2 \Phi}{dx^2} = \frac{-1}{\varepsilon \varepsilon_0} \sum z_i F c_i^0 \exp \left( \frac{-z_i F \Phi}{RT} \right)$$

(2.16)

in which $\Phi$ is potential, $z_i$ is the charge of each ionic specie, $c_i$ is the concentration of the ionic specie, $\varepsilon$ and $\varepsilon_0$ are the permittivity of the electrolyte and the permittivity of free space, respectively. $R$, $T$ and $F$ have their usual meanings.

The space charge (diffuse double layer) capacitance is derived from the solution of the Poisson equation,

$$C_d = \left[ \sum \frac{z_i^2 F^2 \varepsilon \varepsilon_0 c_i^0}{RT} \right]^{1/2} \cosh \left( \frac{z F \Phi_0}{2RT} \right)$$

(2.17)

The extension of the perturbation of concentration of charge due to the electrical field is known as the Debye length, $L_D$.

$$L_D = \left[ \frac{RT \varepsilon \varepsilon_0}{\sum z_i^2 F^2 c_i^0} \right]^{1/2}$$

(2.18)

In terms of the Debye length, the capacitance can be expressed as:

$$C_d = \frac{\varepsilon \varepsilon_0}{L_D} \cosh \left( \frac{z F \Phi_0}{2RT} \right)$$

(2.19)

Neither the Helmholtz nor the Gouy-Chapman models give quantitative agreement over a large potential range. Stern combined both ideas and developed a new model which included the electrical and convective effects with two capacitors in series. In this model, each capacitor represents one of the layers described previously; that is, Helmholtz and Gouy-Chapman’s layers which are denoted with subscripts in Equation 2.20 [27].

$$\frac{1}{C_s} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

(2.20)
From this expression, it is clear that the smallest of the capacitances determines the behavior of the system.

Many techniques can be used to determine the capacitance of the electrical layer, including electrochemical impedance spectroscopy which will be described in Subsection 2.4.3.

2.3.5 Butler-Volmer Equation

Butler-Volmer equation, named after the workers from whose work it comes from, relates the dependance of the current density across a metal-solution interface with the difference of the non equilibrium potential, $\eta$, with respect to the equilibrium potential for the particular electrochemical reaction.

As other thermal activated process, the rate of reaction of the anodic and cathodic reaction follows the Arrhenius equation. The rate of reaction is given by Equation 2.21.

$$ \tau = \frac{i}{nF} = k'c_i \exp \left\{ \frac{-G^+}{RT} \right\} $$

in which, $\tau$, is the rate of electrochemical reaction, $i$, is the current density, $n$, is the number of electrons, $F$, is Faraday’s constant, $k'$, is a pre-exponential factor associated to the frequency of occurrence, $c_i$, is the reactant concentration, $G^+$, is the free energy of activation, $R$, is the gas constant, and, $T$, is temperature.

For a reaction such as $O^+ + e^- \leftrightarrow R$, the change of free energy involved in the process is depicted in Figure 2.4. Figure 2.4 shows how an energy barrier must be overcome so that a change of state (reduced/oxidized) may be achieved.

The diagram includes a schematic of the potential drop that corresponds to the free energy plot. The importance of this simple diagram is that it shows clearly the meaning of the symmetry factor, $\beta$. Because the energy barrier is different when going from left to right and from right to left, then the potential change is also different. The total change of potential given by $\Delta \phi$, is divided in two parts not necessarily equal.
Figure 2.4: Change of free energy and potential as the ionic reactant moves from the surface toward the bulk of the solution [29].
Thus, the equations of rate of reaction are given by Equations 2.22 and 2.23.

\[
ra = \frac{i_a}{nF} = k_a c_R \exp \left\{ \frac{(1 - \beta) nF \phi}{RT} \right\}
\] (2.22)

\[
rc = \frac{i_c}{nF} = k_c c_O \exp \left\{ -\frac{\beta nF \phi}{RT} \right\}
\] (2.23)

The potential and pre exponential factors have changed because a reference potential has been used, and the resulting exponential can be accommodated in the pre exponential factor.

The net current density is given by, \( r = r_a - r_c \), which yields to Equation 2.24.

\[
r = \frac{i}{nF} = k_a c_R \exp \left\{ \frac{(1 - \beta) nF \phi}{RT} \right\} - k_c c_O \exp \left\{ -\frac{\beta nF \phi}{RT} \right\}
\] (2.24)

At this point, it is important to define a standard state that serves as a potential reference and corresponds to the equilibrium potential. The equilibrium condition is given by a net rate of reaction equal to zero. Thus, Equation 2.24 can be solved for the potential \( \phi^0 \) at which the net current density equals zero. The result is given in Equation 2.25.

\[
\phi^0 = \frac{RT}{nF} \ln \left\{ \frac{k_c/k_a}{c_O/c_R} \right\}
\] (2.25)

Overpotential, \( \eta \), is defined as a departure from the equilibrium potential and it is given by, \( \eta = \phi - \phi^0 \). Rearranging, one obtains Equation 2.26.

\[
i = nFk^1\beta k^\beta c^{1-\beta} c^\beta_R \left[ \exp \left\{ \frac{(1 - \beta) nF}{RT} \eta \right\} - \exp \left\{ -\frac{\beta nF}{RT} \eta \right\} \right]
\] (2.26)

Often times, instead of using the symmetry factor, \( \beta \), a transfer coefficient, \( \alpha \), is used. The transfer coefficient can be defined as follows:

\[
\alpha_a = (1 - \beta)n
\] (2.27)

\[
\alpha_c = \beta n
\] (2.28)

although some authors leave \( n \) out of the equation allowing \( \alpha_a + \alpha_c = 1 \) whereas, as defined above, \( \alpha_a + \alpha_c = n \).
In terms of the transfer coefficients, and summarizing all the pre exponential factors into a single factor known as exchange current density, \( i_o \), the Butler-Volmer equation becomes:

\[
i = i_o \left[ \exp \left\{ \frac{\alpha_c F}{RT} \eta \right\} - \exp \left\{ \frac{-\alpha_c F}{RT} \eta \right\} \right] \quad (2.29)
\]

This mathematical expression is the fundamental equation that describes the current-overpotential relationship for an electrode at a specific temperature, pressure, and concentration of ionic species [27, 29–31].

Two approximations are made depending on the order of magnitude of overpotential. The most important approximation corresponds to large overpotentials. For large positive overpotential, the second term of the Butler-Volmer equation tends to zero. For large negative overpotential, the first term tends to zero. In any case, overpotential can be solved as a function of current density as follows:

\[
\eta = \pm \frac{RT}{\alpha_i F} \ln \left( \frac{i}{i_o} \right) \quad (2.30)
\]

The above expression is better known as the Tafel equation and it is usually written in terms of the Tafel slope, \( \beta_z \), according to Equation 2.31.

\[
\eta = \pm \beta_z \ln \left( \frac{i}{i_o} \right) \quad (2.31)
\]

Therefore, at sufficiently high overpotential, the logarithm of current density-overpotential plot is a straight line of slope \( \beta_z = \pm \frac{RT}{\alpha_i F} \) [32]. The positive slope corresponds to anodic processes and the negative slope to the cathodic processes.

### 2.3.6 Mixed Electrodes

The utilization of the mixed-potential theory can be explained by considering a metal electrode in contact with one or more reduction-oxidation systems. Consider for example zinc immersed in hydrochloric acid where it rapidly corrodes. The electrochemical reactions occurring are represented in Figure 2.5.
A zinc electrode in equilibrium with its ions can be represented by a reversible potential corresponding to the Zn/Zn$^{2+}$ electrode reaction at a certain concentration (1 molar, for example) and a corresponding exchange current density. Likewise, the H$_2$/H$^+$ electrode reaction equilibrium is characterized by an equilibrium potential (at a certain concentration of 1 molar and partial pressure of hydrogen of 1 atm, for example) and exchange current density.

However, for a situation where a piece of zinc is immersed in an acidic solution containing some ions of zinc, the electrode cannot remain at either of the mentioned equilibrium potentials but some other value.

Two conditions must be satisfied: first, provided that zinc is a good electric conductor and that the sample is small, that the whole metal surface is at the same potential; second, that the rate of oxidation and reduction are equal at equilibrium. The first condition is undoubtedly satisfied at a laboratory scale, however, the sec-
ond condition is true only at one point. The point is designated in the diagram by $E_{corr}$ and $i_{corr}$. At this point the rate of zinc dissolution equals the rate of hydrogen evolution.

It must be noted that at this common potential, the reverse reactions $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ and $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$, do not occur. As the corrosion potential lies between the equilibrium potentials 0.0 and -0.76V. Zinc reduction can only occur below -0.76V and hydrogen oxidation can only occur above 0.0V.

2.4 Analytical Techniques

Several analytical techniques are available for the study of corrosion and electrochemistry. The techniques used in this research will be briefly discussed below.

2.4.1 Open Circuit Potential

Open circuit potential (OCP) is the potential measured between the corroding metal and a reference electrode. When the working electrode is immersed in an electrolyte, the surface has to adjust to the new environment going through different stages of adsorption, hydration, and maybe formation of corrosion products. Meanwhile, if the potential of the electrode is measured with respect to a reference electrode, a change in time will be observed. The potential will change at first and tend to stabilize after several minutes or hours. At this point, it is assumed that the metal has reached equilibrium with its environment.

When the OCP reaches a stable value it is said to have reached $E_{corr}$; only then they are equal.

Monitoring the OCP is a technique widely used in corrosion engineering. The OCP potential is used as a reference; for example, potentials below OCP fall in the cathodic polarization regime and potentials above OCP fall in the anodic regime in which metal loss at higher rates can be expected.
2.4.2 Potentiodynamic Polarization

Potentiodynamic polarization consists of a potential scan at a fixed scan rate, usually 0.166 mV/sec (ASTM G61 - 86(2009) standard), at the same time the electrical current is measured. The measurement requires the use of at least two other electrodes besides the one in study known as the working electrode. The counter electrode closes the electrical circuit and its role is to conduct current. The reference electrode does not conduct current; however, it serves as reference to the potentiostat which performs the polarization by controlling the potential difference between the working and reference electrode.

The data obtained from the scan is plotted with the potential at the ordinate and the absolute value of current density at the abscissa in a logarithmic scale. A schematic drawing has been provided in Figure 2.6.

The curve from OCP toward higher values of potential is known as the anodic branch, where the anodic reaction rate is predominant. The anodic branch is often divided in three sections: from OCP (point A) to passivation potential (point C) is...
known as the active zone, from passivation potential to pitting potential (point D) is known as the passive region, and above the pitting potential is known as transpassivation region (region designated as E). The point B in the active region is a critical point where the corrosion rate reaches a maximum but once reached, the corrosion rate decreases rapidly. It is believed that at this point the solution on the surface of the metal saturates and the metal oxide precipitates which serves as a diffusion blocking layer further reducing the corrosion rate.

The curve from OCP toward lower potential values is known as the cathodic branch where the rate of cathodic reactions dominates the net current density. A limiting current range has been depicted (region designated as F) where the current is controlled by diffusion of species in the electrolyte. It usually indicates the transition from one cathodic reaction whose reactants deplete and whose reaction rate is diffusion controlled, to a new reaction which is not diffusion controlled which in turn allows the current density to increases again.

This analytical technique allows for the study of the passive behavior of metals. Very important parameters for corrosion can be extracted from the potential-current density curves like corrosion potential, pitting potential, repassivation potential, and the corresponding current densities at these potentials.

The potentials mentioned before can be compared to the actual potential measured under the conditions of interest. Using Faraday’s law, corrosion rates can be calculated from the current densities measured.

Figure 2.5 shows the Tafel lines corresponding to the zinc oxidation and reduction (red), the hydrogen oxidation and reduction (blue), and the theoretical net current is depicted with a black line. If a potentiodynamic scan was made, the polarization curve would follow the black line.
2.4.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy, EIS, is a widely used tool in the study of electrochemical systems. EIS is applied to materials in which ionic conduction strongly predominates, such as corrosion cells. One of the most attractive features of the technique is that it allows a direct connection between an idealized equivalent electrical model with a real system [33].

The technique measures the impedance of the interface metal-electrolyte usually with a small potential excitation of 5-10 mV. A frequency sweep is performed and the impedance is measured with a frequency response analyzer. The data can be modeled to an equivalent electrical circuit and the physical phenomena occurring at the interface can be better understood.

Several microscopic processes which have a specific impedance signature, occur throughout the cell when it is electrically stimulated. These processes include the transport and transfer of electrons at the electrode-electrolyte interfaces to or from atomic species originated from oxidation or reduction reactions, and the flow of charged atoms in the electrolyte. Often times, the processes can be modeled with electrical elements. The analogies between electrical circuit elements will be addressed and additional elements with no electrical equivalent will be introduced as well.

Resistors represent conductive pathways for ions or electrons. They represent the resistance of the electrolyte to the conduction of ions. On the other hand, resistors also indicate how fast an electrochemical reaction occurs. In the first case, resistors relate to conductivity whereas in the second case, resistors relate to electron exchange due to electrochemical reactions.

Although resistors, capacitors and inductances are usually used in equivalent circuits, these elements only approximate ideality over a limited frequency range. In fact, an actual resistor always exhibits some capacitance and inductance as well, and
acts somewhat like a transmission line. Its output response to an electrical perturbation is always delayed compared to its input [34]. These residual properties are negligible over a broad frequency range and, in general, it is possible to represent a physical resistive pathway with its equivalent ideal resistor which is a resistance independent of frequency [28].

The non ideal characteristics of the electrode-electrolyte and particularly to the spatial finite extension of any real system give rise to the distributed elements. One type of distribution is found when non local processes occur, such as diffusion, even when the mobility of the species is not dependent on position. Another type of distribution occurs when properties differ at a microscopic level, which gives rise to a constant-phase element (CPE). Differences on the surface relative to smoothness (kinks, jags, and ledges), composition or microstructure contribute to the distributed behavior observed. As a result, reaction resistance and capacitance contributions differ with position and only an averaged effect is effectively measured.

The infinite-length Warburg impedance was the first distributed element developed. It was obtained from the solution of one-dimensional particle diffusion equation, Fick’s second law, in a semi-infinite space, see Equation 2.32 [28, 35].

\[
Z_{W\infty} = \sigma (j\omega)^{-1/2}
\]  

(2.32)

Other solutions were later developed for more specific conditions such as the finite-length Warburg diffusion, which was developed for the diffusion of an uncharged particle diffusing through a finite length region. The expression for impedance under finite-length constraints is presented in Equation 2.33

\[
Z_{W} = R_{DO} \left[ \frac{\tanh \left( \sqrt{j\delta} \right)}{\sqrt{j\delta}} \right]
\]  

(2.33)

in which \( s = \frac{l^2\omega}{D}, D \) is the diffusion coefficient of the particle, and \( R_{DO} \) is the diffusion resistance that equals \( Z_{W} \) when \( \omega \) approaches zero [36].

Different constraints applied to the mass transport equation will lead to different solutions, in particular, when the diffusion length is considered and compared to the
frequency-dependent diffusion length, \( l_D = \sqrt{D/\omega} \). For example, the fact that \( R_{DO} \)
is an extensive quantity dependent on the diffusion length should be considered if the
diffusion length is much larger than the Nernst diffusion layer [28].

An additional case corresponds to the open-circuit (blocked) diffusion. Here, at
high frequencies the response is similar to the infinite-length Warburg impedance
(straight 45° line), and at lower frequencies the behavior changes to a capacitor
(straight 90° line) which simulates the open circuit caused by the blocked diffusion.
The response described has been found in studies of thin films [37, 38]. The impedance
corresponding to open-circuit diffusion follows in Equation 2.34

\[
Z_{DOC} = \left( \frac{\tau_{DOC}}{C_{DOC}} \right) \left[ \frac{\coth(\sqrt{j\omega}s)}{\sqrt{j\omega}s} \right]
\]  

(2.34)

where \( \tau_{DOC} = \frac{i^2}{D} \) and \( s = \frac{i^2\omega}{D} \).

In the process of circuit fitting, the element that models the blocked diffusion
behavior is known as the generalized finite-length (GFL) element.

Although Warburg and blocked-diffusion effects are usually observed, often times
one finds straight line behaviors with angles different than 45°. The impedance is no
longer a function of \( \omega^{1/2} \) but to some other power of \( \omega \). The constant-phase element,
CPE, is introduced to describe such situations. The impedance of CPE is defined as
in Equation 2.35.

\[
Z_{CPE} = CPE^{-1}(j\omega)^{-N}
\]  

(2.35)

In which, CPE and \( N \) are not frequency-dependent values, and \( 0 \leq N \leq 1 \).
Notice that CPE yields a resistor when \( N = 0 \), a perfect capacitor when \( N = 1 \), and
a Warburg impedance (diffusion control) when \( N = 0.5 \). The common agreement is
that when \( 0.8 \leq N \leq 1 \), the CPE represents a non perfect capacitor. The meaning of
\( 0.5 < N < 0.8 \) and of \( 0 < N < 0.5 \) is subject of debate and it has been proposed that
anomalous diffusion is responsible for this behavior [39].

The expression to convert CPE with units of sec^n/ohm, to capacitance with units
of sec/ohm or Farads is presented in Equation 2.36 [35].
The radial frequency $\omega_m$ is the frequency at which the imaginary part of the impedance reaches a maximum.

The most fundamental electrical equivalent circuit used to simulate the metal-electrolyte interface of a corroding metal is the Randles circuit. It consists of a solution resistance in series with a parallel of three elements: a capacitor representing the electrical layer, which is in parallel with the series connection of an infinite-length Warburg impedance and the charge transfer resistance, often known as polarization resistance (See Figure 2.7). The last two elements model the possible diffusion control, and the charge transfer resistance, respectively.

![Randles circuit](image)

Figure 2.7: Randles circuit: solution resistance in series with the capacitance of the electrical double layer and the charge transfer resistance and Warburg impedance.

In summary, the solution resistance represents the resistance to the conduction of the ionic species in solution. Polarization resistance, or charge transfer resistance, controls the amount of current that can be transferred via electrochemical reaction when the electrode is polarized away from the OCP. Its value is intrinsic to electrochemical reactions occurring at the interface; it also depends on the electrode, electrolyte, and temperature. Two equivalent resistances, polarization resistance and solution resistance, are of great importance for this study. Solution resistance is related to the conductivity of the electrolyte whereas polarization resistance is related to the rate of electrochemical reactions occurring on the electrode.
The electrical layer present at the interface electrode-electrolyte is represented by a capacitor. The plane where the positive ions are aligned and the plane where the negative ions are aligned, represent the plates of the capacitor where charge is stored. Those planes are separated by molecules of water surrounding the ions and this separation is of the order of a few Angstroms [27]. The capacitance of the electrical layer is affected by the electrode potential, temperature, ionic concentration, presence of oxide layers, and roughness of the surface. For this reason, often times, the electrical layer is represented by the distributed element CPE instead of a perfect capacitor.

Diffusion elements appear depending on several variables such as the concentration of the ionic species, the diffusivity of the ionic species, thickness of the diffusion layer, and others. It remains a responsibility of the user to know and understand the physical reality of the system to properly choose (or propose) the element and equivalent circuit that best describes the conditions of the real system.

2.5 Direct Electrical Heating System

The formation of methane hydrates in subsea oil production is a well known problem. The well stream contains considerable amounts of water and methane mixed with oil, and as the stream cools down on its way up to the platform, methane hydrates can form.

Methane hydrate is a compound in which methane is enclosed in a crystal structure of water. The solid structure looks physically like ice. Methane hydrates have received some attention in recent years as a potential gas resource in the future [40]. When the methane hydrate is either depressurized or warmed, the structure destabilizes becoming water and methane gas.

However, as desirable as methane hydrate may be as an energy source, it can be catastrophic if it forms inside pipelines causing a reduction of the flow and ultimately completely blocking the pipeline. It is essential to maintain the stream above the
critical temperature at which the methane hydrate starts to form.

