Chapter#5
Polarization Methods for Corrosion Rate Measurements

ME 472

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Measurement of Corrosion Rate

- **Corrosion Coupons for Mass Loss Tests**
  - A weighed sample (coupon) of the metal is introduced into the process, and later removed after a specific exposure time.
  - The coupon is cleaned of all corrosion product and is reweighed.
  - The weight loss is converted to a average corrosion rate (mm/y or mpy)
    - Faraday's law; i_{corr} (amp/cm^2) = {mass loss*n*F/(area*exposure time*AW)}
    - P.R. (mm/y) = 0.00327*i_{corr} *AW/nD
    - P.R. (mpy) = 0.129*i_{corr}*AW/nD

Measurement of Corrosion Rate

- For iron and steel alloys, the following equation is used to calculate the penetration rate in mm/y:

$$P.R.(mm/y) = \frac{mass\ loss\ (g) * 8.76x10^4}{density\ (g/cm^3) * area\ (cm^2) * exposure\ time(hr)}$$

- Example: what is the corrosion rate for a steel coupon, 2 cm^2 in area, which has lost 0.03 g in 20 hrs.
- Answer
  - PR = $0.03*8.76x10^4/(7.87*2*20)$= 8.3 mm/y

Corrosion Coupon Test Standards

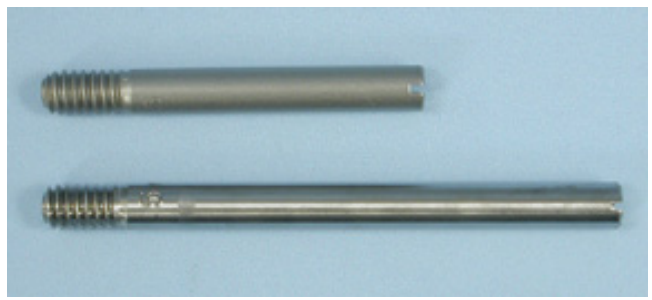
- ASTM G1 "Preparing, Cleaning, and Evaluating Corrosion Test Specimens," American Society for Testing and Materials (ASTM).
- ASTM G4 "Conducting Corrosion Coupon Tests in Plant Equipment,"
- ASTM G31 "Laboratory Immersion Corrosion Testing of Metals,"

Measurement of Corrosion Rate

- Using corrosion coupons to measure corrosion rate has several advantages:
  - Simple and inexpensive.
  - Can be done in the lab or directly in service equipment (pipes, tanks, ..ext.)
  - Provides a physical example of corrosion when removed from a system.
  - Allows an analysis of corrosion products.
- Disadvantages
  - Short-term exposure might be misleading (minimum exposure should be 1 week).
  - Requires easy access to install and collect coupons.

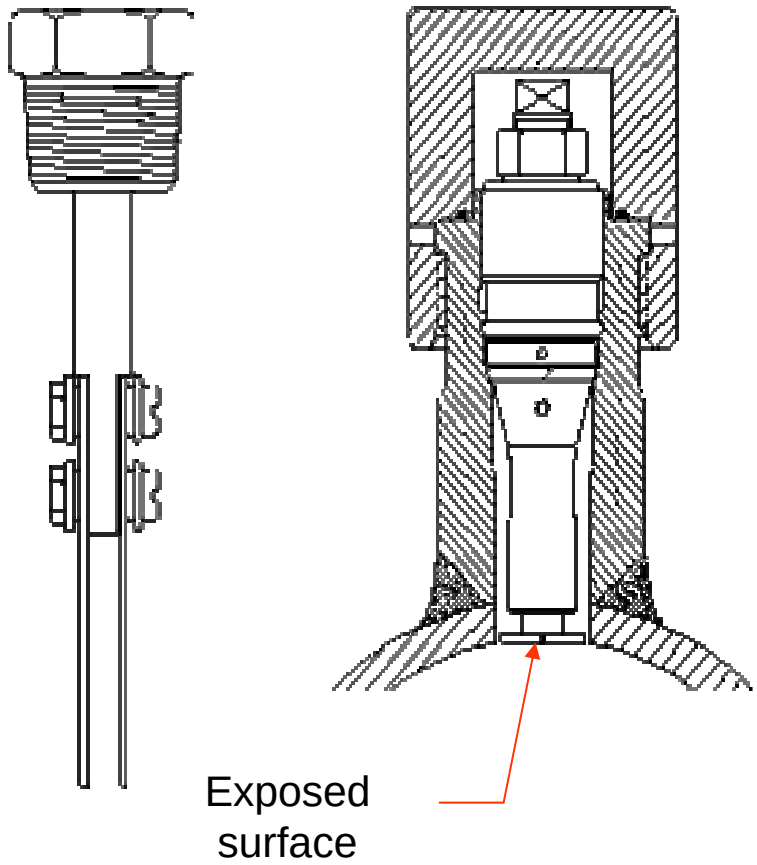
Corrosion Coupons

- There are different shapes of corrosion coupons for different materials shapes:
  - Flat
  - Rings
  - Cylindrical



Coupon Position and Orientation

- Coupons are placed in plant equipment using holders without causing turbulence in the flow stream
- Coupons must be electrically isolated from the holder and from the system to be monitored.



