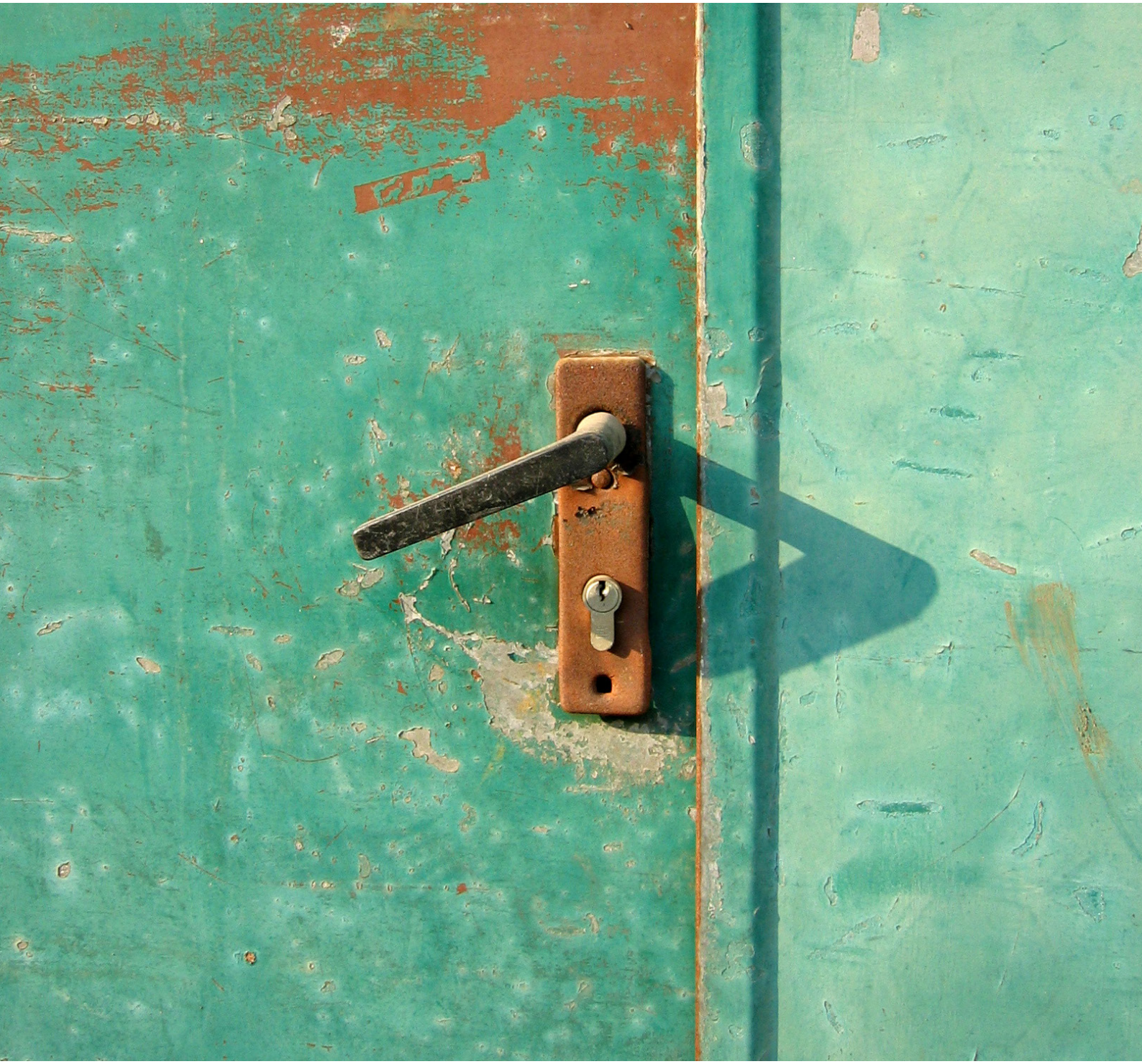
Metrohm White Paper

Fundamentals of Electrochemical Corrosion Research



Metrohm Autolab

Introduction

Corrosion refers to a process that involves deterioration or degradation of metal. The most common example of corrosion is the degradation of metals or alloys. Most corrosion phenomena are electrochemical in nature and consist of at least two reactions on the surface of the corroding metal. One of the reactions is the oxidation (e.g., dissolution of iron), also referred to as the anodic partial reaction. The other is a reduction reaction (e.g., reduction of oxygen), and is referred to as the cathodic partial reaction. The products of the electrochemical reactions can react chemically with each other to form the final product (e.g., rust). For example, the corrosion of iron to form rust proceeds according to the overall reaction:

$$2\,Fe + 2\,H_2O + O_2 \rightarrow 2\,Fe(OH)_2$$

This reaction includes the dissolution of iron, the reduction of oxygen and formation of rust:

$Fe \rightarrow Fe^{2+} + 2\,e^-$ (Anodic)

$2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^-$ (Cathodic)

$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2$ (Chemical)

Types of Corrosion

Uniform Corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the area of the metal under attack. Uniform corrosion results in the loss of material until failure. This is the most widespread form of corrosion that is observed.

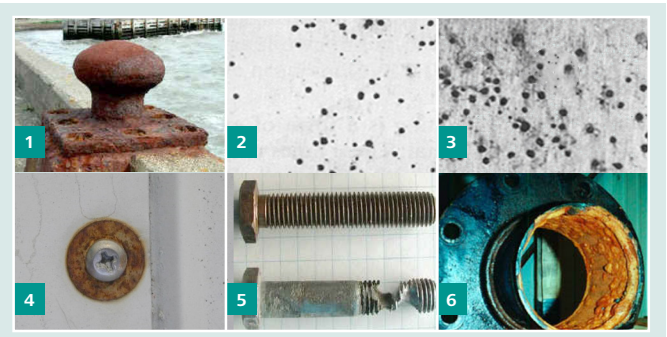


Figure 1. Different types of corrosion:

1. Uniform corrosion **2. and 3.** Pitting corrosion **4.** Galvanic corrosion
5. Crevice corrosion **6.** Microbiologically induced corrosion

Pitting Corrosion

Pitting corrosion is a localized form of corrosion by which pits or pin holes are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to predict and design against. Corrosion products often cover the pits making the detection often very difficult. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system.

Crevice Corrosion

Crevice corrosion is a localized form of corrosion that occurs in the presence of stagnant solution in a small (micro) crevice. Local chemistry changes in crevices (shielded areas) such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, disbonded coatings, threads, lap joints and clamps, can result in crevice corrosion.

Galvanic Corrosion

Galvanic corrosion refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte. For example, it occurs when two (or more) dissimilar metals are brought into electrical contact under water. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. Either metal in the couple may corrode when in seawater.

Microbiologically Induced Corrosion (MIC)

Microbiologically Induced Corrosion or MIC refers to corrosion caused by biological organisms or microbes. These microbes are categorized by common characteristics such as their by-products (i.e., sludge producing) or compounds they effect (i.e., sulfur oxidizing). They all fall into one of two groups based upon their oxygen requirements; one being aerobic (requires oxygen) such as sulfur oxidizing bacteria, and the other being anaerobic (requires little or no oxygen) such as sulfate reducing bacteria.

Electrochemical Characterization Methods for Corrosion

Linear sweep voltammetry (LSV)

Linear sweep voltammetry or LSV is one of the most commonly used methods for characterizing corrosion phenomenon. It involves sweeping the potential of the working electrode and measuring the current response. With LSV valuable information can be discovered about the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in various environments.

Electrochemical impedance spectroscopy (EIS)

In recent years, Electrochemical Impedance Spectroscopy or EIS has been successfully applied to the study of corrosion systems. One of the advantages of EIS over direct current (DC) techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured.

Electrochemical Noise (ECN)

During localized corrosion, electrochemical noise is generated by a combination of stochastic (random) processes, such as the breakdown of passive films and repassivation. ECN involves the measurement of the current and/or potential noise and analysis of the data using Fast Fourier Transform (FFT).

Measurement of Corrosion Rates

The simplest way of measuring the corrosion rate of a metal is to expose the sample to the test medium (e.g., sea water) and measure the loss of weight of the material as a function of time. Although these tests are simple, there is no easy way to extrapolate the results to predict the lifetime of the system under investigation. Moreover, some corrosion processes occur with no significant mass change (e.g., pitting corrosion) making them difficult to detect by gravimetric methods.

Electrochemical methods provide an alternative to traditional methods used to determine the rate of corrosion. Direct and quantitative determination of corrosion rates can be determined from simple electrochemical measurement like LSV.

