Chapter 2
Principles of Corrosion Processes

K. A. Natarajan

Abstract In this chapter, principles of corrosion processes are illustrated with special emphasis on electrochemical aspects. Galvanic and electrolytic cells implicated in various corrosion and protection processes are analyzed with examples. Concentration cells are outlined with reference to galvanic corrosion and formation of differential aeration (oxygen) regions leading to pitting corrosion. Electrochemical kinetics and mixed potential theory are discussed. Active-passive transition in metals and alloys is brought out. Anodic and cathodic protection based on electrochemical principles find technological applications in industrial corrosion protection. Mechanisms involved in biofouling and microbially influenced corrosion are critically analyzed. Human body as a corrosion environment with reference to implanted biomaterials is also brought out.

Corrosion is the deterioration or destruction of metals (and alloys) in the presence of an environment brought about by chemical or electrochemical means.

Microbiologically-influenced corrosion (MIC) has now assumed great significance and can be defined as deterioration or destruction of metals and alloys by electrochemical or biological means in the presence of microorganisms [1–5].

Corrosion types can be classified into dry and wet in general, while the environments can be liquid (aqueous), underground, atmospheric and high temperature. Electrochemical principles come into play in all cases.

Different forms of corrosion can occur depending on wide range of possible environments.

Common industrial classifications are as follows.

(a) Uniform corrosion
(b) Galvanic corrosion
(c) Localized corrosion such as Crevice corrosion, Pitting, Filiform corrosion
(d) Selective leaching as in alloys such as brass (Dezincification)
(e) Intergranular/Transgranular attack

K. A. Natarajan (✉)
Department of Materials of Engineering, Indian Institute of Science, Bangalore 560012, India
e-mail: kan@iisc.ac.in

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(f) Erosion, Impingement and Cavitation corrosion
(g) Stress cracking and Stress corrosion cracking (Hydrogen embrittlement, Sulfide stress cracking, Liquid metal embrittlement)
(h) Fretting corrosion, Corrosion fatigue
(i) High temperature oxidation.

Although biological or microbial corrosion cannot be classified under types of corrosion, it has become an industrially relevant, widespread, catastrophic form of corrosion.

Electrochemical and microbial corrosion reactions involve electrochemical cells (corrosion cells) consisting of anode, cathode and an electrolyte and anodic (oxidation) and cathodic (reduction) reactions. When the electrodes are interconnected, a potential difference is developed (see Fig. 2.1).

Anode: Electrode where oxidation (corrosion) occurs

$$M = M^{++} + 2e \tag{2.1}$$

Cathode: Electrode where reduction (deposition) occurs

$$M^{++} + 2e = M \tag{2.2}$$

For every oxidation reaction, there is a reduction reaction as well, and the net reaction represents the total electrochemical process.

As an example, in the corrosion of zinc metal in an acid solution, the respective reactions are

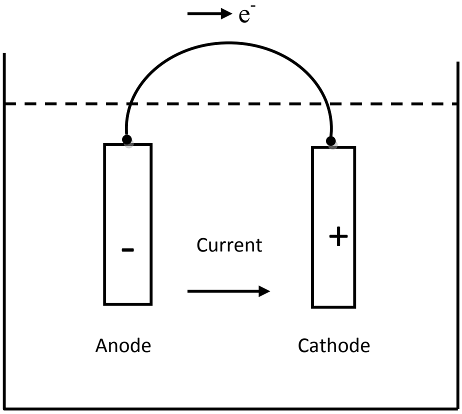


Fig. 2.1 Basic galvanic corrosion cell

$$\mathrm{Zn} \ = \mathrm{Zn}^{++} + 2\mathrm{e} \quad (\mathrm{Anode}) \tag{2.3}$$

$$2\mathrm{H}^{+} + 2\mathrm{e} = \mathrm{H}_2 \quad (\mathrm{Cathode}) \tag{2.4}$$

$$\mathrm{Zn} + 2\mathrm{H}^{+} = \mathrm{Zn}^{++} + \mathrm{H}_2 \ (\mathrm{Net}) \tag{2.5}$$

Several types of electrodes such as

Metal-metal ion	Fe/Fe^{++}
Ion/Ion (redox)	Pt/Fe^{+++}, Fe^{++}
Gas	Pt/H_2, H^+
Metal-insoluble salt come into play	Hg/Hg_2Cl_2, KCl

Electrochemical cells can be divided into galvanic and electrolytic cells and differentiated as follows [1–5].

Galvanic	**Electrolytic**
• Chemical to electrical energy	• Electrical to chemical energy
• Spontaneous/reversible reactions	• Non-spontaneous/Kinetic cell
• Cathode (+), Anode(−)	• Cathode (−), Anode (+)
• $\Delta G^0 < 0$, $E^0_{Cell} > 0$	• $\Delta G^0 > 0$, $E^0_{Cell} < 0$
• Eg: Dry cell, Daniel Cell	• Eg: Electroplating, Cathodic protection by impressed current

Sign conventions are followed to denote half-cell electrode reactions.

European convention, American convention and International (IUPAC) conventions are followed since long.

In this chapter, IUPAC convention is followed, where the half-reaction is expressed as a reduction reaction and 'Plus Right Rule' used to estimate total cell EMF.

Free energy concepts as thermodynamic fundamentals are used to estimate relationships between

- Free energy change and equilibrium constant
- Free energy change and cell EMF

And the Nernst expression derived as follows

$$E = E^0 + \frac{RT}{nF}\ln\frac{[Ox]}{[Red]} \tag{2.6}$$

$$E = E^0 + \frac{0.059}{n} \log \frac{[Ox]}{[Red]} \, (\mathit{Simplified\ to\ room\ temperature\ conditions})$$

where

E = Half-cell potential
E^0 = Standard Electrode Potential

$$\frac{[Ox]}{[Red]} = \mathit{ratio\ of\ activities\ of\ oxidised/reduced\ species}.$$

Daniel cell can be taken as a typical example to illustrate cell EMF calculation and to establish criterion for spontaneity.

Daniel cell consists of zinc and copper electrodes in a diaphragm cell configuration, immersed in 1M $ZnSO_4$ and 1M $CuSO_4$ respectively.

$$-\mathrm{Zn}|\mathrm{Zn_{(1M)}}^{++}||\mathrm{Cu}^{++}{}_{(1M)}|\mathrm{Cu}+$$

$$\mathrm{Zn} = \mathrm{Zn}^{++} + 2\mathrm{e} \quad \mathrm{E}^0 = -0.76\mathrm{V} \tag{2.3}$$

$$\mathrm{Cu}^{++} + 2\mathrm{e} = \mathrm{Cu} \quad \mathrm{E}^0 = +0.34\mathrm{V} \tag{2.7}$$

$$\mathrm{Zn} + \mathrm{Cu}^{++} = \mathrm{Zn}^{++} + \mathrm{Cu} \tag{2.8}$$

$$\mathrm{E_{Cell}} = E_{\frac{1}{2}}(Right) - E_{\frac{1}{2}}(Left)$$

$$E_{\frac{1}{2}}(\mathrm{Zn}) = -0.76 + \frac{0.059}{2} \log[\mathrm{Zn}^{++}] \tag{2.9}$$

$$E_{\frac{1}{2}}(\mathrm{Cu}) = +0.34 + \frac{0.059}{2} \log[\mathrm{Cu}^{++}] \tag{2.10}$$

$$E_{Cell} = +0.34 - (-0.76) = +1.10\,\mathrm{V}$$

(The above cell is spontaneous).

The driving force for the corrosion reaction is the potential difference (cell EMF) between anode and cathode. In a corroding metal, several anodic and cathodic sites exist.

Since absolute potential of a single electrode cannot be measured, all potential measurements in electrochemical corrosion cells are made relative to a reference electrode.

Basic electrochemical aspects of commonly used reference electrodes are illustrated below.

2.1 Silver–Silver Chloride Reference Electrode

The redox reaction at the electrode is

$$\mathrm{AgCl} + \mathrm{e} = \mathrm{Ag} + \mathrm{Cl}^- \tag{2.11}$$

The electrode consists of a silver wire coated with silver chloride immersed in chloride solution.

$$E = E^0 + \frac{RT}{nF}\log\frac{1}{\mathrm{Cl}^-} \tag{2.12}$$

Variations in chloride ion concentrations influence the potential.

2.2 Saturated Calomel Electrode (SCE)

The redox reaction for the electrode is

$$\mathrm{Hg_2Cl_2} + 2\mathrm{e} = 2\mathrm{Hg} + 2\mathrm{Cl}^- \tag{2.13}$$

$$E = E^0 + \frac{RT}{nF}\log\frac{1}{[\mathrm{Cl}^-]^2} \tag{2.14}$$

$$E^0 + \frac{0.059}{2}\log\frac{1}{[\mathrm{Cl}^-]^2} \tag{2.15}$$

2.3 The Hydrogen Electrode (NHE)

A platinum wire contacted with an acid solution of unit H^+ activity. Pure H_2 gas at one atmosphere is bubbled into solution at room temperature.

$$2H^{+} + 2e = H_2 \tag{2.4}$$

$$E = E^0 + \frac{0.059}{2}\log[H^{+}]^2 \tag{2.16}$$

$$E = E^0 - 0.059\,pH \tag{2.17}$$

The Standard Hydrogen Electrode (SHE) is also referred to as Normal Hydrogen Electrode (NHE) with the standard potential, E^0 = 0.00 V.

2.4 Copper–Copper Sulfate Electrode

Very robust and stable reference electrode, often used in cathodic protection systems to measure pipe to soil potentials. Copper metal is placed in a solution of copper sulfate (saturated)

$$Cu^{++} + 2e = Cu \tag{2.7}$$

$$E_{Cu^{++}/Cu} = 0.34 + \frac{0.059}{2}\log[Cu^{++}] \tag{2.10}$$

The standard potential for the electrode is +0.316 V

Standard potentials of different reference electrodes are summarized below:

System	Electrolyte	E^0V
Calomel $2Hg + 2Cl^- = Hg_2Cl_2 + 2e$	Sat'd KCl 1.0 N KCl 0.1 N KCl	0.241 0.280 0.333
Silver–Silver chloride $Ag + Cl^- = AgCl + e$	Sat'd KCl 1.0 N KCl 0.1 N KCl	0.199 0.234 0.288
Copper–Copper sulfate $Cu^{++} + 2e = Cu$	Sat'd $CuSO_4$	0.316

Diagrammatic representations of various reference electrodes are given in Figs. 2.2, 2.3, 2.4 and 2.5.