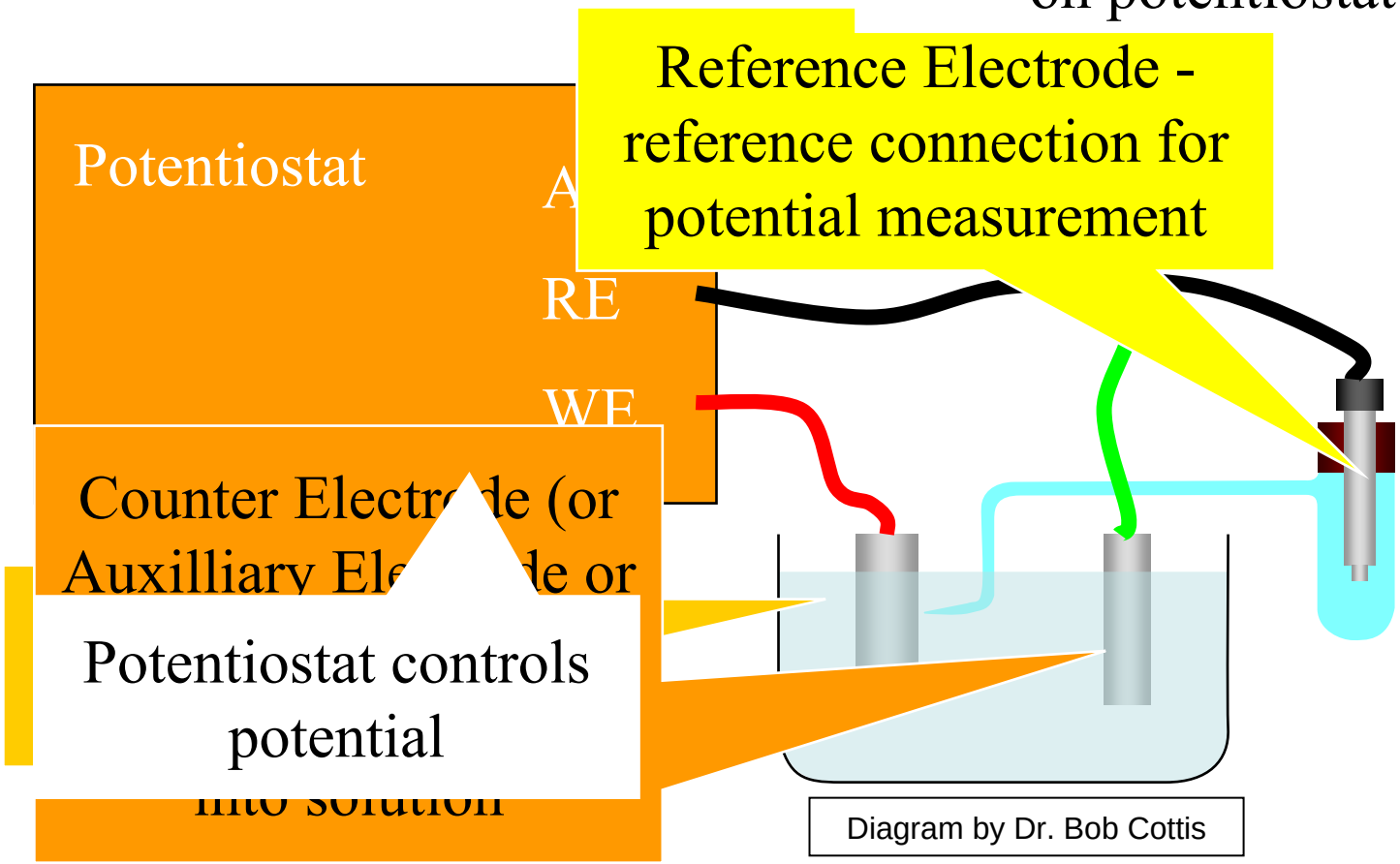
Polarization Methods

- Objective
  - determine corrosion current density under **steady-state** conditions using polarization methods
- Measuring corrosion rates using polarization methods provide several advantages:
  - Quick results
  - High sensitivity
  - Non-destructive
- Two electrochemical techniques:
  - Tafel Extrapolation (for lab measurements)
  - Electrochemical Linear Polarization (for lab and in-service equipment)