Most corrosion phenomena are electrochemical in nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterize corrosion mechanisms and predict corrosion rates.

Calculation of corrosion rates

The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, R_M, and the corrosion current i_{corr}:

$$R_M = \frac{M}{nF\rho A} i_{corr}$$

where M is the atomic weight of the metal, ρ is the density, n is the charge number which indicates the number of electrons exchanged in the dissolution reaction and F is the Faraday constant, (96.485 C/mol), A is the area of the sample. The ratio M/n is also sometimes referred to as equivalent weight.

Calculation of corrosion currents

Calculation of corrosion rates requires the determination of corrosion currents. When reaction mechanisms for the corrosion reaction are known, the corrosion currents can be calculated using Tafel Slope Analysis.

The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation:

$$i = i_{corr}\left(e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}}\right)$$

$$\eta = E - E_{corr}$$

In the above equation E is the applied potential and i the measured current density. The overpotential η is defined as the difference between applied potential and the corrosion potential. The corrosion potential, E_{corr} is the open circuit potential of a corroding metal. The corrosion current, i_{corr}, and the Tafel constants b_a, and b_c can be measured from the experimental data.

For large anodic overpotentials (η/b_a >> 1) the Butler-Volmer equation simplifies to the Tafel equation for the anodic reaction:

$$\eta = b_a \cdot log\left(\frac{i}{i_{corr}}\right)$$

Analogously, for large cathodic overpotentials (η/b_c << -1) the Tafel equation for the cathodic reaction is given by:

$$\eta = -b_c \cdot log\left|\frac{i}{i_{corr}}\right|$$

The Tafel equations predict a straight line for the variation of the logarithm of current density with potential. Therefore, currents are often shown in semilogarithmic plots known as Tafel plots. This type of analysis is referred to as Tafel Slope Analysis.

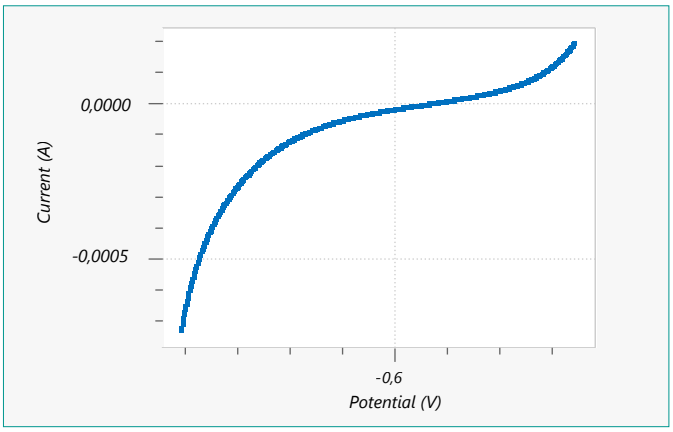


Figure 2 - Current potential plot for iron screw immersed in seawater.

To perform Tafel analysis it is necessary to have information on the electrode surface area, equivalent weight and the density of the material. The Tafel slope analysis provides the corrosion rate and polarization resistance. However a correct estimate of the Tafel slopes is possible if the linear Tafel region covers at least 1 decade in current.