Fig. 2.2 Silver-Silver chloride electrode

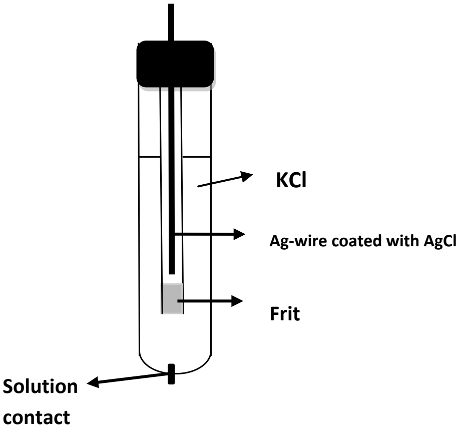


Fig. 2.3 Saturated calomel electrode (SCE)

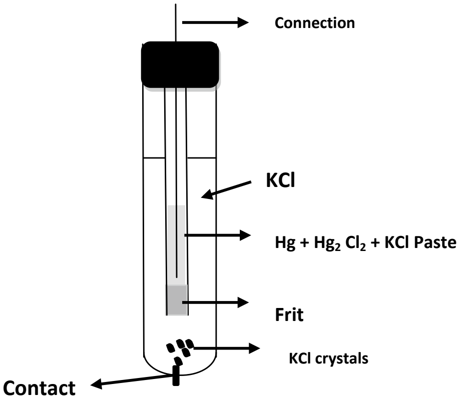
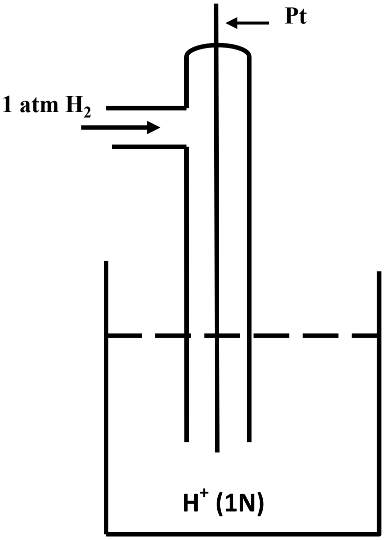


Fig. 2.4 Standard (normal) hydrogen electrode



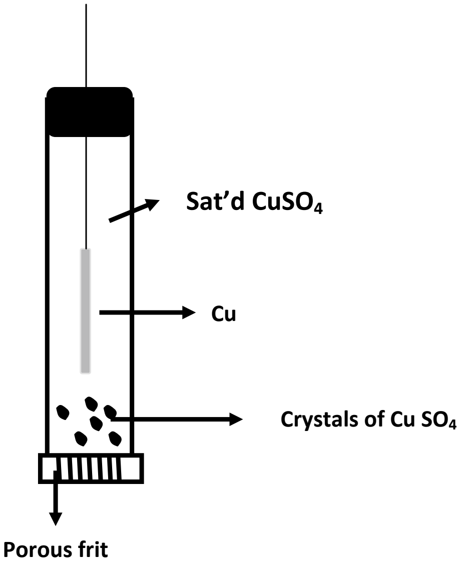


Fig. 2.5 Copper-copper sulfate electrode

2.5 Junction Potentials

A small potential difference that develops at the interface (junction) of two electrodes arises due to different ionic compositions. Liquid junction corrections need to be made to avoid interferences in measured electrode potentials.

2.6 Concentration Cells [1–5]

Besides dissimilar electrode cells (bimetallic), concentration cells can also be considered galvanic corrosion cells. In concentration cells, the EMF arises due to changes in concentrations of the electrolytes as well as reactants such as oxygen. There is no net chemical reaction and the electrical energy arises from the transfer of a reactant in varying concentrations from electrolytes.

For example:

- Differences in metal ion concentrations.
- Differences in oxygen partial pressures.

Example:

$$- \mathrm{Ag} \left| \mathrm{Ag}_{(C_1)}\,\mathrm{NO_3} \right\| \left. \mathrm{Ag}_{(C_2)}\,\mathrm{NO_3} \right| \mathrm{Ag} +$$

c_1 and c_2 are the Ag^+ concentrations in the anode and cathode compartments.

$$\begin{aligned} E_{Cell} &= E_{\frac{1}{2}(R)} - E_{\frac{1}{2}(L)} \\ &= \left[E^0 + \frac{0.059}{n}\log C_2\right] - \left[E^0 + \frac{0.059}{n}\log C_1\right] \end{aligned} \tag{2.18}$$

$$= \frac{0.059}{n}\log\frac{C_2}{C_1} \tag{2.19}$$

The EMF is developed due to transfer of metal ions from the area of higher concentration to that of lower concentration. The silver electrode in contact with a lower silver ion concentration serves as anode, the other being the cathode.

Differential aeration corrosion occurs when a metal surface is exposed to differential air or oxygen concentrations. The part of the metal exposed to higher O_2 concentration acts as cathode, while the part exposed to lower oxygen concentration serve as anodic regions. Poorly oxygenated regions thus undergo corrosion and oxygen-enriched areas are protected,

$$\text{Anode} = \text{M} = \text{M}^{++} + 2\text{e}(\text{Low}\,\text{O}_2) \tag{2.1}$$

$$\text{Cathode} = 1/2\,\text{O}_2 + \text{H}_2\text{O} + 2\text{e} = 2\text{OH}^-(\text{High}\,\text{O}_2) \tag{2.20}$$

Diagrammatic illustrations of the above concentration cells are given in Figs. 2.6 and 2.7.

Water line corrosion is a case of differential aeration corrosion which is prevalent in sea going vessels, water storage tanks and submerged structures. Oxygen concentration cells are formed in this type of corrosion. The part of the metal below the water line is exposed to lower oxygen levels while the part above the water is

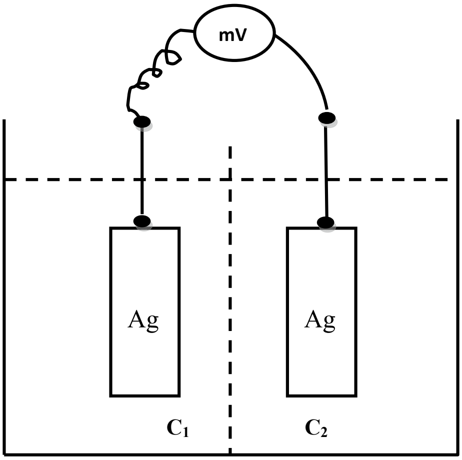


Fig. 2.6 Metal–ion concentration cell

Fig. 2.7 Differential oxygen (aeration) cell

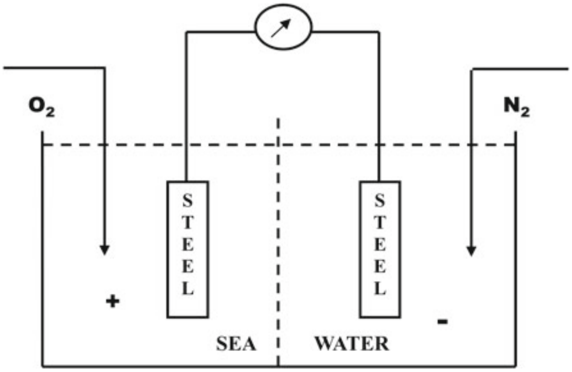
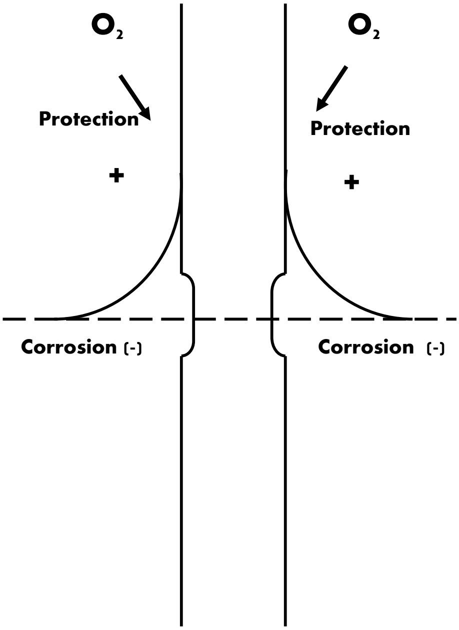


Fig. 2.8 Water-line corrosion (oxygen concentration cell)



exposed to higher oxygen partial pressures and consequently, the metal part below water line acts as anode and undergo corrosion (see Fig. 2.8).