Measurement Methods

- Potential control

Connect electrodes to corresponding terminals on potentiostat

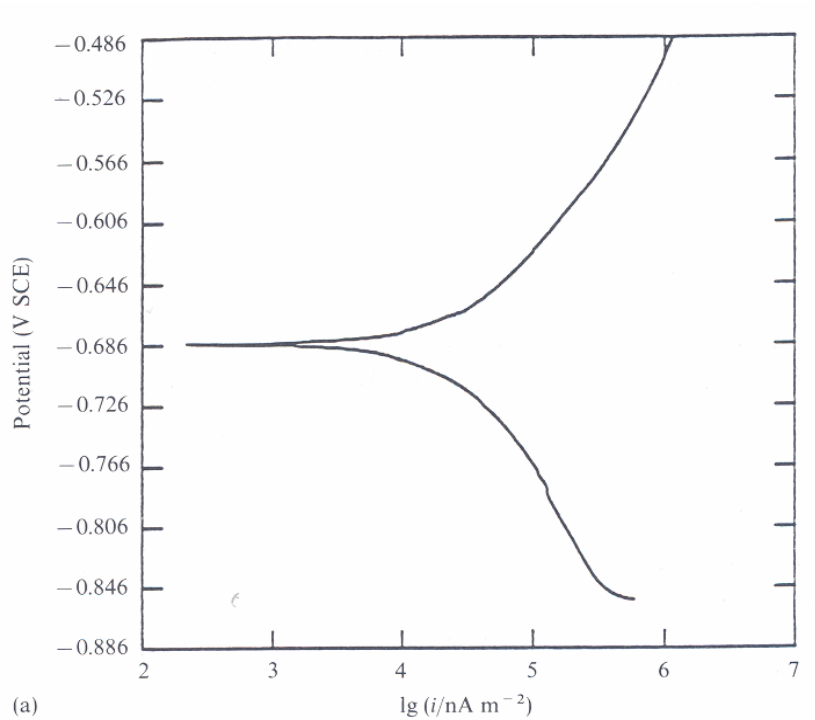


Tafel Extrapolation

- For an electrochemical reaction under activation control, the polarization curves usually show linear behavior of E vs. log (i). This is called Tafel behavior.
- Example: corrosion of metals in de-aerated strong acid where the reduction reaction is due to hydrogen reduction.
- A specimen of the metal is exposed in the same electrolyte and the anodic and cathodic polarization curves are generated (± 100-200 mV from E_{corr}).
- The anodic and cathodic polarization linear curves are extrapolated to E_{corr} to get i_{corr}.

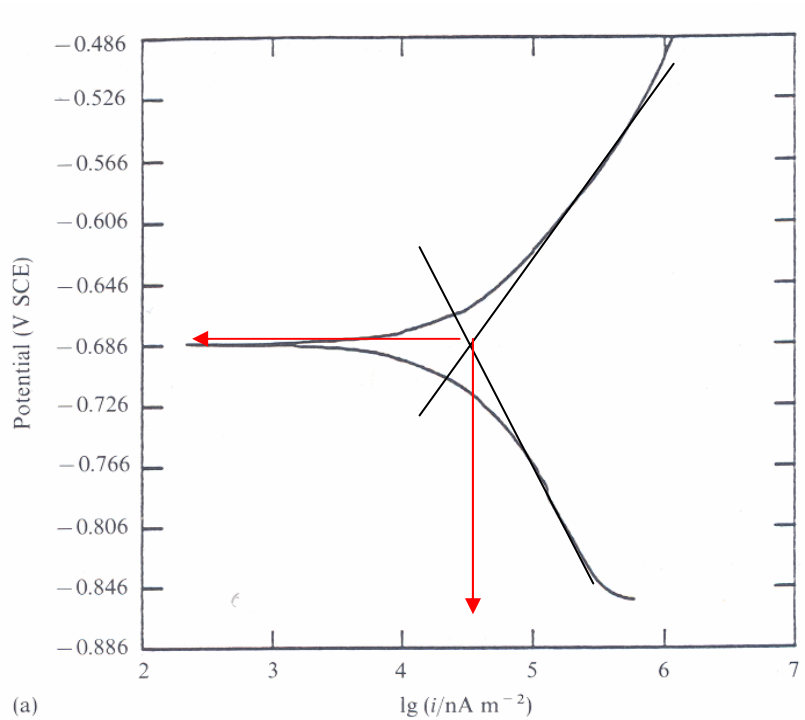
Tafel Extrapolation

- The figure shows the potentiodynamic scan for a steel alloy in de-aerated chemical reactor environment (pH=5) at 25C.
- Note the presence of the linear curve in E vs. Log (i) plots.
- Extrapolate the anodic and cathodic Tafel regions back to the point of intersection (E_{corr}).

