Chapter (4-A)

Corrosion Kinetics- Part (A):

Corrosion Rates Expressions And Measurement

Sept. 16th , 2017

Thermodynamics to Kinetics

1. **Thermodynamics** –
   - the equilibrium between metals and their environment
   - Corrosion tendency of metals.
   - Qualitative picture of what can happen at a given pH and potential.
2. But…
   - Considerations of equilibrium are irrelevant to the study of corrosion rates.
     - Some metals with pronounced tendency to react (such as aluminum) react so slowly that they meet the requirements of a structural metal.
3. Need to know **Electrode kinetics** to predict the corrosion rates for the actual conditions

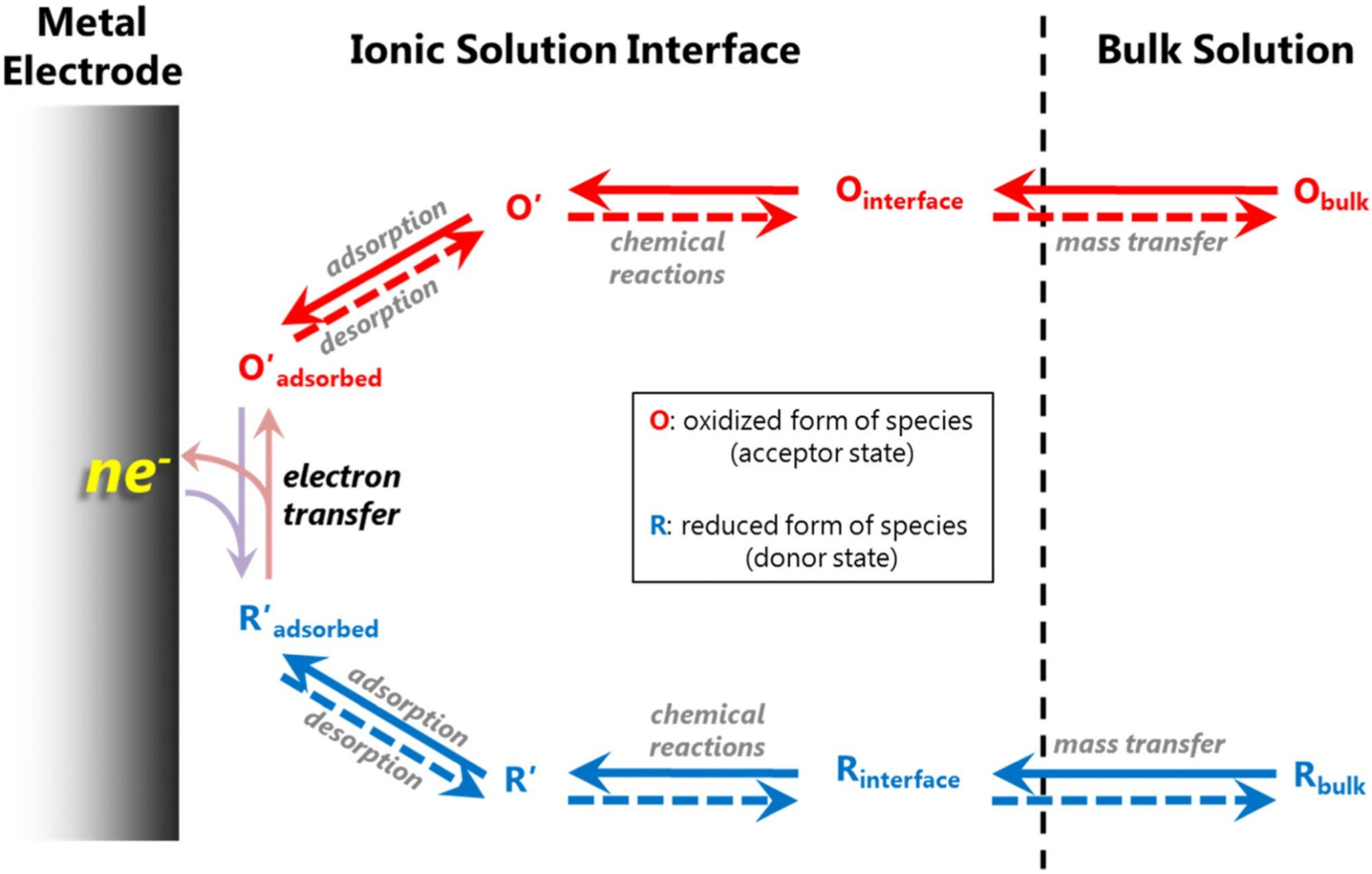
Steps in Electrochemical Reaction

- The following steps are involved in an electrochemical reaction:

  1. Mass transfer (e.g., of O from the bulk solution to the electrode surface).
  2. Electron transfer at the electrode surface.
  3. Other surface processes, e.g. adsorption.

- One or more of these steps will affect the overall corrosion rate. Details will be discussed later.