The Nernst relationship can be used to estimate the potential difference generated due to oxygen concentration cells. When two portions of the same metal are in contact with a solution having differential oxygen concentration areas,

$$O_2 + 2H_2O + 4e = 4OH^- \tag{2.21}$$

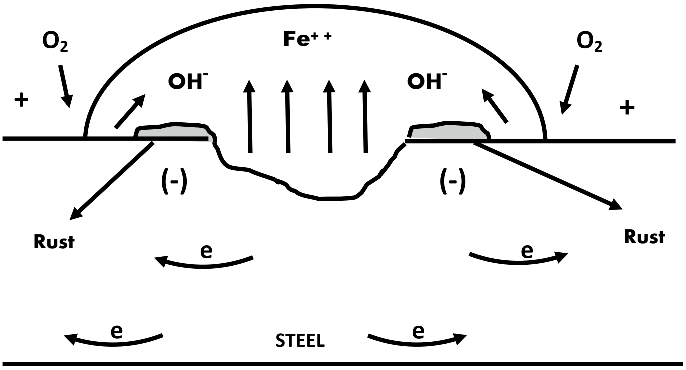


Fig. 2.9 Rusting of iron through oxygen concentration cell formation

$$E_1 = E^0 + \frac{0.059}{4} \log \frac{PO_{2(a)}}{[OH^-]^4} \tag{2.22}$$

$$E_2 = E^0 + \frac{0.059}{4} \log \frac{PO_{2(b)}}{[OH^-]^4} \tag{2.23}$$

$PO_{2(a)}$ and $PO_{2(b)}$ are different oxygen partial pressures while pH being the same for both half cells

$$E_2 - E_1 = \frac{0.059}{4} \log \frac{PO_{2(b)}}{PO_{2(a)}} \tag{2.24}$$

If $PO_{2(a)} < PO_{2(b)}$, then $E_2 > E_1$

Electrode in contact with lower O_2 concentration is anode (corrosion) and the one in contact with higher O_2 is cathode (protection)

A model for role of oxygen concentration cells (differential aeration) on rusting of iron exposed to oxygen and moisture is illustrated in Fig. 2.9.

2.7 EMF Series [1–5]

The EMF series is an arrangement of various metals in order of their electrochemical activities based on their standard electrode potentials. It is a thermodynamic series where the E^0 is calculated from free-energy data. The most active metal in the series possesses the highest negative E^0 (anode) while the nobler metal having less negative or more positive electrode potential (cathode)

There are exceptions to the thermodynamically predicted metal activities as listed in Table 2.1.

Table 2.1 EMF series

Reaction	**E^0,V(SHE)**	
$Au^{+++} + 3e = Au$	+1.42	Noble
$Pt^{++} + 2e = Pt$	+ 1.2	
$O_2 + 4H^+ + 4e = 2H_2O$	+1.23	
$Pd^{++} + 2e = Pd$	+0.83	
$Ag^+ + e = Ag$	+0.799	
$O_2 + 2H_2O + 4e = 4OH^-$	+0.401	
$Cu^{++} + 2e = Cu$	+0.34	
$Sn^{+++} + 2e = Sn^{++}$	+0.154	
$2H^+ + 2e = H_2$	0.00	Reference
$Pb^{++} + 2e = Pb$	−0.126	
$Sn^{++} + 2e = Sn$	−0.140	
$Ni^{++} + 2e = Ni$	−0.23	
$Co^{++} + 2e = Co$	−0.27	
$Cd^{++} + 2e = Cd$	−0.402	
$Fe^{++} + 2e = Fe$	− 0.44	
$Cr^{+++} + 3e = Cr$	− 0.71	
$Zn^{++} + 2e = Zn$	−0.763	
$Al^{+++} + 3e = Al$	– 1.66	
$Mg^{++} + 2e = Mg$	–2.38	
$Na^+ + e = Na$	–2.71	
$K^+ + e = K$	–2.92	Active

Example: Aluminum, chromium and titanium though active in the EMF series are practically highly corrosion resistant due to the presence of stable metal oxide passive surface films.

2.8 Applications of EMF Series

(a) A more active metal would displace a nobler metal from its dissolved state in an aqueous solution. For example, both iron and zinc (being placed lower to copper in the EMF series) can displace cupric ions (reduce) from an acid solution.

$$\mathrm{Zn} + \mathrm{CuSO_4} = \mathrm{ZnSO_4} + \mathrm{Cu} \tag{2.25}$$

$$\mathrm{Fe} + \mathrm{CuSO_4} = \mathrm{FeSO_4} + \mathrm{Cu} \tag{2.26}$$

$$\text{Oxidation} \quad \mathrm{Fe} = \mathrm{Fe}^{++} + 2\mathrm{e} \tag{2.27}$$

$$\mathrm{Zn} = \mathrm{Zn}^{++} + 2\mathrm{e} \tag{2.3}$$

$$\text{Reduction} \quad \mathrm{Cu}^{++} + 2\mathrm{e} = \mathrm{Cu} \tag{2.7}$$

(b) Electrode potentials indicate tendency for corrosion and deposition. Metals (ions) above hydrogen in the series are more readily reduced. Metals below hydrogen exhibit higher oxidation tendency.

(c) Use of hydrogen as a reducing agent under different pressures as well as that of oxygen (or other oxidants) under various partial pressures as an oxidizer for different metal ions and metals can be predicted.

In a bimetal combination, the metal with the nobler potential will act as cathode while the one with a relatively active potential will serve as anode. For example, in Fe–Zn couple, Fe will be cathodic to anodic Zn.

2.9 Limitation of EMF Series

- The series list only pure metals and not alloys and other composites.
- Rather than the thermodynamic electrode potentials for the various metal/metal ion concentrations, it is the corrosion potentials of metals and alloys in a defined corrosive environment which is of practical use and interest.

- EMF series predicts only the tendency for corrosion. There are metals in the EMF series such as chromium, aluminum and titanium which are listed as very active (negative potentials), but never the less do not corrode significantly due to passive oxide surface films. EMF series are silent on effect of environment on metal activity.

2.10 Galvanic Series [1–5]

Galvanic series overcome many of the drawbacks of the EMF series. Here the actually measured corrosion (rest) potentials of metals and alloys are listed in the order of their increasing—(or decreasing) activity in a defined environment (such as sea water) as shown in Table 2.2. It is of great practical importance since corrosion behavior of different alloys in combination can also be predicted.

Some alloys (such as 18-8 stainless steels) are shown as existing both in active and passive states. This could be seen in the light of the nature of surface passive films (whether stable or unstable (scratched surfaces).

The galvanic series would differ from environment to environment as well as to whether the media. (sea water, for example) is static or turbulent.

2.11 Electrochemical Aspects of Bimetallic (Galvanic) Corrosion [3, 6, 7]

Some basic conditions essential for bimetallic corrosion to occur are:

- Presence of continuous bridging between two metals (or alloys) through an electrolyte.
- Presence of concentration cells.
- Proper electrical contact and large potential difference among contacted metals (alloys).
- Sustained cathodic reaction at the nobler metal (alloys).

Major factors influencing galvanic corrosion in bimetallic couples include [6]

(a) Electrode potentials and electrode efficiency.
(b) Reactions such as metal dissolution, oxygen/hydrogen reduction.
(c) Metallurgical conditions such as composition, microstructure, alloy components, types of heat-treatment and mechanical working.
(d) Surface conditions like treatment, corrosion products and passive layers
(e) Electrolytic properties such as presence of various types of ions, pH, temperature, conductivity, aeration, flow rate and volume.

Table 2.2 Galvanic series

Platinum	↑
Gold	
Graphite	
Silver	
Hastelloy C	Noble
18-8 stainless steel (passive)	
Chromium steel> 11% Cr (passive)	
Inconel (passive)	
Nickel (passive)	
Monel	
Bronzes	
Copper	
Brasses	
Inconel (active)	
Nickel (active)	
Tin	
Lead	
Lead-tin solder	
18-8 Mo stainless steel (active)	Active
18-8 stainless steel (active)	
Ni-resist	
Chromium steel <11% Cr (active)	
Cast iron	
Steel or iron	
2024 aluminium	↓
Cadmium	
Commercially pure aluminium	
Zinc	
Magnesium and its alloys	

(f) Environmental factors such as dry-wet cycles, water content, climatic and seasonal conditions as well as solar radiation.

(g) Geometrical aspects such as distance, positions, surface area, shape and orientations.

The compatibility of two different metals (or alloys) may be assessed through what is referred to as 'anodic index' [8], which is a measure of the electrochemical potential that is realized between the desirable metal and gold.

Typical anodic indices of some metals and alloys relative to most noble gold is given in Table 2.3.

To estimate the relative potential of a pair of metals or alloys it is only essential to subtract their anodic indices. For normal conditions, there should not be not more than 0.25 V difference.

The extent of galvanic effect need not always be related to differences in the electrode potentials as listed in the EMF series. The galvanic potentials measured in a given environment could be a better guide for assessing effect of potential differences on galvanic activity.

Titanium, aluminum and chromium possess highly active reversible potentials as projected in the EMF series, but occupy relatively nobler positions in the galvanic series. Galvanic corrosion of steel is higher when coupled to nickel and copper than when contacted with 304 stainless steel and Ti-6Al-4 V alloy. Reaction kinetics as well as nature of corrosion products may thus determine galvanic corrosion rates. Smaller quantities of alloying additions to a metal would not result in any significant shift in reversible potential, even though it could significantly influence the electrochemical kinetics. Multiphase microstructures can influence galvanic activity. Strange as it may seem, enhanced cathodic corrosion in a couple may happen as in the case of Zn–Al couple in saline solutions prematurely due to increased alkalinity near the electrode surface, when aluminum is not stable. Galvanic corrosion can occur in metal as well as multi-metal combinations. Presence of 'mixed metals' in piping is an example. In multi-contact situations, the most anodic metal would remain active whatever may be position of other metals, while the noblest metal would serve as cathode, irrespective of the different arrangements. However, the dissolution behavior of metals (and alloys) exhibiting intermediate potentials, depend on their relative positions in the multi-metal combination. Galvanic

Table 2.3 Anodic indices (V) [8]

Gold	0.00
Silver, high Ni–Cu alloys	0.15
Nickel, Ti and alloys	0.30
Copper, Ni–Cr alloys	0.35
2000 series wrought Al	0.75
Plain C and low alloy steels	0.85
Zinc	1.25
Magnesium and its alloys	1.75

corrosion can also occur in metal-nonmetallic material contacts such as metal-reinforced polymer matrix composites and metal-graphite composites.

Corrosion currents can be generated due to several reasons in metals and alloys.

- Presence of impurities.
- Grain boundaries and orientation.
- Differential temperatures/gradients.
- Surface roughness, surface product layers.
- Metallographic/micro-structural defects, inclusions, precipitates.
- Alloying elements and different phases.
- Differential stress/strain.