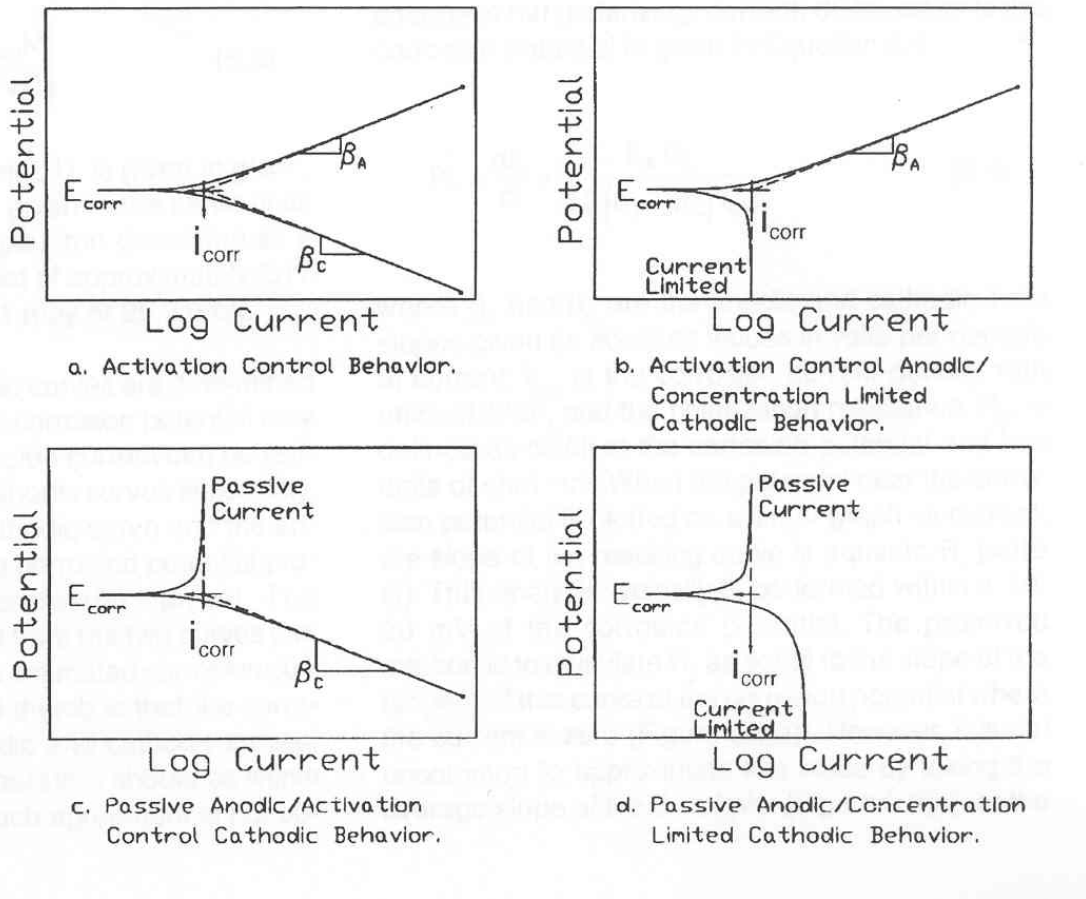


Tafel Extrapolation

- Tafel extrapolation indicates that $i_{corr} = 10^{4.5}$ nA/m^2 = 31 μA/m^2 and
- E_{corr} = -0.686 V vs. SCE

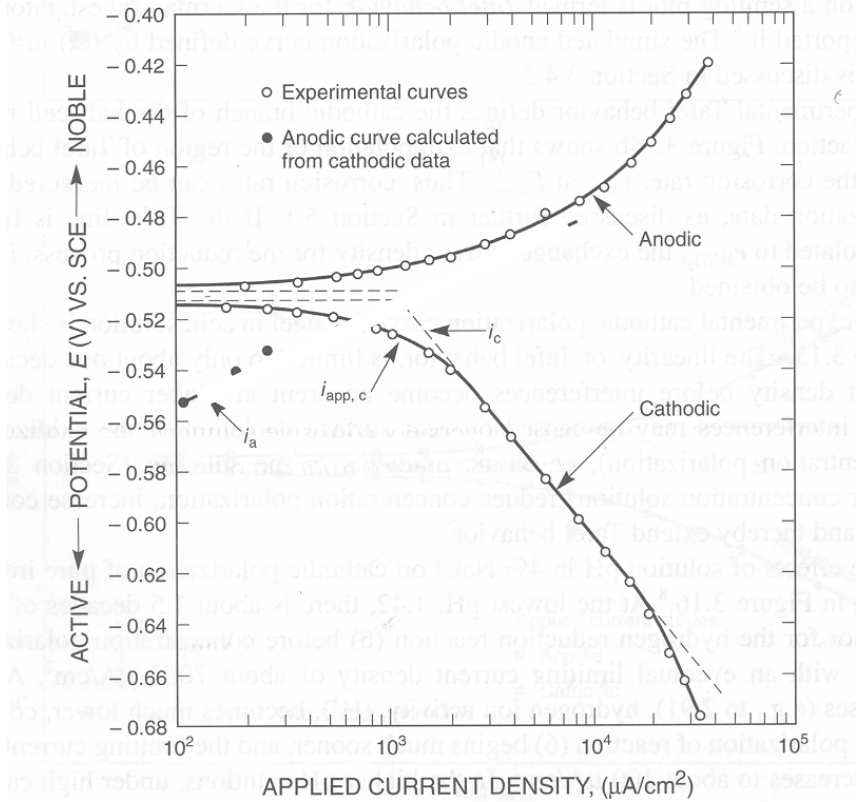


- Typical polarization plots for four different conditions:



Tafel Extrapolation

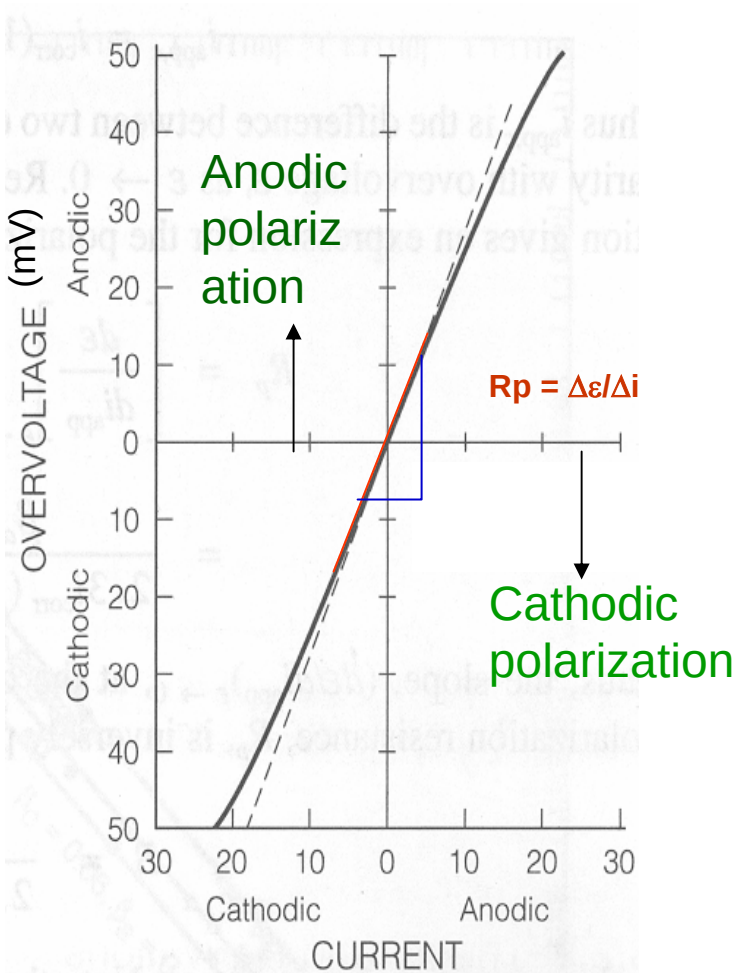
- Disadvantages of Tafel Extrapolation
  - Polarization curves are not reversible and sensitive to many experimental as well as environmental variables which introduce high variability in the Tafel constants.
  - Anodic curves may not show linear behavior near E_{corr}.



