Corrosion: 3. Measurement of Polarization Resistance

In the previous application note, the procedure for estimating corrosion rates was outlined. The calculations were valid under the assumption that the corrosion reactions were under charge transfer control and that the mechanisms of the reactions were known. In real life, often, corrosion is a result of several reactions and it is not possible to *a priori* determine the reaction mechanism. In such cases Polarization Resistance, R_P, can be used to determine the resistance of the metal under investigation against corrosion.

Polarization Resistance, R_P

An electrode is polarized when its potential is forced away from its value at open circuit or corrosion potential. Polarization of an electrode causes current to flow due to electrochemical reactions it induces at the electrode surface. The polarization resistance or R_P is defined by the following equation,

$$R_P = \left.\frac{\Delta E}{\Delta I}\right|_{\Delta E \to 0}$$

where,

ΔE = polarization from corrosion potential
ΔI = polarization current.

Polarization resistance, R_P, behaves like a resistor and can be calculated by taking the inverse of the slope of the current potential curve at open circuit or corrosion potential.

During the polarization of an electrode, the magnitude of the current is controlled by reaction kinetics and diffusion of reactants both towards and away from the electrode. In the previous application note, the Butler-Volmer equation was introduced as

$$i = i_{corr}(\exp(2.303\frac{\eta}{b_a}) + \exp(-2.303\frac{\eta}{b_c}))$$

$$\eta = E - E_{corr}$$

where,

I = measured current,
I_{corr} = corrosion current,
η = over-potential,
b_a = anodic Tafel slope,
b_c = cathodic Tafel slope.

For small η, i.e. for potentials close to corrosion potentials, the above equation can be reduced to:

$$I_{corr} = 2.303\frac{b_a b_c}{(b_a + b_c)}(\frac{1}{R_P})$$

or

$$R_P = 2.303\frac{b_a b_c}{(b_a + b_c)}(\frac{1}{I_{corr}})$$

If the Tafel slopes are known, one can calculate the corrosion currents from the polarization resistance using the above equations. If the Tafel slopes are not known (e.g. when corrosion mechanism is not known), the R_P can still be used as a quantitative parameter to compare the corrosion resistance of metals under various conditions. High R_P of a metal implies high corrosion resistance and low R_P implies low corrosion resistance.

Measurement of R_P using electrochemical methods

Linear Sweep Voltammetry(LSV)

In Figure 1 the results of a LSV experiment performed on an iron screw immersed in seawater are shown. The slope of the curve at corrosion potential (-0.319V) can be calculated by performing a linear regression on data from -0.329 to –0.309V (i.e.10mV cathodic and 10mV anodic to the corrosion potential). The results of the regression are shown in Figure 2. The polarization resistance R_P is calculated from inverse of the slope (1/slope) and is found to be 9.339kΩ.

Electrochemical Impedance Spectroscopy (EIS)

Polarization resistance can also be measured with electrochemical impedance spectroscopy. For simple systems where the Nyquist plot shows one semi circle, a Randles equivalent circuit shown in Figure 3 can be used to estimate R_P. In Figure 4 Nyquist plot of experimental data for the corrosion of iron in sulfate solution is shown. The solid line represents the regression of the Randles circuit to calculate the polarization resistance, R_P.

Figure 1: LSV data for corrosion of iron screw immersed in seawater.

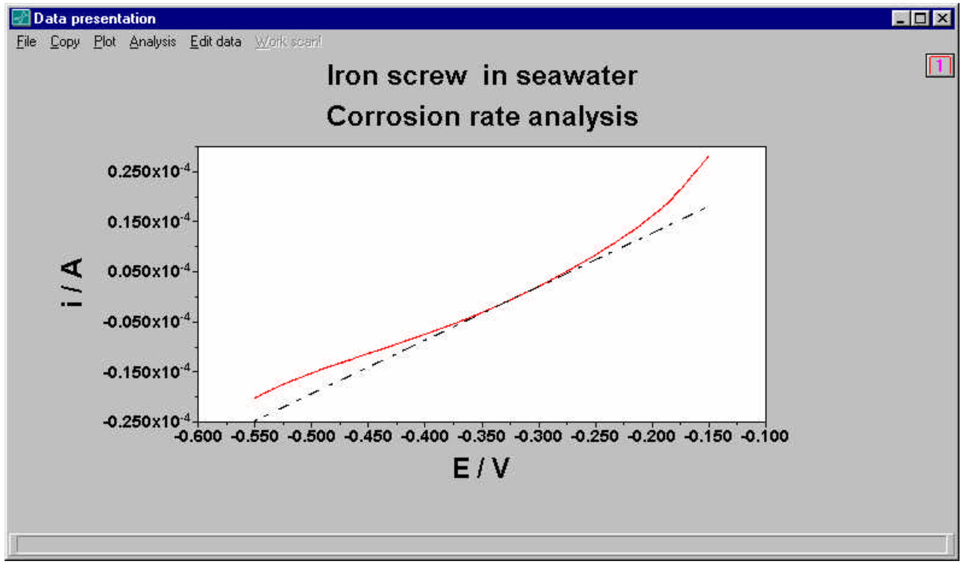
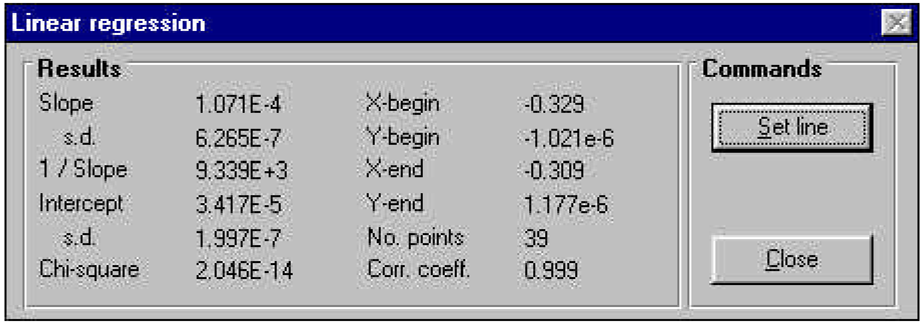


Figure 2: Estimation of R_P for corrosion of iron screw immersed in seawater.



Results

Slope	1.071E-4	X-begin	-0.329
s.d.	6.265E-7	Y-begin	-1.021e-6
1 / Slope	9.339E+3	X-end	-0.309
Intercept	3.417E-5	Y-end	1.177e-6
s.d.	1.997E-7	No. points	39
Chi-square	2.046E-14	Corr. coeff.	0.999

Figure 3: Randles circuit.

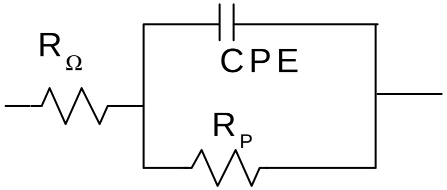


Figure 4: Estimation of R_P for corrosion of iron is sulfate solution using EIS