Bimetallic corrosion in the absence of physical contacts can also occur. Localized corrosion [7] on a metal can lead to formation of soluble corrosion products that can deposit through displacement reactions onto an active metal surface exposed to similar environmental conditions and form local anodic and cathodic cells. For example, in water heating systems, dissolved copper from the pipes can deposit on steel radiators, generating anodic and cathodic areas.

Iron corrosion products from steel fittings can flow over aluminum and deposit as cathodic magnetite.

Area, distance and geometric effects on bimetallic corrosion are very important with respect to design and operation of different industrial components. Highest galvanic corrosion rate in confined at the junction between two metals and severity of corrosion decreases with increased length (distance) as illustrated in Figs. 2.10 and 2.11.

Geometry and design of components would influence galvanic corrosion. Current does not flow around corners, as well.

When a current flows between anode and cathode in a corroding metal, the current will be the same across, independent of surface areas of each region. However, current density would differ depending on anodic and cathodic surface area ratios. The larger the cathode, compared to the anode, higher oxygen reduction (or similar cathodic reactions) can occur and hence the galvanic currents are enhanced. The effect of the ratio of the anodic to cathodic areas thus becomes a

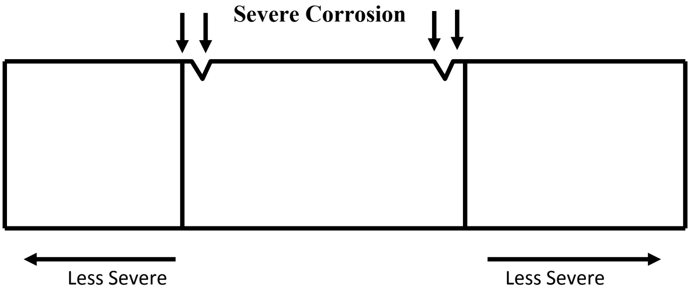


Fig. 2.10 Model showing severe galvanic corrosion at junctions-distance effect

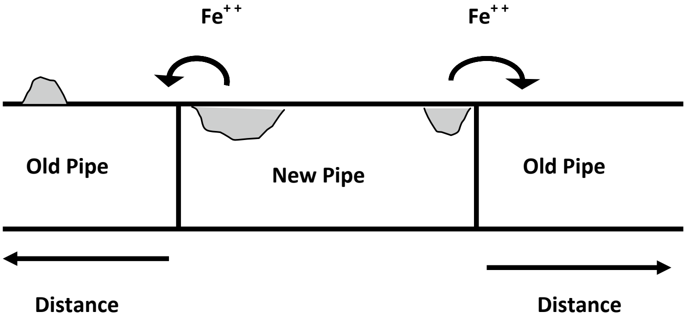


Fig. 2.11 Model showing distance effect in galvanic corrosion

significant factor controlling galvanic corrosion rates. A small anode area in contact with larger cathodic area results in serious bimetallic anodic corrosion due to higher anodic current densities on smaller anodes (see Fig. 2.12). As a general rule of principle, anode area should be larger than that of the cathode to minimize galvanic corrosion. For corrosion protection, the cathode regions in a component should be painted (coated) based on area-effect, discussed above. If the paint is damaged, then a smaller cathode in contact with relatively larger anode would be exposed, minimizing corrosion rates. On the other hand, if the anode is painted, paint damage would result in the formation of a smaller anode in contact with larger cathode, leading to enhanced corrosion rates. For example, in a carbon steel (anode) structural component in contact with stainless steel (cathode), surface coating of only the carbon steel could lead to disastrous corrosion due to unfavorable area effect [2–5].

In this regard, superiority of galvanized steel components need to be stressed. A uniformly zinc coated steel surface when exposed to a corrosive environment will be protected under all conditions of coating damage. Even if large portions of zinc coatings are abraded away, the base steel will still be protected due to favorable area effect! (see Fig. 2.13).

Fig. 2.12 Variation of corrosion rate with increasing catholic area for a fixed small anodic area

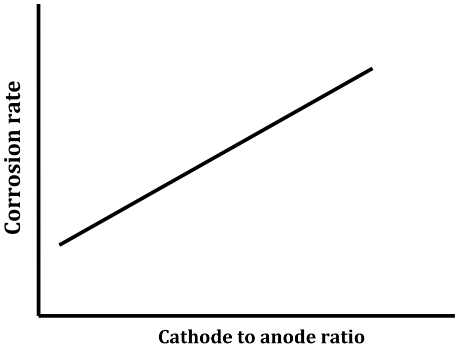


Fig. 2.13 Sacrificial zinc corrosion in contact with iron (Galvanic coating)

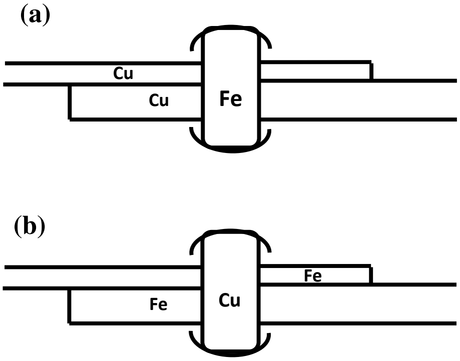


Fig. 2.14 Model showing area effect in galvanic corrosion. **a** Iron rivets on copper plates. **b** Copper rivets on iron sheets

Steel rivets on a copper bar exposed to sea water is yet another example to unfavorable area effect compared to copper rivets on a steel bar (see Fig. 2.14).

Yet another significant observation is polarity reversal under certain environmental conditions with time. Some examples are illustrated below [1–7].

Tinning is used to protect steel containers. Internally tin-coated steel cans are used to preserve vegetable and many types of fruit juices, Tin in nobler to iron in the EMF series. However, tin can dissolve to form Sn^{++} due to the presence of organic acids from the stored vegetable and fruit juices. Stannous ions can form tin complexes with organic acids, leading to reversal of polarity of the

$$\mathrm{Sn} = \mathrm{Sn}^{++} + 2\mathrm{e}\,\text{reaction} \tag{2.28}$$

Reversible Sn/Sn^{++} potential could shift to more active values. $\left[\frac{\mathrm{Sn}^{++}}{\mathrm{Fe}^{++}}\right]$ ratios corresponding to onset of polarity reversal can be estimated from the reaction,

$$\mathrm{Fe}^{++} + \mathrm{Sn} = \mathrm{Fe} + \mathrm{Sn}^{++}\,\text{when}\,\mathrm{E}_{\mathrm{Cell}=0} \tag{2.29}$$

$\left[\frac{\mathrm{Sn}^{++}}{\mathrm{Fe}^{++}}\right]$ must be less than 5×10^{-11} for tin to become more active than iron [5].

Change of surface condition of at least one among the metallic couples can cause polarity reversal. For the zinc–steel couple, the change in the zinc electrode potential is mainly responsible for polarity reversal since the iron potential does not significantly change with time in hot water. Passivation of the zinc surface in presence of oxygen in water lead to cathodic depolarization.

Polarity reversal can occur in aluminum-steel couples as well (used in cathodic protection). In presence of carbonate/bicarbonate ions, aluminum surface passivation may be promoted, shifting potential to nobler values. Polarity reversals as in the zinc-steel and aluminum-steel couples result in loss of cathodic protection of the steel component.

In the light of above bimetallic corrosion fundamentals, the following prevention or control methods can be suggested [2–6]:

(a) Selection of metals or alloy combinations as close together as possible in the galvanic series.
(b) Due importance to be given to surface area ratio effect and contacts to be avoided where the area of the active metal (alloy) is smaller. In case of fasteners, always prefer nobler metal components. Design of anodic parts in an assembly should take into consideration area and geometry.
(c) Wherever possible, dissimilar metal contacts need to be insulated from each other.
(d) Coatings or painting need caution. Do not paint less noble contact portions without also coating the nobler one. If only one contact surface need to be coated, the nobler surface to be coated.
(e) Metals need to be kept as far as possible (distance effect).
(f) Inhibitors could reduce corrosiveness. Cathodic protection can be used wherever suitable.

2.12 Potential-pH Diagrams [1–5]

Eh (Electrode potential with reference to standard hydrogen electrode) and pH ($-\log a_{H+}$) are the major environmental parameters influencing aqueous corrosion of metals. Electrochemical equilibrium diagrams can be constructed based on thermodynamic principles to predict corrosion and protection of different metals in an aqueous medium as a function of Eh and pH for different oxidation/reduction reactions and pH levels. Basic Eh-pH diagram as a two dimensioned representation in an aqueous phase consists of four coordinates representing oxidizing and reducing regions across acidic and pH levels as illustrated in Fig. 2.15. Increasing of Eh towards more positive values indicate enhanced oxidizing environments compared to lower, less positive Eh values, which denote shift towards reducing environment.