Electrochemical Process Mechanisms



Metal Electrode

Ionic Solution Interface

Bulk Solution

O'

$O_{interface}$

O_{bulk}

adsorption

desorption

chemical reactions

mass transfer

$O'_{adsorbed}$

ne^-

electron transfer

$R'_{adsorbed}$

adsorption

desorption

chemical reactions

mass transfer

R'

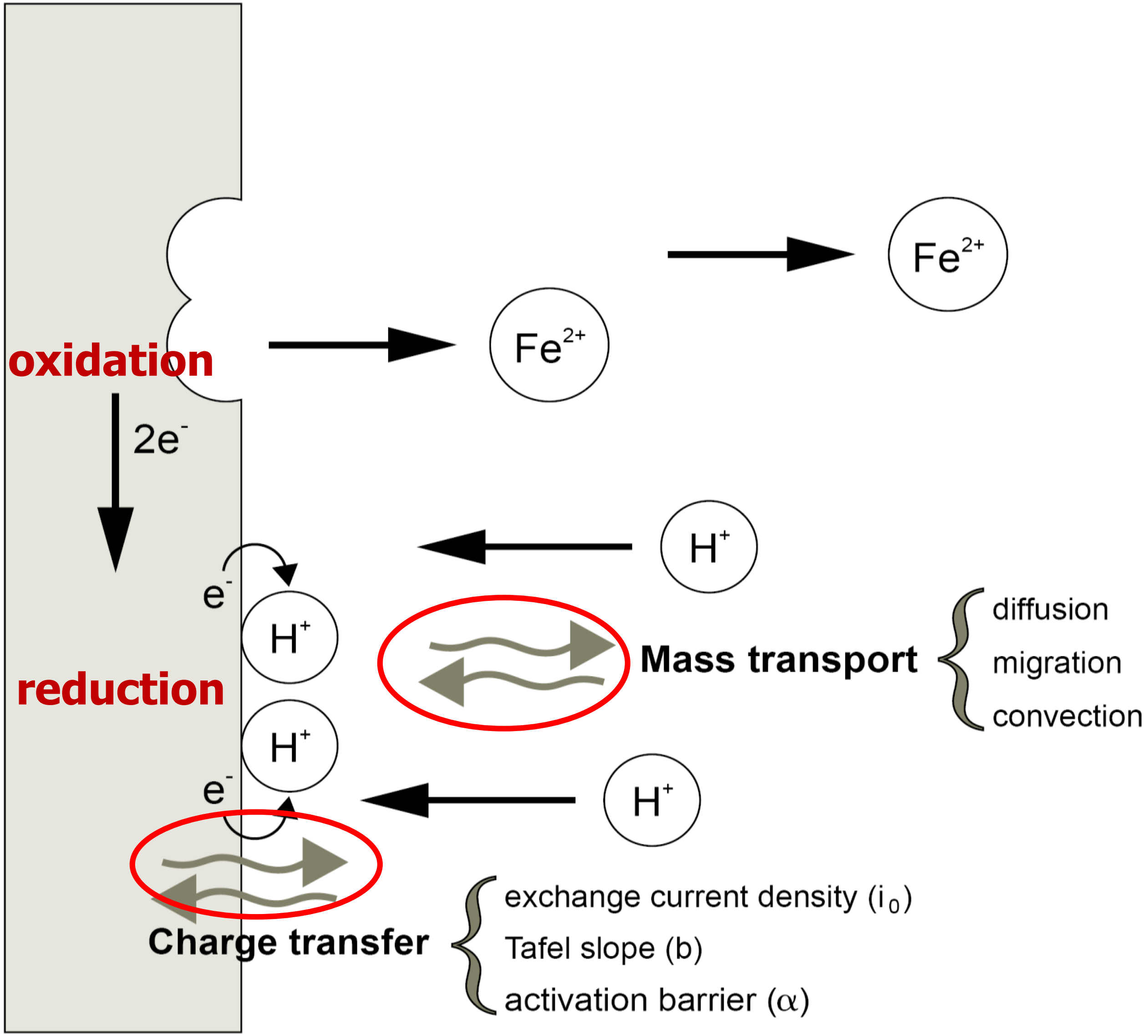
$R_{interface}$

R_{bulk}

O: oxidized form of species (acceptor state)

R: reduced form of species (donor state)

Corrosion Reactions Mechanism



Graphical representation of the processes occurring at an electro-chemical interface.

The corrosion reaction consists of two types of processes:

1. **Charge transfer reactions** … e.g.

anodic

$M_{lattice} \rightarrow M^{+}_{surface} + e$

$M^{+}_{surface} \rightarrow M^{2+}_{surface} + e$

$M_{lattice} \rightarrow M^{n+}_{surface} + ne \qquad (n=1, 2, 3, \ldots)$

cathodic

$O_{2\,surface} + 2H^{+} + 2e \rightarrow H_2O_{2\,surface}$

$H_2O_{2\,surface} + 2H^{+} + 2e \rightarrow 2H_2O_{surface}$

$O_{2\,surface} + 4H^{+} + 4e \rightarrow 2H_2O_{surface}$

2. **Mass transport of ions or molecules involved in the reaction** … e.g.