Linear Polarization Resistance

- Let's change the potential 10-20 mV slightly from E_{corr} and measure the corresponding i.
- Plot a linear graph for the overvoltage ε ($E_{app} - E_{corr}$) vs i assuming:
  - $i_{app,a}$ as +ve current
  - $i_{app,c}$ as -ve current
- The polarization resistance of an electrode is defined as the slope of the potential-current density curve near E_{corr} :
  - the polarization resistance:

$$R_p = \Delta\varepsilon/\Delta i \text{ as } \Delta\varepsilon \rightarrow 0$$

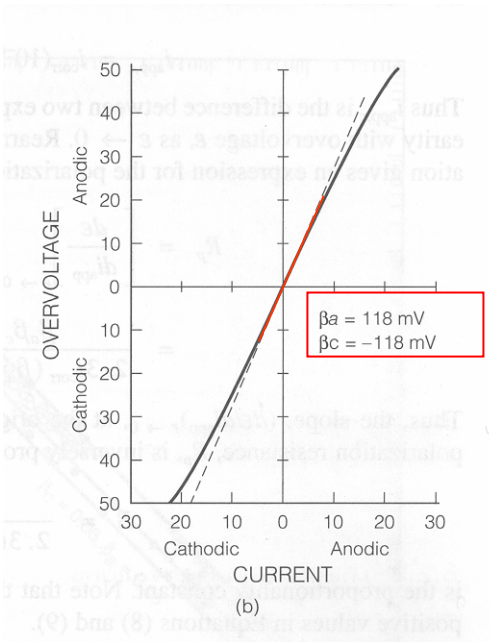


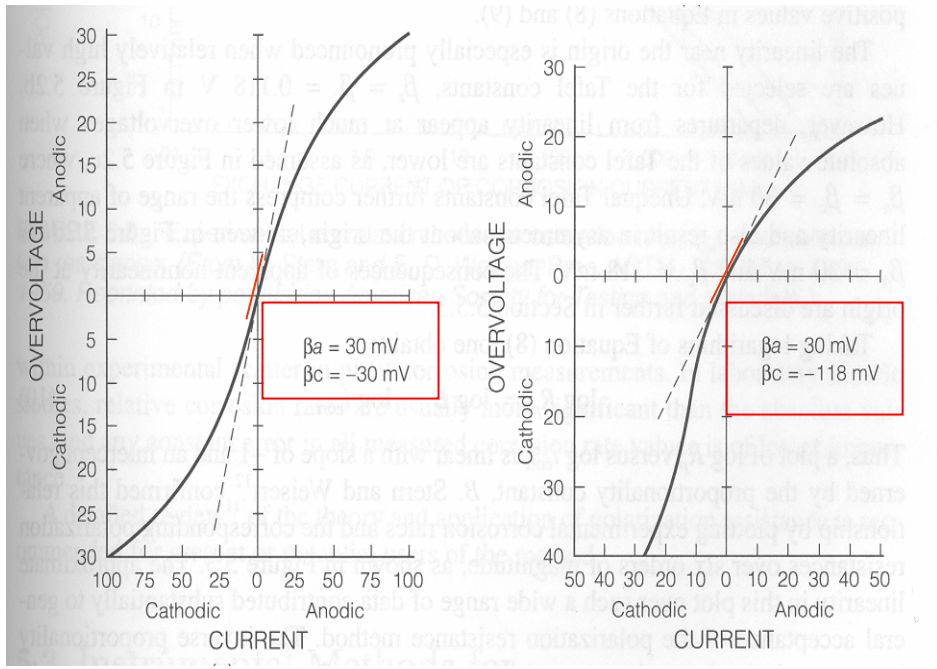
Linear Polarization Resistance

- For reactions under activation control, the polarization resistance R_P can be related to the corrosion current by:
  - $i_{corr} = B/R_P$
    - where B is a constant for a given corrosion system and given by:
    - $B=\beta_a \beta_c /[2.3(\beta_a+\beta_c)]$
      - For $\beta_a=\beta_c=100$mV, B = 21.7 mV = 0.0217 V
      - For $\beta_a=\beta_c=30$mV, B = 6.5 mV

Linear Polarization Resistance

- The range of linearity of the potential-current curve depends on the values of β_a and β_c (wide linear behavior for large β_a and β_c)





Tafel Constants and R_p

- Tafel slopes are required to calculate B.
- For large range of Tafel constants, B varies within a factor of 2 around the average value of 0.065 V.
- Therefore, even if the Tafel constants are not known and can not be measured, i_{corr} can be estimated to within a factor of 2.