Upper and lower stability limits of water can be established for the Eh-pH diagram based on the following redox reactions (Fig. 2.16):

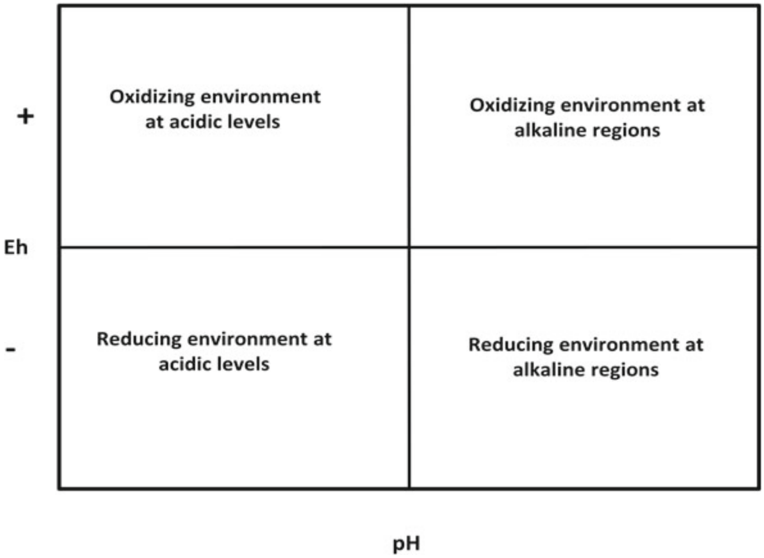


Fig. 2.15 Eh-pH basic coordinates

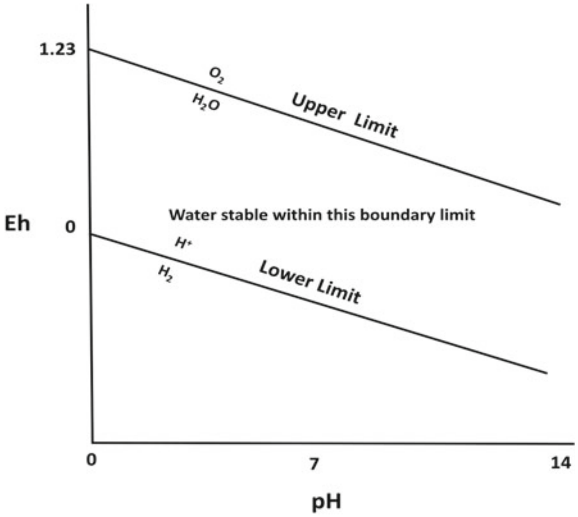


Fig. 2.16 Stability region for water in the Eh-pH diagram

(a) $$O_2 + 4H^+ + 4e = 2H_2O \quad E^0 = +1.23V \tag{2.30}$$

$$Eh = 1.23 - 0.059\,pH\,(at\,pO_2 = 1)$$

(b) $$2H^+ + 2e = H_2 \quad E^0 = 0.00V \tag{2.4}$$

$$Eh = 0 - 0.059\,pH\,(at\,p_{H2} = 1)$$

The stability limits can shift depending on oxygen and hydrogen partial pressures. For complete representation of the above water stability diagram, reactions involving oxygen reduction to form H_2O_2 which further reduces to H_2O need to be considered under neutral and alkaline conditions. Reactions such as

$$O_2 + 2H_2O + 4e = 4OH^- \tag{2.21}$$

$$2H_2O + 2e = H_2 + 2OH^- \tag{2.31}$$

are also likely. For various metal-water-oxygen systems, stability regions for oxidized and reduced species fall within the above marked boundaries.

Three types of equilibrium states can be realized based on the following types of reactions:

(a) Depending only on Eh, but independent of pH (Horizontal line to the X-axis).
(b) Dependent only on pH, but independent of Eh (Vertical to the X-axis).
(c) Dependent on both Eh and pH (line with defined slope).

Various types of reactions are illustrated in Fig. 2.17.

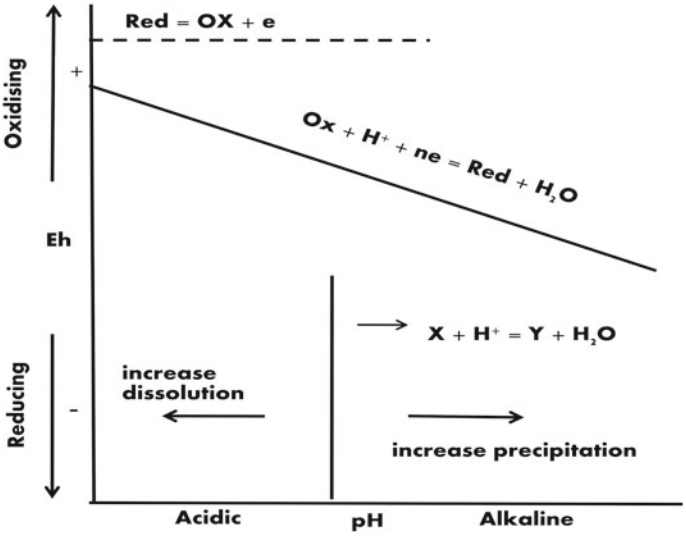


Fig. 2.17 Possible reactions in an Eh-pH diagram

Eh-pH diagrams are drawn for specific ion activities and partial pressures of gases at room temperature from thermodynamic data. For the Fe–H_2O–O_2 system, major thermodynamically feasible reactions are illustrated below, assuming Fe^{++}, Fe^{+++} activities at 1M and gaseous partial pressures as one at room temperature [1].

1\.
$$\begin{gathered}\mathrm{Fe} = \mathrm{Fe}^{++} + 2e \quad E^0 = -0.44\mathrm{V} \\ \text{(Reaction dependent only on Eh, independent of pH)}\end{gathered} \tag{2.27}$$

$$\mathrm{Eh} = -0.44 + \frac{0.059}{2}\log[\mathrm{Fe}^{++}] \tag{2.32}$$

$$\text{For } a_{\mathrm{Fe}^{++}} = 1, \mathrm{Eh} = -0.44\mathrm{V} \tag{2.33}$$

2\.
$$\begin{gathered}\mathrm{Fe}^{++} + 2H_2O = \mathrm{Fe(OH)}_2 + 2H^+ \\ \text{(Reaction dependent only on pH, independent of Eh)}\end{gathered} \tag{2.34}$$

$$\begin{aligned}\Delta F^0 &= -RT\ln K \\ &= -1.364\log K\end{aligned} \tag{2.35}$$

$$2\mathrm{pH} + \log[\mathrm{Fe}^{++}] = 13.28 \tag{2.36}$$

$$\mathrm{Log}[\mathrm{Fe}^{++}] = 13.28 - 2\mathrm{pH} \tag{2.37}$$

$$\mathrm{pH} = 6.64 \tag{2.38}$$

3\.
$$\begin{gathered}\mathrm{Fe}^{++} = \mathrm{Fe}^{+++} + e \quad E^0 = +0.771\mathrm{V} \\ \text{(Eh dependent, but independent of pH)}\end{gathered} \tag{2.39}$$

$$\mathrm{Eh} = 0.771 + 0.059\log\left[\frac{\mathrm{Fe}^{+++}}{\mathrm{Fe}^{++}}\right] \tag{2.40}$$

$$\mathrm{Eh} = 0.771\mathrm{V} \tag{2.41}$$

4\.
$$\begin{gathered}\mathrm{Fe}^{+++} + 3H_2O = \mathrm{Fe(OH)}_3 + 3H^+ \\ \text{(reaction dependent only on pH)}\end{gathered} \tag{2.42}$$

$$\mathrm{Log}[\mathrm{Fe}^{+++}] = 4.81 - 3\mathrm{pH} \tag{2.43}$$

$$\mathrm{pH} = 1.6 \tag{2.44}$$

5.
$$\begin{array}{l}\mathrm{Fe} + 2\mathrm{H_2O} = \mathrm{Fe(OH)_2} + 2\mathrm{H^+} + 2\mathrm{e} \\ \text{(dependent both on Eh and pH)}\end{array} \tag{2.45}$$

$$\mathrm{E}^0 = -\frac{2.19}{23.06X2} = -0.05\mathrm{V} \tag{2.46}$$

$$\mathrm{Eh} = -0.05 + \frac{0.055}{2}\log[\mathrm{H}^+]^2 \tag{2.47}$$

$$\mathrm{Eh} = -0.05 - 0.059\mathrm{pH} \tag{2.48}$$

6.
$$\mathrm{Fe(OH)_2} + \mathrm{H_2O} = \mathrm{Fe(OH)_3} + \mathrm{H^+} + \mathrm{e} \tag{2.49}$$

$$\mathrm{Eh} = 0.27 - 0.059\,\mathrm{pH} \tag{2.50}$$

7.
$$\mathrm{Fe^{++}} + 3\mathrm{H_2O} = \mathrm{Fe(OH)_3} + 3\mathrm{H^+} + \mathrm{e} \tag{2.51}$$

$$\mathrm{Eh} = 1.057 - 0.177\mathrm{pH} - 0.059\log[\mathrm{Fe^{++}}] \tag{2.52}$$

The above seven reactions are then drawn on an Eh-pH diagram. Stability regions for Fe, Fe^{++}, Fe^{+++}, $Fe(OH)_2$ and $Fe(OH)_3$ phases are marked as shown in Fig. 2.18.

The corrosion diagram corresponding to the Fe–H_2O–O_2 equilibrium is shown in Fig. 2.19.

With changes in the ionic concentrations of dissolved iron and partial pressures of oxygen and hydrogen, the phase boundaries would shift.

Regions of corrosion for iron (steels) are not only confined to the acidic region, but also exist in the high alkaline region (beyond a pH of about 12) where dissolution of iron as $HFeO_2^-$ species can occur. Regions of immunity (where metallic iron is stable thermodynamically) and passivation (stability phases for iron oxides which form a protective passive layer) are shown. From the diagram, suitable Eh-pH regions for cathodic and anodic protection could be selected. Similar Eh-pH and corrosion diagrams can be drawn for different metal—H_2O–O_2 systems to understand their corrosion behavior. Representative corrosion diagrams for aluminum, zinc, magnesium, nickel, copper and titanium are shown in Fig. 2.20.

There are some limitations to thermodynamically constructed Eh-pH diagrams.

- The diagrams are thermodynamically derived for room temperature conditions. Corrosion behaviour at higher temperatures cannot be predicted using this diagram.
- Only thermodynamic amenability to corrosion and protection are predicted. Corrosion kinetics cannot be assessed.