anodic

$M^{n+}_{surface} \rightarrow M^{n+}_{solution}$

cathodic

$O_{2\,solution} \rightarrow O_{2\,surface}$

$H_2O_{surface} \rightarrow H_2O_{bulk\ solution}$

Corrosion Rate Expressions

The rate of electron flow to or from a reacting interface is a measure of the reaction rate. From the combination of Faraday's law:

$$m = \frac{ItM}{nF}$$

m = mass reacted (g)
I = current (amp) *obtained from electrochemical measurement*
t = time (s)
M = molar mass (g/mol)
n = number of electrons in electrode reaction
F = Faraday's constant (96485 Coul /mole of electrons)

Corrosion Rate Expressions

For a corrosion reaction:

$$w = \frac{ItM}{nF}$$

I. Corrosion rate (based on metal loss):

$$r = \frac{w}{tA} = \frac{iM}{nF}$$

$$\mathbf{i = I/A}$$

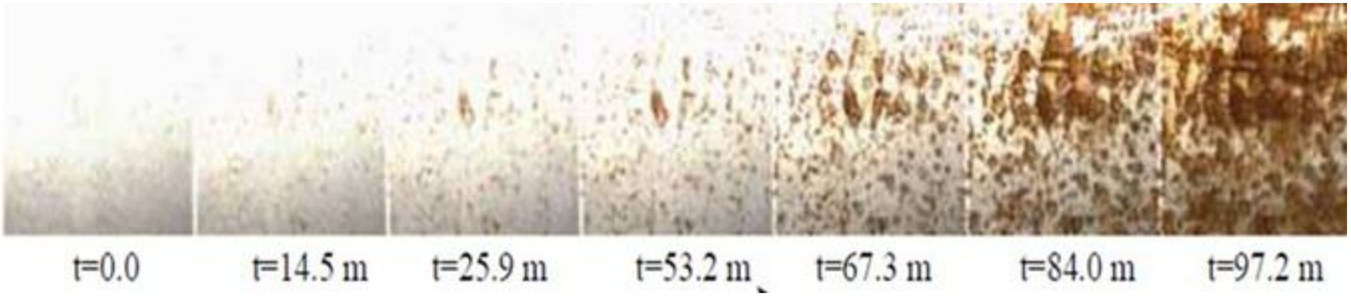
r = corrosion rate of metal (mass/area/time) {mdd: mg/dm^2/d}

w = mass loss (g)

i = current density (amp/cm^2) where $i = i_{CORR}$ *obtained from electrochemical measurement*

A = electrode surface area (cm^2)

This rate expression is useful for uniform corrosion.



Example: Corrosion of Iron

An iron container 10 cm × 10 cm at its base is filled to a height of 20 cm with a corrosive liquid. A current is produced as a result of an electrolytic cell, and after 4 weeks, the container has decreased in weight by 70 g. Calculate the current and the current density involved in the corrosion of the iron.

SOLUTION

1. The total exposure time is:

$$t = (4\ \text{wk})(7\ \text{d/wk})(24\ \text{h/d})(3600\ \text{s/h}) = 2.42 \times 10^6\ \text{s}$$

From Faraday's equation, using *n* = 2 and M = 55.847 g/mol:

$$I = \frac{wnF}{tM} = \frac{(70)(2)(96{,}500)}{(2.42 \times 10^6)(55.847)} = 0.1\ \text{A}$$

2. The total surface area of iron in contact with the corrosive liquid and the current density are:

$$A = (4\ \text{sides})(10 \times 20) + (1\ \text{bottom})(10 \times 10) = 900\ \text{cm}^2$$

$$i = \frac{I}{A} = \frac{0.1}{900} = 1.11 \times 10^{-4}\ \text{A/cm}^2$$

Corrosion Rate (mass/area/time) for an Alloy:

An equivalent weight (M/n) is used in calculating corrosion rate:

$$r = \frac{w}{tA} = \frac{iM}{nF}$$

$M/n = EW = 1/N_{eq}$

$r = i\,.EW/F$

$$N_{eq} = \sum\left(\frac{f_i}{M_i/n_i}\right) = \sum\left(f_i\frac{n_i}{M_i}\right)$$

f_i = mass fraction of ith element

n_i = electrons exchanged in the ith element

M_i = Molar mass (= atomic weight) of ith element

N_{eq} = number of equivalents in unit mass of alloy **(equiv/g)**

EW = equivalent weight of alloy

Example:

For 304 stainless steel (Cr 19%, n=3; Ni 9.25%, n=2; Fe 71.75%, n=2) ; % is mass fraction

$$N_{eq} = \frac{(0.19)(3)}{(52.00)} + \frac{(0.0925)(2)}{(58.71)} + \frac{(0.7175)(2)}{(55.85)} = 0.03981$$

EW =1/ 0.3981 = 25.12 (g/equiv) **r = i .EW/F (mdd)**

II. Penetration Rate (Corrosion rate based on thickness):

$$r_p = C\frac{iM}{n\rho}$$ For metals and $$r_p = C.i.\Sigma[\frac{M_i}{n_i\rho_i} f_i]$$ For alloys

r_p = Penetration rate (length/time)
C = Conversion factor including Faraday's constant.
i = current density of corrosion reaction (μA/cm^2)
ρ = density of metal (g/cm^3)

C = 0.129 {r in mpy; mpy: mils/year ; 1 mil = 0.001 inch}
C =3.27 {r in mm/yr}

Example: What is r (mpy) for iron (ρ=7.87 g/cm^3) which is equivalent to a corrosion current density of of 1 μA/cm^2 ?