To prevent the formation of hydrate, many technological solutions have become available. Chemical injection and thermal insulation are some examples. Both have advantages and disadvantages, and do not represent universal solutions to the problem. For example, chemicals must be removed later on increasing costs. The chemicals also occupy some volume of the stream, which reduces production capacity. Thermal insulation, on the other hand, may be sufficient for short pipelines, but not appropriate for longer distances. Additionally, thermal insulation cannot control the drop of temperature when the stream flow decreases [41].

By heating the pipeline electrically the need of chemical injection is reduced. It is a suitable solution for longer pipelines which can be complemented with chemical injection and thermal insulation.

The direct electrical heating (DEH) system consists of a single phase AC supply connected through rise cables to the near end of the pipe and to the far end of the piggyback cable. The piggyback cable is the conductor of current that runs parallel to the heated pipeline. A diagram of the system can be found in Figure 2.8.

![DEH system diagram](image.png)

Figure 2.8: DEH system diagram [41].
With a current in the range of 1500 A (RMS) the heating capacity is in the range of 70 to 150 W/m. This power is, with a pipeline coating system as the one shown in Figure 2.9, sufficient to avoid hydrate formation [42].

![Coating system for thermally insulated pipelines.](image)

Figure 2.9: Coating system for thermally insulated pipelines. Typical thickness is 50 mm. The layers are different forms of polypropylene (PP) and fusion bonded epoxy (FBE) [42].

Cathodic protection is provided with aluminum sacrificial anodes as depicted in the diagram, with a higher number of them in the transfer zone. The current transfer zone is where the connection pipeline-rise cable is made. The coating is not interrupted by the anodes. The anodes are placed on top of the coating - or flush with the coating, then with a layer of polypropylene coating beneath them.

The DEH is thus connected to the surrounding seawater through the anodes causing the electrical current from the source to divide into two parts: one part returns through the pipe and the other is lost to the water. Typically forty percent of the electrical current does not participate in the heating of the pipe because it is conducted through the water, the current flows parallel to the pipeline from one transfer zone to the other.

Some of the steel properties of great importance in the design of the DEH are the electrical conductivity and magnetic permeability as heat is generated by ohmic losses and inductive effects. Because these properties vary even between manufactured
batches, some sections of the pipeline may be under heated due to variations of the AC resistance. Pipes must be classified, previous to installation, based on magnetic permeability measurements to prevent cold-hot pipe joints, i.e. low-high magnetic permeability joints. The skin effect (Equation 2.3) is responsible of the behavior here described since the magnetic permeability determines the depth of penetration. High magnetic permeability leads to smaller penetration depth and higher resistance, therefore, higher temperatures can be reached.

Transfer zones are equipped with evenly distributed anodes to keep the transfer current density at 40 A/m². This design criteria was based on other studies which showed that there is no significant corrosion for current densities below 240 A/m², provided that the steel is protected by anodes [41].

2.5.1 AC Corrosion Failure Mechanisms

Two main scenarios for potential AC corrosion are identified for a pipeline with a DEH system:

- the current transfer zone where 40pct. of the system current corresponding to approximately 600 A is entering and leaving the pipe is an area of concern. A coating damage here may be exposed to very high AC densities that can lead to corrosion

- the intersections between two permeability groups. Where two permeability groups meet, there will be a voltage gradient from the pipe to the sea that can lead to current transfer in case of a coating damage. This behavior can lead to a considerable AC current density and calculations have shown that the current density can be as high as 1000 A/m² and above.

It is known that the AC density is dependent on the area of the coating damage. Looking at the type of coating on these kinds of pipelines, the most likely coating
damage is cracks located at the field joints. The most likely area of such a potential coating damage is probably around 1 cm$^2$ [42].
CHAPTER 3
AC CORROSION

Many efforts have been made since the early 1900's to understand the role of alternating current in corrosion. Even today some people in the field would argue that AC does not cause corrosion [43]. However, several cases of failure in the field have been reported to be related to AC. The state of awareness of the risks posed by AC corrosion even under cathodic protection has prompted the interest in understanding the mechanism of corrosion due to AC [44].

The research and understanding of the problem has been difficult, due to a lack of theoretical understanding and to the lack of proper equipment for research. The equipment usually found in a corrosion laboratory cannot detect alternating current and they can only apply and measure direct current (DC). Additionally, the knowledge in thermodynamics and electrode kinetics of the corrosion community is mostly related to DC as corrosion has classically been attributed to DC. Text books in corrosion engineering do not treat AC corrosion thermodynamics, kinetics, or even possible mechanisms. The literature is scattered throughout journals and proceedings over a period of almost 100 years, making it more difficult to compile a state-of-the-art of the work made in USA and Europe, where most of the research has been done.

The general agreement is that AC corrosion is manifested in the form of pitting, and that while AC is present a DC potential shift with respect to OCP in absence of AC can be measured. It is also agreed that higher alternating currents lead to higher corrosion rates.

Morphologically, AC corrosion is found in the form of pitting. Agglomerated soil mixed with corrosion products with a higher pH and lower resistivity, generally surrounds the pits [45]. In solutions, AC has resulted in the growth of a thick non-
adhering corrosion product and pitting [46].

In cathodically protected pipelines, AC corrosion occurrence can be summarized as follows [45]:

- does not occur at AC densities below 20 A/m²
- is unpredictable between AC densities of 20 and 100 A/m²
- can be expected at AC densities above 100 A/m².

Corrosion rates in the presence of AC:

- increase in chloride containing or deaerated environments
- increase when decreasing frequency, at frequencies below 100 Hz [5, 6, 45]
- decrease with increasing cathodic protection.

3.1 Early Work on Electrochemistry and AC Voltages

Many mechanisms have been proposed to explain AC corrosion within the past fifty years. The earliest work reported on the effect of AC on electrode kinetics was made by Doss and Agarwal [47]. They discovered that when AC passed between two platinum electrodes immersed in an aqueous solution, a DC potential was developed at each electrode. They referred to this observation as the redoxokinetic effect and to the potential developed as the redoxokinetic potential.

Doss and Agarwal suggested two hypothesis to explain the redoxokinetic effect. According to one of the hypothesis, the effect is caused by the differential effect of the anodic and cathodic half-wave of the current. For example, one of the half waves could be less effective in bringing about the reactive ion than the other half wave (diffusion related). As a result, the ratio of reactive ions at the interface is disturbed causing the redoxokinetic potential.
The second hypothesis proposed that the reactions involved in the anodic and cathodic half-waves do not occur equally fast, resulting in a net potential. The authors finish their work stating that although the second mechanism was successful in explaining most of their experimental results, the two mechanisms cannot be entirely independent.

The redoxokinetic effect was later renamed faradaic rectification by Oldham [48]. The term also refers to the asymmetry of the anodic and cathodic processes manifested in different slopes of the curves current-potential, and in the rectification potential when AC is applied.

In 1960, Delahay et al. expanded the redoxokinetic theory by elaborating on the effect of the electrical layer and the type of control applied (potential or current) [49]. The authors stated that when controlling current to be a symmetrical wave, a DC rectification potential is observed, and that controlling potential to be symmetrical around the equilibrium potential results in a rectification current. Therefore, it is important to control not only the alternating part of the perturbation but also the DC component. Simply stated, symmetrical current results in asymmetrical potential and symmetric potential results in asymmetric current.

The electrical layer should be considered especially for diffusion control boundary conditions. The electrical layer capacitance is, however, not constant and rather potential dependent and its structure will be disturbed by the AC. Transients due to charging of the electrical layer become important in the interpretation of rectification potential measurements, which the authors calculate should be less than 5 mV.

At this point, the rectification theory had become an electrochemical tool to determine electrochemical parameters such as rate constants, corrosion current densities, and transfer coefficients [49–52].

In 1972, Devanathan revisited the work of Doss and Agarwal making some important distinctions that were initially overlooked [53].
Devanathan said that when an overpotential is a periodic function of time, then the current consists of components with periodicities of $\omega$, $2\omega$, $3\omega$, etc. Some aspects of the behavior in the presence of AC potentials have been studied with respect to:

- the fundamental frequency $\omega$, known as faradaic impedance,
- the first harmonic frequency, $2\omega$, called faradaic distortion, and
- the DC component known as faradaic rectification.

Further, up to this point the mentioned phenomena have not been properly correlated and it was always assumed that the transfer coefficients follow the relationship $\alpha_a + \alpha_c = 1$, which is only true for single electron transfer reactions [29, 31].

All the theoretical solutions published up to this point corresponded to the solution of Fick's diffusion equation for a redox system conducting alternating current. Further developments have been obscured because of the difficulty interpreting rather complex mathematical solutions. Moreover, some simplifications made such as $(nF/RT)\eta < 1$ limit the applicability of the equations to 10-20 mV.

From a basic point of view, rectification effects are observed whenever the $i/\eta$ curve is asymmetric. The asymmetry arises from either intrinsic asymmetry of the charge-transfer reaction (faradaic rectification) or from differences in the mass-transfer rates of the ionic species (redoxokinetic rectification). This explicit distinction was first stated by Devanathan [53] and he proposed equations that would describe both situations.

Devanathan's work set the basis for future developments taking the theory of rectification one step further, from electrochemistry to corrosion.

Devay and Meszaros presented one of the first studies about corrosion rate determined by a faradaic distortion method [54]. However, the method shares characteristics with electrochemical impedance spectroscopy and only applies for small amplitudes of voltage. Other authors like Hettiarachchi presented a new method for...
corrosion rate estimation which has the advantage that no previous knowledge of polarization resistance or Tafel slopes is required [51]. It is advantageous that Tafel slopes are not needed in the calculations because of their inherent ambiguity and the difficulty of measuring slopes in a log scale. Several efforts followed aiming to determine the importance of the double layer capacitance effects on the measurements [55]. Depending on the overpotential applied, the effect of the double layer can be more important. However, up to this point, the faradaic rectification theory remained a laboratory technique and was still not appropriately applied to AC corrosion.

3.2 Theoretical Modeling of AC Corrosion

In the present chapter, several models developed for predicting AC corrosion will be discussed.

Lalvani et al. presented theoretical models for corrosion with and without the possible effects of the electrical double layer [56–59]. Lalvani et al. reinforce the fact that systems more susceptible to AC corrosion are those with a high ratio of anodic-to-cathodic Tafel slope. This assertion is not surprising because faradaic rectification arises from the asymmetry of anodic and cathodic processes. The models also predict the shift in corrosion potential (DC potential) as a function of peak potential applied for different ratios of anodic-to-cathodic Tafel slope.

The experimental work made by Lalvani et al. [5, 6, 60–63] could not corroborate the models proposed. The difficulties of the experimental work due to the lack of appropriate equipment and, sometimes, thorough understanding of the problem are revealed through these publications.

For example, part of the experimental matrix consisted of controlling the potential between the working and counter electrodes. This type of control does not provide thermodynamic or kinetic value as it refers to the power of the cell. Moreover, fixing the potential between working and counter electrodes does not mean that the potential of the working electrode with respect to a reference electrode is fixed, so the
experiments are not controlled galvanostatically or potentiodynamically.

Also, in an attempt to make symmetric the alternating current, part of the experimental matrix consisted of applying a potential AC while forcing the DC potential to equal the OCP before the application of AC. As stated in previous sections, the condition of symmetric current necessarily leads to a rectification potential which by definition does not equal OCP in the absence of AC (see Section 6.1.1).

Bosch et al. later expanded the models presented by Lalvani et al. by proposing a model for mixed control [64]. The model predicts that diffusion limits the increase of the corrosion rate up to the point where the limiting current density is reached.

Nielsen et al. [65, 66] proposed setting up electrical equivalent circuits when dealing with AC corrosion, particularly when dealing with real systems. The equivalent circuits seek to take into consideration the physical and chemical aspects relevant to the particular situation. His equivalent circuit considers resistive elements such as soil resistance and charge transfer resistance as well as dynamic elements like interfacial capacitance and diffusion elements. In their discussion, they state that the potential bias is partially the result of potential drop due to the soil resistance not acknowledging the faradaic rectification effect. Furthermore, the author proposes that corrosion occurs due to the alkanization of the soil which takes the metal from the passive region of pH (9 to 13) to the active region (pH > 13).

Pourbaix et al. [9, 67, 68] have also investigated AC corrosion intensively. Their work and theories link the AC corrosion to Pourbaix diagrams. They state that corrosion occurs as the sine half wave goes from the immune to active regions causing corrosion. Also, they acknowledge that the passivation is less effective when AC is present, probably because the oxide film is less protective when formed under AC polarization.

Alkanization theory and several field research studies support the idea that excessive cathodic protection must be avoided and these conclusions have been adopted
by European standards [69].

Lazzari et al. have extensively studied AC corrosion and its effect on overpotential [46, 70–72], and suggest a mixed mechanism. The authors discuss the reversibility of the cathodic and anodic reactions that occur in each half wave. This affects the double layer chemical composition and the corrosion kinetics, leading to changes in the polarization behavior and shifts of corrosion potential [69].
CHAPTER 4
EXPERIMENTAL METHODOLOGY

This experimental work was oriented to study four fundamental aspects of AC corrosion:

1. the type of corrosion that the AC densities of interest produce,

2. the DC response to the application of AC in terms of polarization curves,

3. the effect of magnetic field on corrosion and on AC corrosion, and

4. the true wave form of potential and current while studying cathodic protection criteria.

The sample preparation consisted of grinding the samples with silicone carbide paper of 240, 320, 400 and 600 grit at least 24 hours before the corrosion tests. The samples were cleaned with acetone and left on the top of the table in a safe way so that no scratching could occur. By following this procedure, reaching a stable open circuit potential would only take one to two hours.

The standard calomel electrode (SCE) was used for all the experiments. The electrolyte used was commercial artificial seawater prepared according to the ASTM D 1141 standard of pH of 8.1. The frequency of the alternating current used was always 60 Hz. All the experiments were performed in aerated solution open to the atmosphere.

The equipment used was:

- potentiostat/galvanostat Princeton 253A controlled with the software package CorrWare®, Zplot®, CorrView®, and Zview®.
- high frequency response analyzer SI 1255.
• oscilloscope Tektronix DPO-3012.

• differential probe ADA 400A.

• high impedance multimeter Fluke 8808A.

• AC constant current source from Amp-Line Corp.

• AC insulated power supply

• FW Bell 5180 Gauss/Tesla meter

4.1 AC corrosion

After preliminary testing, it was concluded that the effect of different values of AC should be assessed by exposing the metal to fixed amounts of charge, i.e. the product of current and time. By fixing the amount of charge it is possible to relate the corrosion to the intensity of the perturbation while eliminating time as a variable.

Three values of interest emerged from the DEH system: 40, 240, and 500 A/m². The charge was chosen from the preliminary experiments made with the highest current density, 500 A/m², which always exhibited pitting after two hours. Correspondingly, for the other two current densities, 240 A/m² was applied for 4 hours 10 minutes and 40 A/m² for 25 hours.

The experiments were carried out galvanostatically in artificial seawater. The DC potential between the working electrode and the reference electrode (open circuit potential, OCP) was recorded for one hour previous to the application of the AC. When the potential was stable, the AC was turned on and the DC potential continued to be recorded for the remainder of the experiment.

To prevent the AC from interfering with the correct functioning of the laboratory equipment (Potentiostat/Galvanostat, FRA), an external circuit was used to filter the AC component of the signal. The circuit used is shown in Figure 4.1 which is a modified version of the circuit used in the literature and shown in Figure 4.2.
Figure 4.1: External circuit used to separate AC from DC. The circuit was modified to reduce electromagnetic noise: potentiostat instead of galvanostat, 300 microF capacitor added.

Figure 4.2: Electrical circuit used to study AC corrosion [71–73].
Additionally, special settings of sample rate, data average, and selection of low-pass filters was necessary to complement the noise control.

After the prescribed time, the alternating current stopped and the sample was allowed to reach a stable DC potential again, the OCP was recorded, and the state of the surface was assessed with electrochemical impedance spectroscopy (EIS). The samples were later characterized with the optical microscope.

Three cell configurations were used for these experiments. The major difference of the cell arrangements was geometry and counter to working electrode surface ratio. The top view of the cell arrangement is presented in Figure 4.3.

4.2 DC Response to AC: Polarization Curves

The DC response to AC was measured using the circuit presented in Figure 4.1 and the cell configuration of the flat square sample presented in Figure 4.3. Alternating current densities of 40, 240, and 500 A/m² were used. The previous section proved that pitting was feasible with the three current densities of interest and that the extent of corrosion was different in each case.

To prevent the corrosion and dissimilarity of sample surfaces, the sequence of the present experiments was as follows: the OCP was recorded until stabilization was reached, then a potential scan toward more negative potentials started. When -2V vs SCE was reached (the cathodic protection condition) the potential was held for five minutes. During that time the AC was turned on and the DC current was allowed to stabilize before the polarization scan started in the anodic direction.

The cyclic polarization started at -2 V, scanned forward to +1 V, and then returned to -1 V (all potentials relative to SCE). The data was then corrected for the IR drop and all data points after repassivation were omitted.
- Three graphite counter electrodes
- One surface of the working electrode exposed

Flat square sample

- Three graphite counter electrodes
- Five surfaces of the working electrode exposed

Cubic sample

- One graphite DC counter electrode
- One platinum mesh AC counter electrode
- Four surfaces of the working electrode exposed

Bar sample

Figure 4.3: Top view of the cell configurations.
4.2.1 Cathodic and Anodic Polarization

The difference between these experiments and those described in the previous subsection is the starting potential of the curves and when AC is turned on. In this case, the OCP was recorded until stabilization was reached, and then the AC was turned on allowing some time for the DC potential to become stable at a new shifted value. Five minutes were given for 500 A/m², fifteen minutes for 240 A/m², and thirty minutes for 40 A/m². At this point, and maintaining the AC on, the potential scan started from the new shifted DC potential to -4V vs SCE, in the cathodic scan. For the anodic scan, the potential sweep started at the new shifted DC potential to 1V vs SCE, and then back to the repassivation potential. The data was later corrected for the IR drop produced by the external circuit.

4.3 Effect of AC Magnetic Fields on Corrosion

The effect of alternating magnetic fields on corrosion and on AC corrosion was studied using EIS and polarization curves as follows.

4.3.1 Corrosion under Alternating Magnetic Fields

The alternating magnetic field was created by passing AC through a coil. A calibration curve was drawn to compare the theoretical values of magnetic flux density with those values measured with a Hall probe.

The coil was embedded in epoxy resin to prevent stray currents from leaking to the electrolyte. The space inside the coil was large enough to accommodate the sample and Luggin tube and to allow for diffusion and convection to occur naturally.

The experiments were sequenced as follows: the OCP (no current passing through the coil) was recorded for one hour for stabilization. Then the OCP continued to be recorded for ten minutes while the AC was passing through the coil. Finally, EIS was performed and followed by cyclic polarization (from -1.4 to 0 V back to -1V, vs SCE). Afterward, the surface of the samples were characterized in the optical microscope.
4.3.2 AC Corrosion under Alternating Magnetic Fields

From the experiments described in Section 4.3.1 the highest magnetic field was selected to assess the effect of AC magnetic fields on AC corrosion. The experiments were performed under the same scheme found in Section 4.1 while superimposing the alternating magnetic field. EIS was performed after stopping the AC when the OCP was stable again.

EIS was performed two times at this point, first with the magnetic field still in place and second, without the magnetic field.

4.3.3 DC Response to AC under Alternating Magnetic Fields

The experimental setup was the same as the one used to study the DC response to AC, described in Section 4.2, with the addition of the AC magnetic field. The sequence of steps was also as described in Section 4.2. The AC magnetic field was turned on for the entire experiment.

4.4 True Wave Form and Cathodic Protection Assessment

After analyzing the results from previous Sections it was determined that cathodic protection was only feasible for AC densities of 40 and maybe 240 A/m$^2$. AC density of 500 A/m$^2$ produces DC current densities so high that the necessary DC potential to decrease the corrosion rate is too high to be practical.

Two different criteria of cathodic protection were tested for 40 A/m$^2$. The first criteria was to bring the DC potential down to the passive region of the polarization curve and hold the DC potential there while monitoring the potential with the oscilloscope, which shows the true wave form of the potential. The second criteria consisted of decreasing the potential further to the cathodic region of the polarization curve and monitoring the potential with the oscilloscope.
CHAPTER 5

RESULTS AND DISCUSSION

The results of the experiments described in the previous section will be presented and discussed in the present Chapter.