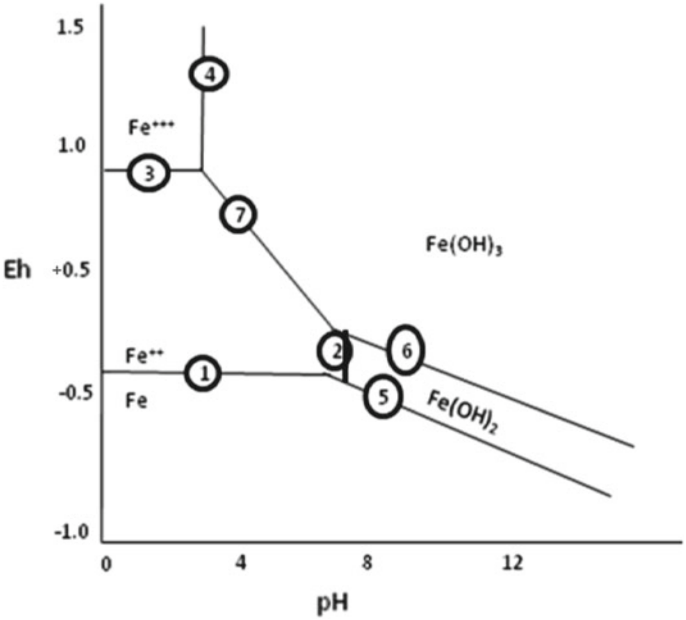


Fig. 2.18 Eh-pH diagram for the Fe–H_2O–O_2 system showing seven reaction boundaries

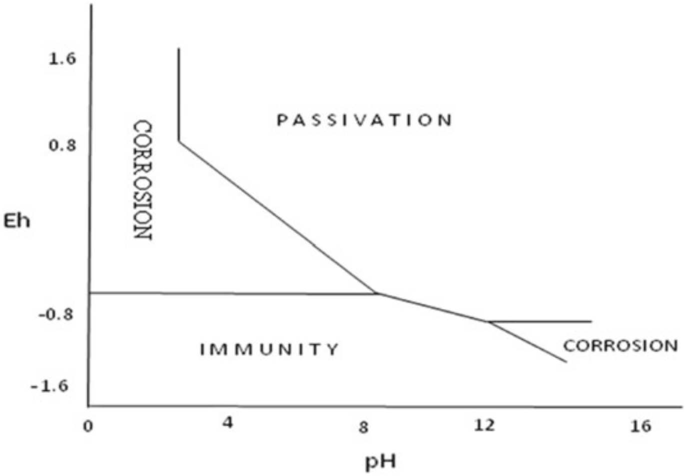


Fig. 2.19 Corrosion diagram for iron

- No consideration for added ions and effect of metal complexation is given.
- Only pure metals are considered. Effects of alloying and metallographic phases and heterogeneities are not considered.

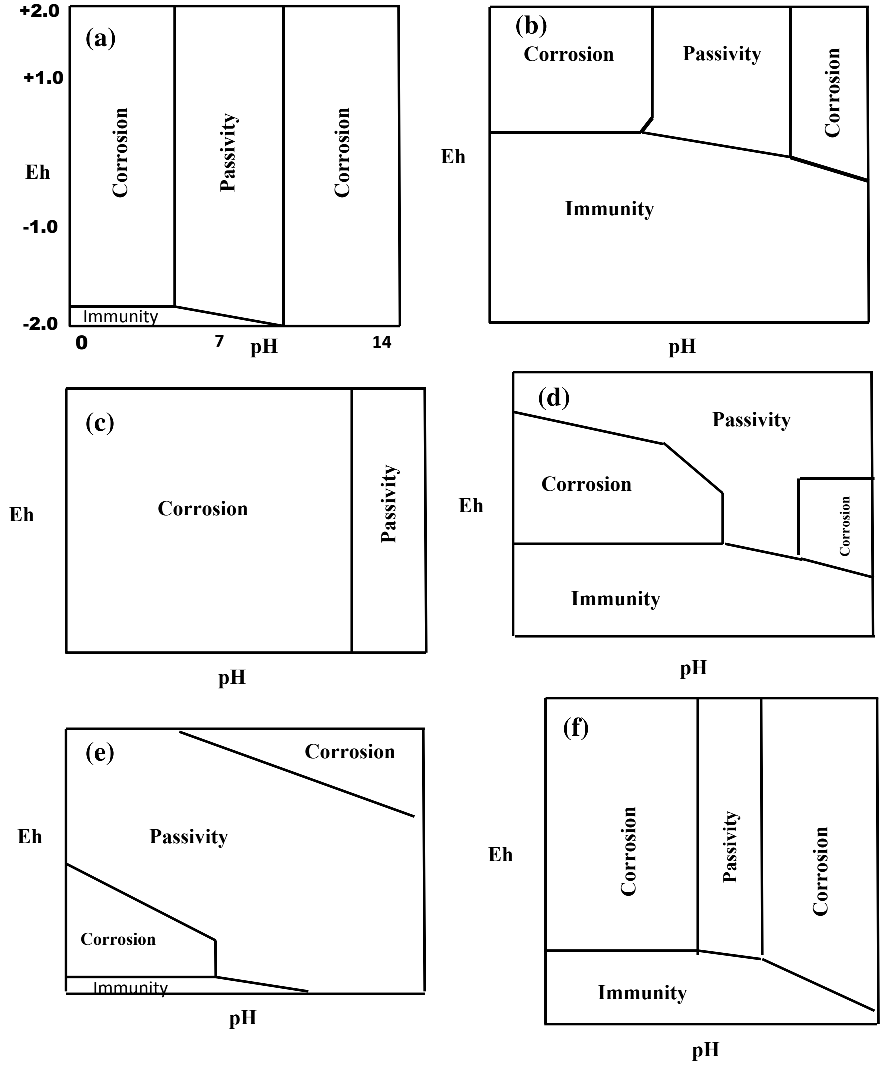


Fig. 2.20 Corrosion diagrams of **a** Aluminum, **b** Copper, **c** Magnesium, **d** Nickel, **e** Titanium, **f** Zinc

Modified Eh-pH diagrams for various metals need to be prepared taking into consideration the effect of alloying additions, presence of complexing agents and higher temperatures. Combined diagrams taking into consideration two or more metals simultaneously present would be more useful. For example, effect of chromium addition to iron to increase corrosion resistance can be represented in a combined Fe–Cr diagram. Similarly Cu–Zn, Cu–Sn and aluminum and magnesium alloy diagrams can be constructed.

Computer programs and soft-ware kits are now available to construct Eh-pH diagrams for various metal systems under different environmental conditions.

2.13 Electrochemical Kinetics [1–5, 9]

When a metal is contacted with an electrolyte containing its ions, either oxidation (loss of electrons) or reduction (gain of electrons) can occur. Equilibrium conditions existing across the metal-solution interface will determine the nature of the reactions. Electron transfer across interface will take place until thermodynamic equilibrium is reached. At equilibrium, the net current is zero while the oxidation-reduction rates are equal. The reversible electrode potential corresponds to the potential at equilibrium while the net equivalent current across the interface when there is no external current is supplied is referred to as the exchange current (i_0). When a metal is at its equilibrium potential in a solution, rates of oxidation and reduction are equal (not zero)

$$r_1 = r_2 = \frac{i_o a}{nF} \tag{2.53}$$

where r_1 and r_2 are rates of forward and reverse reactions and i_o is the exchange current density.

When a net current flows through a corrosion cell, the difference between the measured potential and the reversible half-cell potential ($\Delta E = E - E_{eq}$) is called the over-potential which is a measure of the departure (or deviation) of the potential from its equilibrium value. An electrode is not in equilibrium when a net current flows from or to its surface and to enable the current flow, the electrode potential should shift off its equilibrium value.

Polarization essentially results from a slow step in an electrode process. Considering transport processes at a metal-solution interface, diffusion of electroactive ions from the bulk to the interface and their subsequent interaction at the electrode surface resulting in charge transfer can be considered to understand the type of polarization.

A slow step in diffusion transport of reactants to and from the electrode interface results in concentration polarization, while a slow step in the charge transfer step results in activation polarization.

$$\eta_{Total} = \eta_{concentration} + \eta_{activation}$$

Depending on as to whether the polarization is significantly at the anode or cathode or at both anode and cathode, anodic, cathodic and mixed control electrode processes can be realized. Anodic, cathodic and mixed controls are represented in polarization diagrams shown in Fig. 2.21.

Exchange current densities can only be determined experimentally.

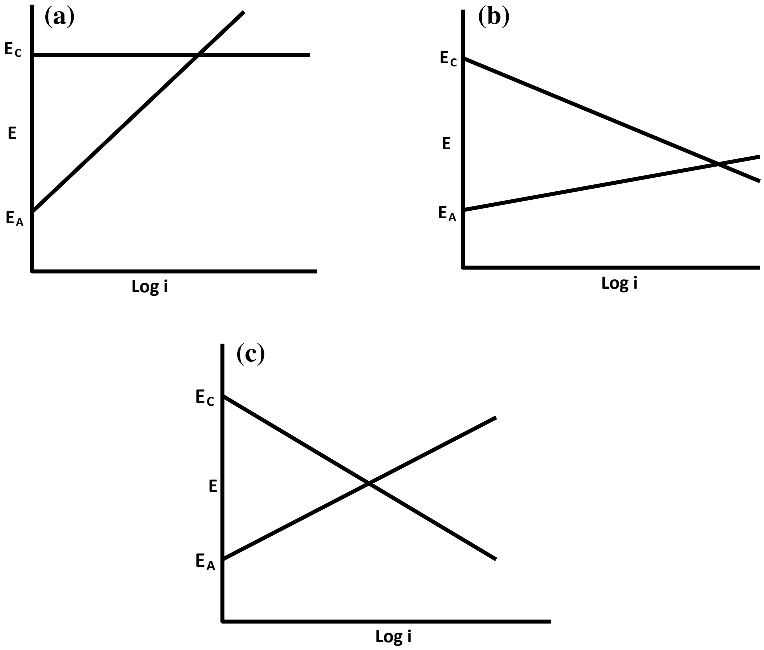


Fig. 2.21 Anodic (**a**), Cathodic (**b**) and Mixed (**c**) Control

A kinetic expression for exchange current density can be derived as

$$i_o = nFAK_s(c_{ox})^{1-\propto}(c_{red})^{\propto} \tag{2.54}$$

where

K_s is a rate constant.
A = surface area.
$\propto$ = transfer coefficient.

Exchange current depends on the following

- Nature of the redox reaction.
- Electrode surface and composition.
- Temperature.
- Concentration of redox species.