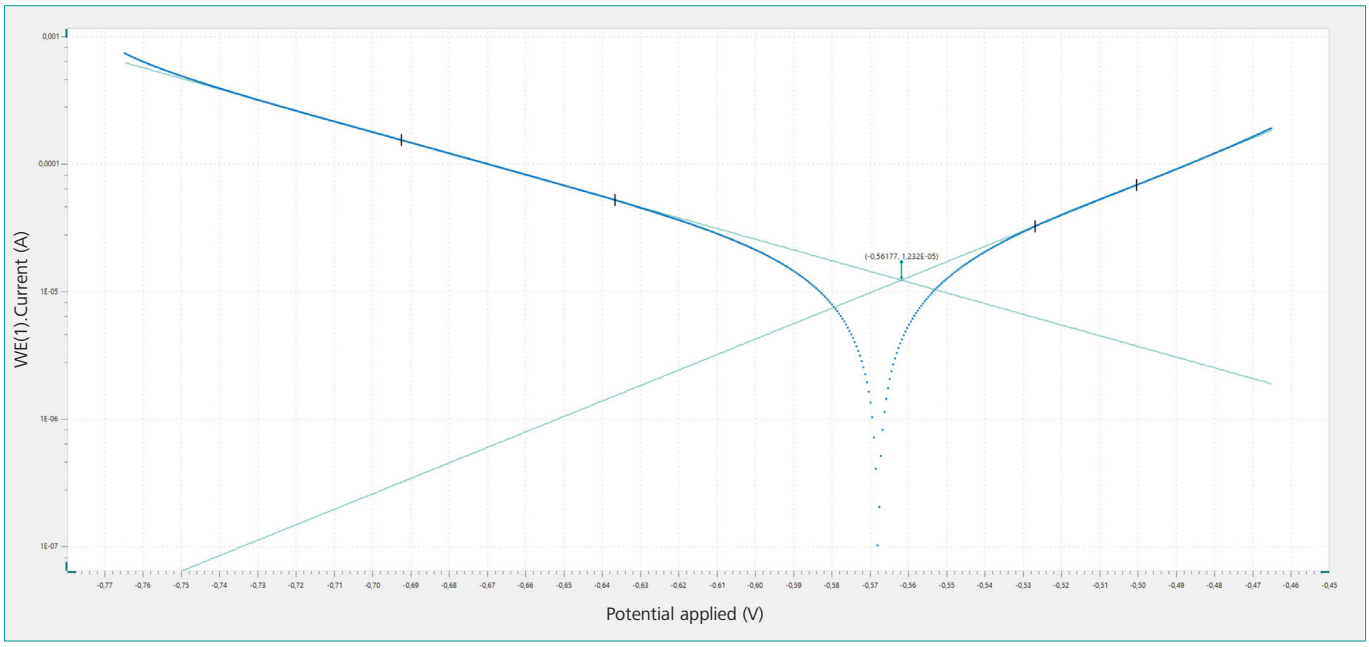


Figure 3 - Tafel plot for iron screw immersed in seawater. The linear parts of the Tafel plot are identified.

Measurement of Polarization Resistance

Polarization Resistance, R_p

An electrode is polarized when its potential is forced away from its value at open circuit or corrosion potential. Polarization of an electrode causes current to flow due to electrochemical reactions it induces at the electrode surface. The polarization resistance is defined by the following equation:

$$R_p = \left(\frac{\Delta E}{\Delta i}\right)_{\Delta E \to 0}$$

Where ΔE is the variation of the applied potential around the corrosion potential and Δi is the resulting polarization current. The polarization resistance, R_p behaves like a resistor and can be calculated by taking the inverse of the slope of the current potential curve at open circuit or corrosion potential. During the polarization of an electrode, the magnitude of the current is controlled by reaction kinetics and diffusion of reactants both towards and away from the electrode.

Considering the Butler-Volmer equation for small η, i.e. for potentials close to corrosion potential, the Butler-Volmer equation can be reduced to:

$$i_{corr} = \frac{1}{2.303}\frac{b_a b_c}{b_a + b_c}\left(\frac{1}{R_p}\right)$$

Or, when the expression is rearranged:

$$R_p = \frac{1}{2.303}\frac{b_a b_c}{b_a + b_c}\left(\frac{1}{i_{corr}}\right)$$

If the Tafel slopes are known, one can calculate the corrosion currents from the polarization resistance using the above equations.

If the Tafel slopes are not known (e.g. when corrosion mechanism is not known), the R_p can still be used as a quantitative parameter to compare the corrosion resistance of metals under various conditions. High R_p of a metal implies high corrosion resistance and low R_p implies low corrosion resistance.

Measurement of R_p using LSV

In Figure 4 the results of a LSV experiment performed on an iron screw immersed in seawater are shown. The slope of the curve at corrosion potential (- 0.319 V) can be calculated by performing a linear regression on data from - 0.329 V to - 0.309 V (i.e. 10 mV cathodic and 10 mV anodic relative to the corrosion potential).

The results of the regression are shown in Figure 5.
The polarization resistance R_p is calculated from inverse of the slope (1/slope) and is found to be 9.442 kΩ.