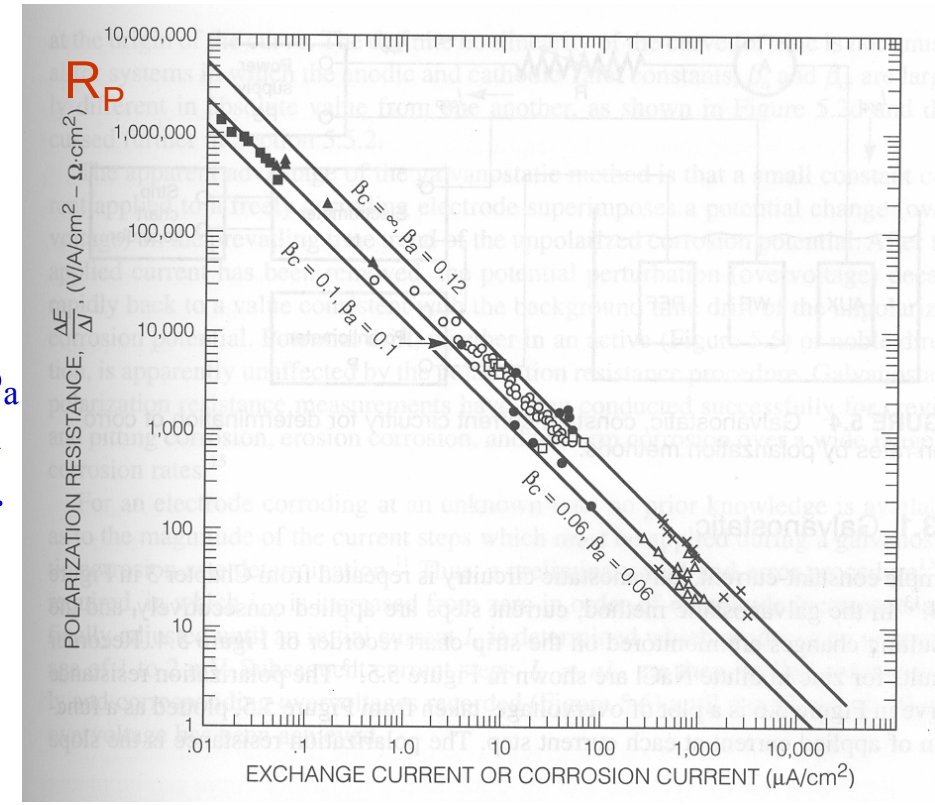
TABLE 5.2
CORRESPONDING RATE VALUES FOR TYPICAL TAFEL CONSTANTS AND POLARIZATION RESISTANCES

b_a (V)	b_c (V)	B	R_p (ohm-m²)	i_{cor} (A/m²)	μm/y*
0.120	0.120	0.026	10	2.6E-03	3.3
0.300	0.120	0.037	10	3.7E-03	4.7
0.300	0.300	0.065	10	6.5E-03	8.3
0.500	0.120	0.042	10	4.2E-03	5.3
0.500	0.500	0.109	10	1.1E-02	14
0.120	0.120	0.026	1	2.6E-02	33
0.300	0.120	0.037	1	3.7E-02	47
0.300	0.300	0.065	1	6.5E-02	83
0.500	0.120	0.042	1	4.2E-02	53
0.500	0.500	0.109	1	1.1E-01	138
0.120	0.120	0.026	0.1	2.6E-01	331
0.300	0.120	0.037	0.1	3.7E-01	473
0.300	0.300	0.065	0.1	6.5E-01	828
0.500	0.120	0.042	0.1	4.2E-01	534
0.500	0.500	0.109	0.1	1.1E+00	1,380

