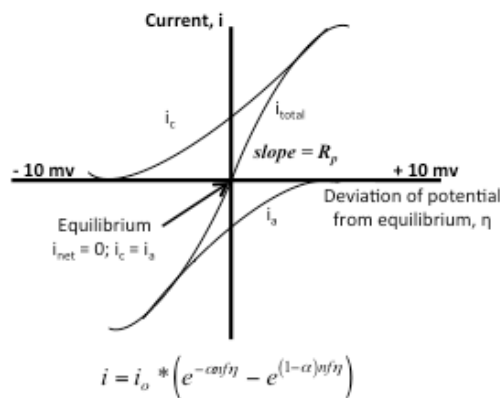# Falex Litigation Technical Investigations
# **Electrochemical Corrosion Test Methods**

The four electrochemical corrosion measurements we use are linear polarization (LP), Tafel analysis, harmonic analysis (CASP, but also called electrochemical frequency modulation (EFM), and electrochemical impedance spectroscopy (EIS).

Linear polarization is a classical, direct current (dc) corrosion measurement method. The electrochemical corrosion test current – potential relationship is linear only within 10 mv to 20 mv of the free corrosion potential, and the measurable current is very small in this region, the significance of which is that modern, higher performing instrumentation has made this technique more practical.
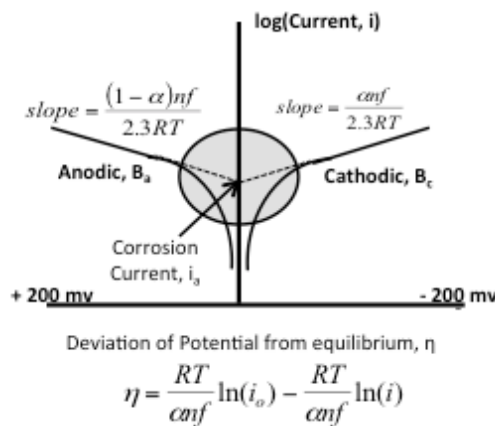


$$i = i_o * \left( e^{-\alpha nf \eta} - e^{(1-\alpha)nf \eta} \right)$$

Measuring the slope, $R_p$, of line obtained in the "Linear Polarization" plot provides the corrosion current, but quantities called the Tafel coefficients, $B_a$ and $B_c$, are required for this computation. The Tafel coefficients are often assumed to have certain values, but this causes an error whose extent is unknown and that can be large.

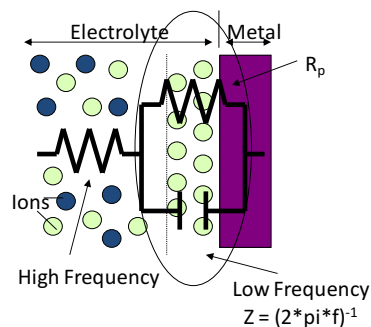$$i_{corr} = \frac{\frac{1}{R_p} * B_a * B_c}{2.303 * (B_a + B_c)}$$

Tafel analysis is a conventional dc technique in which larger, applied potentials are used. This produces larger, measurable currents, but the current – potential relationship is non-linear, so a semi-log plot is used, which is called a "Tafel" plot (next Figure). The Tafel plot shows an anodic branch for the oxidation reaction, and a cathodic branch for the reduction reaction. Each branch shows a linear portion and extrapolation to the free corrosion potential provides the corrosion current at the free corrosion potential. The slopes of the anodic and cathodic lines are the Tafel coefficients. The problems with this approach are that large potentials can sometimes drive unwanted reactions that obscure the linear portion of the anodic or cathodic branch, making extrapolation inaccurate, and irreversibly altering the electrode surface.