Exchange current densities (amp/cm^2) for various metals for the hydrogen reduction reaction are given below [1–5]:

Pb, Hg	10^{-12} to 10^{-13}
Zn	10^{-10} to 10^{-11}
Ag, Cu	10^{-7}
Fe, Au	10^{-6}
Pd, Rh	10^{-4}
Pt	10^{-2}

It becomes 10^{12} times easier for hydrogen to evolve on a platinum cathode compared to lead and mercury surfaces. Thus, the magnitude of exchange current density indicates the reversibility or irreversibility of a redox reaction at an electrode surface.

Electrochemical kinetics of corrosion can be derived in terms of activation and concentration polarization for anodic and cathodic reactions.

From the rate theory equations, relationships between applied current density, exchange current density and activation over potentials can be derived.

A general relationship for the polarization of an electrode for a specific redox reaction is given by the Butler-Volmer equation [2].

$$i_a = i_o \exp\left[\frac{\propto nF\eta}{RT}\right] \tag{2.55}$$

$$i_c = i_o \exp\left[\frac{-(1- \propto)nF\eta}{RT}\right] \tag{2.56}$$

$$\mathrm{I}_{\mathrm{applied}} = i_0\left[\mathit{exp}\left(\frac{\propto nF\eta}{RT}\right) - \exp\left(\frac{-(1- \propto)nF\eta}{RT}\right)\right] \tag{2.57}$$

where

$\mathrm{I}_{\mathrm{applied}}$ = net reaction current
$\propto$ = charge transfer or symmetry coefficient for the anodic/cathodic reaction

The factors $\propto$ and $(1 - \propto)$ are the fractions of over- potential (η) taken by discharge and ionization reactions (forward and backward)

n = number of electrons
F = Faraday constant
T = Absolute temperature.

For high over-potentials, the above equation can be simplified as the Tafel equation

$$\eta_{\mathrm{act(anode)}} = \mathrm{a} + \mathrm{b_a} \log \frac{\mathrm{i_a}}{\mathrm{i_o}} \tag{2.58}$$

$$\eta_{\mathrm{act(cathode)}} = \mathrm{a} - \mathrm{b_c} \log \frac{\mathrm{i_c}}{\mathrm{i_o}} \tag{2.59}$$

$$\eta_{\mathrm{act}} = \pm \mathrm{b} \log \frac{\mathrm{i}}{\mathrm{i_o}} \tag{2.60}$$

$\propto$ = 0.5 for $\mathrm{b_a}$ and $\mathrm{b_c}$ of 0.12 V

Anodic and cathodic slopes can be estimated as

$$\mathrm{b_c} = -2.303 \frac{RT}{\propto nF} \tag{2.61}$$

$$\mathrm{b_a} = 2.303 \frac{RT}{(1- \propto)nF} \tag{2.62}$$

Tafel equation is applicable to each electrode half reaction separately.

At low over-potentials, the dependence of current on over-potential is linear and the linear region is referred to as ‘polarization resistance’.

As per the Stern-Geary equation, applicable to the linear region at lower over potentials,

$$i_{Corr} = \frac{B}{R_p} \text{ and } B = \frac{b_a . b_c}{2.3(b_a + b_c)} \tag{2.63}$$

where $\mathrm{R_p}$ = polarization resistance = $\frac{\Delta E}{\Delta I}$.

Tafel and stern-Geary equations are used to estimate corrosion currents (corrosion rates) by the Tafel plots and linear polarization methods.

Similarly, from Faraday’s laws and Fick’s laws of diffusion, a relationship for concentration polarization with reference to limiting (diffusion) current and cathodic current can be derived.

$$\eta_{Conc} = \frac{RT}{nF} \ln \left[1 - \frac{i_C}{i_L} \right] \tag{2.64}$$

where $\mathrm{i_L}$ = limiting (diffusion) current density.

Total cathode polarization consisting of activation and concentration over-potentials can be written as

$$\eta_{total} = -\beta \log \frac{i_C}{i_O} + 2.3 \frac{RT}{nF} \log \left[1 - \frac{i_c}{i_L} \right] \tag{2.65}$$

Figure 2.22 illustrates corrosion of a metal where cathodic reaction is under activation and concentration polarization.

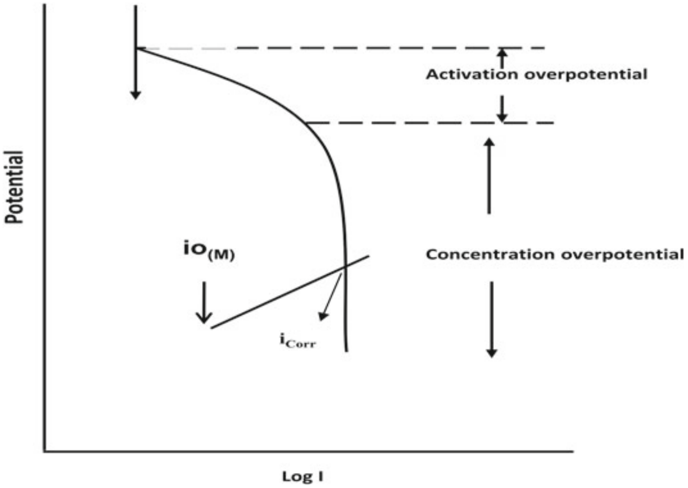


Fig. 2.22 Polarization diagram showing activation and concentration over-potentials [2, 4]

2.14 Theory of Mixed Potentials [1–5, 10]

Electrochemical fundamentals governing mixed potential theory are based on the following concepts:

- Principle of charge conservation: There cannot be any net accumulation of charge during an electrochemical reaction. Total rate of oxidation must be equal to total rate of reduction. i.e. Sum of anodic oxidation currents must be equal to sum of cathodic reduction currents.
- Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.

Consider a general anodic reaction,

$$M = M^{++} + 2e \tag{2.1}$$

Possible cathodic reactions depending on environment are:

(a) Hydrogen reduction from acid or neutral/alkaline solution.

$$2H^{+} + 2e = H_2(\text{acid}) \tag{2.4}$$

$$2H_2O + 2e = H_2 + 2OH^{-}(\text{neutral or alkaline}) \tag{2.31}$$

(b) Oxygen reduction in acid or neutral solution.

$$O_2 + 4H^+ + 4e = 2H_2O(\text{acid}) \tag{2.30}$$

$$O_2 + 2H_2O + 4e = 4OH^-(\text{neutral}) \tag{2.21}$$

(c) Reduction of other added oxidizers such as ferric ions

$$Fe^{+++} + e = Fe^{++} \tag{2.39}$$

As per the mixed potential theory using the zero current criterion, $\sum i_a = \sum i_c$

$$i_a^M = i_c^{H(M)} + i_{c\,2}^{O\,(M)} + i_c^{Fe^{+++}(M)} \tag{2.66}$$

At equilibrium, the total anodic oxidation rate is equal to total cathodic reduction rate.

Assuming corrosion of an divalent metal, M in an acid solution,

$$M = M^{++} + 2e(\text{anodic reaction}) \tag{2.1}$$

$$\underline{2H^+ + 2e = H_2(\text{cathodic reaction})} \tag{2.4}$$

$$M + 2H^+ = M^{++} + H_2 \text{ (net reaction)} \tag{2.67}$$

The metal M corrodes with the evolution of hydrogen. The two half-reactions as indicated above cannot coexist as separate entities on the same metal surface. Each reaction has its own half-cell electrode potential and exchange current density.

Due to polarization, potentials shift in anodic and cathodic directions to an intermediate value (between the two half-cell potentials).

Since such a polarized potential is a combination of the two half-cell potentials, it is referred to as MIXED POTENTIAL. The electrode potential at steady state for a freely corroding metal is referred to as corrosion potential (E_{Corr}). See Fig. 2.23.

At E_{corr}, rates of anodic and cathodic reactions are equal.

$$i_c = i_a = i_{corr,}(\text{at } E_{corr}) \tag{2.68}$$

i_{corr} is the corrosion rate of the metal and also the rate of hydrogen liberation at the metal surface (H^+ oxidizes the metal).

Kinetic parameters such as the exchange current density for the redox reaction at a metal surface need to be considered to understand the reversibility of a redox reaction at metal surfaces.

For example, in dilute hydrochloric acid solutions, zinc dissolution is expected to be higher than that of iron from a thermodynamic view point ($E^{0++}_{Zn/Zn} = -0.76$ V compared to E^0 for $Fe|Fe^{++} = -0.44$ V). However, from a kinetic view point, the

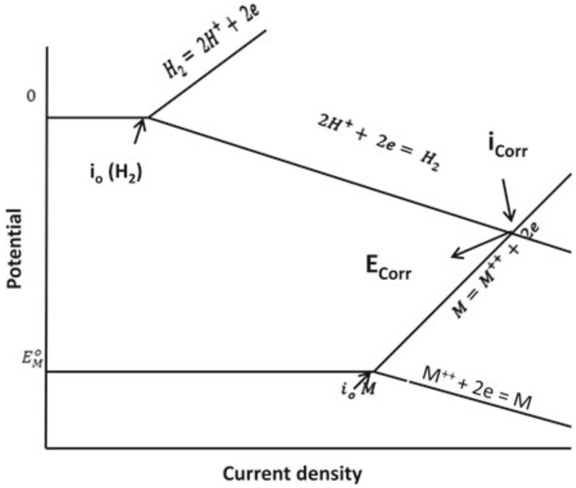


Fig. 2.23 Polarization of anodic and cathodic reactions resulting in a mixed potential

corrosion rate of iron will however be higher than that of pure zinc, due to differences in their exchange current densities for hydrogen liberation reaction. Exchange current density for hydrogen reduction on zinc is lower than that on iron.

Engineering systems are heterogeneous and complex. The zero current criterion in such multi-electrode systems in a corrosive environment becomes all the more relevant.

Consider two electrodes X and Y with one reduction reaction in an acid solution [11].

$$i_a^X + i_a^Y = i_c^{H(X)} + i_c^{H(Y)} \tag{2.69}$$

Relative areas of the anode and cathode are important in the prediction of anodic corrosion rates and current density (current/unit area) need to be considered.

