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, $\rho$ 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, $(96.485 \text{ C/mol})$. 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:

$$ i = i_{corr}\left(e^{\frac{2.303n}{E - E_{corr}}} - e^{-\frac{2.303n}{E - E_{corr}}}ight) $$

where $E$ is the applied potential and $i$ the measured current density. The overpotential, $\eta$, 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 ($\eta/b_a >> 1$) 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 ($\eta/b_c << -1$) 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](image)

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](image)

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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>7.06</td>
</tr>
<tr>
<td>Equivalent weight (g/mol)</td>
<td>27.825</td>
</tr>
<tr>
<td>Surface area (cm²)</td>
<td>1</td>
</tr>
<tr>
<td>Number of significant digits</td>
<td>5</td>
</tr>
</tbody>
</table>

![Figure 3 – The working electrode parameters used in the Tafel slope analysis](image)

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](image)

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, icorr, obtained from the intercept of the two linear segment of the Tafel slope.
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).

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.