5.1 AC corrosion

The discussion of the experiments will be divided into six subsections: open circuit potential shift or DC potential, photomicrographs, EIS of the surfaces after applying AC, IR drop correction, polarization curves while applying AC starting at cathodic potentials, and starting at shifted DC potential.

5.1.1 Open Circuit Potential - DC Potential

Three different cell configurations were used as indicated in Figure 4.3. The motivation for studying three cell configurations was that preliminary results usually exhibited pitting in specific areas of the samples which led to the belief that the current distribution was not uniform over the sample surface. In an attempt to improve current distribution and assure that the current applied corresponds to the current density targeted, these three cell configurations were studied.

The DC potential was recorded before, during and after applying the corresponding AC density. The plots presented include only the data of two of the cell configurations: cubic and square samples (Figure 4.3). The third cell configuration data, the bar sample, was not included because of an incompatibility of data formats but the results were consistent with those observed with the other two cell configurations. The DC potential as a function of time plots are shown in Figures 5.1, 5.2, and 5.3.

Since the term open circuit potential refers to zero current flowing in an external circuit, it is contradictory to use that term here. The direct current may be zero, but
Figure 5.1: DC potential with respect to the SCE. AC density applied was 40 A/m².

Figure 5.2: DC potential with respect to the SCE. AC density applied was 240 A/m².
Figure 5.3: DC potential with respect to the SCE. AC density applied was 500 A/m². The alternating current is not. For this reason, the potential measured will be referred to as DC potential.

The DC potential shifted as soon as the AC was turned on. The shift occurred toward more negative potentials, and it was more negative for higher alternating current densities. For the smallest current density the shift oscillated between slightly positive or slightly negative with respect to the OCP; i.e., the potential before applying AC.

For 40 A/m² the potential experiences a slight negative or positive shift with periodic peaks which is most likely related to passivation and breaking of the passivation layer. For 240 A/m² there is a great difference between both curves. One curve stabilizes within the first thirty minutes and remains stable until AC is turned off. The other curve rapidly decreases when AC is applied but increases and stabilize at a potential slightly below the OCP. In the case of 500 A/m², the potential drops as AC starts flowing and increases becoming relatively stable at values 100-200 mV below the OCP.
The potential shift that occurs when applying AC indicates that the system is provided with a potential or driving force for certain processes (such as chemical reactions and mass transport) that do not correspond with what a cathodic shift would usually signify, i.e. cathodic protection. Notice that for the current densities tested a negative potential shift is observed, and with sufficient time pitting occurred along with the formation of corrosion products.

In the context of the rectification theory, it is confirmed that controlling AC to be symmetrical produces a rectification potential. However, the complexity of the corrosion process leads to some variations. For example, multiple reactions are possible and their rate is potential dependent. Possibly, during each half cycle the contribution of the reactions varies: in the case of the cathodic half cycle, during high potential values the reaction of oxygen reduction may predominate, while at valley values the water hydrolysis reaction could predominate. In the case of the anodic half cycle, it is possible that preferential dissolution of iron or formation of non protective iron oxides may occur during the higher potentials of the wave, while dissolution of chromium or formation of chromium-rich oxides may occur at the peak values of potential.

Figure 5.4 shows the corrosion products that can form at potentials above the immune zone. It is evident that the sinusoidal wave form can cross different stability regions which can lead to the formation of mixed oxides, possibly unstable and non protective.

Passivation and pitting are important aspects of the corrosion process which cannot be predicted mathematically and are empirical observations. Passivation and pitting can affect the electron transfer rate due to the dielectric properties of the oxide, ionic exchange and diffusion and the total surface area. The complexity of the previously described phenomena are possibly responsible for the variations observed in the DC potentials. As corrosion proceeds and the metal surface changes, the DC
Figure 5.4: Pourbaix diagram for iron species in the ternary system of Fe-Cr-Ni at 25°C and $(\text{Fe}_{\text{aq}})^{\text{tot}} = (\text{Cr}_{\text{aq}})^{\text{tot}} = (\text{Ni}_{\text{aq}})^{\text{tot}} = 10^{-6}$ molal [74].

potential also changes.

It is important to note that the potential shift and severity of corrosion observed is related only to the intensity of the AC. The time was controlled so as to allow the same amount of charge to be transferred to cathodic and anodic processes. After passing the AC, the metal was allowed to recover from the polarization and again reach the rest potential.

The effect of the AC on the pitting behavior is more clearly understood by analyzing the photomicrographs taken after the application of the AC in Figure 5.5 (flat square sample).

5.1.2 Photomicrographs of the Metal Surfaces after Applying AC

Judging by visual inspection of the cell configuration of the bar sample, only the two smaller current densities exhibited pitting but not the one at 500 A/m$^2$. However, under the microscope the reality was that the sample tested with 500 A/m$^2$ had micro
pits all over the surface but not many big pits. On the contrary, the samples tested at the lower AC densities exhibited a few big pits but no micro pitting.

The other two cell configurations exhibited pits at a glance for the three AC densities. Clearly, these two configurations allow a better control of the current distribution and consequently of the current density. The tendency, as expected was more extensive pitting at 500 A/m², followed by 240 and 40 A/m² with the least amount of pits mostly on the edges of the sample. The pictures presented in Figure 5.5 correspond to the flat square sample cell configuration.

It seems that for higher AC densities, pitting has a higher driving force for nucleation and growth of pits, whereas for lower AC densities pitting occurs maybe assisted by defects already present on the surface. The pits most likely grow from those defects. Nucleation and growth of pits seems to be more difficult for the two smallest AC densities used.

It can be said that the severity of corrosion increases with the intensity of AC. More pitting occurs at higher current densities even when the same amount of charge is passed. It is also possible that different reactions take place, not only because the degree of DC polarization is different for the AC densities applied, but because the alternating part of the potential polarization can cross different fields of the Pourbaix diagram, i.e. immunity, passivity, corrosion.

5.1.3 EIS Results after Applying AC

The results from the assessment of the surface with EIS for the three cell configurations are presented next.

The Nyquist plots are presented in Figure 5.6. The plots of magnitude of impedance as a function of frequency are presented in Figure 5.7. The plots corresponding to the phase angle as a function of frequency are presented in Figure 5.8.

From the Nyquist plots (Figure 5.6), where the imaginary impedance (Y-axis) and real impedance (X-axis) are represented, it is clear that the cell configuration of the
(a) After applying an AC density of 500 A/m$^2$ for two hours

(b) After applying an AC density of 240 A/m$^2$ for four hours and ten minutes

(c) After applying an AC density of 40 A/m$^2$ for twenty five hours

Figure 5.5: Photomicrographs of square flat samples after applying AC densities of 500, 240 and 40 A/m$^2$. 
Figure 5.6: Nyquist plots of all three cell configurations and AC densities.
square and cubic samples exhibit similar behaviors for the three current densities. The samples tested at 40 A/m$^2$ produced the semicircle typical of a Randles circuit whereas the other two AC densities curves look like straight lines. In all cases, the highest impedance was found in the sample tested at 40 A/m$^2$ whereas the plots of 240 and 500 A/m$^2$ are more similar to each other in behavior and magnitude.

From the Nyquist plots it is not possible to determine the frequency at which the data was acquired; and often times the data points obtained at high frequencies are not visible in the full scale. The Bode plots are helpful for this purpose as they show the magnitude of impedance as a function of frequency. Figure 5.7 shows the Bode plots of the three current densities. At high frequencies, the first properties sensed by EIS are the bulk properties, in this case, the solution resistance. Resistances are independent of frequency so they appear as horizontal sections of the plot (Figure 5.7). The charge transfer resistance would be found as a horizontal line in the low frequency range. However, the horizontal section is too small for a good estimation of the charge transfer resistance.

In the Nyquist plot, the charge transfer resistance is the diameter of the semicircle. Because the plot is only one portion of a semicircle in the frequency range used, a good approximation is to extrapolate and estimate the value of the impedance where the semicircle would have intersected the real axis.

Figure 5.7 is in agreement with the Nyquist plots. The plots start at high frequencies with the resistance-like response, i.e. independent of frequency, and as the frequency decreases, a change in behavior is observed: the slope of the curve becomes negative and the magnitude of the impedance increases.

In the impedance magnitude plots corresponding to 40 A/m$^2$ no further change of slope is observed, while 500 A/m$^2$ and in a smaller degree 240 A/m$^2$, exhibit more changes of slope at medium and low frequencies. The changes of slope usually indicate the presence of additional frequency-dependent elements.
Figure 5.7: Impedance magnitude as a function of frequency from Figure 5.6.
Figure 5.8: Phase angle as a function of frequency from Figure 5.6.
Figure 5.8 better reveals the number of possible frequency-dependent elements. This figure shows the phase angle as a function of frequency. The plot of 40 A/m² only exhibits one broad maximum which is consistent with one frequency-dependent element. Because the maximum angle is negative and higher than 45°, the element must be capacitive. The plots of 240 and 500 A/m², exhibit two peaks which is an indication of two frequency-dependent elements.

Four equivalent circuits have been proposed to fit the data. Two of the circuits propose the presence of a generalized finite-length Warburg element (GFL) to account for possible diffusion control through the oxide film. In one case, the GFL is in series with a Randles circuit simulating a diffusion process occurring in the region between the electrical layer and the metal surface where the passive film exists. In the second case, the Warburg impedance of the Randles circuit that is in series with the polarization resistance is substituted by the GFL. The equivalent circuits are presented in Figure 5.9. GFL was used because of the open circuit type of response observed in the Nyquist plots at low frequencies, particularly for 240 and 500 A/m².

Figure 5.9: Equivalent circuits proposed with generalized finite-length Warburg element simulating possible diffusion control, a) of the oxide layer following the electrolyte-oxide interface, b) diffusion control in series with the charge transfer resistance.
The other two proposed equivalent circuits look at the passive film as a CPE in virtue of its dielectric properties instead of a diffusion controlling barrier. In one case, the CPE is connected in series with the Randles circuit and in the second case, it is in series with the polarization resistance as shown in Figure 5.10.

Each spectrum was fitted to the four models and the results are detailed in Appendix A.1. The best fit was decided by analyzing the error values, not only of the overall fit, but also the error of each parameter of the fit. The model that best fitted most of the spectra corresponds to the circuit where the CPE simulates the dielectric oxide layer on the surface metal in series with the Randles circuit (Figure 5.10, a). The physical representation of the electrical equivalent model is presented as a schematic in Figure 5.11.

The equivalent circuit in Figure 5.11 consists of a solution resistance followed by a parallel of charge transfer resistance with an electrical layer capacitance that represents the interface solid-electrolyte. This parallel is followed by a capacitor which represents the corrosion product layer formed during the application of the AC.
In a Nyquist plot, an RC parallel produces a semicircle. A series capacitor appears as a straight vertical line whereas a CPE would produce a straight line of finite slope. The Nyquist plot of the model in Figure 5.11, from high to low frequencies, starts by measuring the solution resistance as a point on the real axis; it is followed by a semicircle or a portion of it which is detected by the frequency sweep through the RC parallel. Finally, at lower frequencies the second CPE is detected resulting in a straight line of angle $< 90^\circ$. The described behavior is observed for 240 and 500 A/m$^2$ for all cell configurations.

The spectra corresponding to 40 A/m$^2$ and the reference sample were fitted to the Randles circuit because the plot indicated the presence of only one frequency-dependent element, in this case, the electrical double layer capacitance. It should be noted that the Nyquist plot of 40A/m$^2$-bar sample is hardly a semi circle, as a result, the error of the polarization resistance of the corresponding circuit fit is very large.

Figure 5.12 summarizes the results of the data fitting where the values of each element of the equivalent circuit for the three cell configurations can be found.

In Figure 5.12 a), there is an evident decrease of the charge transfer resistance from 40 A/m$^2$ to higher current densities. A reduced $R_p$ results in accelerated corrosion.
Figure 5.12: EIS fitted parameters for all cell configurations after undergoing AC corrosion at three AC densities: a) charge transfer resistance, b) CPE parameters for double layer, and c) CPE parameters for oxide layer.
rates and it is consistent with previous observations that indicate the higher corrosion rates correspond to higher AC densities.

The expression that relates corrosion current density and charge transfer resistance is given by Equation 5.1 [78]. Where \( \beta_a \) and \( \beta_c \) are the anodic and cathodic Tafel slopes, respectively. The corrosion current density, and consequently the corrosion rate, increase as the polarization rate decrease.

\[
i_{corr} = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c) R_p}
\]

The moderate increase of the polarization resistance from 240 to 500 A/m² was unexpected because the weight loss data show higher corrosion rates as the AC density increases as shown in Figure 5.13. This behavior is an indication that AC corrosion is a complex phenomena and that other parameters, besides charge transfer resistance, must be considered. Equation 5.1 was developed for DC corrosion so it may not be appropriate to describe corrosion rates of AC corrosion as it only incorporates the Tafel slopes and polarization resistance as variables. From Figure 5.13 it is clear that the AC density or AC potential play and important role in determining the corrosion rate. However, although both curves grow as AC density increases, the corrosion rate curve grows in a exponential manner while the DC \( i_{pass} \) curve increases more slowly.

Figure 5.12 b), which shows the CPE\(_{dl}\) values and corresponding N parameters, demonstrates a very complex behavior that cannot simply be attributed to the thickness of the electrical double layer. At the point when EIS was performed, the samples had undergone relatively intense corrosive conditions that can hardly result in similar values of capacitance.

For example, the diffuse layer structure mimics the topological conditions of the oxide layer between the electrolyte and the metal, worsening the non uniformity of the double layer. Also, the composition of the electrolyte changes due to the metal dissolution, in consequence, metallic ions will form part of the double layer structure.
It was shown in Equations 2.17 and 2.18, that the concentration and charge of the ions that form the electrical double layer are fundamental in determining the length and capacitance of the double layer. The two mentioned conditions, i.e. roughness of the surface and chemical composition of the double layer, increase the complexity of the electrical double layer and can result in great variability as seen in Figure 5.12 b).

Three of the CPE$_{dl}$ values presented in Figure 5.12 b) have errors above ten percent which is the conservative limit of the researcher to consider the fit acceptable. For this particular circuit element, the high error values further increase the uncertainty of the trends and values measured.

Figure 5.12 c) shows the CPE$_{ox}$ fitted values corresponding to the oxide layer formed on the surface of the samples during the application of AC. All cell configurations present an increment of the value CPE from 240 to 500 A/m$^2$. The parameter
N decreases with the exception of the square sample configuration.

These results are less variable than the \( \text{CPE}_{\text{dl}} \), possibly because \( \text{CPE}_{\text{ox}} \) only relates to the oxide layer structure and not to the electrolyte. One possibility to explain the increase of \( \text{CPE}_{\text{ox}} \) is that the thickness of the layer is thinner for 500 A/m². However, because the parameter N is less than 0.9 in both cases, the interpretation of CPE as capacitor may not be the best. For values of \( 0.8 < N < 0.6 \) a better alternative is to see CPE as responsible for anomalous diffusion through the oxide layer [39].

Because CPE is a distributed element, another possible reason for these low values of parameter N can be the structure of the oxide layer itself. It is known that the kinetics of the electrode reaction determine the physical characteristics of the deposit layer [9]. For example, copper reduction at high reduction rates results in dendritic deposits, whereas lower reduction rates result in more uniform planar deposits [79]. Similarly, a less uniform deposit is expected at 500 A/m² than at 240 A/m² of AC density and this seems to be confirmed by the small values of N.

Other scientists who have studied the passivity of stainless steels have reported other important structural characteristics. Layers of different oxides, where the oxygen concentration decreases from the metal-environment interface to the metal-oxide interface, are not unusual [10]. The chemical composition of the passive layer also changes over time of immersion and potential at which the passive layer is formed [80]. Figure 5.14 illustrates the mentioned structural features of passive films.

Particularly the later example, which addresses the differences in the oxide nature depending on the potential at which they form, is of great importance when analyzing the passivity of a metal corroded by AC. A layered oxide structure of iron-rich and chromium-rich oxides may form due to the different potentials that the metal is exposed to during the AC cycles.

The oxide formed on the electrode under AC is very complex and difficult to study. Several attempts were made to study the oxide layer, however, the layer was usually
(a) Proposed models for iron having single or double layers containing combinations of oxides, hydroxides, and oxyhydroxides [10].

(b) Capacitive behavior of Type 316 L stainless steel after different immersion times in artificial seawater [80].

Figure 5.14: Structural features of oxide layers.
destroyed when removed from the electrolyte. When immersed in the electrolyte, it looked as if an orange cloud extending toward the solution surrounded the surface, when removed, the layer was washed away and even touching it with the finger tips would remove most of it.

In summary, the most general observations are:

- All cell configurations showed similar DC potential as a function of time behaviors

- In terms of pitting distribution and corrosion uniformity throughout the electrode surface, the flat square sample configuration was the most appropriate cell configuration. The bar and cubic samples presented more variability and not all the facets were corroded to the same extent

- In terms of EIS results, the $R_p$ trend is the same independently of the cell geometry. Both $\text{CPE}_{\text{dl}}$ and $\text{CPE}_{\text{ox}}$ are more dependent on the cell geometry

- The cell configurations of the bar and cubic samples follow the same trends for all the elements and parameters, as observed in the three graphs of Figure 5.12

Considering all the results presented, it was decided that the bar sample configuration was the least convenient of all. The flat sample configuration was adopted for the following experiments with the exception of the true wave form experiments, which were performed using the cubic sample cell configuration.

### 5.1.4 IR Potential Compensation

The DC polarization response to the application of AC is the study of potentiodynamic polarization curves while AC is being applied simultaneously.

The studies found in the literature are limited to the galvanostatic control of both AC and DC which does not permit the study of the passivation behavior [70–72].
The experimental set up used in this research, where AC is controlled galvano-
statically and a DC potential sweep is performed, allows the study the passivation
behavior of the metal while AC is being applied.

Several preliminary experiments were done to optimize the system. The most
important features that were taken into account have been:

1. The potential drop compensation due to the external circuit
2. Noise control, filters, and data acquisition parameters
3. Anodic to cathodic surface area ratio
4. Symmetry of the cell which was optimized, thanks to the results shown in
   Subsection 4.1.

The potential drop compensation proved to be of great importance. The data was
corrected by subtracting the potential drop caused by the current passing through
the external circuit.

The resistance of the external circuit was determined separately by following this
procedure: with the external circuit connected to the potentiostat and electrochemical
 cell, a stair case type of polarization was done (potential scan-potential hold). In
addition to the potentiostat, a high impedance multimeter was connected in parallel
between the working electrode and the reference electrode.

During each hold step of the scan, the current, the potential measured by the
potentiostat (uncompensated), and the potential measured by the multimeter (com-
pensated) were recorded. The value of the total resistance, $R$, was calculated using
Equation 5.2.

$$E_{\text{compensated}} = E_{\text{uncompensated}} - i \times A \times R$$  \hspace{1cm} (5.2)

To illustrate how important it is to perform the correction of the potential when
using the external circuit, Figure 5.15 is included. It is demonstrated that the po-
tential drop across the external circuit can be very significant, particularly for higher
current densities. However, it is possible to perform a complete study of the cathodic, anodic, passive, and transpassive behavior of the metal. Galvanostatic control does not allow to study the passive behavior which is of major importance for stainless steels. The discussion of the curves will be presented in the next Subsection.

The noise created by the AC was controlled using the low pass 590 Hz built-in filter of the potentiostat, which filters all frequencies above 590 Hz. Following the recommendation of the potentiostat's manual to avoid 60 Hz noise, the data acquisition rate was reduced to 240 samples per second. Additionally, a 300 $\mu$F capacitor was placed between the working and the DC counter electrodes. The capacitor aimed to confine any AC in the right side mesh of the circuit to the loop conformed by the capacitor, working and counter electrodes (see Figure 4.1).

