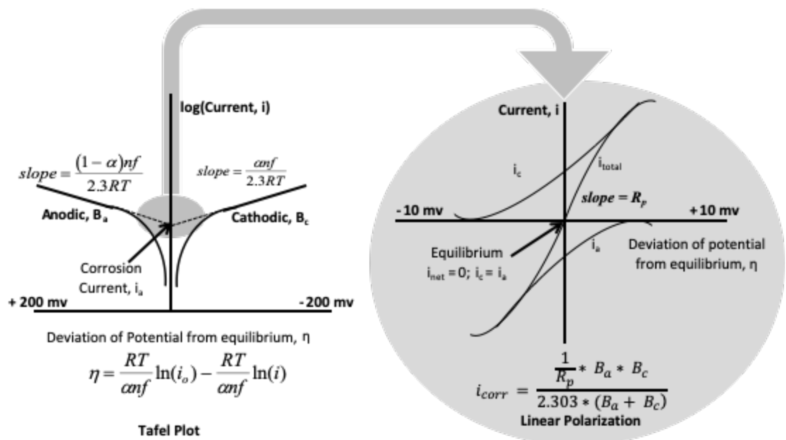
Spotlight Business Consulting LLC
Scientific, Technical, and Business Consulting

John Fildes, Ph.D.
Spotlight Business Consulting LLC
www.SpotlightBC.com
jfildes@SpotlightBC.com
(630) 248-0836

Corrosion engineering provides guidance on the selections of metals to resist corrosion but does not explain why corrosion occurred. Corrosion testing that exposes a sample to an environment with periodic inspection can screen corrosion resistance but is limited for corrosion failure analysis because it may not precisely identify the onset of corrosion and it does not offer insight as to the mechanism by which a coating failed or corrosion occurred. Electrochemistry is required to gain more insight.

Electrochemistry provides the underpinnings for corrosion science and the means to effectively determine the cause and origin of corrosion and coating failures. There are several electrochemical techniques to measure corrosion rates, which differ in their complexity, the equipment needed, the mathematical methods used for analyzing the data, their applicability, and their ability to provide mechanistic information. The four electrochemical corrosion measurements we use are linear polarization, Tafel analysis, harmonic analysis, also called electrochemical frequency modulation, and electrochemical impedance spectroscopy.

<u>Direct Current (DC) Methods</u>



Tafel analysis (left above) is a dc technique in which a relatively large voltage is applied to the sample. This produces a relatively large non-linear current that is measured and plotted on a semi-log plot, which is called a "Tafel" plot. 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. Large potentials can drive unwanted reactions that obscure the linear portion of the anodic or cathodic branch and can also irreversibly alter the electrode.

Linear polarization (right in the Figure above) uses the linearity of the electrochemical current –potential relationship within 10 mv to 20 mv of the free corrosion potential. The measured current is very small in this region, but modern instrumentation has made this technique practical. The slope, R_p, of the line 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. Tafel coefficients are sometimes assumed to have certain values, which causes an error whose extent is unknown and can be large.

Experience and Case Studies

Dr. John Fildes has conducted electrochemical studies including ones for corrosion that span the beginning of his career at Borg Warner's Corporate Research Center through his most recent research under funding by the Army.

Dr. John Fildes was brought-in to a case after several metallurgical experts had produced their reports. John applied a broader multidisciplinary approach and collected information that was known about the behavior of the metal in several other chemical processes where similar conditions would exist and concluded that the material should not have corroded, an aspect that none of the metallurgical experts had considered. John also collected information that was known about the nature of conditions in the chemical process in which the equipment was used and concluded that the type of corrosion that occurred should not have happened under these conditions.

These insights, which had been unrecognized, resulted in a request for documents and information about the way in which this specific chemical process was operated. This produced materials that showed the process was operated with non-typical conditions that would cause corrosion, but that could not have been anticipated by the maker of the supplied equipment.

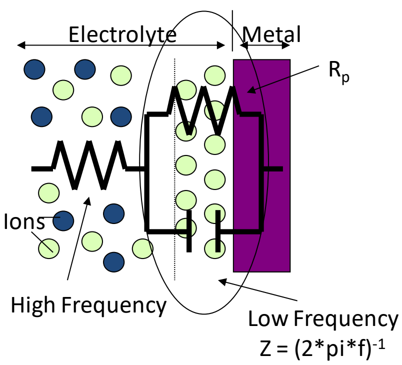
This took the supplier of the equipment from a difficult defense based on not being responsible for the selection of the material to a far easier to understand issue of the equipment being used in a way that was never specified for its use. A favorable settlement resulted in a case that was headed to trial.

Spotlight Business Consulting LLC
Scientific, Technical, and Business Consulting

John Fildes, Ph.D.
Spotlight Business Consulting LLC
www.SpotlightBC.com
jfildes@SpotlightBC.com
(630) 248-0836

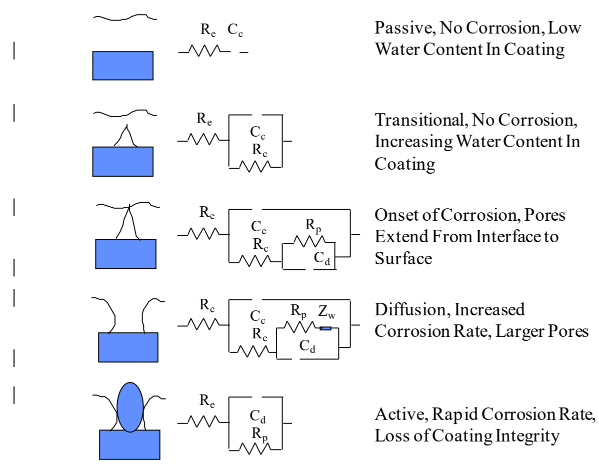
AC Methods

DC methods like linear polarization and Tafel analysis are easy to perform, but there are limitations when the corrosion rate is very low, the electrolyte has low electric conductivity, or when an electrically insulating coating is used. These limitations exist because 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 contribution that comes from the potential error caused by $R_{solution}$ and can be appreciable if $R_{solution}$ is large, and a component that comes from charging of the capacitance; both are unrelated to the corrosion rate.



This situation is exploited by ac methods. The instrumentation for ac methods is more complex, the mathematics are more sophisticated, extensive modeling is required, and it takes experience to identify the correct model. Nonetheless, ac methods can provide superior, often unique, insight about the corrosion rate and mechanism.

For example, electrochemical impedance spectroscopy with equivalent circuit modeling has been shown to be very instructive as to the degradation of paint coatings on metal surfaces. Paint coatings typically go through a number of stages as shown in following Figure, and these stages can be identified and quantified by equivalent circuit modeling.



Another method we use 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. 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 of the fundamental. 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.

Dr. John Fildes has a Ph.D. in physical chemistry, a B.S. in chemistry, and he was a post-doctoral research associate in a chemical engineering department. Physical chemistry provides the scientific basis for many engineering disciplines. Thermodynamics provides the basis for metallurgy, materials science, fire and explosion science, and others. Chemical bonding provides the basis for the strength of materials and electronic materials and devices. Electrochemistry provides the basis for corrosion science, and chemical kinetics provides the basis for chemical compatibility, reactivity, volatility, and chemical processes. Dr. Fildes has conducted over $27.5 million of R&D and/or litigation-related investigations in these areas because he is well experienced in the fundamental scientific principles as well as in analytics and chemical safety. He led a large group of scientists and engineers at Northwestern University and two scientific/engineering firms licensed to practice professional and structural engineering that conducted thousands of litigation-related technical investigations, so he is also an expert in the conduct of these types of investigations.