* Calculated for iron

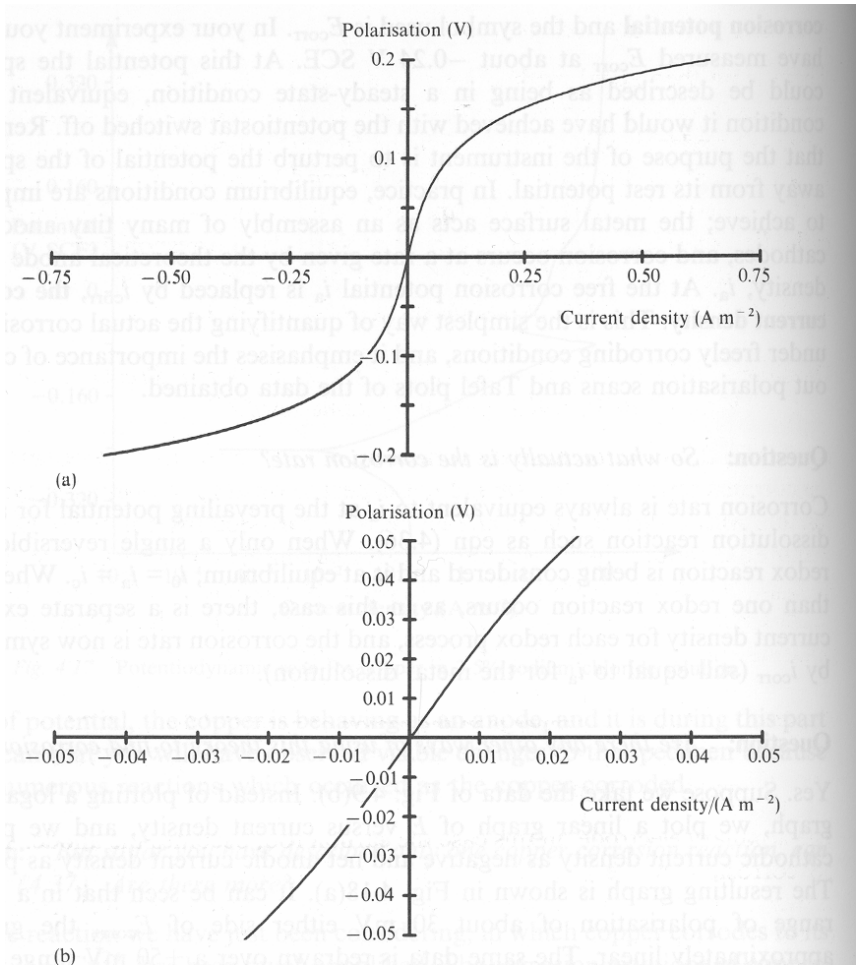
Linear Polarization Resistance

- The inverse relationship between R_P and i_{corr} has been verified experimentally for a variety of corrosion systems.
- $i_{corr}=B/R_P$ or $R_P = B/i_{corr}$
- Log R_p = log B- log i_{corr}
- If the actual values for the Tafel slopes are not known, assuming β_a and β_c =0.1 V for any system will introduce an error of a factor of 2.
- Hence, this method of estimating the rate of corrosion is not very sensitive to the exact values of β_a and β_c, contrary to Tafel extrapolation method.



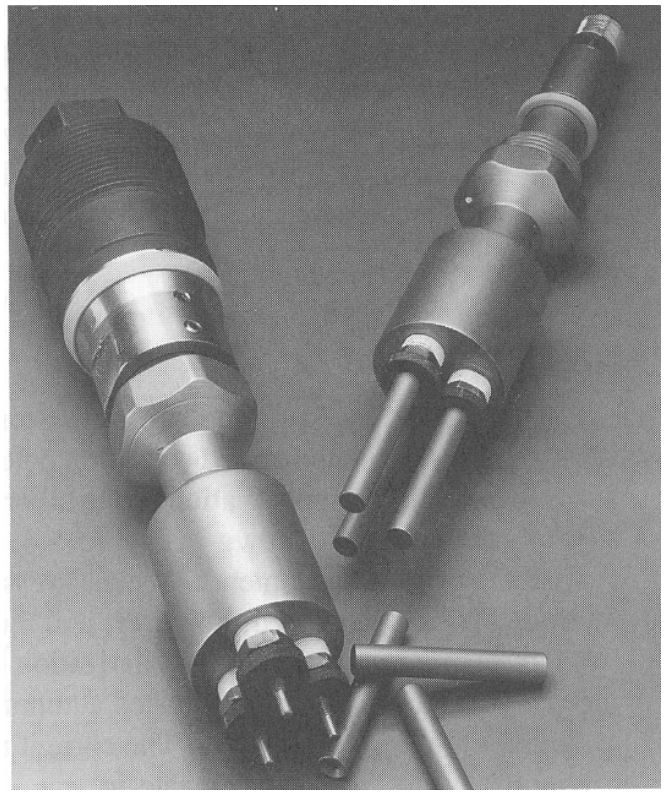
Linear Polarization Resistance

- Example: What is the corrosion current for a steel alloy exposed to a corrosive environment. The linear polarization curve measured in the environment is shown.
- Sol:
  - R_P = 0.04V/0.018A=2.2 V/A
  - Assume $\beta_a=\beta_c$=100 mV
  - B=0.022 V
  - i_{corr}= 0.022/2.2=0.01 A/m^2



LPR for Corrosion Monitoring

- The measurement of polarization resistance in the laboratory is done using 3-electrode cell.
- Linear polarization resistance (LPR) corrosion probes are commonly used in chemical-process and water treating industry where on-line corrosion rate readings are required. The technique is used in:
  - **Cooling water systems**
  - **Potable water treatment and distribution systems**
  - **Waste water treatment systems**
- The measurement may be made using:
  - a conventional three-identical electrodes (working, reference and counter).
  - two identical electrodes (a two-electrode system).

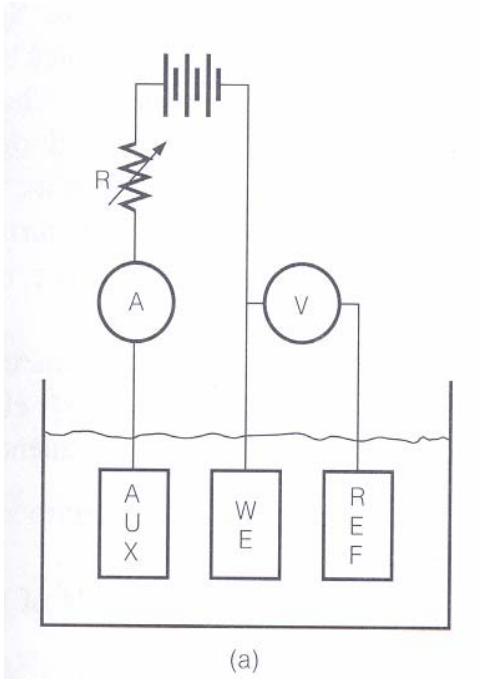


LPR for Corrosion Monitoring

- Linear polarization resistance (LPR) corrosion probes can be two electrodes or three electrodes:

•Three electrode

use conventional counter, reference and working electrodes. Provides lower solution resistance, therefore better for low conductivity solutions more complex instrumentation



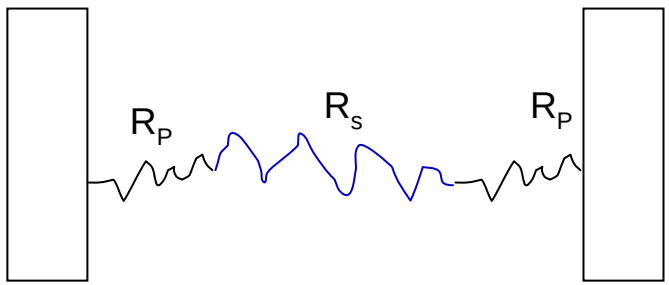
(a)