The success of these experiments is very important as, up to this date, there have not been reported polarization curves that reveal the passive behavior of the metals undergoing AC corrosion. As an example, Figure 5.16 is presented. It was a failed attempt to obtain polarization curves while applying AC which lacked noise control. In the corrosion community, the most common approach has been to use galvanostatic control (set current and measure potential) to draw the graphs as shown in Figure 5.17. As a result, passivity cannot be studied and only active metals can be used. It should be noted that both examples presented were obtained using the external electrical circuit presented in Figure 4.2.

Several surface area ratios and cell symmetry were tested. Because the AC densities are so high with respect to the DC densities, stray currents are more likely to occur. Any short path will result in the concentration of current to a small area, and the actual AC density will be different from the one that was calculated. The surface area of the AC counter electrode was increased to at least ten times that of the working electrode.
Figure 5.15: Effect of potential drop compensation due to external circuit.
Figure 5.16: Polarization curves of a coated steel containing a 10 mm defect in the concentrated carbonate/bicarbonate solution at various AC current densities [81]. Excessive noise.
5.1.5 Polarization Curves while Applying AC: Starting at Cathodic Potentials

The three alternating current densities were applied during the DC polarization curves and the resulting cyclic polarization curves are shown in Figure 5.18. From the graph several corrosion-related parameters were extracted and summarized in Table 5.1.

Although the four polarization curves were performed with the same polarization parameters, the curves are modified when correcting for the IR drop of the external circuit as shown in Figure 5.15.

Figure 5.18 includes a reference polarization curve where no AC was applied. In the cathodic branch of this curve, two distinctive regions are separated by a limiting current. Because the experiments were performed in air, the cathodic reaction that takes place from $E_{corr}$ to the limiting current region is most likely the hydrolysis of water in the presence of dissolved oxygen, $2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^-$. From the limiting current regime to more negative potentials, a new cathodic reaction takes place, most likely the hydrolysis of water to produce hydroxyl ions and hydrogen gas, $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$. The only reactant in later reaction is water, which is
Figure 5.18: Cyclic polarization curves while applying AC after compensating the potential drop due to the external circuit.

Table 5.1: Electrochemical parameters extracted from cyclic polarization curves in Figure 5.18

<table>
<thead>
<tr>
<th>AC density, A/m²</th>
<th>No AC</th>
<th>40</th>
<th>240</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$, V</td>
<td>-0.503</td>
<td>-0.923</td>
<td>-0.816</td>
<td>-0.721</td>
</tr>
<tr>
<td>$E_{pass}$, V</td>
<td>-0.450</td>
<td>-0.880</td>
<td>-0.780</td>
<td>-0.660</td>
</tr>
<tr>
<td>$E_{pit}$, V</td>
<td>0.093</td>
<td>-0.106</td>
<td>-0.279</td>
<td>-0.394</td>
</tr>
<tr>
<td>$E_{pit} - E_{corr}$, V</td>
<td>0.411</td>
<td>0.819</td>
<td>0.537</td>
<td>0.327</td>
</tr>
<tr>
<td>$i_{pass}$, µA/cm²</td>
<td>1.038</td>
<td>17.66</td>
<td>69.97</td>
<td>105.2</td>
</tr>
</tbody>
</table>
unlikely to experience a limiting current regime, i.e. diffusion control.

\[
\begin{align*}
O_2 + 4H^+ + 4e^- &= 2H_2O \\
E_{(SHE)} &= 1.23V
\end{align*}
\]

\[
\begin{align*}
2H_2O + 2e^- &= H_2 + 2OH^- \\
E_{(SHE)} &= 0.00V
\end{align*}
\]

Figure 5.19: Schematic representation of possible cathodic reactions occurring when AC is not applied.

Figure 5.19 is a schematic representation of the cathodic branch of the curve in which no AC was applied. However, because the electrolyte is artificial seawater, one cannot discard other reactions in which different ions participate. In fact, a white deposit forms on the surface of the metal electrode at lower potentials, but XRD analysis was inconclusive on identifying the compound or mixture of compounds.

None of the curves obtained while applying AC exhibits a cathodic branch similar to the curve obtained without AC. It is possible that for those curves the reaction of water hydrolysis in which hydroxyl ions and hydrogen gas are produced, \(2H_2O + 2e^- \rightarrow H_2 + 2OH^-\), is dominant; whereas the dissolved oxygen may be used in the metal passivation reaction. Since limiting currents are observed when the reaction rate is controlled by diffusion, it is possible that at higher rates, water hydrolysis becomes dominant and the effect of depletion of dissolved oxygen is not observed.
The curves when AC was applied appear shifted toward higher current densities. The shift is larger for the higher AC densities. Considering that the metal is experiencing a DC current and an AC current, one must keep in mind that corrosion is not only due to the anodic DC current density but also due to the anodic half cycle of the AC current.

The higher current densities observed while AC increases indicate that the metal corrodes faster, not only because of the anodic half cycle of the AC component of the current, but because the DC component has a higher current density. Possibly, AC provides additional energy to the reactions, so they proceed faster when AC is present.

The potential known as $E_{\text{corr}}$ is found in the graph at the point where the net DC current is zero (or very small in a logarithmic scale). The potential appears shifted toward more negative potentials when compared to the curve where no AC was applied, which is consistent with the observation that the DC potential shifts to more cathodic potentials when AC is applied.

Interestingly, the order of the $E_{\text{corr}}$ of the curves as AC density increases, challenges the observations presented in Subsection 5.1.1. Usually, the DC potential measured before starting the potential scan (frequently referred to as OCP because no DC current is flowing) coincides with $E_{\text{corr}}$. This behavior was not observed in the polarization curves. Moreover, the larger the AC, the bigger the DC potential shift. However, in Figure 5.18 $E_{\text{corr}}$ is more negative when the AC density of 40 A/m$^2$ was applied, but it was the highest when the AC density of 500 A/m$^2$ was used.

This observation can be explained by considering how the curves were obtained. The corrosion potential observed in these curves is not equivalent to the DC potentials presented in Section 5.1 because the way the polarization was carried out was different.

So that the curves could start with similar surfaces, the AC was applied at the lowest DC potential and a window of five minutes was provided to allow for stabilization.
The corrosion of the surface is considered to be minimal under these circumstances and the curves comparable. The DC potential presented in Figures 5.1, 5.2, and 5.3 was recorded while accelerated corrosion was occurring. As a consequence, the $E_{\text{corr}}$ observed in the present experiments and the DC potential from the experiments presented in Subsection 5.1.1 are not equivalent, as the metal surfaces are very different.

The changes in the passivation behavior are possibly the most interesting effects of AC. When studying the passivation of a metal, two critical parameters are considered: the passivation current density ($i_{\text{pass}}$ in Table 5.1) and the passive range ($E_{\text{pit}} - E_{\text{corr}}$ in Table 5.1). The passivation current density is consistently higher as AC increases which indicates a less protective passive behavior of the metal.

The passive range, however, shows a peculiar tendency. When comparing the curve without AC with the one corresponding to 40 A/m$^2$, the passive range is larger when 40 A/m$^2$ AC density was applied. There is an increase in the range from $E_{\text{corr}}$ to $E_{\text{pit}}$ which is 411 mV when no AC was applied and 819 mV when 40 A/m$^2$ AC density was applied. Generally speaking, this behavior is desirable because it implies a reduced tendency to localized corrosion; however, because the change comes along with an increased passivation current density it should be treated carefully. In fact, all the curves where AC was applied are shifted to the right (toward higher current densities) which also corresponds to higher corrosion rates.

The apparently contradictory behavior observed when 40 A/m$^2$ is applied can be explained by considering how the experiment was performed. While the DC potential scan was done, the AC portion of the potential was probably reaching the passive range and the metal surface was passivating. As a result, the $E_{\text{pass}}$ is experienced earlier. In fact, the amplitude of the AC potential wave when 40 A/m$^2$ was being applied was approximately 440 mV, so indeed while the cathodic branch was drawn, the anodic half cycle of the potential was crossing the passivation region.

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When compared with 40 A/m², this range is smaller for 240 A/m² (537 mV), and even smaller for 500 A/m² (327 mV). At these current densities the AC portion of the potential is most likely exceeding the pitting potential at virtually all points of the DC scan. Actually, the amplitude of the AC potential wave was 920 mV and 1620 mV, respectively. Even when the cathodic branch was drawn, the anodic half cycle of the potential was exceeding the pitting potential. As a result, passivation is less effective, higher DC densities are experienced, and smaller passive ranges are observed. In Appendix B, the three graphs are presented with a superimposed shadow that represents the AC potential variation at all times during the data acquisition. It is shown clearly that the AC potential may cross the passivation region during cathodic polarization at low current densities which further results in a lower \( E_{corr} \) or \( E_{pass} \) and in a broader passive range. However, at higher AC densities the AC potential may cross the pitting potential even during cathodic polarization which results in an ineffective cathodic protection and in a smaller passive range.

The decrease of the pitting potential as AC density increases is very evident and possibly a consequence of the high corrosion rates and the lessened passivation ability.

It has been recognized that \( E_{pit} \) depends on temperature, alloy, and halide concentrations [25]; however, these variables remain equal for all experiments. If the pitting potential is related to the stability of oxygen gas, \( O_2(g) + 4 H^+ + 4e^- \rightarrow 2H_2O \ (E^o = 1.23 \text{ V}) \), and if this reaction also shifts to the right when AC is applied, then it is possible that it would cause the new pitting potential to become more negative [78].

In Figure 5.20 can be found a schematic drawing of the different shifts observed from a small to a high AC density. When AC is present, all the reaction rates are increased resulting in shifted potentials as shown in Figure 5.20 and the shift is more significant for higher AC densities. As a result, \( E_{corr} \) becomes more positive while \( E_{pit} \) becomes more negative, the passive range is reduced, and the DC current densities are higher.
5.1.6 Polarization Curves while Applying AC: Starting at the Shifted DC Potential

The anodic, cathodic and cyclic polarization curves are presented in Figures 5.21, 5.22, and 5.23. The same curve from the previous subsection is included for comparison (black). The anodic and cathodic curves are red dotted lines and red dashed lines, respectively. All the data has been corrected for the potential drop of the external circuit.

It is pertinent to recall that the anodic and cathodic polarization curves were performed differently than those described in the previous subsection. There, the AC was turned on right before the beginning of the potential scan, at a cathodic potential. In the case of the anodic and cathodic curves, the AC was turned on and the potential was allowed to stabilize for a short period of time to minimize the corrosion of the surface. After this short period of time, the potential scan began toward cathodic or anodic potentials while the AC continued passing. Each anodic and cathodic curve was obtained from new samples so that each experiment had similar surfaces.
Figure 5.21: Polarization curves while applying an AC density of 40 A/m$^2$. Curve started at cathodic potentials, black. Anodic cyclic polarization curve, red dotted line. Cathodic polarization curve, red dashed line.

Notice that the DC potentials at which the scans started are in the same range of values as those observed in Figures 5.1, 5.2, and 5.3, roughly -0.200 V for 40 A/m$^2$, -0.450 V for 240 A/m$^2$, and -0.550 for 500 A/m$^2$. Moreover, it can be observed that the DC potential at which the cathodic and anodic curves start, falls somewhere between $E_{pit}$ and $E_{repass}$, or lower in the case of Figure 5.23. This observation is in agreement with previous experiments which showed that the three AC current densities studied exhibit pits with sufficient time, as the alternating portion of the potential is constantly exceeding the pitting potential. The peak value of the potential continuously crosses the pitting potential which has an accumulative effect on the metal causing pits over time.

Two of the cathodic curves in Figures 5.21 and 5.22, start off with some noise. This behavior is nothing but an artifact and it is not related to the true behavior of the corrosion cell.
Figure 5.22: Polarization curves while applying an AC density of 240 A/m². Curve started at cathodic potentials, black. Anodic cyclic polarization curve, red dotted line. Cathodic polarization curve, red dashed line.

The cathodic curves tend to overlap the black curve showing very similar behaviors although the curves were obtained in different ways.

However, the cathodic curves experience a change of the slope around 1.2 V, -1.0 V and -0.9 V in Figures 5.21, 5.22, and 5.23, respectively. Although the change of slope could be interpreted as a transition to limiting current (concentration polarization), it could also be caused by the formation of the white precipitate mentioned before, which reduces the surface area available for reaction. This deposit appeared in all experiments at low potentials. Because the conductivity of the deposit is probably lower, the total current density is reduced producing a change of slope.

It has been reported that in seawater, the high pH developed at the metal surface, as result of the cathodic reaction, promotes the precipitation of magnesium hydroxide [82]. This is actually favorable as the necessary current (power demand) of the cathodic protection is smaller as less current is required to produce the same current.
Figure 5.23: Polarization curves while applying an AC density of 500 A/m². Curve started at cathodic potentials, black. Anodic cyclic polarization curve, red dotted line. Cathodic polarization curve, red dashed line.

density.

The cyclic anodic polarization curves do not exhibit the passive range inherent to passive metals, such as stainless steel. The passive behavior of the alloy in the presence of AC is only revealed when the polarization starts at cathodic potentials as was shown in Figure 5.18.

The transpassive nose drawn in during the anodic polarization tends to overlap with the black curve at \( E_{\text{pit}} \) and \( E_{\text{repass}} \). The areas are different mainly because the potential at which the scan reversed was higher for the anodic polarization curves. This behavior confirms the validity of the potentials reported, \( E_{\text{pit}} \) and \( E_{\text{repass}} \).

Polarization scans starting at cathodic potentials seem to be advantageous to study the passive behavior in the presence of AC as a complement of the anodic and cathodic polarization curves. Corrosion scientists tend to overlook the cathodic branch and concentrate on the anodic branch; however, it was demonstrated that
starting the scan at cathodic potentials is necessary to reveal the passive behavior of
the alloy in the presence of AC.

5.2 Corrosion under Alternating Magnetic Fields

The study of the effect of magnetic fields on corrosion was divided into two parts:
first, the EIS analysis at open circuit potential; that is, free corrosion in the presence of
different AC magnetic fields; second, the polarization curves performed under different
AC magnetic fields.

5.2.1 EIS Assessment of the Effect of Magnetic Fields on Corrosion

The applied magnetic fields had no effect on the OCP; thus it remained stable. However, the results from EIS proved to be influenced by the magnetic fields. The corresponding plots are shown in Figure 5.24. The data was fitted to the Randles circuit, and the values of the fitted parameters are presented in Table 5.2.

Table 5.2, shows the values of the parameters derived from fitting the data to
the Randles circuit: solution resistance, $R_s$; charge transfer resistance or polarization
resistance, $R_p$; and constant-phase element parameters CPE and N, which simulate
the electrical double layer.

Notice that the charge transfer resistance decreases as the magnetic field density
increases indicating an enhanced ability of electron transferring and hence a faster
reaction rate.

Although the magnetic fields used in these experiments were small, particularly
in comparison to those used in other research studies of 800 mT or less (800 G) [83–86], they were capable of reducing the polarization resistance by 30 and 90 pct. approximately, for 49.1 G and 56.8 G, respectively. It is not surprising, then, why corrosion of pipelines near high tension lines has received so much interest [87–90].

Magnetic fields influence the movement of charges, as it was pointed out in Section 2.2. Thus, magnetic fields are capable of influencing the mass transport of ions in the
Figure 5.24: EIS results on the effect of alternating magnetic fields on free corrosion.

Table 5.2: Circuit fit elements corresponding to EIS of experiments assessing the effect of alternating magnetic fields on corrosion

<table>
<thead>
<tr>
<th></th>
<th>0 Gauss</th>
<th>Error, %</th>
<th>49.1 Gauss</th>
<th>Error, %</th>
<th>56.8 Gauss</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs, omh cm$^2$</td>
<td>3.667</td>
<td>0.8032</td>
<td>3.747</td>
<td>1.3847</td>
<td>1.972</td>
<td>1.9203</td>
</tr>
<tr>
<td>Rp, omh cm$^2$</td>
<td>714,560</td>
<td>4.5554</td>
<td>503,310</td>
<td>5.6875</td>
<td>71,859</td>
<td>10.062</td>
</tr>
<tr>
<td>CPE, S$^{-1}$ (sec rad$^{-1}$)$^n$</td>
<td>$4.65 \times 10^{-5}$</td>
<td>0.1007</td>
<td>$4.44 \times 10^{-5}$</td>
<td>0.7845</td>
<td>$21.96 \times 10^{-5}$</td>
<td>1.3738</td>
</tr>
<tr>
<td>N</td>
<td>0.87134</td>
<td>0.4542</td>
<td>0.84781</td>
<td>0.1748</td>
<td>0.81115</td>
<td>0.3217</td>
</tr>
</tbody>
</table>
solution and of the electrons in the metal.

Magnetic field stirring of electrolytes has been described and used as is the case of the magneto-hydrodynamic (MHD)-based micro pumps [91]. The theory states that when a potential difference is applied across two opposing electrodes, a current flux flows through the solution. In the presence of a magnetic field, the current flow interacts with the magnetic field following Lorentz law, Equation 5.3.

\[ \vec{F}_M = \vec{J} \times \vec{B} \]  

A force is created by the cross-product of the flux, \( \vec{J} \), and the magnetic field density, \( \vec{B} \), according to the right-hand rule. Thus, the generated force drives fluid motion. A magnetic field can modify the trajectory and velocity of the ions in solution, affecting corrosion kinetics due to different diffusion conditions.

Although the fluid motion is expected to influence the corrosion rate, it cannot explain the fact that different magnetic field orientations have a more intense effect than others [86].

Moreover, the structure of the electrical double layer must be sensitive to the magnetic field applied. Table 5.2 shows that the CPE values are essentially the same for 0 G and 49.1 G, but it is larger for 56.8 G. This observation seems to indicate that a magnetic field density of 49.1 G is too weak to induce changes in the electrolyte, but strong enough to influence the electron transfer kinetics as indicated by the reduced charge transfer resistance. A magnetic field density of 56.8 G is, however, strong enough to influence both metal and electrolyte.

In a perfect capacitor, capacitance is inversely proportional to the thickness of the dielectric layer where the charge accumulates. An increase of CPE, which is comparable to the capacitance, C, could be the result of the thinning of the electrical double layer. The relationship of capacitance per unit of area and thickness, \( d \), of the dielectric medium is given by Equation 5.4.

\[ C = \frac{\varepsilon \varepsilon_0}{d} \]  

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In this case, the metal has not experienced severe corrosion and the metal surfaces are possibly comparable. More importantly, the passive behavior of the metal relies on the passive chromium oxide film of only 300-600 nm thick [80, 92]. The dramatic change of CPE is possibly more influenced by a reduction of thickness of the double layer due to the presence of the magnetic field.

In absence of external perturbations other than temperature, the Debye length (distance over which significant charge separation can occur) is given by Equation 2.18.

\[
L_D = \left[ \frac{RT\varepsilon_0}{\sum z_i^2 F^2 c_i} \right]^{1/2}
\]

Here, the charge and concentration of the ions near the interface are inversely proportional to the thickness of the layer. Furthermore, this one dimensional model considers only coulombic forces, drag forces and temperature. Assuming that the relationship \( L_D \propto 1/z^2 c_i \), is still valid, it is possible that the additional force that the magnetic field exerts on the ionic charges may influence the product \( z^2 c_i \), reducing the length of the Debye layer.

Additionally, the potential across the electrical double layer, under normal circumstances, falls exponentially with distance. Simplifying, the potential drop in the diffuse layer (Equation 2.16) follows the expression, \( \Phi(x) = \Phi_0 \exp(-\tau x) \). Further, as the ionic concentration increases, \( \tau \) increases and \( \Phi(x) \) falls more sharply [29].

The behavior of the charge transfer resistance implies an increase of the corrosion rate as the AC magnetic field is increased. The parameter N decreases as the magnetic field intensity increases, revealing more heterogeneity of the surface. Indeed, higher corrosion rates can lead to rougher surfaces.