Function description	y = 3.3767E-05 + 0.00010538x
Correlation coefficient	0.99891
a	3.3767E-05
b	0.00010538
1/Slope	9489.3

Figure 5 – The calculated regression line equation for the corrosion of an iron screw in seawater

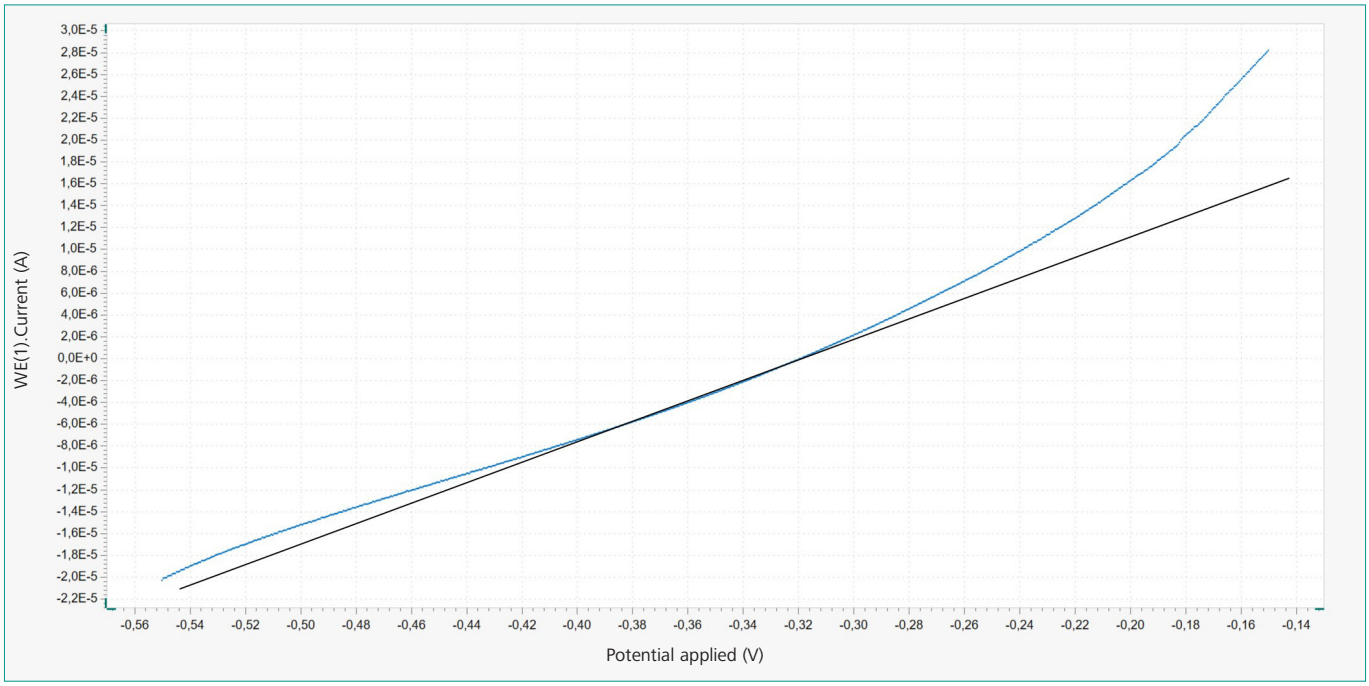


Figure 4 – LSV data for the corrosion of an iron screw in seawater

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Measurement of R_p using Electrochemical Impedance Spectroscopy (EIS)

Polarization resistance can also be measured with electrochemical impedance spectroscopy. For simple systems where the Nyquist plot shows one semicircle, a Randles equivalent circuit shown in Figure 6 can be used to estimate R_p. In Figure 7, the Nyquist plot of experimental data for the corrosion of iron in sulfate solution is shown. The solid line represents the regression of the Randles circuit to calculate the polarization resistance R_p.