Solution: r = 0.129 [(55.84)(1) / ((2)(7.87)] = 0.46 mpy

Explanation:

For single metal:

$r_p = r/\rho$

(length/time) = (mass/area/time) / (mass/volume)

"volume = area x length"

$r_p = r/\rho = (i\ M/n\ F)/\rho = (i\ M/n\ \rho\ F)$

$r_p = (i/F)(C')\ (M/n.\rho) = (C.i)\ (M/n.\rho)$ C′ = unit conversion factor

$r_p = 0.129\ i\ (M/n.\rho)$ mpy

For alloys:

Replace $(M/n.\rho)$ by $\Sigma(f_i.M_i/n_i.\rho_i)$ in the last equation above:

$r_p = 0.129\ i\ \Sigma(f_i.M_i/n_i.\rho_i)$

Corrosion Penetration Rate (CPR)

1. If a metal exposed to a corrosive environment, dissolves uniformly, the thickness removed can be calculated.
2. If a sample with a surface area of A (in^2) is exposed for t (hours) and a weight loss of w (mg) is measured, then the CPR is the rate of thickness loss.
3. CPR<20 mil/yr or about 0.5 mm/yr is acceptable.

$$Weight\ loss = w\ (mg) = 10^{-3} w\ (g)$$

$$Density = \rho\ (g/cm^3)$$

$$Volume\ loss = \frac{10^{-3} w}{\rho}$$

$$Exposed\ area = A\ (in^2) = 2.54^2 A\ (cm^2)$$

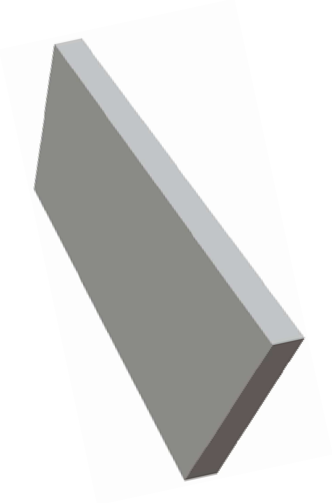
$$Thickness\ loss = \frac{10^{-3} w}{2.54^2 A \rho}\ (cm)$$

$$Rate\ of\ thickness\ loss = \frac{10^{-3} w}{2.54^2 A \rho t}\ (cm/hr)$$

$$= \frac{10^{-3} w}{2.54^2 A \rho t} \times 24 \times 365 \times 10\ (mm/year)$$

