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Electrochemical Corrosion Case Study

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. He conducts failure analysis investigations for insurers and litigators, which sometimes involve testing of metals, coatings, lubricants, and fuels to determine the cause of corrosion and the failure of protective coatings. This case study demonstrates a comprehensive approach based on four electrochemical techniques to obtaining reliable corrosion rate data for difficult to measure systems.

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. Sometimes these techniques are complementary, and sometimes certain techniques are not applicable such as using dc methods for painted metals.

Electrochemistry may be complex, but the outcome is easy to understand and provides compelling insight as to the reason for corrosion or coating failure.
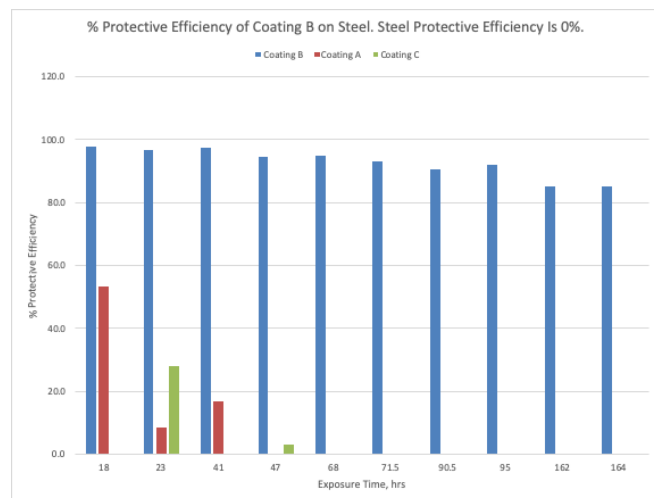
The measured corrosion rates for the bare steel and a coated steel are shown in the Figure below. The corrosion rate was measured by three techniques [harmonic analysis (CASP), linear polarization (LP), electrochemical impedance spectroscopy (EIS)] of the four techniques described on the next page. There is variation between absolute values of the three measurement techniques which is typical, but there is good agreement in the trends for the techniques and the conclusions for the corrosion resistance of the specimens are the same for all of the technique, providing additional support for any conclusions. The results show that the corrosion current for bare steel is substantial throughout the test that involved exposure to 3.5 wt. % NaCl in water. The corrosion current for the Coating B on the same steel starts out substantially lower than for bare steel, and remains very low throughout the test, showing excellent corrosion resistance and durability.
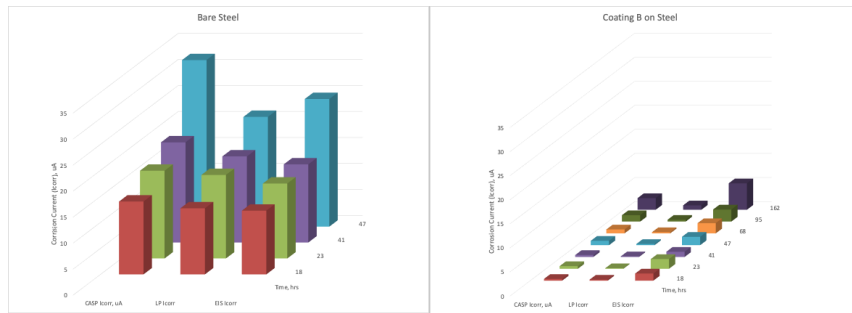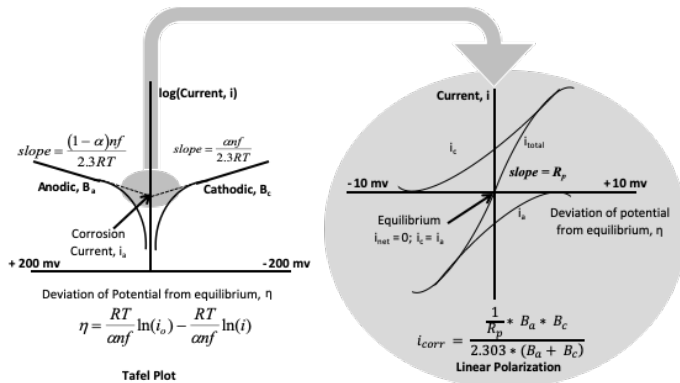

The protective efficiency, *P%*, of a coating is defined as:

$$P\% = \left(1 - \frac{I_{corr-coating}}{I_{corr-steel}}\right) * 100 \ .$$

The next Figure shows the protective efficiencies of the coating above (Coating C) and two others. The protective efficiencies are all relative to 2 hours exposure of bare steel. This may be an easier to understand presentation of the data than showing actual corrosion rates above. Coating C provides excellent protection that is much better than the other two coatings.

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Direct Current (DC) Methods

Tafel analysis (left Figure 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. A semi-log plot, called a "Tafel" plot, is used. 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 limitations 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 can also irreversibly alter the electrode surface.

Linear polarization (right in the Figure above) exploits the linearity of the electrochemical corrosion 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 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.

DC methods are easy to perform but have limitations when the corrosion rate is very low, the electrolyte has low electric conductivity, or when an electrically insulating coating is used.

Alternating Current (AC) Methods

The dc method limitations exist because the corroding metal in an electrochemical test is part of an equivalent electric circuit that, in addition to the polarization resistance, R_p that is related to the corrosion rate, 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, both of which are unrelated to the corrosion rate.
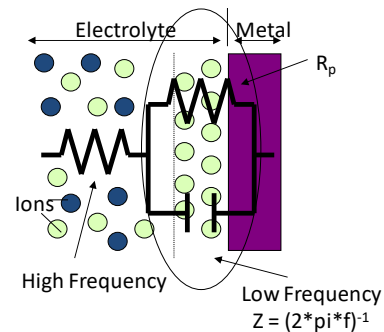
AC methods exploit this situation. Electrochemical impedance spectroscopy uses the frequency response of the corroding sample to construct an electrical circuit whose components model the electrochemical processes that are occurring.

Another more recent technique, Harmonic Analysis (CASP) also called electrochemical frequency modulation (EFM), provides an uncontaminated value of the corrosion current, as well as of the Tafel coefficients without requiring use of large dc potentials. This technique 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. The results of harmonic analysis are fairly immune to contributions of circuit elements other than R_p which is proportional to the corrosion rate, so the corrosion rate is not affected by unrelated electrochemical processes that may also occur.

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.

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