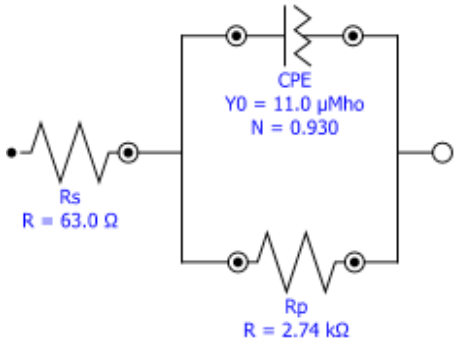

Figure 6 – The Randles equivalent circuit

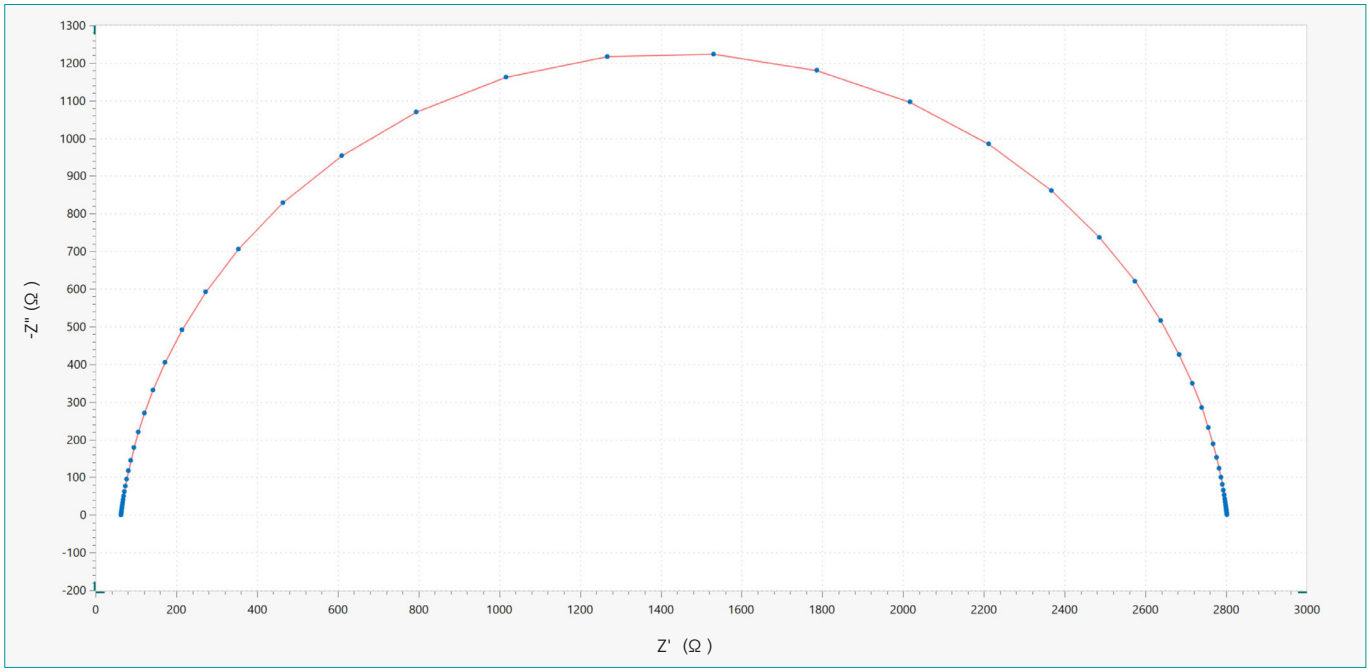

Figure 7 – Nyquist Plot for Estimation of Rp for corrosion of iron in seawater using EIS

Corrosion Inhibitors

A corrosion inhibitor is a substance that when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defense against corrosion.

Anodic inhibitors

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

Cathodic inhibitors

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface.
The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging.
The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

Mixed Inhibitors

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly.
Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal forming a protective film.
The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required.

Volatile Corrosion Inhibitors

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used.
When these inhibitors come in contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility.

Evaluation of Corrosion Inhibitors

Electrochemical methods are used routinely for the evaluation of the efficiency of corrosion inhibitors. The advantages of electrochemical methods are short measurement time and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new inhibitors.

The LSV experiments can evaluate the performance of the corrosion inhibitor. Beginning the experiments at cathodic potentials ensured that any oxide layer present prior to the start of the experiments was reduced.

Figure 8 shows the polarization curves for solutions with and without inhibitor, in red and in blue, respectively. The anodic part of the polarization curve without inhibitor is typical for active metal dissolution.