$$= \frac{87.6 w}{A \rho t}\ (mm/year)$$

$$= \frac{534 w}{A \rho t}\ (mil/year)$$



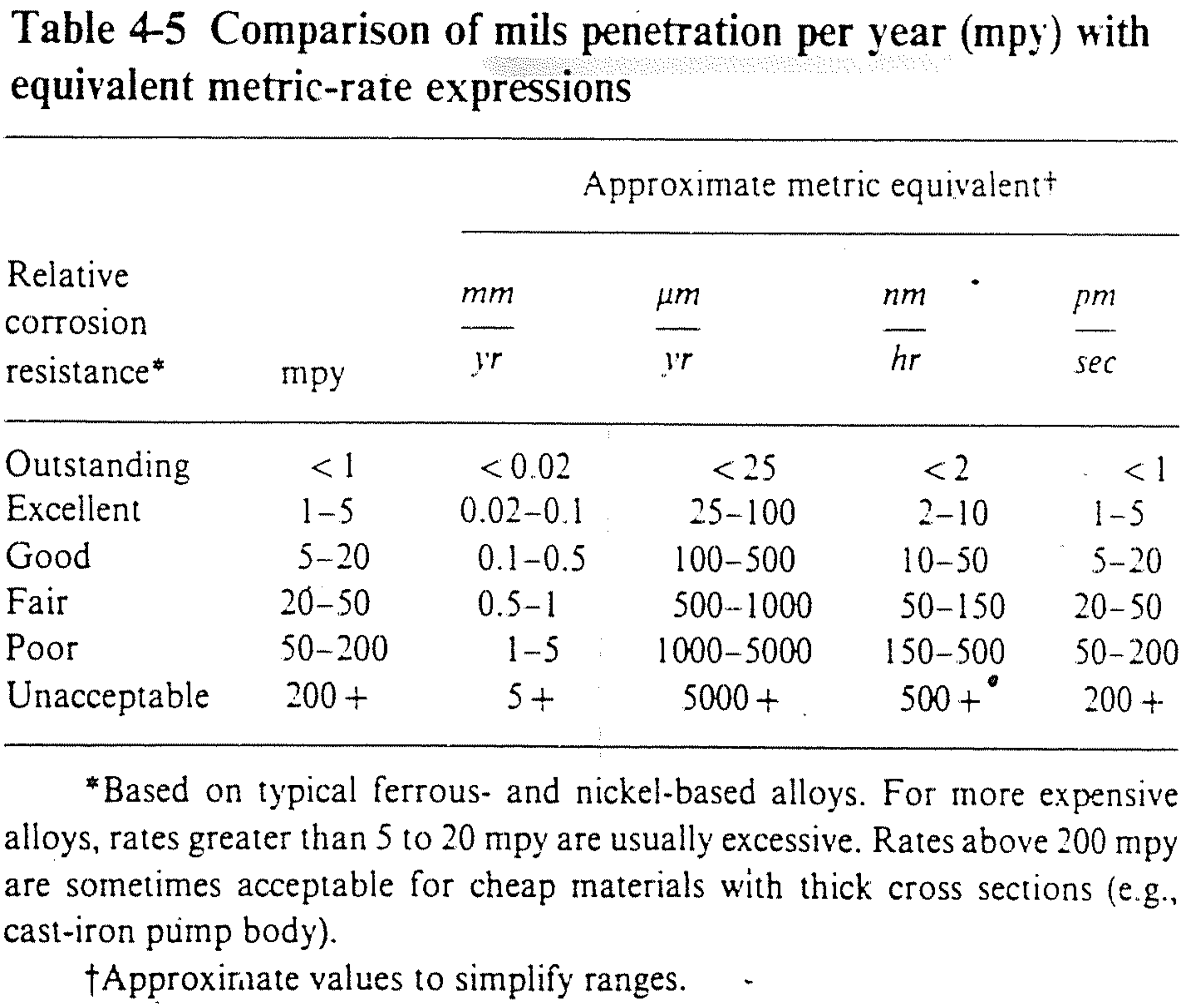


Table 4-5 Comparison of mils penetration per year (mpy) with equivalent metric-rate expressions

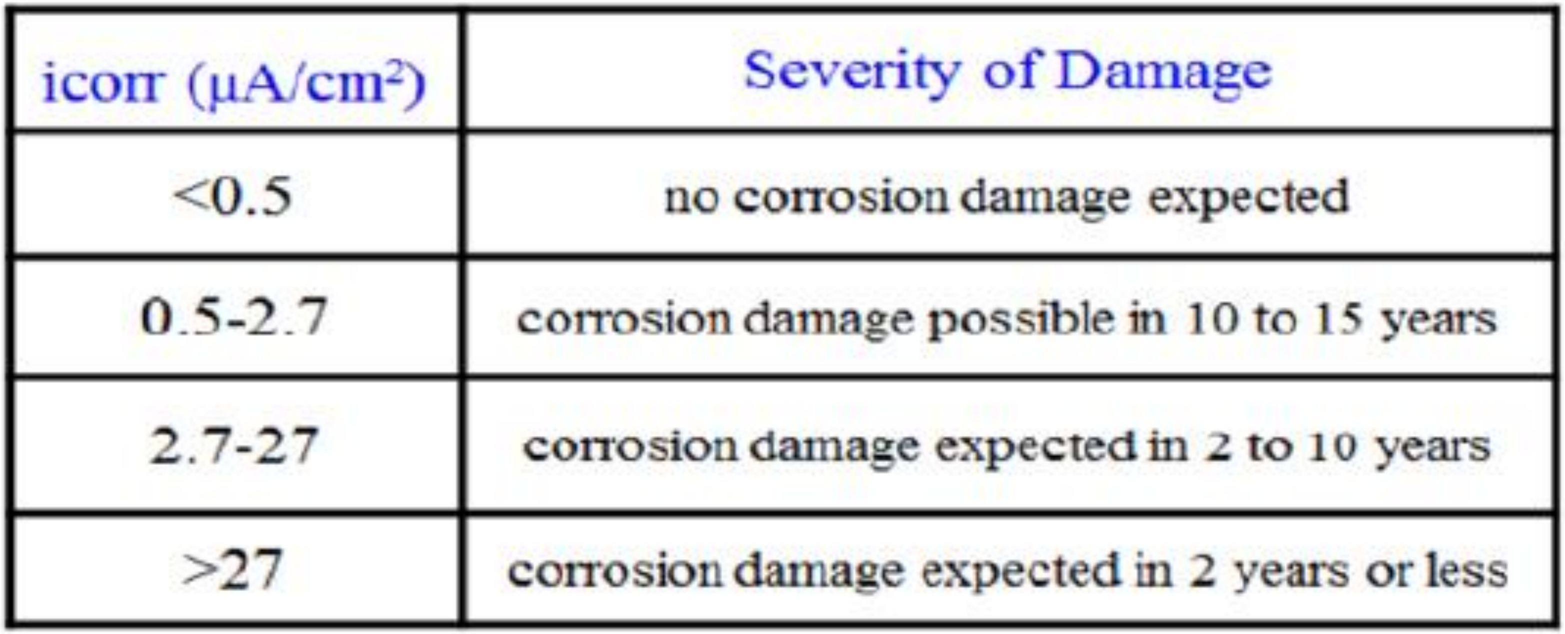
		Approximate metric equivalent†			
Relative corrosion resistance*	mpy	$\frac{mm}{yr}$	$\frac{\mu m}{yr}$	$\frac{nm}{hr}$	$\frac{pm}{sec}$
Outstanding	< 1	< 0.02	< 25	< 2	< 1
Excellent	1–5	0.02–0.1	25–100	2–10	1–5
Good	5–20	0.1–0.5	100–500	10–50	5–20
Fair	20–50	0.5–1	500–1000	50–150	20–50
Poor	50–200	1–5	1000–5000	150–500	50–200
Unacceptable	200 +	5 +	5000 +	500 +	200 +

*Based on typical ferrous- and nickel-based alloys. For more expensive alloys, rates greater than 5 to 20 mpy are usually excessive. Rates above 200 mpy are sometimes acceptable for cheap materials with thick cross sections (e.g., cast-iron pump body).