The charge transfer resistance depends on characteristics of the metal such as free-electrons density and conductivity. It also depends on variables related to the reaction itself such as symmetry factor, number of electrons transferred, and temperature. Next, the response of metals to magnetic fields will be analyzed.
When a metal is in the presence of a magnetic field, different effects occur. *Diamagnetism* is experienced when the magnetization induced opposes that of the applied magnetic field. It is a feeble magnetic response consisting on the acceleration of the orbital electrons due to electromagnetic induction caused by the penetration of the external magnetic field to the orbit. According to Lenz's law, the magnetic flux produced by this acceleration is always opposite to the change to the external magnetic field [93]. Materials containing no atomic magnetic moment tend to behave in this manner.

Suppose that a magnetic field is applied to a diamagnetic atom (filled up to s- or p- orbitals). The resultant intrinsic angular momentum of the electrons remains zero but the orbital motion is slightly changed. When a magnetic field $\vec{B}$ is switched on, the force on the electron is increased by an amount $-e \vec{v} \times \vec{B}$, where $\vec{v}$ is the velocity of the electron. This extra force will be assumed here to be small enough that the electron remains in its original orbit. The angular speed of the electron in the orbit changes to the value $\omega'$, where $\omega' \approx \left( \frac{se^2}{4\pi\varepsilon_0 m_e r^3} \right)^{1/2} + \frac{eB}{2m_e}$.

In the presence of a magnetic field, the angular velocity of the electron is increased by an amount $eB/\pi\varepsilon_0 r^3$, a quantity known as the Larmor angular frequency [19]. Although these equations are simplified and were developed for fixed magnetic fields, it is expected that the AC magnetic fields could potentially have similar effects. It is expected that the frequency of the AC magnetic field would have a similar effect on the final $\omega'$.

*Paramagnetism* describes a feeble magnetism where the magnetization induced has the same direction of the applied magnetic field. It is observed in materials that contain magnetic atoms or ions widely separated so that they exhibit no appreciable interaction with one another. The magnetic moments are randomly oriented in the absence of an external field due to thermal agitation.
If there is sufficient energy exchange between dipoles they will interact, and may spontaneously align to form magnetic domains (ferromagnetism or antiferromagnetism). Thermal agitation of the dipoles may destroy the magnetic domains of ferromagnetic materials when they are above their Curie temperature; at this point, the available thermal energy overcomes the interaction energy between the spins.

When exposed to an external magnetic field, the electrons close to the Fermi level will respond to the field resulting in a small surplus of spins (up or down). This effect is known as Pauli-paramagnetism. The net effect is the balance between the paramagnetic response from the outer electron spin alignment and the diamagnetic response opposite to the applied field (diamagnetism), produced by the core electrons of the atom.

Stronger magnetic effects are typically observed when d- or f-electrons are involved. The origin of the strong response is the presence of spontaneous magnetization produced by a parallel alignment of spins.

Figure 5.25 shows two plots of the density of state distribution of nickel. In Figure 5.25 (a), the parabola represents the s-band which is totally filled (gray). Above the energy axis, the spin up states are depicted and below the line, the spin down states can be found. Some overlap occurs between the d- and the s-band. Notice also that the d-band is partially empty. The vertical line that separates the gray (full states) and white area (empty states) indicates the Fermi energy level.

Figure 5.25 (b) shows the new distribution of states and the new Fermi energy level as a result of the spin redistribution in response to the magnetic field. When a magnetic field, $H$, is applied parallel to the spin down, the spin band is lowered by an amount $E_H = 2M_B H$. Therefore the electrons at the top of the spin up band will be transferred to the spin down band by reversing their spins, bringing their Fermi energy levels to a common value. The number of electrons, $\Delta n$, which will be transferred is given by the area between the old and new Fermi energy levels \([93, 94]\).
Figure 5.25: Density of states distribution in nickel (a) in the absence of a magnetic field and (b) under a magnetic field [94].
The 13 Cr supermartensitic alloy is an iron-chromium-nickel based alloy, as such, its magnetic response is expected to be dictated by the unpaired d-shell electrons, mainly by the spin alignment of the d-electrons in response to the magnetic field, and in a smaller degree, by the induced changes in the orbital angular frequency of the electrons of inner shells. Thus, the metal becomes magnetized and a redistribution of energy states and new Fermi energy level occurs.

Other possible effect of the magnetic field on the electrochemical charge transfer process is related to the Fermi energy of the involved species.

It was mentioned in Subsection 2.3.4 that a charge will be transferred across a metal-electrolyte interface, provided that the Fermi energy levels of the donor and acceptor are appropriate. The tunneling of electrons through barriers has a special feature when the transition occurs radiation-less: the electron has to have the same energy on both sides of the barrier. This condition is depicted in Figure 5.26.

![Diagram](https://example.com/diagram.png)

Figure 5.26: Condition for tunneling: $E_R$ must be equal or larger than the Fermi energy [29].
In Figure 5.26, the reference level of energy is that of an electron isolated in vacuum. $\Phi$ is the energy necessary to bring an electron from the Fermi energy to a different resting place, and $E_R$ is the energy necessary to bring an isolated electron from vacuum to a new position in the solution near the metal [29].

Oscillations of the Fermi energy of iron due to magnetic fields has been documented in the literature [95, 96]. Because the magnetic field influences the density of states distribution, then, it is possible that the available number of electrons with higher energy for the electrochemical reaction would increase in turn, and with that, the reaction rate.

### 5.2.2 Polarization under Alternating Magnetic Fields

The effect of the magnetic field on polarization curves was also studied. Because the results in the passive range (lowest current densities) were influenced by electromagnetic noise, they are not reported. However, the transpassive region (higher current densities) was strongly influenced by the magnetic fields and is shown in Figure 5.27.

The potential sweep that produced each curve was done with the same parameters, i.e. initial potential, vertex potential, final potential, and scan rate. The data is presented in the form of current density as a function of time, although it is understood that the time at which each data point was obtained corresponds also to the same potential.

It can be seen in the graph how the magnetic field increases the transpassive current density and hence the extent of pitting. Photomicrographs of the pitted samples are presented in Figure 5.28. Not only the amount and size of the pits increases; additionally, the pits appear in a vertical array which is perpendicular to the magnetic field lines. These results show that the interaction of the magnetic field, even at this low intensity, is probably more complex than simply Lorentz force stirring.
Possibly, the distorted magnetic field lines around the pits have a catalytic effect on their neighbors. It has been stated that the corrosion rate in magnetized pipelines (after inspection with smart pigs) can increase around the defects, precisely due to the residual magnetic field [87–90]. On the other hand, the ions in solution which move according to the paths dictated by the Lorentz force, are stirred. Inside the pits, the solution is continuously replenished which further accelerates the metal dissolution.

5.3 AC Corrosion under Alternating Magnetic Fields

The effect of alternating magnetic fields on AC corrosion was studied with EIS at OCP after applying AC in the presence of 56.8 G alternating magnetic field, and with cyclic polarization curves performed while applying an AC density of 40 A/m² and different magnetic fields.
5.3.1 EIS Assessment of the Effect of Alternating Magnetic Fields on AC Corrosion

One of the most noticeable differences of these experiments with respect to those where no magnetic field was applied (Subsection 2.4.3), is that pitting was always visible. However, superimposing the magnetic field to the AC resulted in micropitting and hardly any macropits.

The DC potential was not influenced by the presence of the magnetic field, the behavior observed was the same presented in Subsection 4.2.

The samples were analyzed with EIS after undergoing AC corrosion in the presence of a magnetic field of 56.8 G. EIS was performed two times: the first time with the magnetic field on, and the second time right after that, without the magnetic field. The results from EIS, while the magnetic field was on, are shown in Figure 5.29. Because the plots from both measurements are so similar, only one of them is shown here (measurement with magnetic field turned off) and the other is presented in
Appendix C.1.

Similarly to the data from Subsection 5.1.3, the data was fitted to four different electrical equivalent circuits (Figures 5.9 and 5.10). The results of the four circuit fit are presented in Appendix C.2, but only the best fit is presented and discussed here.

The electrical circuit that best fitted the data corresponds to the model presented in Figure 5.10. The parameters of the circuit fit are presented in Figure 5.30 for both measurements, with and without the magnetic field. To facilitate comparison, the values have been included in the graph: data labels above the point correspond to the measurement with the magnetic field on (red), and the data label below the point.
Figure 5.30: EIS fitted parameters after undergoing AC corrosion in the presence of alternating magnetic field of 56.8 G. EIS performed with the magnetic field off (data values below, blue), and EIS performed a 56.8 G magnetic field (data values above, red).
corresponds to the measurement without the magnetic field (blue).

Figures 5.6, 5.7, 5.8, 5.29, and C.1 in Appendix C.1, are very similar. The Nyquist plots Figure 5.29 (top) show the imaginary impedance (Y-axis) and real impedance (X-axis). The curve corresponding to the smallest AC density is a semicircle typical of a process controlled by the charge transfer occurring at the interface metal-electrolyte. The other two results look like straight lines in the low frequency range. This behavior could be attributed to diffusion control if the angle were 45° or to a constant-phase element (CPE) if the angle were slightly less than 90°, which occurs when the parameter N is less than 1. The high frequency response is not visible in the full scale Nyquist plots of the samples corresponding to 240 and 500 A/m².

Figure 5.29 (bottom left) shows the magnitude of the impedance as a function of frequency. The plot corresponding to the smallest current density is a Z-shaped curve which is in correspondence to a charge transfer controlled process. On the other hand, the curves of 240 and 500 A/m² exhibit changes of slope after the high frequency horizontal section of the curve (solution resistance).

The smallest current density seems to have only one slope; the plots corresponding to 240 and 500 A/m² more clearly show two slopes. As it was mentioned before, changes of slope in the curve between the high and low frequency region indicate the number of frequency-dependent elements present in the electrical circuit.

The presence of two frequency-dependent elements is further confirmed by analyzing the phase angle plot in Figure 5.29 (bottom right). Here, each frequency-dependent element produces a peak for a total of two, for the plots corresponding to 240 and 500 A/m², and only one for 40 A/m².

Again, the equivalent circuit that best fits the data corresponds to the one presented in Figure 5.11. It has been used in the literature in the study of anodized or passivated metals [75–77].
In the Nyquist plots corresponding to 240 and 500 A/m², the RC semicircle is too small to appear in the full scale plot; however, their presence was confirmed. These two spectra fully satisfy the predicted behavior of the selected model.

The values of the electrical equivalent elements and parameters are presented in Figure 5.30. The fitted parameters and errors can be found in Appendix C.2.

Similarly to the results in Subsection 5.1, the spectrum corresponding to the smallest current density does not end with the CPE behavior at low frequencies (straight line); therefore, this element was not included in the circuit fit. Both the reference sample and the one tested at 40 A/m² fitted to a simple Randles circuit [28].

Because the electrolyte is the same for all experiments, the solution resistance is a trivial value, and it was not included in Figure 5.30. For the sake of verification, one can inspect the plots of impedance magnitude as a function of frequency (Figures 5.7 and 5.29) in their high frequency region and notice that, as expected, the curves converge to a similar value.

However, the values vary slightly, probably due to evaporation of the solution and subsequent concentration of ionic species. The longest experiment exhibits the lowest solution resistance and the shortest experiment exhibits the highest. This is particularly evident for the experiments discussed in in the present section and the exact values can be found in the Appendix C.3.

The charge transfer resistance of the reference sample (no AC) and 40 A/m² experiences a decrease, indicating that the charge transfer due to electrochemical reactions occurs more easily in the second case. This behavior was also observed when studying corrosion due to AC in the absence of magnetic fields.

Similarly to what was observed in Subsection 5.2.1, $R_p$ is smaller when measured in the presence of the magnetic field, and this is true for all the measurements, although to different extents. For 240 and 500 A/m², the values are so small that further decrease may not be possible. The effect in corrosion of the magnetic field
densities used in this research, seems to be more noticeable when small AC densities are present.

Again, the behavior of the CPE that simulates the double layer is very complex and can hardly be attributed solely to the thickness of the layer. At this point, roughness of the surface and electrolyte composition can also contribute to the complex behavior observed. The low values of the parameter N support this idea.

Only 240 and 500 A/m\(^2\) fit the model of Figure 5.11, which simulates the oxide layer with a CPE. The oxide layer does not impose diffusion control, which is evidenced by parameters N closer to 1. When compared to the N parameter of the reference sample, they are actually very close (0.84 versus 0.83, and 0.77). It is possible that the magnetic field promoted the growth of a more compact but thinner layer of corrosion products. Both effects have been reported in the literature in previous investigations, particularly for magnetic fields oriented perpendicularly to the surface [97-99].

It was already observed that the EIS results in this section are very similar to those found in Subsection 5.1.3. In both cases, the electrical model presented in Figure 5.11 best fits the results obtained when 240 and 500 A/m\(^2\) were applied. The values of the N parameter have been summarized in Table 5.3. It is revealed that the parameter N of the oxide layer is closer to 1 for the samples exposed to AC under a magnetic field.

<table>
<thead>
<tr>
<th>AC density</th>
<th>240 A/m(^2)</th>
<th>500 A/m(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No magnetic field</td>
<td>0.64</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>0.77</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>0.69</td>
</tr>
<tr>
<td>56.8 G</td>
<td>0.83</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>0.77</td>
</tr>
</tbody>
</table>
This observation confirms what was observed by visual inspection, the surfaces seemed smoother when undergoing AC in the presence of the magnetic field than in absence of it. It also confirms the assertion that oxide layers grown under the influence of magnetic fields are more homogeneous than those grown in the absence of the magnetic fields.

The effect of the magnetic field on the electrical double layer is confirmed by the fact that the CPE\textsubscript{dil} values, obtained with the magnetic field on, are smaller than those obtained without the magnetic field (with only one exception, 500 A/m\textsuperscript{2}). This behavior is imitated by the CPE\textsubscript{ox}. The strain caused by the magnetic field (magnetostriction) and the coulombic forces, may be responsible for this observation [24, 100]. This result suggests that the oxide layer is thinner when in the presence of the magnetic field. Magnetostriction, as illustrated in Figure 5.31, is the phenomenon whereby the shape of a ferromagnetic specimen changes during the process of magnetization.

![Magnetostriction](image)

Figure 5.31: Magnetostriction: rotation of domain magnetization accompanying rotation of the axis of spontaneous strain [93].

Five aspects of passivation are relevant: chemical composition, thickness, structure, electronic and mechanical properties of the passive layer [10]. Magnetic fields are known to particularly influence the structure of deposited products. The oxides grown in the presence of magnetic fields tend to be more uniform and planar [86, 99, 101, 102]. If modeled with a CPE, the parameter N would be closer to
1. In contrast, fractal and porous structures are known to influence the distributed properties measured by impedance [28].

In summary, at 40 A/m², a rather high polarization resistance, still offers some corrosion resistance, whereas when AC densities of 240 and 500 A/m² are applied, the metal corrodes 450 to 670 times faster, respectively. It was verified that magnetic fields have the potential of modifying the corrosion behavior; that is, anodic dissolution and passivation, even at low field intensities as shown here.

5.3.2 Polarization Curves under Alternating Magnetic Fields and Alternating Current

The following polarization curves were obtained while applying 40 A/m² of AC density and different magnetic fields. The polarization curves are shown in Figure 5.32 and Table 5.4 summarizes the critical parameters extracted from Figure 5.32.

Figure 5.32: Cyclic polarization curves while applying an AC density of 40 A/m² under a magnetic field of 56.8 G.
Table 5.4: Electrochemical parameters from polarization curves while applying an AC density of 40 A/m$^2$ and different alternating magnetic fields

<table>
<thead>
<tr>
<th>Magnetic Field</th>
<th>$E_{\text{corr}}, \text{V}$</th>
<th>$E_{\text{pit}}, \text{V}$</th>
<th>$E_{\text{repass}}, \text{V}$</th>
<th>$i_{\text{corr}} = i_{\text{pass}}, \mu\text{A/cm}^2$</th>
<th>Corrosion rate, mm per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 G</td>
<td>-0.925</td>
<td>-0.105</td>
<td>-0.295</td>
<td>17.7</td>
<td>0.20</td>
</tr>
<tr>
<td>49.1 G</td>
<td>-0.926</td>
<td>-0.105</td>
<td>-0.299</td>
<td>23.5</td>
<td>0.27</td>
</tr>
<tr>
<td>56.8 G</td>
<td>-0.922</td>
<td>-0.123</td>
<td>-0.286</td>
<td>48.6</td>
<td>0.56</td>
</tr>
</tbody>
</table>

When comparing the curves obtained without the magnetic field and the one in which 49.1 G was applied, no significant difference is observed. This result is in compliance with those reported in Subsection 5.2 in which an alternating magnetic field of 49.1 G produced a small, yet measurable, change on polarization resistance. However, when a magnetic field of 56.8 G was applied, the polarization resistance dropped dramatically. In the polarization curves, this fact is evidenced by an increment in the anodic current density.

The curve obtained without a magnetic field started at a more negative potential, and a layer of a white deposit formed on the working electrode. This deposit is most likely the result of cathodic reactions occurring at lower potentials or the result of precipitation of magnesium hydroxide due to increased pH. It is possible that the presence of this layer is partially responsible for the lower current density measured when no magnetic field is applied.

The cathodic branch of the two curves, where magnetic fields were applied, almost overlap, whereas important differences are observed for the anodic branches. It can be said that the magnetic field effect is more accentuated in the anodic reaction than in the cathodic reaction.

During the cathodic polarization, the effect of the magnetic field must be moderated because of the low intensity applied. In this case, the metal is the substrate upon which the cathodic reaction occurs and it serves as a conductive surface for the
electron transfer. During the anodic reaction, \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \), the d-shell electrons are participating on the reaction. It has been stated before that the magnetic field influences particularly those electrons, particularly, their energy state distribution and Fermi energy level. Whereas the electrolyte stirring effect should influence both anodic and cathodic processes, the electronic effects are more likely to be seen in the anodic process for the reasons explained above. Further, the increased reaction rate of the anodic branch may be related to this electronic interactions of the metal and the magnetic field. Another possibility is the enhanced diffusion of iron ions through the passive layer which would also result in faster passive current densities.

It is possible that the cathodic reaction takes advantage of the stirring proportioned by the low AC magnetic fields. On the other hand, the anodic reaction takes advantage not only of the stirring, but particularly of the magnetic force which effects the thickness, the structure and possibly the composition of the deposit, as was mentioned in the previous subsection.

The three curves exhibit the same corrosion potential and the DC potential was not influenced by turning on or off the magnetic field. However, some studies have reported variations as high as 40 mV even in systems where diamagnetic and paramagnetic ions are involved [103]. Most likely, the magnetic field densities used in this research were too small to have a measurable effect on the DC potential or \( E_{corr} \).

The anodic branches of the polarization curves are similar, except that the one corresponding to 56.8 G, occurs at higher current densities. Although the corrosion, pitting, and repassivation potentials are the same for the three curves, the higher passivation current density experienced with the highest magnetic field indicates an accelerated corrosion rate.

The difference between the two magnetic fields is relatively small, and yet \( R_p \) and \( i_{corr} \) exhibit measurable differences. The result suggests that, at higher magnetic fields, higher corrosion rates can be expected, and according to the literature, even
$E_{\text{corr}}$ shifts of the potentials could be expected [73, 84, 85]. The increment of current density experienced for the highest alternating magnetic field is in agreement with observations made by other scientists [86].

In the present research, only one cell configuration was used where the magnetic field lines were parallel to the sample surface, so it is possible that a different configuration, for example, field lines perpendicular to the sample surface, could produce different results, as suggested by the literature. Some studies indicate, however, that parallel magnetic fields have stronger influence than perpendicular magnetic fields [86, 97].

The magnetic fields used in this study are very small compared to others used in the literature [84, 85]. One of the reasons for using smaller magnetic fields was to avoid the excessive heat generation of higher magnetic fields, for instance, the temperature variation throughout the experiments never exceeded 5 °K. Additionally, the sponsor company of this research did not provide any range of interest, so it was decided to study relatively small field densities, to prove if there was an influence of alternating magnetic fields on corrosion and on AC corrosion.

In summary, many researchers justify their results of higher reaction rate with the Lorentz force created by the magnetic field (electrolyte stirring). However, other observations suggest that more complex interactions also occur. The modified structures observed in the deposits formed under parallel magnetic fields, which tend to be more compact and uniform, have been attributed to preferential next neighbor atomic pair-ordering in the direction of the magnetic field, particularly when the deposit formed has ferromagnetic properties [85].