$$\eta = \frac{RT}{\alpha nf} \ln(i_o) - \frac{RT}{\alpha nf} \ln(i)$$

# Falex Litigation Technical Investigations
## Electrochemical Corrosion Test Methods

DC methods like linear polarization and Tafel analysis are easy to perform, but they have additional severe limitation when the corrosion rate is very low, the electrolyte has low electric conductivity, or when an electrically insulating coating is used. The next Figure helps explain why these limitations exist. The corroding metal in an electrochemical test is part of an equivalent, electric circuit that contains contributions from the resistance of the solution (or an electrically insulating coating) and from the double layer capacitance that forms from the accumulation of ions at the surface of the electrode, in addition to the polarization resistance, $R_p$, that is related to the corrosion rate. The electric current that is measured contains a component that comes from $V/R_{solution}$ and that is appreciable if $R_{solution}$ is large, and a component that comes from charging of the capacitance, if present, both of which have nothing to do with corrosion.
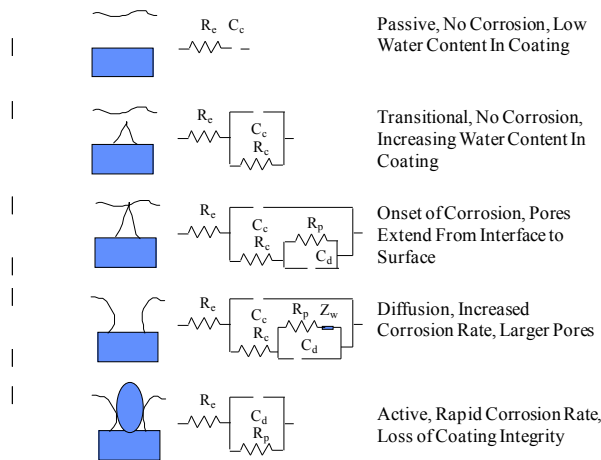


This situation is exploited in electrochemical impedance spectroscopy (EIS) to obtain a more accurate measure of the corrosion current by using an ac potential excitation rather than a dc potential excitation, and by measuring the relationship between the ac current and the applied ac potential for a variety of frequencies. The data from this approach allows for construction of an equivalent circuit model, including determination of the values of the various elements of the model of the electrochemical system, such that a value of $R_p$ is obtained that is related only to the corrosion current.

For example, electrochemical impedance spectroscopy with equivalent circuit modeling has been shown to be very instructive about the degradation of paint coatings on metal surfaces. Paint coatings typically go through a number of stages as shown in the following Figure, and these stages can be identified and quantified by equivalent circuit modeling. Although very powerful, the instrumentation for electrochemical impedance spectroscopy is more complex, the mathematics are more sophisticated, there are a multitude of models, it takes experience to identify the correct model, and extensive modeling is required. Nonetheless, when done properly, EIS provides superior, often unique, insight about the corrosion rate and mechanism.

The fourth method we use is also an alternating current (ac) method that is relatively recent. It provides an uncontaminated value of the corrosion current, as well as of the Tafel coefficients, without requiring use of large dc potentials that can alter the surface of the electrode, and it does not require extensive modeling, but also does not provide mechanistic insight.

This technique is called harmonic analysis (CASP), or electrochemical frequency modulation (EFM). It uses the same instrumentation as electrochemical impedance spectroscopy, but simultaneously applies two sine waves of different frequency. The non-linear nature of corrosion processes introduces harmonics and intermodulation components into the current response of the corroding system due to the dual sine wave stimulus. Although the math to analyze the harmonics is somewhat complex, it is not necessary to tailor it to each system as has to be done for EIS.

The results of harmonic analysis are fairly immune to contributions of circuit elements other than $R_p$, but it can be challenging to obtain a valid measurement because the excitation amplitude cannot be very large and the magnitudes of the current harmonics are much smaller than those of the fundamental frequency. The choice of the two frequencies also is important, and has to fulfill certain requirements that depend on the nature of the corroding system. By coupling electrochemical impedance spectroscopy with harmonic analysis, we are able to identify the appropriate frequencies and overcome this limitation.