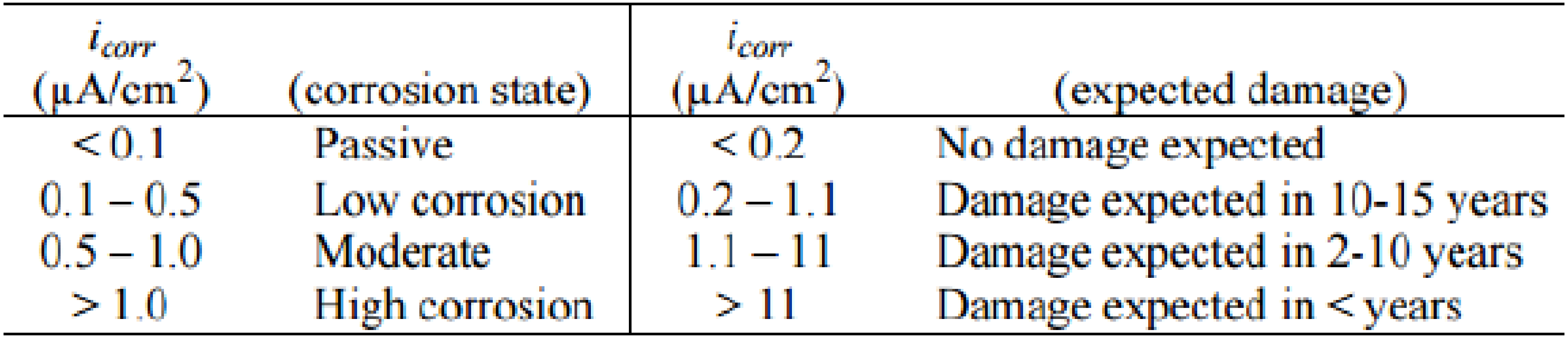
†Approximate values to simplify ranges.

Ref. Fontana's Text: Corr Eng 1986

Example on Steel Corrosion rates



icorr ($\mu A/cm^2$)	Severity of Damage
<0.5	no corrosion damage expected
0.5-2.7	corrosion damage possible in 10 to 15 years
2.7-27	corrosion damage expected in 2 to 10 years
>27	corrosion damage expected in 2 years or less



i_{corr} ($\mu A/cm^2$)	(corrosion state)	i_{corr} ($\mu A/cm^2$)	(expected damage)
< 0.1	Passive	< 0.2	No damage expected
$0.1 - 0.5$	Low corrosion	$0.2 - 1.1$	Damage expected in 10-15 years
$0.5 - 1.0$	Moderate	$1.1 - 11$	Damage expected in 2-10 years
> 1.0	High corrosion	> 11	Damage expected in < years

Measurement of Corrosion Rate

(Corrosion Potential, Current Density and Rate)

- ☐ Weight Loss Measurement
- ☐ Electrochemical Polarization Methods (ECPM)
  - Galvanostatic Measurement (current control)
  - Potentiostatic Measurement (potential control)
    1) Tafel Extrapolation Method (TEM)
    2) Linear Polarization Resistance Method (LPRM)

- ECPM are used for studying corrosion (e.g., evaluating the performance of a metal specimen in a test solution)

- Often involve the construction of *potential vs. current curves* … i.e., they involve the study of polarization characteristics.