Another possible contribution of the magnetic fields could be its influence on the charge exchange process occurring on the surface. This possible contribution has been evidenced through the reduction of the charge transfer resistance when EIS has been performed in the presence of magnetic fields. Further, the polarization
curves in the presence of magnetic fields showed an increased reaction rate in the transpassive nose (no AC applied) and on the anodic branch (AC applied). These effect is more accentuated than the moderate change of reaction rate observed in the cathodic branches.

5.4 True Wave Form and Cathodic Protection Assessment

The objective of the present group of experiments was to study cathodic protection in combination with AC.

Cathodic protection can be performed by sacrificial anodic protection, as in the DEH system, by impressed current, or by potential control.

The more complex case study consists of sacrificial anodic protection in the presence of AC. Both the metals protected and the sacrificial anode will experience the DC potential shifts that result from the AC polarization. Also, both metals will develop anodic direct currents (rectification currents) and will have anodic half-cycle contributing to the corrosion rate. In short, a very well known cathodic protection system becomes complex and basic research is needed.

The other two systems, current or potential control in the presence of AC, polarize the metal either by imposing a direct cathodic current or by imposing a cathodic DC potential. The value of the applied current or potential are usually standardized for the metal, environment and length-area of the structure to be protected. Most of the standards, however, have not been developed considering AC corrosion.

It was demonstrated in previous sections that the AC shifts the critical potentials (DC potential, $E_{corr}$, and $E_{pit}$) and also increases the DC current densities.

Even for small current densities, such as $40 \, \text{A/m}^2$, using the regular criteria of cathodic protection may result in underprotection. The DC anodic current may not be low enough to achieve the targeted current density (corrosion rate); additionally, the anodic half wave adds up to the anodic current, further increasing the real anodic current density.
For higher current densities such as 500 A/m², the same criteria may be even more inappropriate as the cathodic protection potential will reduce the DC potential but will not be sufficient to prevent the alternating portion of the potential from exceeding $E_{pit}$. In this particular case, not only the overall anodic current density is higher than predicted, also, there is an additional complication: the pitting potential is exceeded so pitting is likely to occur.

The power necessary to energize the cathodic protection system is wasted as the cathodic protection is insufficient, in the case of the small AC density. In the case of high AC density, cathodic protection may not be appropriate and some form of reduction of AC must be considered in combination with cathodic protection.

Figure 5.33 shows three polarization curves: one reference curve in which no AC was applied (gray dashed), one obtained while applying 500 A/m² (red), and one obtained while applying 40 A/m². If the cathodic polarization criteria, $E_{CP} = -1.100V$ vs SCE, were the same for the three curves, the cathodic protection would work for the reference and possibly for 40 A/m² (black). For the reference curve, at $E_{CP} = -1.100V$ vs SCE, the anodic current would potentially be smaller than the $i_{pass}$ (gray vertical line) and that is precisely the objective of the cathodic protection.

When analyzing the other two curves, it is revealed that polarizing to similar values of $E_{CP}$; that is, -0.970V for 500 A/m² or -1.060V for 40 A/m², can only bring down the anodic current density to values near $i_{pass}$ of the reference curve, but hardly less than that. It is confirmed then, that with the same cathodic protection criterion, the DC anodic current density is higher when AC is present. At the same time, the anodic half wave is also larger as the AC density increases; in consequence, the corrosion rate is further increased.

In contrast to corrosion in absence of AC, in which uniform corrosion is the usual form of corrosion in cathodic polarization, when AC is present the morphology of corrosion may be different. The AC potential, particularly at high AC densities,
Figure 5.33: Cathodic protection criteria in the presence of different AC densities.

may exceed the pitting potential and pitting could be expected even under cathodic protection.

Considering the previous analysis, cathodic protection experiments were set up for the following conditions: 1) for a AC density of 40 A/m², $E_{CP} = -0.890$ V vs SCE (uncompensated), 2) for a AC density of 40 A/m², $E_{CP} = -1.215$ V vs SCE (uncompensated), and 3) for a AC density of 240 A/m², $E_{CP} = -1.135$ V vs SCE (uncompensated).

The AC was applied as soon as the $E_{CP}$ was reached. The plots of potential as a function of time are presented in Figure 5.34.

Although the potentiostat maintained the potential fixed at the values indicated above, the potential effectively applied is not a fixed value due to variations of the current. The DC current changes are caused by the formation and breakdown of bubbles that grow on the metal surface, reducing the contact area metal-electrolyte, and also because at low potentials the white deposit forms on the surface of the metal, which also grows and peels off.
Figure 5.34: $E_{CP}$ (compensated) as a function of time.
Figure 5.35 shows two pictures of the cell: the first one when the white deposit was on the surface and the second one when the deposit detached (the scale can be seen in the bottom of the cell).

Comparing the potential after performing the potential compensation (plot) and the uncompensated potential, one observes that the potential drop due to the external circuit varies from 20 mV to almost 200 mV. This observation reveals how important it is to know the resistance that causes the potential drop so that, in real systems, the actual $E_{CP}$ may be calculated. Particularly in the presence of AC corrosion, which makes the current densities higher, the problem of the potential compensation becomes more critical.

Using an oscilloscope and a differential probe, it was possible to monitor the potential between the working and reference electrodes. The potential measured has the form, $E = E_{DC} + E_{V} \sin(\omega t)$, and it was confirmed that $E_{DC}$ and $E_{CP}$ (compensated) were equal. This observation is an important validation of the procedure followed up to this point regarding the potential compensation.

The values of the amplitude of the AC potential wave can be found in Figure 5.36.

Figure 5.36 reveals that the amplitude of the potential may change over time, adding a new factor of complexity.

The experiments described in this section should take several days or weeks. Since the corrosion rate is reduced under cathodic protection, the evaluation of corrosion with mass loss becomes more difficult to sense. The experiments were originally designed to last at least ten days; however, in two of the experiments the duration was less than ten days. In one case, the computer rebooted and in the other case, the length of the steps was miscalculated when setting up the software that controls the equipment. In consequence, besides what is suggested by the graph, it should not be concluded that at 40 A/m$^2$ and a $E_{CP} = -1135$ mV, the amplitude will remain unchanged for longer times.
Figure 5.35: Pictures of the cell when the metal surface is coated with the white salt deposit and later, when the deposit falls off the surface.
Figure 5.36: Amplitude of the potential wave measured during the cathodic protection experiments.

Most likely, the amplitude variation corresponds to the change of impedance of the interface that results from the corrosion or salt precipitation on the surface.

By the end of the experiment in which an AC density of 240 A/m² was applied, the AC potential exceeded the pitting potential:

\[ E_{\text{pit}} = -0.279 \text{ V}, \quad E_{\text{CP-compensated}} = -0.930 \text{ V}, \quad A = 2.5 \text{ V} \]
\[ E_{\text{max}} = -0.930 \text{ V} + 1.25 \text{ V} = 0.320 \text{ V}. \]

\( E_{\text{max}} > E_{\text{pit}} \) is precisely the condition that could prove that pitting is feasible under cathodic protection. This condition was met for nine days. However, because the surface was coated with the mentioned deposit, the metal was either at a different potential (due to the potential drop across the deposit), or relatively protected from corrosion due to the barrier of the deposit. Longer times would be needed to assess the extent of corrosion under the circumstances described.
Because of the uncertainty about what causes the amplitude to increase, these experiments should be repeated in an electrolyte, such as diluted sulfuric acid, where the number of possible reactions is reduced, specifically the reactions that result on the formation of the solid salt on the metal surface would be avoided.

Additionally, the pH of the electrolyte was measured before and after the experiment. The pH went from 8.10 to 4.41, at the end of the 10-day-long experiment. The only reaction that could explain this change of pH is the the reverse of the reaction \[ HOCl + H^+ + 2e^- = Cl^- + H_2O \ (E^0 = +1.490 \text{ V}) \] [104]. The metal dissolution reaction does not affect the pH, while the two cathodic reactions mentioned in Subsection 5.1.5 tend to increase pH, as they produce OH\(^-\) (or consume H\(^+\)). Not only the pH was lower, also the cell emanated the distinctive smell of bleach.

Appendices D.1 and D.2 show two examples of the wave form data collected by the oscilloscope. The oscilloscope has the ability of performing several different measurements, from which, frequency, amplitude and maximum value, were selected. Both examples are in the same scale of 500 mV/div and the sensitivity of the measurements is in the order of 0.1 mV.

To perform true-wave-form studies of current, the order of magnitude of the AC and DC parts of the current must be considered, as it will affect the equipment to be used and the ranges that can be measured. Current probes available in the market at the present, can measure currents as low as 1 mA [105]; however, in these experiments the DC currents are usually between \(10^{-6}\) and \(10^{-3}\) A. For this reason, at the present time, current probes are not appropriate for the study of the true wave form of the current.

Another option consists of using the same differential probe with which the potentials have been measured. With a resistor connected in series to the working electrode, and the differential probe measuring the potential drop across the resistor, the current can be calculated according to the schematic presented in Figure 5.37.
Figure 5.37: Possible experimental set up to measure current true wave form with an oscilloscope.

However, the sensitivity of the measurement may be compromised. The AC densities presented in this work were in the order of 3 to 80 mA (RMS).

If a resistor of 100 ohms is used, for 80 mA (RMS) of AC: a potential drop of 8 V (RMS) would be produced. In consequence, the amplitude of the wave would be 22.62 V and the scale of the oscilloscope should be at least of 4 V/div. The sensitivity of the measurement would be 10 mV; in turn, the smallest DC current that could be sensed would be 1 mA.

Using the same 100 ohms resistor and 3 mA (RMS) of AC: a potential drop of 0.3 V (RMS) would be produced. In consequence, the amplitude of the wave would be 0.848 V and the scale of the oscilloscope should be at least of 0.2 V/div. The sensitivity of the measurement would be 0.1 mV; in turn, the smallest DC current that could be sensed would be 0.001 mA.

It is evident that the study of the true wave form of the current can only be done for low alternating currents and relatively large direct currents. The person
conducted the research must be aware of these limitations and always make sure that the readings fall within the ranges that the scale of the oscilloscope can measure.

Using higher resistors may be an alternative which must be treated carefully. The impedance of the resistor must not exceed that of the differential probe (1 M ohm) or else, it would damage the probe. Also, the resistance amplifies the DC and AC parts of the signal, so resolution will be lost if the amplification makes it necessary to use a higher scale.

True waveform studies of the current is definitely more difficult than that of the potential, at least with the laboratory equipment usually found in a corrosion laboratory. In the present study, the alternating current was controlled with a constant power supply and the direct current was measured with a potentiostat/galvanostat, which is suited for measurements or the order of micro amperes.
CHAPTER 6
THEORETICAL MODELING

A historical review of the evolution of the knowledge and understanding of AC corrosion was presented in Chapter 3.

Although the electrochemical society has worked with the AC polarization for many years, the corrosion society has worked separately from their developments. Many theories have been proposed such as the alkanization model, proposed by Pourbaix et al, which is one of the most popular models in Europe.

Some attempts have been made by other scientists which aimed to apply the rectification theory to the corrosion failed, which for several reasons have failed up to this point. The present chapter aims to collaborate in the efforts to use the rectification theory to the study of AC corrosion.

6.1 Definition of Overpotential

Overpotential is defined as the deviation of the electrode potential from its equilibrium potential to a different value, \( \eta = E - E^0 \). This parameter is a fundamental concept which relates to the thermodynamics (Nernst equation) and to the kinetics (Butler-Volmer equation) of the electrochemical system.

6.1.1 Equilibrium Potential

In a corrosion cell, the potential is determined by the mixed potential theory. The potential falls somewhere between the equilibrium potential of the redox systems: one redox system, for example \( \text{H}/\text{H}^+ \), is responsible for the cathodic reaction, and the other redox system, for example \( \text{Zn}/\text{Zn}^{2+} \), is responsible for the anodic reaction.

In a redox system, in which the anodic reaction is the reverse of the cathodic reaction, the equilibrium potential is determined by the Nernst equation. In Subsection
2.3.2, it was shown how the Nernst equation can be modified when additional external work is done. Later, the rectification theory was presented, and it was observed that an alternating current induces a rectification potential.

In the present study, it is postulated that other effects may add to the external work of an electrochemical cell. Such is the case of alternating current, which produces a bias potential when applied. The potential developed is the result of a new situation of surface charging that respond to the inequalities of the rate or anodic and cathodic reactions, as Doss et al. first observed [47]. This quantity modifies the Nernst equation as shown in Equation 6.1,

\[
E = E^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) + \sum \text{other } w_{\text{external}} \frac{nF}{nF} - \sum \delta w_{\text{internal}} \frac{nF}{nF}
\]

Equation 6.1

Now, including the term magnetization work which counts as internal work [22, 23], \( w = B \Delta M \), Equation 6.1 becomes,

\[
E = E^o + \Delta E_{\text{bias}} - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right)
\]

Equation 6.2

Because the magnetic fields used in this study were very small and no change of potential was observed with the magnetic field on or off, Equation 6.1 is probably a good approximation.

The consequences of the new term, \( \Delta E_{\text{bias}} \), in the Nernst equation are of great impact. The Pourbaix diagram, which is a key player in the design of cathodic protection, will have its lines shifted and the extent of the shift will depend on the AC density, as was demonstrated by the experimental work.

Figure 6.1 shows that even though the desirable polarization would be such that the metal is in the position D, if the lines of the Pourbaix diagram have shifted, the reality might be that the metal is polarized to zones A, B or C.
Figure 6.1: Pourbaix diagram of iron. A and C are regions where metal dissolution occurs, B is a passive region where the metal may be protected, and D is the immune region desirable for cathodic protection.

Further, the consequences of Equation 6.1 on the mixed potential theory, will be presented.

Consider a redox reaction 1 which has an equilibrium potential given by,

\[ E_1 = E_1^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) \]

and a redox reaction 2 which has an equilibrium potential given by,

\[ E_2 = E_2^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) \]

A system where both reactions are coupled is presented in Figure 6.2. The captions no AC have been added to emphasize the fact that AC has not been applied yet. A common potential where one anodic branch meets the cathodic branch of the second reaction is designated as \( E_{\text{corr}} \). The darker black lines represent the net current density of the couple.

When AC is applied, a bias potential is experienced as a result. The new equilibrium potentials of the reactions are given by,

\[ E_{1(AC)} = E_1^o + \Delta E_{\text{bias,1}} - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) \]

\[ E_{2(AC)} = E_2^o + \Delta E_{\text{bias,2}} - \frac{RT}{nF} \ln \left( \frac{a_{\text{prod}}}{a_{\text{react}}} \right) \]
Figure 6.2: Mixed potential theory applied to two hypothetical reactions 1 and 2, in the absence of alternating current.

It has also been stated that a rectification current results due to the presence of the AC. Figure 6.3 depicts the final diagram. Considering the potential shift and the increased current density, a new diagram is obtained, which describes the new couple situation in the presence of AC.

The blue lines are shifted with respect to their originals, which appear in gray in this diagram. The extent of the vertical shift is different for each redox reaction. Also, the rectification current, which contributes to the shift of $i_{corr}$, is different. A new shifted $E_{corr (AC)}$ is obtained and a higher current density is also experienced. For clarity, only the shifts of reaction 2 are indicated in the diagram.

The results of the polarization curves presented in Section 5.1.5 agree with the presented diagram.
Figure 6.3: Mixed potential theory applied to two hypothetical reactions 1 and 2 in the absence of AC (gray) and in the presence of AC (blue).

6.1.2 Alternating Potential

In an electrochemical cell, there is an applied potential between the working and the counter electrodes, however, it is not a thermodynamic quantity. In turn, it is related to the power of the cell and, if a regular power supply is used, it has the form, $E_{\text{power}} = E_p \sin(\omega t)$. Substantial research has been done controlling this potential, however, it has no thermodynamic value. There is also the potential measured between the working and the reference electrode, this quantity has a thermodynamic and kinetic value and it is of great interest.

The cell potential with respect to the reference electrode is measured according to, $E_{\text{measured}} = \phi_{W.E.} - \phi_{R.E.}$. Because the reference electrode is a DC reference, and because of the rectification potential, the potential measured has the form, $E_{\text{measured}} = E_{\text{bias}} + E_V \sin(\omega t)$, where $E_{DC} = \phi_{DC-W.E.} - \phi_{R.E.}$. 
In the experimental work performed, the alternating current was controlled, so the potential measured was a response to the alternating current applied. The current applied had the form \( i = i_{DC} + i_V \sin(\omega t) \).

The Butler-Volmer equation works in a situation where the potential is controlled and the current is the output measured. In a experimental set up, a control loop must exist so that the potential between the working and reference electrodes has the form of interest, \( E(t) = E_{bias} + E_V \sin(\omega t) \), and to achieve this, the power supply must be able to regulate the \( E_{power} = E_{DC} + E_p \sin(\omega t) \) while monitoring \( E(t) \). The hypothetical power supply must have the ability of adjusting the intensity of the wave and the DC potential.

The experimental set up may consist of a function generator, an amplifier and a LabVIEW® controlled computer. A restriction of this set up is usually the power capacity of the amplifier, which limits the intensity of the current that may pass. Another limitation is the fact that the cell load (impedance) is unknown and variable, while the function generator requires the load to be known. If this set up were to succeed, the current response registered could be used to fit the solution of the Butler-Volmer equation for a shifted sinusoidal overpotential.

6.1.3 Overpotential Resulting from AC

The overpotential definition, \( \eta = E - E_{eq} \) or \( \eta = E - E_{corr} \), is quite simple in the absence of AC as depicted in Figure 6.4. However, when AC is applied, the potential response is depicted in Figure 6.5. Different authors of AC corrosion models have defined overpotential in different ways, and the general idea is that the overpotential should be measured with respect to the \( E_{corr} \) when no AC is being applied. In contrast, Figures 6.3 and 6.5, indicate that the appropriate description of overpotential, in the context of AC corrosion and the mixed potential theory, would be,

\[
\eta(t) = [E_{bias} + E_V \sin(\omega t)] - E_{corr(AC)}
\]
Figure 6.4: Overpotential due to the application of a DC potential: $\eta = E - E_{\text{corr (no AC)}}$.

Figure 6.5: Overpotential due to the application of alternating current.
where $E_{\text{corr}}(AC)$, as depicted in Figure 6.3, corresponds to the equilibrium potential in the presence of AC. That is, the potential predicted by the mixed potential theory.

In the case where the potential wave form is controlled, $E(t) = E_{\text{bias}} + E_V \sin(\omega t)$, overpotential is $\eta(t) = [E_{\text{bias}} + E_V \sin(\omega t)] - E_{\text{corr}}(AC)$. In this particular scenario, $E_{\text{bias}}$ is not the response to AC, in this case, it is the DC component of the potential measured between the working and reference electrode.

The distinctions made so far are of great importance, however, they have been overlooked and the models presented up to date in the literature are very difficult to follow. The notation used in the literature varies significantly and also the definitions.

### 6.2 Current True Wave Form

The Butler-Volmer equation was discussed in Subsection 2.3.5. The present section aims to modify the Butler-Volmer equation by substituting the recently defined overpotential function. The application of this expression is limited to processes under activation polarization; that is, they obey Equation 6.3. The concentration at the electrode of the ionic species involved in the reaction equals their bulk values; that is, there is no diffusion control and the mass transfer occurs rapidly.