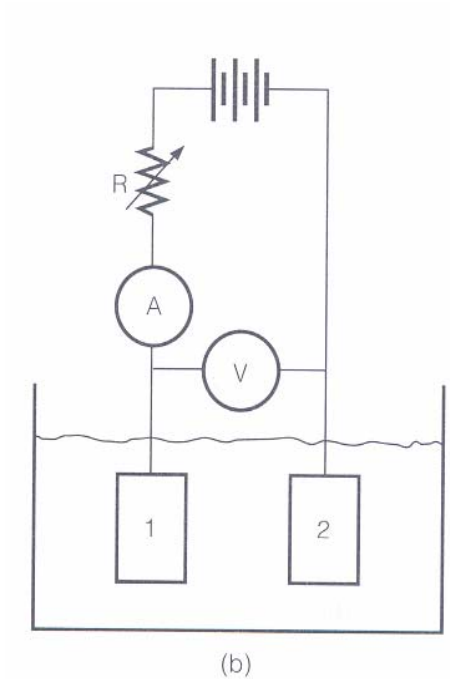
LPR for Corrosion Monitoring

- Linear polarization resistance (LPR) corrosion probes can be two electrodes or three electrodes:

•Two electrode

assume R_p is the same for two similar electrodes and measure cell resistance (= $2R_p + R_{sol}$).
Easy, no reference electrode required





LPR for Corrosion Monitoring

- Galvanostatic approach to meaure linear polarization resistance for three-electrode prope:
  - A small current is applied (few μA)
  - The electrode potential will change
  - The potential change is measued
  - Plot the overvoltage vs. current and calculate the slope
  - Apply the relationship between R_P and i_{Corr}

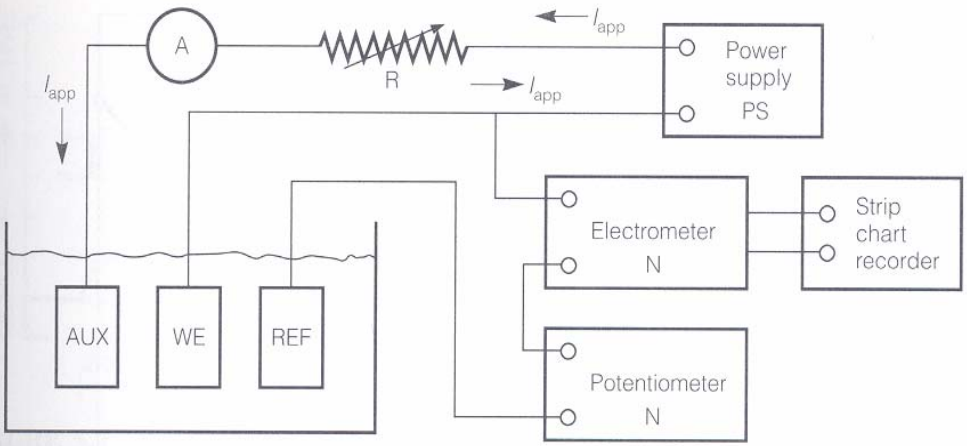
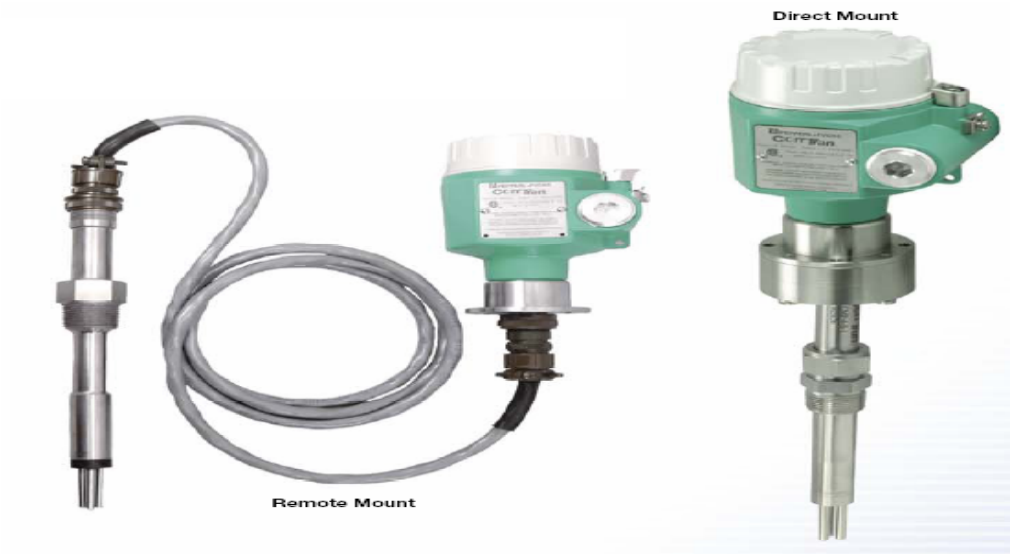


FIGURE 5.4 Galvanostatic, constant-current circuitry for determination of corrosion rates by polarization methods.

Commercial probes for on-line Monitoring of Corrosion



Probe mounted above the rebar
Electrode length 1.25" (32 mm)

A LPR probe installed in a concrete structure