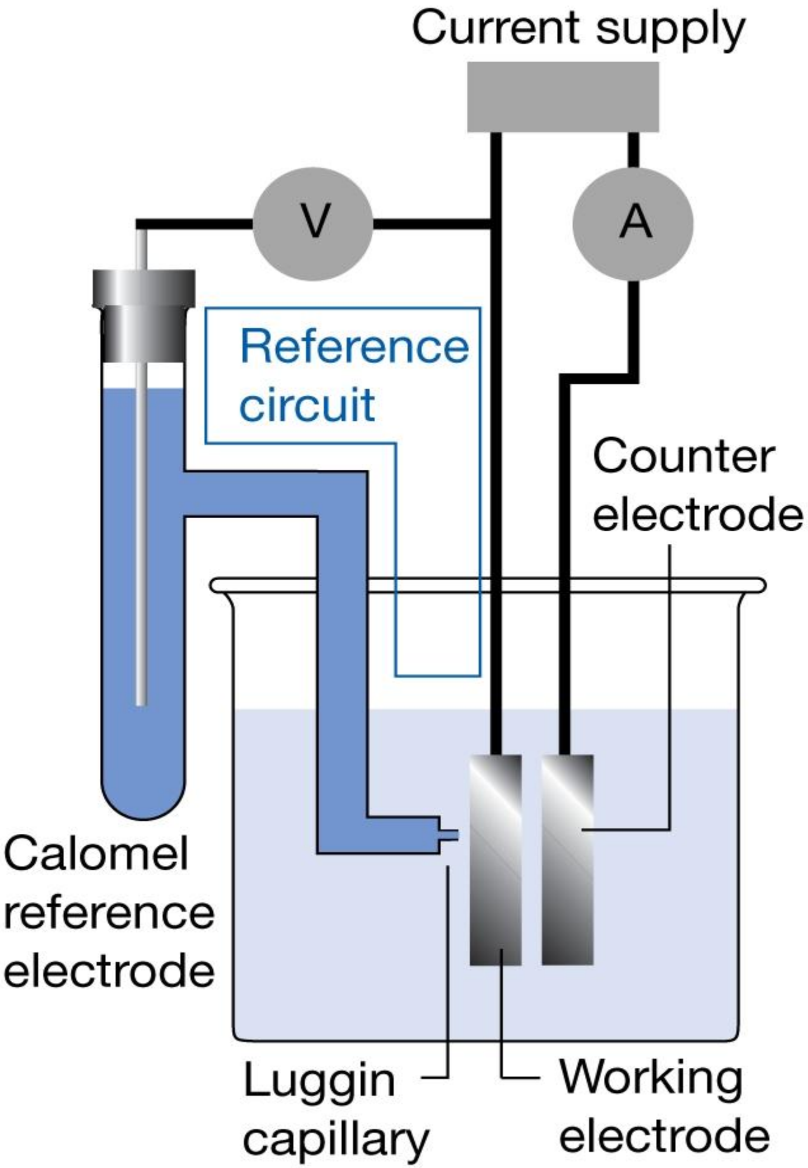
Potentiostat

1. A potentiostat is an electronic instrument that *controls the voltage difference between a Working Electrode and a Reference Electrode*. Both electrodes are contained in an electrochemical cell.
2. The potentiostat implements this control by injecting current into the cell through an Auxiliary or Counter electrode.

Polarization Measurement

A potentiostat typically functions with an electrochemical cell containing three electrodes, by:

- Applying a fixed potential (relative to a reference electrode), and
- Measuring the current (flowing from the working electrode to the counter or auxiliary electrode).



Working Electrode (Test Specimen)

- Requirements
  - reproducible
  - representative
  - free of shape defects
  - Free of galvanic effects.

- Properties
  - Often a small sphere, small disc or a short wire.
  - Has a useful working potential range
  - Usually < 0.25 cm^2 surface area
  - Smooth with well defined geometry for even current and potential distribution

Auxiliary (Counter) Electrodes

- Function *to supply current* required by the W.E.
- Products of the C.E. reaction should <u>not</u> interfere with the reaction being studied.
- Counter electrode should allow current to pass with tolerable polarization
- Usually use platinum or graphite, although stainless steel can be used in some situations (e.g. where only anodic polarization of specimen is used)

Reference Electrode

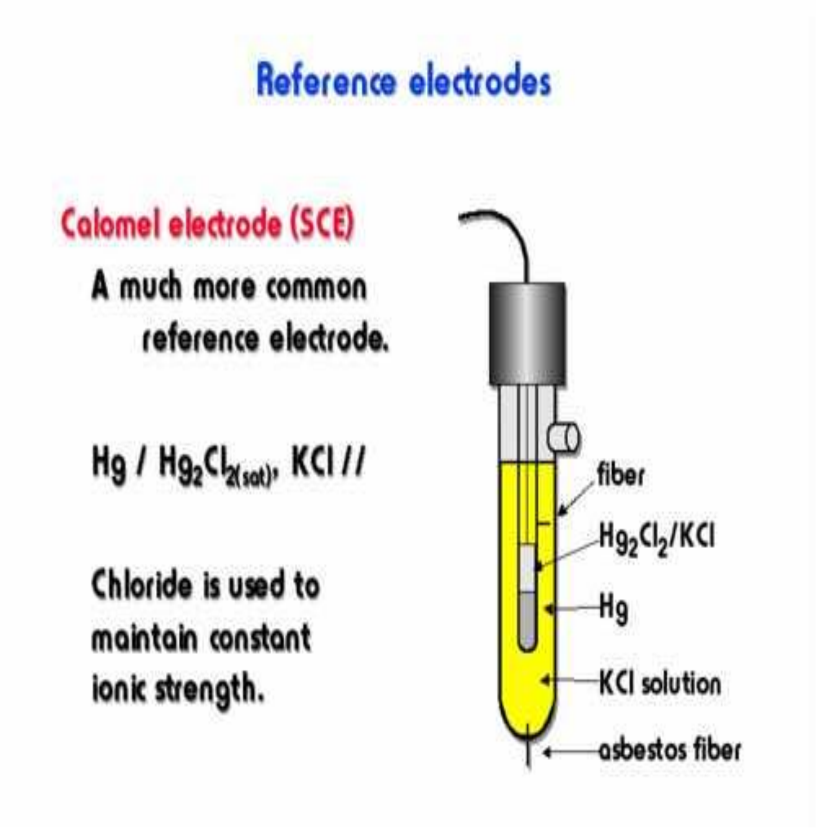
- The role of the R.E. is to provide a fixed potential which does *not vary* during the experiment.
- A good R.E. should be able to maintain a constant potential even if a few micro-amps are passed through its surface.