For corrosion, where both processes are controlled by activation control, Equation 2.29 is written as [64],

$$i = i_{\text{corr}} \left\{ \exp \left[ \frac{\eta}{\beta_a} \right] - \exp \left[ -\frac{\eta}{\beta_c} \right] \right\} \quad (6.3)$$

Substituting the definition of overpotential resulting from an applied potential of the form, $E(t) = E_{\text{bias}} + E_V \sin(\omega t)$, the expression becomes,

$$i = i_{\text{corr}}(AC) \left\{ \exp \left[ \frac{[E_{\text{bias}} - E_{\text{corr}}(AC)] + E_V \sin(\omega t)}{\beta_a} \right] - \exp \left[ -\frac{[E_{\text{bias}} - E_{\text{corr}}(AC)] + E_V \sin(\omega t)}{\beta_c} \right] \right\} \quad (6.4)$$
For very small potential amplitudes (small $E_V$), Equation 6.4 yields Equation 6.3. Now, the DC potential difference, $E_{bias} - E_{corr(AC)}$, will be referred to as $\eta_{DC}$. Rewriting Equation 6.4,

$$i = i_{corr(AC)} \left\{ \exp \left[ \frac{\eta_{DC} + E_V \sin(\omega t)}{\beta_a} \right] - \exp \left[ -\frac{\eta_{DC} + E_V \sin(\omega t)}{\beta_c} \right] \right\} \quad (6.5)$$

Using the expansion series of the exponential function, $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$, for each exponential term of Equation 6.5:

- Anodic exponential: substitute $\frac{\eta_{DC}}{\beta_a} = A$, and $\frac{E_V}{\beta_a} = V_A$

$$\exp [A + V_A \sin(\omega t)] = 1 + (A + V_A \sin(\omega t)) + \frac{(A + V_A \sin(\omega t))^2}{2} + \frac{(A + V_A \sin(\omega t))^3}{6} + \frac{(A + V_A \sin(\omega t))^4}{24} + ...$$

- Cathodic exponential: substitute $\frac{\eta_{DC}}{\beta_c} = C$, and $\frac{E_V}{\beta_c} = V_c$

$$\exp [C + V_c \sin(\omega t)] = 1 + (-C - V_c \sin(\omega t)) + \frac{(-C - V_c \sin(\omega t))^2}{2} + \frac{(-C - V_c \sin(\omega t))^3}{6} + \frac{(-C - V_c \sin(\omega t))^4}{24} + ...$$

The difference of the anodic series minus the cathodic series becomes:

$$\{\exp [A + V_A \sin(\omega t)] - \exp [-(C + V_c \sin(\omega t))]\} \approx [A + C] + [V_A \sin(\omega t) + V_C \sin(\omega t)] + \frac{1}{2} [((A + V_A \sin(\omega t))^2 - (C + V_C \sin(\omega t))^2]$$
$$+ \frac{1}{6} [(A + V_A \sin(\omega t))^3 + (C + V_C \sin(\omega t))^3] + \frac{1}{24} [-(C + V_C \sin(\omega t))^4] + ... \quad (6.6)$$

Form this expression, it is evident that:

- the term $A + C = \frac{\eta_{DC}}{\beta_a} + \frac{\eta_{DC}}{\beta_c}$ is the first term that contributes to the rectification current, but it is not the only one. Figure 6.6 shows how other terms of the series also contribute to the rectification, specifically, the even powers of the series. To estimate their contribution to the rectification current, the terms must be re written using other trigonometric identities.
(a) Odd powers of the Sine function: contribute to distortion but not to rectification.

(b) Even powers of the Sine function: contribute to rectification and distortion.

Figure 6.6: Plots of $\sin^n(x)$ for odd and even values of $n$. 
• Since the Taylor series was developed up to the fourth term, additional rectification terms (DC or independent terms), fundamental-frequency terms (sine to the power of 1), even-powered and odd-powered terms, will appear as the third and fourth terms of Equation 6.6 are solved.

From Equation 6.6, grouping the independent terms yields,

\[ R_{e1} = [A + C] + \frac{1}{2} [A^2 - C^2] + \frac{1}{6} [A^3 + C^3] + \frac{1}{24} [A^4 - C^4] + \ldots \]

Grouping the terms of \( \sin(\omega t) \) yields,

\[ F_{F1} = \sin(\omega t) \left( (V_A + V_C) + (A V_A - C V_C) + \frac{1}{2} (A V_A^2 + C V_C^2) + \frac{1}{6} (A^3 V_A - C^3 V_C) \right) \]

Grouping the terms of \( \sin^2(\omega t) \) yields,

\[ P2 = \sin^2(\omega t) \left[ \frac{1}{2} (V_A^2 - V_C^2 + A V_A^2 + C V_C^2) + \frac{1}{4} (A^2 V_A^2 - C^2 V_C^2) \right] \]

Grouping the terms of \( \sin^3(\omega t) \) yields,

\[ P3 = \sin^3(\omega t) \frac{1}{6} \left( (V_A^3 + V_C^3) + (A V_A^3 - C V_C^3) \right) \]

Grouping the terms of \( \sin^4(\omega t) \) yields,

\[ P4 = \sin^4(\omega t) \frac{1}{24} (V_A^4 - V_C^4) \]

Using the trigonometric identity, \( \sin^2(x) = \frac{1 - \cos(2x)}{2} \), the terms of sine to the power of two yield,

\[ P2 = \left[ \frac{1}{2} (V_A^2 - V_C^2) + \frac{1}{2} (AV_A^2 + CV_C^2) + \frac{1}{4} (A^2 V_A^2 - C^2 V_C^2) \right] \left[ \frac{1 - \cos(2\omega t)}{2} \right] \]

From this expression, grouping the independent terms, which contribute to the rectification, the following expression is obtained:

\[ R_{e2} = \frac{1}{4} (V_A^2 - V_C^2) + \frac{1}{4} (AV_A^2 + CV_C^2) + \frac{1}{8} (A^2 V_A^2 - C^2 V_C^2) \]

Using the trigonometric identity, \( \sin^3(x) = \frac{3 \sin(x) - \sin(3x)}{4} \), the terms of sine to the power of three yield,
\[ P_3 = \left[ (V_A^3 + V_C^3) + (AV_A^2 - CV_C^3) \right] \frac{3 \sin(\omega t) - \sin(3\omega t)}{24} \]

This expression contributes to the fundamental frequency term and to the 3\(\omega\) harmonics. The contribution to the fundamental frequency is,

\[ FF_2 = \sin(\omega t) \frac{1}{8} \left[ (V_A^3 + V_C^3) + (AV_A^3 - CV_C^3) \right]. \]

Using the trigonometric identity, \(\sin^4(x) = \frac{3 - 4\cos(2\omega t) + \cos(4\omega t)}{8}\), the term of sine to the power of four yields,

\[ P_4 = \frac{1}{24} (V_A^4 - V_C^4) \left[ \frac{3 - 4\cos(2\omega t) + \cos(4\omega t)}{8} \right]. \]

From this expression, the contribution to the rectification is,

\[ Re_3 = \frac{1}{64} (V_A^4 - V_C^4). \]

Finally, adding both expressions, \(FF_1 + FF_2\), the final expression for the fundamental frequency term is,

\[ FF = i_{corr(AC)} \sin(\omega t) \left\{ (V_A + V_C) + (AV_A - CV_C) + \frac{1}{2} (AV_A^2 + CV_C^2) \right. \]

\[ + \frac{1}{6} (A^3V_A - C^3V_C) + \frac{1}{8} \left[ (V_A^3 + V_C^3) + (AV_A^3 - CV_C^3) \right] \right\} \]

The expression for current density at the fundamental frequency is,

\[ i_\omega = i_{corr(AC)} \sin(\omega t) \left\{ (V_A + V_C) + (AV_A - CV_C) + \frac{1}{3} (AV_A^2 + CV_C^2) \right. \]

\[ + \frac{1}{6} (A^3V_A - C^3V_C) + \frac{3}{24} (V_A^3 + V_C^3 + AV_A^3 - CV_C^3) \right\} \quad (6.7) \]

On the other hand, the rectification current equals, \(i_{rectf} = i_{corr} \sum Re_i\),

\[ i_{rectf} = \frac{i_{corr(AC)}}{192} \left\{ 192 (A + C) + 96 (A^2 - C^2) + 32 (A^3 + C^3) + 8 (A^4 - C^4) \right. \]

\[ + 24 \left[ 2 (V_A^2 - V_C^2 + AV_A^2 + CV_C^2) + (A^2V_A^2 - C^2V_C^2) \right] + 3 (A^4 - C^4) \right\} \quad (6.8) \]

Now, \(\nu p C_{\beta a} = A, \nu p C_{\beta c} = C, \frac{\nu C}{\beta a} = V_A, \text{ and } \frac{\nu C}{\beta c} = V_C\), thus, the rectification current density is a function of the DC overpotential, potential wave amplitude and Tafel
slopes. Next, the effect on the rectification current previously derived (Equation 6.8) of the Tafel slopes, $\beta_A$ and $\beta_C$, overpotential, and potential wave amplitude, $E_V$, will be demonstrated.

From Equation 6.8, and assuming $i_{corr} = 10^{-6}$ A/cm$^2$, Figures 6.7 and 6.8 were generated to show the effect of the potential wave amplitude and the asymmetry of the Tafel slopes on the rectification current.

Figure 6.7 shows that the rectification current follows the behavior typical of the Butler-Volmer equation. Also, the two graphs with asymmetric Tafel slopes exhibit an asymmetric behavior. The plot corresponding to symmetric Tafel slopes exhibits symmetric anodic and cathodic branches. This plot was obtained with a relatively small AC amplitude. It was expected that at low potential wave amplitude, the Butler-Volmer behavior would dominate.
Figure 6.8: Effect of $E_V$ on the rectification current: a) $E_V < \eta_{DC}$ and b) $E_V > \eta_{DC}$. 

(a) Rectification current as a function of DC overpotential, $\eta_{DC}$, for $\beta_A = 0.1V$ and $\beta_C = 0.12V$. The plots correspond to the following AC potential intensity: $E_V = 0.180V$ (black), $E_V = 0.120V$ (blue), and $E_V = 0.020V$ (red).

(b) Rectification current as a function of DC overpotential, $\eta_{DC}$, for $\beta_A = 0.1V$ and $\beta_C = 0.12V$. The plots correspond to the following AC potential intensity: $E_V = 1.0V$ (blue), $E_V = 0.8V$ (red), and $E_V = 0.7V$ (black).
Figure 6.8 shows the effect of different potential wave amplitudes on the rectification current. Asymmetric Tafel slopes of $\beta_A = 0.1V$ and $\beta_C = 0.12V$ were arbitrarily chosen for this plot. Figure 6.8(a) shows that the rectification current density increases as the potential wave amplitude increases. This behavior is more noticeable in the anodic branch, which has a higher Tafel slope, than in the cathodic branch.

Figure 6.8(b), which was obtained using the same parameters as the previous plot, is the result of higher potential wave amplitudes. The behavior observed does not correspond to the Butler-Volmer typical behavior. The anodic branch (higher Tafel slope) grows at small negative overpotentials, as the overpotential becomes more negative, the rectification current reaches a maximum and decreases again to a minimum (equivalent to a zero in a logarithmic scale) and grows again. It was confirmed that for a situation where $\beta_C > \beta_A$, the same behavior was observed in the cathodic branch. This complex behavior is the result of the dominant effect of the sine function on the exponentials of Equation 6.5.

It is confirmed that the Butler-Volmer behavior is attained provided that the DC potential is more dominant on the exponential than the sine term.

It becomes evident that Equation 6.5 has some mathematical and physical limitations. The argument of the exponential function should be small, for example, $\frac{n_{DC} + E_v \sin(\omega t)}{\beta_A} < 1$ and $\frac{n_{DC} + E_v \sin(\omega t)}{\beta_C} > -1$, so that the current density does not reach unreasonable values. From a physical point of view, at large overpotentials, and most likely at large potential wave amplitudes, the mass transport of the ionic species is expected to dictate the behavior of the current. However, the effect of mass transport control will not be developed.

To exercise different situations where the DC overpotential or the sine term are dominant, Figures 6.9, 6.10, and 6.11 are presented. In these figures the true wave form of the current, given by Equation 6.5, will be analyzed considering the relative
Figure 6.9: Plot of $i(\eta, t)$ as a function of time calculated from Equation 6.5: $\beta_A = 0.12 \, V$, $\beta_C = 0.1 \, V$, $i_{corr} = 10^{-6} \, A/cm^2$, small potential amplitude: $E_V = 0.180 \, V$ (black), $E_V = 0.120 \, V$ (red), and $E_V = 0.020 \, V$ (blue).
Figure 6.10: Plot of $i(\eta, t)$ as a function of time calculated from Equation 6.5: $\beta_A = 0.1 \, V$, $\beta_C = 0.12 \, V$, $i_{corr} = 10^{-6} \, A/cm^2$, small potential amplitude: $E_V = 0.180 \, V$ (black), $E_V = 0.120 \, V$ (red), and $E_V = 0.020 \, V$ (blue).
order of magnitude of the potential wave amplitude, $E_V$, and the DC overpotential, $\eta_{DC}$.

Consider Figures 6.9 and 6.10 a). When no overpotential is applied, the distorted sine wave response is obtained and a near DC response is observed for the smaller potential wave amplitude. In both cases, the larger half cycle occurs for the process with higher Tafel slope.

Using the same parameters, a small anodic overpotential is applied and Figures 6.9 and 6.10 b) were obtained. In both cases, the overpotential applied is enough to take the whole wave to the anodic region (positive current), however, the maximum value of current reached corresponds to the anodic half wave of smaller Tafel slope.

Figures 6.9 and 6.10 c) were obtained by applying a cathodic overpotential and the same parameters as in the later case. Again, the potential shift is enough to take the whole wave to the cathodic region (negative currents). Similarly to the previews figure description, the lower value of current reached corresponds to the cathodic half wave of smaller Tafel slope.

The behavior predicted in Figures 6.9 and 6.10 reveals that in the absence of a DC overpotential, the Tafel slope asymmetry is enough to cause accelerated corrosion in the presence of a sinusoidal potential, due to a larger anodic half wave, when the anodic Tafel slope is smaller than the cathodic Tafel slope. In the same manner, hydrogen take up may be increased, due to a larger cathodic half wave, in a situation where the cathodic Tafel slope is smaller and when the cathodic reaction is the reduction of hydrogen.

Moreover, a great underestimation of the corrosion rate would result from using only the rectification current density to calculate the corrosion rate. This practice has two origins: in the absence of AC, it is a common practice to calculate the corrosion rate from $i_{corr}$ (Equation 5.1); also, it has been frequently stated that the AC portion of the current cannot contribute to the corrosion rate as the reaction rate is not as fast.
as the polarization changes due to the frequency applied. For a range of frequencies, 60 Hz included, this statement is erroneous and accelerated corrosion is observed due to AC as many studies in the literature indicate. It becomes necessary to study the true wave form of the current for corrosion rate estimations.

Particularly at 60 Hz and less, the risk of underestimation of corrosion rate exists. In fact, it has been reported that the corrosion rate increases when the AC amplitude increases, but it decreases at higher frequencies [60]. From a physical point of view, higher frequencies may also influence the mass transport in the solution further contributing to the corrosion rate decrease. This effect is what Doss et al. called the redoxokinetic effect.

Further, continuing the analysis of the effect of the ratios, $\eta_{DC} + \frac{E_V \sin(\omega t)}{\beta_A} < 1$ and $-\frac{\eta_{DC} + E_V \sin(\omega t)}{\beta_C} > -1$, Figure 6.11 is presented. In this figure, Equation 6.5 will be analyzed in situations where the potential wave amplitude, $E_V$, has the same values as of Figure 6.8(b) and the same small DC overpotentials of the two previous figures.

Figures 6.11 a and b) were obtained at small overpotentials, anodic for a) and cathodic for b). The figures evidence how the asymmetry of the Tafel slopes is amplified by the amplitude of the sine of the exponential. When the anodic overpotential is applied, the anodic half wave increases and the cathodic half wave is very small. When the cathodic overpotential is applied, the cathodic half wave increases while the anodic half wave is very small. This behavior is dominated by the overpotential applied and the potential wave amplitude (the three curves were obtained for the same values of Tafel slopes). The risks of hydrogen charging when high current densities are experienced are clear. On the other hand, the reported higher consumption rate of sacrificial anodes can be more clearly understood by examining these plots.

A closer examination of Figure 6.11 b) is presented in Figure 6.11 c). It consists of a semi-logarithmic plot of the absolute value of the rectification current when a small cathodic overpotential is applied. This figure reveals that at higher potential wave
Figure 6.11: Semi-logarithmic plot of the absolute value of $i(\eta, t)$ as a function of time calculated from Equation 6.5: $\beta_A = 0.12\,V$, $\beta_C = 0.1$, $i_{corr} = 10^{-6}\,A/cm^2$, large potential amplitudes: $E_V = 1\,V$ (black), $E_V = 0.8\,V$ (red), and $E_V = 0.7\,V$ (blue).
intensities, the periodicity and amplitude of the resulting current wave, are different.

Indeed, a more complex behavior is observed in both, the rectification current density and the true wave form of the current density, when the sine term dominates the behavior of the exponential function. The strong wave distortions observed (intensity and periodicity) are most likely due to the increasing effect of the harmonics:

- First harmonic distortion: $2\omega$, from the terms of $\sin^2(\omega t)$ and $\sin^4(\omega t)$
- Second harmonic distortion: $3\omega$, from the term of $\sin^3(\omega t)$
- Third harmonic distortion: $4\omega$, from the term of $\sin^4(\omega t)$.

The model presented here has considered only a process under activation polarization. The effects of diffusion and electrical double layer have not been considered. In consequence, the validity of the model presented is restricted to relatively small DC overpotentials and potential wave amplitudes because of mathematical and physical considerations. Passivation and its effect of the current density is not included in the model either.
CHAPTER 7
CONCLUSIONS

• The mechanism of corrosion in presence of AC in the context of the DEH; that is, at the three current densities of interest in artificial seawater on 13 Cr supermartensitic stainless steel, is pitting. This observation is most likely due to the fact that the potential wave continuously crosses the pitting potential.

• Polarization scans were successfully performed in the presence of AC. The scans revealed the passivation behavior of the metal undergoing AC corrosion, which has never been reported before in the literature.

• The steel under study exhibited a passive behavior even in the presence of AC. However, as AC increased, the passive current was higher and the passive range of potential became smaller, resulting in a poor passivation ability under AC.

• AC magnetic fields seemed to accelerate the corrosion rate. Two cooperating mechanisms may be responsible for this behavior: electrolyte stirring due to the Lorentz force effect on the ionic species in solution, and accelerated electron transfer rate due to the magnetic field influence on the energy state of the electrons in the metal.

• The effect of AC magnetic fields on the oxide layer formed when AC was applied revealed that a thinner and more compact oxide layer was created, as compared to the one formed in the absence of the magnetic field. Also, when EIS is performed in the presence of the magnetic field, the oxide film appeared to be thinner, as result most likely caused by magnetostriction. Polarization curves revealed that the layer may be less protective because the passive current was higher when in the presence of the magnetic fields.
• The experiments of cathodic protection criteria assessment were inconclusive
due to the unavoidable formation of a salt deposit on the metal surface and the
continuous increase of the potential wave amplitude.

• The theoretical analysis of the cathodic protection criteria indicated that low AC
densities may be effectively protected. However, the corrosion rate experienced
would potentially be higher than in the absence of AC.

• A thermodynamic model, considering the effect of AC on the DC potential, was
presented. The effect of the new DC potential on the mixed potential theory
was introduced. The concept of overpotential was re-defined and then, a kinetic
model was presented.

• The kinetic model predicts the rectification current that results from the appli-
cation of AC. The model also predicts the true wave form of the current, \( i(t) \),
and the asymmetry that results from the different Tafel slopes of the anodic and
cathodic reactions. The model indicates a change to more complex behaviors
when the sine amplitude is higher than the DC overpotential.
In a potential continuation of the present research, it is recommended to perform the following experiments:

- Weight loss experiments in the presence of AC and alternating magnetic fields, which would prove how much the corrosion rate is actually increased by the presence of alternating magnetic fields.

- Cathodic protection criteria assessment experiments, which should be performed with the following modifications: use a larger solution volume (consider a system where the solution is continuously replaced), test for several weeks, and use an electrolyte such as diluted sulfuric acid. These variations from the original set up would prevent many of the complications found. The modifications suggested would better assess the effectiveness of the cathodic protection in the presence of AC.

- Hydrogen content assessment, which would complement the cathodic protection criteria by determining the risk to overprotection.

- Polarization curves at higher magnetic field densities, which could be done with an electromagnet equipped with a cooling system. To prevent induced AC currents from negatively affecting the measurements, the modified external circuit should be used.

