

Autolab Application Note COR02

Corrosion

Part 2 – Measurement of Corrosion Rates

Keywords

Corrosion; Electrochemical methods; Corrosion rate; Kinetics

Summary

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 a linear sweep voltammetry (LSV).

Weight loss measurements

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 simple 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 tests

As mentioned in the previous application notes, most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterise 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} :

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

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). The ratio M/n is also sometime 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 E_{corr} . 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 ($\eta/b_a \gg 1$) the Butler-Volmer equation simplifies to the Tafel equation for the anodic reaction:

$$\eta = \log(i_{corr}) + b_a \cdot \log(i)$$

Analogously, for large cathodic overpotentials ($\eta/b_c \ll -1$) the Tafel equation for the cathodic reaction is given by:

$$\eta = \log(i_{corr}) - b_c \cdot \log|i|$$

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.

Calculation of corrosion currents in NOVA

The NOVA software provides a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. In Figure 1 the current potential curve for an iron screw immersed in seawater is shown.

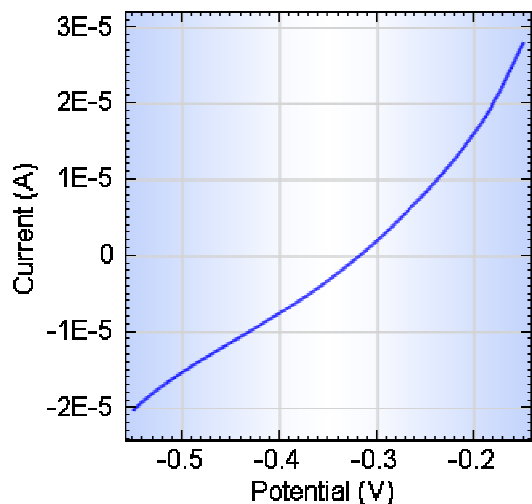


Figure 1 – Current potential curve for iron screw immersed in seawater

Selecting the Corrosion Rate Tafel Slope analysis tool from the Analysis menu, a Tafel plot is added as shown in Figure 2.

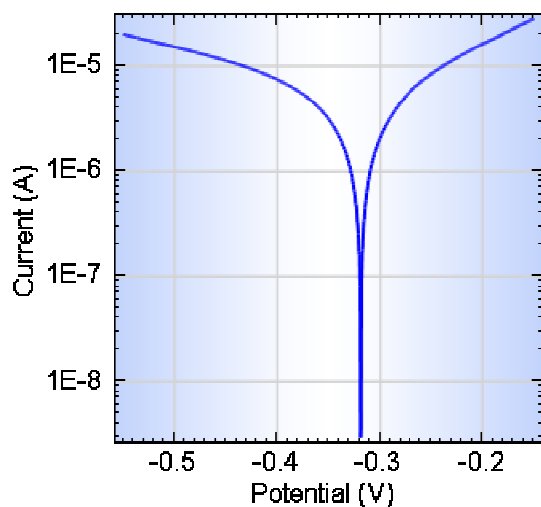


Figure 2 – Tafel plot for iron screw immersed in seawater

The user can specify the equivalent weight, density of the electrode material, the surface area of the electrode and the number of significant digits to use in the calculation as shown in Figure 3.

Density (g/cm ³)	<input type="text" value="7.86"/>
Equivalent weight (g/mol)	<input type="text" value="27.925"/>
Surface area (cm ²)	<input type="text" value="1"/>
Number of significant digits	<input type="text" value="5"/>
<input type="button" value="Reset"/>	

Figure 3 – The working electrode parameters used in the Tafel slope analysis

The user, with the help of markers, needs to specify the anodic and cathodic Tafel region. Once the regions are selected the NOVA software automatically calculates the Tafel slopes and the corrosion currents. The Tafel slopes are then automatically plotted on the Tafel Plot as shown in Figure 4 and the results are tabulated as shown in Figure 5.

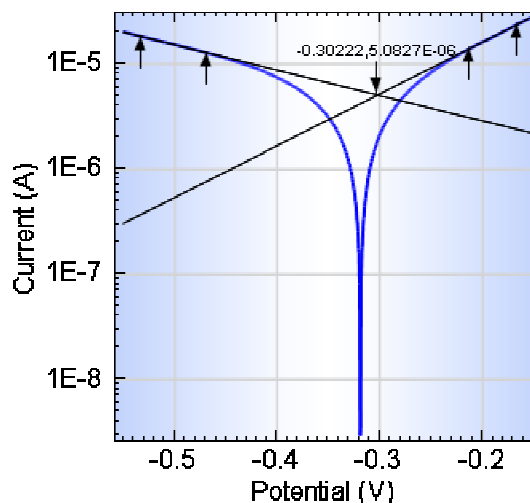


Figure 4 – The linear parts of the Tafel plot are identified by placing markers

The Tafel slope analysis tool provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated from the estimated corrosion current, i_{corr} , obtained from the intercept of the two linear segment of the Tafel slope.

Corrosion rate, tafel slope

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ba (V/dec) = 201.630 mV/dec
bc (V/dec) = 405.020 mV/dec
Ecorr, Calc (V) = -303.270 mV
Ecorr, Obs (V) = -318.740 mV
jcorr (A/cm²) = 4.97200 µA/cm²
icorr (A) = 4.97200 µA
Corrosion rate (mm/year) = 0.057774
Polarization resistance (Ω) = 11.7580 kΩ
E Begin (V) = -531.850 mV
E End (V) = -164.950 mV
  
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Figure 5 – NOVA displays the results of the Tafel Slope analysis

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Selecting the Corrosion Rate Fit analysis tool from the Analysis menu performs a similar analysis as with the Corrosion Rate Tafel Slope tool. The fit tool also performs a curve fit based on the Butler-Volmer expression which allows for a more accurate determination of the corrosion current, polarization resistance and corrosion rate.

The Corrosion Rate Fit tool works in the same fashion as the Corrosion Rate Tafel Slope tool. Using markers the linear Tafel region can be identified. After the markers have been placed on the plot, the software performs the curve fit and calculates the characteristic corrosion values using the specified density, equivalent weight and surface area (see figure 6).

Corrosion rate, fit

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ba (V/dec) = 693.370 mV/dec
bc (V/dec) = 322.520 mV/dec
Ecorr, Calc (V) = -303.620 mV
Ecorr, Obs (V) = -318.740 mV
jcorr (A/cm²) = 9.87250 µA/cm²
icorr (A) = 9.87250 µA
Corrosion rate (mm/year) = 0.11472
Polarization resistance (Ω) = 9.68350 kΩ
E Begin (V) = -532.910 mV
E End (V) = -166.020 mV
χ² = 1.0222E-11
Iterations = 8
  
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Figure 6 – NOVA displays the results of the Corrosion rate fit analysis

In choosing the regions for Tafel slope analysis, care must be taken. A correct estimate of the Tafel slopes is possible only if the linear Tafel region (region between markers in Figure 3) covers at least 1 decade in current. In certain cases (e.g., passivation of iron shown in Figure 6) the Tafel slope analysis is not possible.