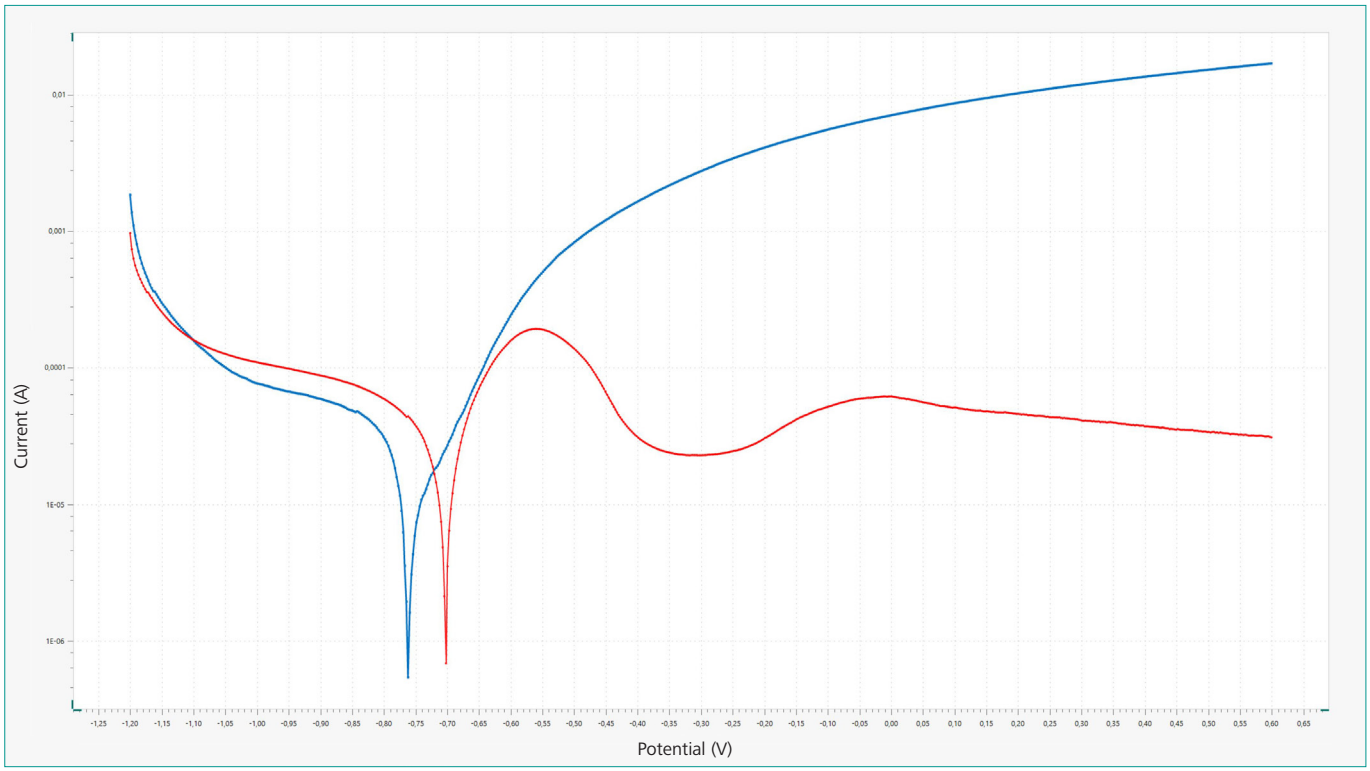

Figure 8 – Linear polarization measurement in the absence (blue) and presence (red) of a corrosion inhibitor

The data suggests that when an anodic inhibitor is added to the solution there is a shift of the corrosion potential in the anodic direction and a reduction in the anodic current. The corrosion inhibitor also results in the formation of the passive film evidenced by the appearance of the passivation plateau.

Resources

Now that you have been introduced to the fundamental corrosion concepts you may like to explore the topic more thoroughly. We offer this list of resources to help you deepen your knowledge of the topic.

ASTM International – Standards Worldwide
www.astm.org/Standard/standards-and-publications.html

NACE International Standards
nace.org/resources

Introduction to Corrosion Science
Author: E. McCafferty
Springer 2010

The Fundamentals of Corrosion
Author: JC Scully
Pergamon 3e 1990

Principles and Prevention of Corrosion
Author: Denny A Jones
Pearson 2e 2013

Application Notes

We created a number of application notes that can help you explore corrosion electrochemically in your laboratory:

- Critical Pitting Temperature (CPT) as per ASTM G150
- Electrochemical impedance spectroscopy (EIS) of three coated aluminum samples
- Equivalent circuit models
- Hydrogen permeation experiments
- Stepwise dissolution measurement

Log on to **www.metrohm.com/applications** to find these notes. The list above is subject to change and you can use a **Full Text Search** *AN-COR* to discover additional corrosion applications as they become available.

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