- Impedance and polarization curves under magnetic fields, should be performed on the same alloy with different heat treatments (different magnetic properties).
These experiments would complement the assessment of the effect of the magnetic fields on the anodic and cathodic process. The results might bring more light on the separation of the effects: electrolyte and electron stirring.

• Using the experimental set up described at the end of Section 5.4, additional experiments could be performed which would help to corroborate the model presented and the actual range of validity of the equations, in terms of DC overpotential and potential wave amplitude.
REFERENCES CITED


APPENDIX A - AC CORROSION-EIS CIRCUIT FIT

A.1 EIS Results from Subsection 5.1.3

The data was fitted to the four equivalent circuits in Figures 5.9 and 5.10. The results are presented in Tables A.1, A.2, A.3, and A.4.

Table A.1: Model: GFL in series with Randles circuit. Errors higher than 10 pct. are highlighted in red.

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155
Table A.2: Model: GFL in place of Warburg impedance in the general Randles Circuit. Errors higher than 10 pct. are highlighted in red.

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Table A.3: Model: CPE in series with Randles circuit. Errors higher than 10 pct. are highlighted in red.

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<td>CPEox</td>
<td>-</td>
<td>7.53E-05</td>
<td>1.76E-04</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
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<td>0.65265</td>
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<tr>
<td>Chi sq</td>
<td>0.02277</td>
<td>0.0050479</td>
<td>0.021524</td>
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<td>Wt Sum of sq</td>
<td>2.5502</td>
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### Cubic sample

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<th>500A/m²</th>
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<tbody>
<tr>
<td>Rs</td>
<td>3.569</td>
<td>2.524</td>
<td>1.417</td>
</tr>
<tr>
<td>RP</td>
<td>472,720</td>
<td>96.7</td>
<td>262.5</td>
</tr>
<tr>
<td>CPEdl</td>
<td>6.27E-05</td>
<td>2.47E-04</td>
<td>2.51E-05</td>
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<tr>
<td>N</td>
<td>0.88995</td>
<td>0.71588</td>
<td>0.8219</td>
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<tr>
<td>CPEox</td>
<td>-</td>
<td>2.11E-04</td>
<td>3.24E-04</td>
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<tr>
<td>N</td>
<td>-</td>
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<td>0.69494</td>
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<td>Chi sq</td>
<td>0.0038389</td>
<td>0.0029294</td>
<td>0.014744</td>
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<td>Wt Sum of sq</td>
<td>0.46835</td>
<td>0.38083</td>
<td>1.9462</td>
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Table A.4: Model: CPE in place of Warburg impedance in the general Randles Circuit. Errors higher than 10 pct. are highlighted in red.

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<td>500A/m²</td>
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<td>Value error</td>
<td>Value error</td>
<td>Value error</td>
<td>Value error</td>
<td>Value error</td>
</tr>
<tr>
<td>Rs</td>
<td>3.917</td>
<td>1.1258%</td>
<td>6.588</td>
<td>1.8496%</td>
<td>8.461</td>
</tr>
<tr>
<td>RP</td>
<td>93,122.0</td>
<td>2.5304%</td>
<td>92.4</td>
<td>3.1695%</td>
<td>629.9</td>
</tr>
<tr>
<td>CPEdl</td>
<td>9.79E-06</td>
<td>0.1806%</td>
<td>9.71E-06</td>
<td>10.6000%</td>
<td>1.50E-04</td>
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<tr>
<td>N</td>
<td>0.85750</td>
<td>2.5340%</td>
<td>0.82880</td>
<td>1.2360%</td>
<td>0.65734</td>
</tr>
<tr>
<td>CPEox</td>
<td>-</td>
<td>-</td>
<td>2.35E-04</td>
<td>0.7658%</td>
<td>2.49E-04</td>
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<tr>
<td>N</td>
<td>-</td>
<td>-</td>
<td>0.64248</td>
<td>0.3782%</td>
<td>0.83071</td>
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<tr>
<td>Chi sq</td>
<td>0.00041936</td>
<td>0.0026025</td>
<td>0.00614</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.52</td>
<td>0.35393</td>
<td>0.79757</td>
<td></td>
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</tr>
<tr>
<td>Rs</td>
<td>13.12</td>
<td>0.9357%</td>
<td>9.361</td>
<td>3.2720%</td>
<td>10.19</td>
</tr>
<tr>
<td>RP</td>
<td>186.8</td>
<td>14.1100%</td>
<td>939.4</td>
<td>12.7700%</td>
<td>517.2</td>
</tr>
<tr>
<td>CPEdl</td>
<td>7.10E-06</td>
<td>10.1097%</td>
<td>2.91E-05</td>
<td>10.9429%</td>
<td>1.02E-05</td>
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<tr>
<td>N</td>
<td>0.98881</td>
<td>1.1770%</td>
<td>0.77361</td>
<td>1.5022%</td>
<td>0.81420</td>
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<td>CPEox</td>
<td>1.01E-05</td>
<td>7.8959%</td>
<td>4.52E-05</td>
<td>6.6748%</td>
<td>1.62E-04</td>
</tr>
<tr>
<td>N</td>
<td>0.82764</td>
<td>0.4033%</td>
<td>0.75523</td>
<td>1.4035%</td>
<td>0.62336</td>
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<tr>
<td>Chi sq</td>
<td>0.0016936</td>
<td>0.0074164</td>
<td>0.015271</td>
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<tr>
<td>Wt Sum of sq</td>
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<td>0.91963</td>
<td>1.8936</td>
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<tr>
<td>Rs</td>
<td>3.569</td>
<td>1.0284%</td>
<td>2.732</td>
<td>1.9010%</td>
<td>1.541</td>
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<tr>
<td>RP</td>
<td>472,720</td>
<td>5.0850%</td>
<td>107.3</td>
<td>3.6523%</td>
<td>314.4</td>
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<td>CPEdl</td>
<td>6.27E-05</td>
<td>0.58622%</td>
<td>5.73E-05</td>
<td>5.7000%</td>
<td>1.99E-05</td>
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<tr>
<td>N</td>
<td>8.90E-01</td>
<td>0.1322%</td>
<td>0.82394</td>
<td>0.8130%</td>
<td>0.82064</td>
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<tr>
<td>CPEox</td>
<td>-</td>
<td>-</td>
<td>1.48E-04</td>
<td>2.5566%</td>
<td>3.04E-04</td>
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<tr>
<td>N</td>
<td>-</td>
<td>-</td>
<td>0.75215</td>
<td>0.5367%</td>
<td>0.67963</td>
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<tr>
<td>Chi sq</td>
<td>0.00383839</td>
<td>0.005812</td>
<td>0.01239</td>
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<tr>
<td>Wt Sum of sq</td>
<td>0.46835</td>
<td>0.76137</td>
<td>1.63480</td>
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</table>
APPENDIX B - AC CORROSION-POLARIZATION CURVES

The following figure presents the polarization curves performed while applying different AC densities. The blue shadow superimposed to the polarization curves represents the AC portion of the potential.

Figure B.1: Polarization curves from Subsection 5.1.5.
APPENDIX C - AC CORROSION UNDER MAGNETIC FIELDS-EIS RESULTS

EIS results from measurement made after applying AC and 56.8 G alternating magnetic field.

C.1 EIS Data Obtained after Experiment

EIS was performed two times after the experiment, first with the magnetic field on (Figure 5.29) and a second time with the magnetic field off, Figure C.1.

Figure C.1: EIS assessment after applying different AC densities in the presence of an alternating magnetic field of 56.8 G. EIS performed in the presence of magnetic field.
C.2  EIS Results after Applying AC in the Presence of Alternating Magnetic Field from Subsection 5.3.1

Data was fitted to four equivalent circuits according to Figures 5.9 and 5.10. Results are summarized in Tables C.1, C.2, C.3, and C.4. Errors higher than 10 pct. have been highlighted in red.

Table C.1: Model: GFL in series with Randles circuit.

<table>
<thead>
<tr>
<th>MAGNETIC FIELD ON DURING EIS</th>
<th>40A/m²</th>
<th>Value</th>
<th>error</th>
<th>240A/m²</th>
<th>Value</th>
<th>error</th>
<th>500A/m²</th>
<th>Value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>3.571</td>
<td>1.112%</td>
<td></td>
<td>5.027</td>
<td>1.962%</td>
<td></td>
<td>6.949</td>
<td>3.432%</td>
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<td>RP</td>
<td>9,013.0</td>
<td>1.290%</td>
<td></td>
<td>87.8</td>
<td>6.263%</td>
<td></td>
<td>153.0</td>
<td>4.653%</td>
<td></td>
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<td>CPEdl</td>
<td>1.97E-04</td>
<td>0.958%</td>
<td></td>
<td>2.81E-04</td>
<td>9.230%</td>
<td></td>
<td>1.24E-04</td>
<td>11.065%</td>
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<tr>
<td>N</td>
<td>0.77382</td>
<td>0.239%</td>
<td></td>
<td>0.65278</td>
<td>1.698%</td>
<td></td>
<td>0.64905</td>
<td>2.007%</td>
<td></td>
</tr>
<tr>
<td>W-R</td>
<td>308880</td>
<td>3.951%</td>
<td></td>
<td>308880</td>
<td>3.951%</td>
<td></td>
<td>171570.0</td>
<td>199.123%</td>
<td></td>
</tr>
<tr>
<td>W-T</td>
<td>151.0</td>
<td>4.737%</td>
<td></td>
<td>151.0</td>
<td>4.737%</td>
<td></td>
<td>327.3</td>
<td>259.200%</td>
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<tr>
<td>W-P</td>
<td>0.82434</td>
<td>0.392%</td>
<td></td>
<td>0.82434</td>
<td>0.392%</td>
<td></td>
<td>0.76850</td>
<td>0.815%</td>
<td></td>
</tr>
<tr>
<td>Chi sq</td>
<td>0.003123</td>
<td></td>
<td></td>
<td>0.003559</td>
<td></td>
<td></td>
<td>0.008509</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.39953</td>
<td></td>
<td></td>
<td>0.45913</td>
<td></td>
<td></td>
<td>1.1147</td>
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</table>

<table>
<thead>
<tr>
<th>MAGNETIC FIELD OFF DURING EIS</th>
<th>40A/m²</th>
<th>Value</th>
<th>error</th>
<th>240A/m²</th>
<th>Value</th>
<th>error</th>
<th>500A/m²</th>
<th>Value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>4.373</td>
<td>1.495%</td>
<td></td>
<td>5.031</td>
<td>1.979%</td>
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<td>3.410%</td>
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<td>18,636.0</td>
<td>2.510%</td>
<td></td>
<td>104.2</td>
<td>6.551%</td>
<td></td>
<td>170.5</td>
<td>4.824%</td>
<td></td>
</tr>
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<td>CPEdl</td>
<td>2.21E-04</td>
<td>1.100%</td>
<td></td>
<td>2.54E-04</td>
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<td></td>
<td>1.06E-04</td>
<td>11.043%</td>
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<td>0.297%</td>
<td></td>
<td>0.66034</td>
<td>1.625%</td>
<td></td>
<td>0.66287</td>
<td>1.967%</td>
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<tr>
<td>W-R</td>
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<td>4.114%</td>
<td></td>
<td>345640</td>
<td>4.114%</td>
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<td>250490.0</td>
<td>267.6.000%</td>
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<tr>
<td>W-T</td>
<td>152.2</td>
<td>4.893%</td>
<td></td>
<td>152.2</td>
<td>4.893%</td>
<td></td>
<td>499.4</td>
<td>3521.600%</td>
<td></td>
</tr>
<tr>
<td>W-P</td>
<td>0.82532</td>
<td>0.411%</td>
<td></td>
<td>0.82532</td>
<td>0.411%</td>
<td></td>
<td>0.75985</td>
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<tr>
<td>Chi sq</td>
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<td>0.003763</td>
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<td></td>
<td>0.008888</td>
<td></td>
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<tr>
<td>Wt Sum of sq</td>
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Table C.2: Model: GFL in place of Warburg impedance in the general Randles Circuit.

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<th>MAGNETIC FIELD OFF DURING EIS</th>
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<td>40A/m²</td>
<td>Value</td>
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<td>3.971</td>
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<td>RP</td>
<td>9.013</td>
<td>1.290%</td>
</tr>
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<td>CPEDl</td>
<td>1.97E-04</td>
<td>0.958%</td>
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<tr>
<td>N</td>
<td>0.77382</td>
<td>0.239%</td>
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<td>W-R</td>
<td>17.4</td>
<td>203.73%</td>
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<td>0.000556</td>
<td>248.95%</td>
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<td>0.41201</td>
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<td>Wt Sum of sq</td>
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<th>Value</th>
<th>error</th>
<th>240A/m²</th>
<th>Value</th>
<th>error</th>
<th>500A/m²</th>
<th>Value</th>
<th>error</th>
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<tbody>
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<td>Rs</td>
<td>4.373</td>
<td>1.495%</td>
<td>5.444</td>
<td>1.790%</td>
<td>8.097</td>
<td>1.524%</td>
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<tr>
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<td>18.636</td>
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<td>106.6</td>
<td>7.93</td>
<td>5.150%</td>
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<tr>
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<td>1.100%</td>
<td>7.69E-05</td>
<td>1.786%</td>
<td>2.44E-05</td>
<td>10.675%</td>
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<td>0.80249</td>
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</tr>
<tr>
<td>W-R</td>
<td>169.6</td>
<td>12.587%</td>
<td>168.9</td>
<td>11.927%</td>
<td>168.9</td>
<td>11.927%</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>W-T</td>
<td>0.0008156</td>
<td>10.821%</td>
<td>0.028453</td>
<td>18.658%</td>
<td>0.028453</td>
<td>18.658%</td>
<td></td>
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</tr>
<tr>
<td>W-P</td>
<td>0.42096</td>
<td>0.688%</td>
<td>0.42096</td>
<td>0.688%</td>
<td>0.37503</td>
<td>0.894%</td>
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</tr>
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<td>Chi sq</td>
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<td>0.010844</td>
<td>0.00583</td>
<td>0.010844</td>
<td>0.00583</td>
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<tr>
<td>Wt Sum of sq</td>
<td>0.606666</td>
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</table>
Table C.3: Model: CPE in series with Randles circuit.

### MAGNETIC FIELD ON DURING EIS

<table>
<thead>
<tr>
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<th>40A/m²</th>
<th>Value</th>
<th>error</th>
<th>240A/m²</th>
<th>Value</th>
<th>error</th>
<th>500A/m²</th>
<th>Value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>3.971</td>
<td>1.1122%</td>
<td>4.922</td>
<td>1.9758%</td>
<td>6.755</td>
<td>3.7806%</td>
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</tr>
<tr>
<td>RP</td>
<td>9.013</td>
<td>1.3899%</td>
<td>94.3</td>
<td>5.9513%</td>
<td>157.3</td>
<td>4.6008%</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CPEdl</td>
<td>1.97E-04</td>
<td>0.9577%</td>
<td>3.03E-04</td>
<td>8.2358%</td>
<td>1.34E-04</td>
<td>0.9213%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.77</td>
<td>0.2396%</td>
<td>0.64</td>
<td>1.5594%</td>
<td>0.64</td>
<td>1.9887%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chi sq</td>
<td>0.0031233</td>
<td>0.0092316</td>
<td>0.0077133</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.33353</td>
<td>0.36516</td>
<td>1.0007</td>
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</table>

### MAGNETIC FIELD OFF DURING EIS

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<tr>
<th></th>
<th>40A/m²</th>
<th>Value</th>
<th>error</th>
<th>240A/m²</th>
<th>Value</th>
<th>error</th>
<th>500A/m²</th>
<th>Value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>4.395</td>
<td>0.6871%</td>
<td>4.373</td>
<td>1.4945%</td>
<td>4.927</td>
<td>2.0019%</td>
<td>6.99</td>
<td>3.6001%</td>
<td></td>
</tr>
<tr>
<td>RP</td>
<td>75.234</td>
<td>1.5985%</td>
<td>18.656</td>
<td>2.5100%</td>
<td>112.3</td>
<td>6.2578%</td>
<td>163.3</td>
<td>4.7602%</td>
<td></td>
</tr>
<tr>
<td>CPEdl</td>
<td>1.02E-04</td>
<td>0.4972%</td>
<td>2.21E-04</td>
<td>1.0990%</td>
<td>2.78E-04</td>
<td>7.9515%</td>
<td>1.09E-04</td>
<td>10.9202%</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.84</td>
<td>0.1213%</td>
<td>0.74</td>
<td>0.2568%</td>
<td>0.05</td>
<td>1.4550%</td>
<td>0.06</td>
<td>1.5403%</td>
<td></td>
</tr>
<tr>
<td>Chi sq</td>
<td>0.0017</td>
<td>0.008314</td>
<td>0.0030278</td>
<td>0.00780</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.2176</td>
<td>0.40656</td>
<td>0.38725</td>
<td>0.99885</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table C.4: Model: CPE in place of Warburg impedance in the general Randles Circuit.

<table>
<thead>
<tr>
<th></th>
<th>MAGNETIC FIELD ON DURING EIS</th>
<th>MAGNETIC FIELD OFF DURING EIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40A/m²</td>
<td>240A/m²</td>
</tr>
<tr>
<td></td>
<td>Value</td>
<td>error</td>
</tr>
<tr>
<td>Rs</td>
<td>3.971</td>
<td>1.112%</td>
</tr>
<tr>
<td>Rp</td>
<td>9,013.0</td>
<td>1.290%</td>
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<tr>
<td>CPEdl</td>
<td>1.97E-04</td>
<td>0.958%</td>
</tr>
<tr>
<td>N</td>
<td>0.77182</td>
<td>0.239%</td>
</tr>
<tr>
<td>CPEox</td>
<td>1.24E-04</td>
<td>3.756%</td>
</tr>
<tr>
<td>N</td>
<td>0.81934</td>
<td>0.689%</td>
</tr>
<tr>
<td>Chi sq</td>
<td>0.003123</td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.39353</td>
<td></td>
</tr>
<tr>
<td>Rs</td>
<td>4.373</td>
<td>1.495%</td>
</tr>
<tr>
<td>Rp</td>
<td>18,636.0</td>
<td>2.510%</td>
</tr>
<tr>
<td>CPEdl</td>
<td>2.21E-04</td>
<td>1.100%</td>
</tr>
<tr>
<td>N</td>
<td>0.73815</td>
<td>0.297%</td>
</tr>
<tr>
<td>CPEox</td>
<td>1.07E-04</td>
<td>10.302%</td>
</tr>
<tr>
<td>N</td>
<td>0.82313</td>
<td>1.887%</td>
</tr>
<tr>
<td>Chi sq</td>
<td>0.004814</td>
<td></td>
</tr>
<tr>
<td>Wt Sum of sq</td>
<td>0.60656</td>
<td></td>
</tr>
</tbody>
</table>
Examples of the data acquired during the measurements of potential between the working and reference electrodes with the oscilloscope, are presented next.

The potential wave is given by \( E = E_{DC} + E_V \sin(\omega t) \). The oscilloscope measures different values of the wave such as the maximum value of potential, \( \text{Max} \) or \( E_{\text{MAX}} \), and the amplitude of the wave, \( A \). Therefore, the DC potential can be calculated:

\[
E_{DC} = E_{\text{MAX}} - \frac{A}{2}.
\]

D.1 Data Acquired during Polarization with an AC Density of 40 A/m\(^2\) and a \( E_{\text{CP}} = -0.890 \text{V vs SCE (uncompensated)} \)

Figure D.1: Example of the data acquired during the measurements of potential between the working and reference electrodes with the oscilloscope. AC density of 40 A/m\(^2\) and a \( E_{\text{CP}} = -0.890 \text{V vs SCE (uncompensated)} \).
D.2 Data Acquired during Polarization with an AC Density of 240 A/m² and a $E_{CP} = -1.135$ V vs SCE (uncompensated)

Figure D.2: Example of the data acquired during the measurements of potential between the working and reference electrodes with the oscilloscope. AC density of 240 A/m² and a $E_{CP} = -1.135$ V vs SCE (uncompensated).