Examples of Reference electrodes

- **Calomel (Hg/Hg_2Cl_2)**
  - the most popular R.E. in aq. solutions;
  - usually made up in saturated KCl solution (SCE);
- **Silver - silver chloride**
  - gives very stable potential;
  - easy to prepare;
  - may be used in non aqueous solutions

Solution in SCE (or Ag/AgCl electrode) is saturated KCl

- beware of chloride contamination of test solution by Cl^- leaking from reference electrode
- make sure solution remains saturated



Reference electrodes

Calomel electrode (SCE)

A much more common reference electrode.

$Hg\ /\ Hg_2Cl_{2(sat)},\ KCl\ //$

Chloride is used to maintain constant ionic strength.

The electrolyte solution

1. Consists of solvent and a high concentration of an ionized salt and electroactive species

2. **High conductivity** of the solution and reduced resistance:
   - between W.E. and C.E. to help maintain a uniform current and potential distribution
   - between W.E. and R.E. to minimize the potential error due to solution resistance
   - add supporting electrolyte, such as sodium perchlorate

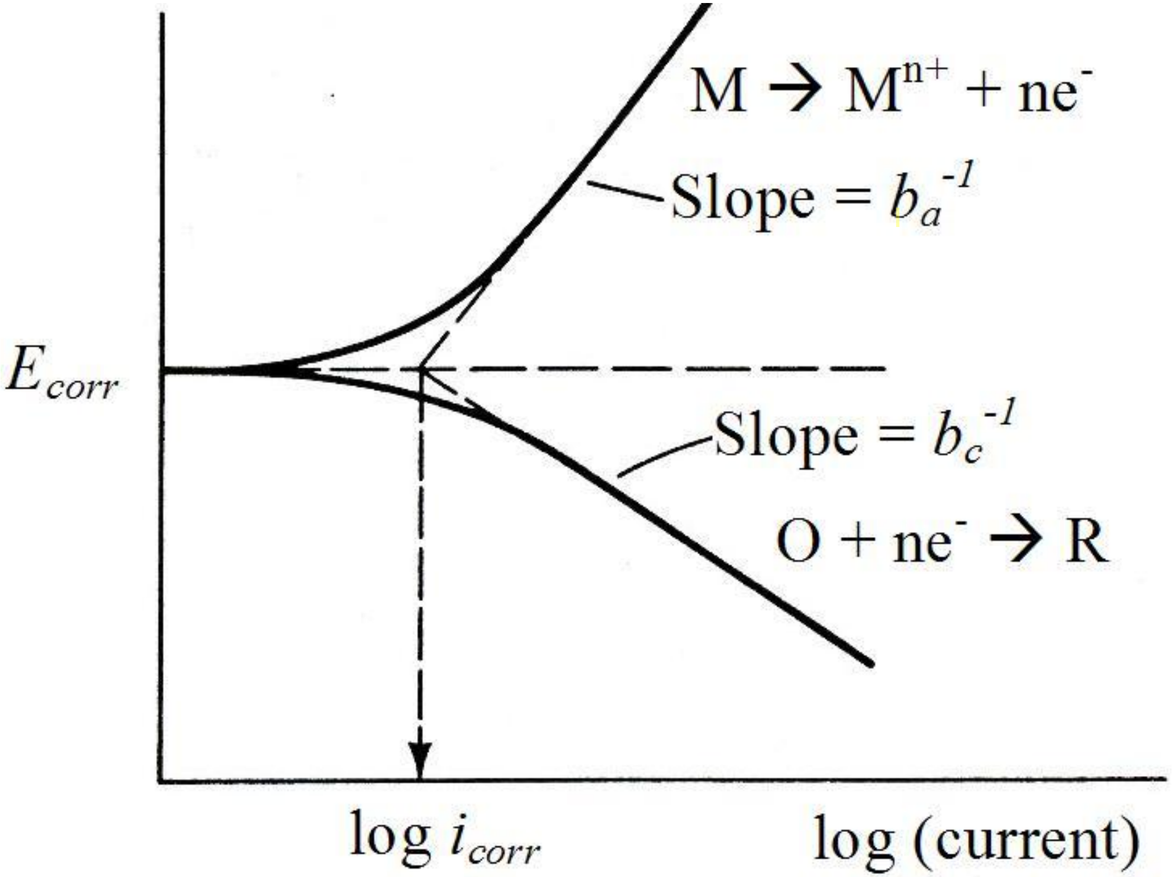
3. Oxygen concentration often critical - aerate by bubbling air or O_2 or deaerate with N_2 or Ar

4. Most reactions temperature sensitive. So, control or at least record temperature.

Corrosion Rate Measurement

1. Corrosion rates are determined by applying a current to produce a polarization curve (the degree of potential change as a function of the amount of current applied) for the metal surface whose corrosion rate is being determined.
2. When the potential of the metal surface is polarized by the application of the current in a positive direction, it is said to be anodically polarized; a negative direction signifies that it is cathodically polarized.
3. The polarization curves is used to find the corrosion current by applying Tafel's extrapolation technique. Tafel equation and slope will be discussed later.

Tafel's Method: Polarization Curve



Plot of the total current versus potential, showing the extrapolation of the Tafel regions to the corrosion potential, E_{corr}, to yield the corrosion current, i_{corr}.