The driving force for corrosion is enhanced on addition of a strong oxidizer such as ferric ions to the acid solution. The corrosion potential E_{corr}, is shifted to more noble direction with increasing corrosion rate of the metal. Hydrogen reduction rate is correspondingly decreased due to the added oxidizer. See Fig. 2.24.

$$\begin{aligned} & I_{corr}(\text{Corrosion rate on addition of ferric ion}) \\ & = i_C^{Fe^{+++}/Fe^{++}} + i_C^{H^+/H_2}(\text{at steady state}) \end{aligned} \tag{2.70}$$

It may however be borne in mind that the above shown effect of an added oxidizer will be significant only if the exchange current density for the added oxidizer reduction is higher than that for hydrogen reduction. If the exchange current for the added oxidizer reduction is lower, no increase in corrosion rate of metal would be observed.

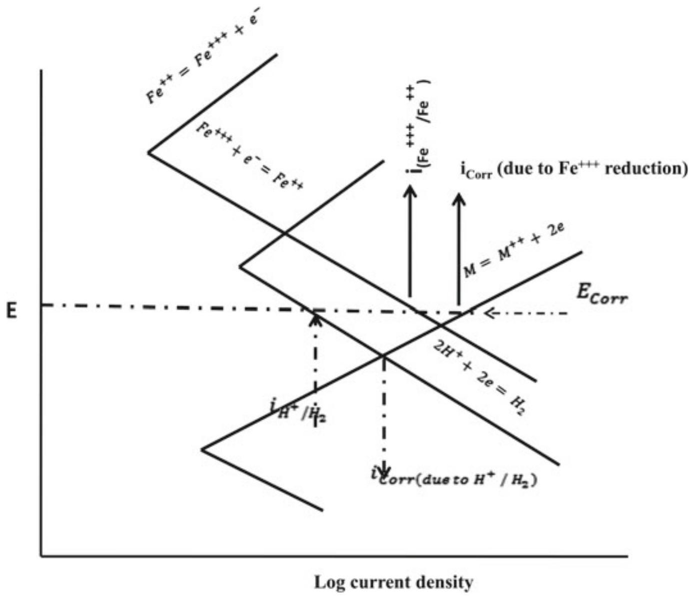


Fig. 2.24 Mixed potential diagram illustrating effect of addition of ferric ions to acid solution on the corrosion rate of a metal [9, 10]

Let us examine the corrosion behavior of active-noble metal couples under the mixed potential theory.

2.15 Platinum-Iron Couple in Acid Solution [11]

$$i_a^{Fe} = i_c^{H(Pt)} \frac{A(Pt)}{A(Fe)} + i_c^{H(Fe)} \tag{2.71}$$

where i_a and i_c represent anodic and cathodic current densities and A is relative surface area. Corrosion rate of platinum in the couple is negligible, while that of iron is enhanced due to very high exchange current density for hydrogen reduction on platinum. Surface area effect also needs to be considered. Platinum provides additional cathode surface for efficient hydrogen reduction.

The corrosion rate of an active metal (Fe, Zn) depends on the nature of the coupled noble metal in relation to the exchange current density for the reduction reaction. pH of the medium and nature of the oxidizer will also influence rate of anodic oxidation. If the Fe–Pt couple (having higher cathode to anode surface area ratio) is exposed to neutral pH solution where oxygen reduction is the cathodic reaction (instead of H_2), the expected effect of noble metal (Pt) would be not so significant since the exchange current densities for oxygen reduction on both the surfaces are nearly the same. Also, if lead metal is coupled with iron instead of platinum in acid solution, the effect of coupling on anodic oxidation of iron would be rather negligible, since the exchange current density for hydrogen reduction on lead is very much lower than that on iron.

2.16 Iron-Zinc Couple [11]

Corrosion behavior of the iron-zinc couple can be examined with respect to role of zinc as a sacrificial anode

$$i_a^{\mathrm{Fe}} = i_c^{\mathrm{H(Zn)}} \frac{A(\mathrm{Zn})}{A(\mathrm{Fe})} + i_c^{H(\mathrm{Fe})} - i_a^{\mathrm{Zn}} \frac{A(\mathrm{Zn})}{A(\mathrm{Fe})} \tag{2.72}$$

$$i_a^{\mathrm{Zn}} \gg i_c^{\mathrm{H(Zn)}} \tag{2.73}$$

Enhanced zinc oxidation rate would decrease the rate of iron oxidation and the effect zinc depends on the ratio of $\frac{i_c^{\mathrm{H(Zn)}}}{i_a^{\mathrm{Zn}}}$ and iron will be protected as long as this ratio is smaller.

The relative areas of the two metals in a couple influence its galvanic corrosion rate. Increasing cathodic surface areas for a fixed anode area will increase the anodic corrosion rate.

While $\mathrm{E_{corr}}$ can be directly measured, $\mathrm{i_{corr}}$ need to be determined by polarizing the electrode from the corrosion potential.

The entire corroding metal is made either anodic or cathodic in an electrolytic cell through application of an external potential (or current) and steady state conditions deduced from the polarized condition [2].

$$\eta_{\mathrm{act}} = \mathrm{b_a} \log \frac{i_{net}}{i_{corr}} \text{ at higher anodic over-potentials} \tag{2.74}$$

For cathodic reaction,

$$\eta_{\mathrm{act}} = \mathrm{b_c} \log \frac{i_{net}}{i_{Corr}} \tag{2.75}$$

$$\mathrm{i} = \mathrm{i_{corr}} \text{ when } \eta = \mathrm{O} \tag{2.76}$$

Anodic and cathodic Tafel lines can be extrapolated back to $\mathrm{E_{corr}}$ to get $\mathrm{i_{corr}}$(corrosion rate).

When the cathodic reaction is diffusion controlled as in the case with oxygen reduction at neutral pH,

$$O_2 + 2H_2O + 4e = 4OH^- \tag{2.21}$$

solution velocity influences corrosion rate (unlike in activation control). Corrosion rate of normal metals initially increases with solution velocity up to a certain value, there after becoming independent of velocity.

2.17 Determination of Corrosion Rates [2]

Electrochemical reaction rate can be measured in terms of rate of electron transport from or to the electrode interface.

As per Faraday's law,

$$M = \frac{It.a}{nF} \tag{2.77}$$

where

M = mass reacted
a = atomic weight
I = current, in amperes
t = time
n = number of exchanged equivalents
F = Faraday constant

Proportionality between mass loss per unit area per time and current density can be given as

Corrosion rate,

$$\mathrm{r} = \frac{M}{A.t} = \frac{ia}{nF} \tag{2.78}$$

where

$$\mathrm{i} = \text{current density}\left(\frac{i}{A}\right)$$

$$\text{Penetration rate} = 0.129\frac{a.i}{nd}\text{in mpy(mils per year)} \tag{2.79}$$

where

d = density of metal/alloy in g/cm^3
i = μA/cm^2 and 0.129 is the proportionality constant

For expressing penetration rate in other units such as mm/year or µm/year appropriate proportionality constants need to be used.

As an example, the relationship between penetration rate in mpy and current density of 1µA/cm^2 for iron can be calculated as

$$0.129\left[\frac{55.8x1}{7.9x2}\right] \approx 0.5mpy = 1\ \mu\text{A/cm}^2$$

To determine the corrosion penetration rate for alloys, respective metallic compositions need to be considered and the equivalent weight determined in terms of sums of fractions of equivalents of all alloying elements.

$$\text{Total equivalents } \mathrm{N_t} = \Sigma\frac{f_i n_i}{a_i} \tag{2.80}$$

where

$\mathrm{f_i}$ = mean fraction of the element in the alloy
$\mathrm{n_i}$ = exchanged electrons
$\mathrm{a_i}$ = respective atomic weights

From corrosion current densities derived from polarization plots, equivalent penetration rates in mass loss per unit area per time can be estimated.

Typical Tafel extrapolation and linear polarization plots for determination of corrosion currents and other electrochemical parameters are illustrated in Figs. 2.25 and 2.26.

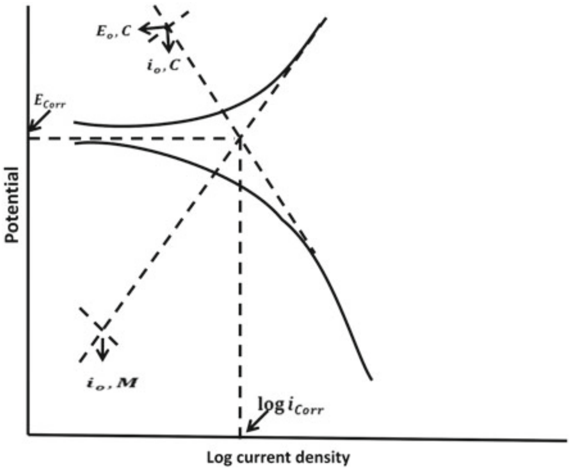


Fig. 2.25 Estimation of Tafel parameters

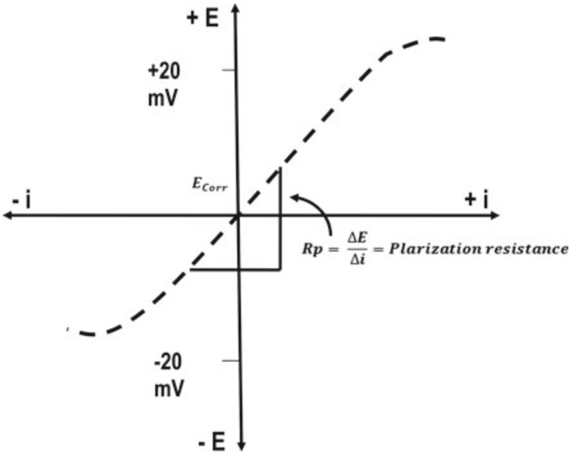


Fig. 2.26 Linear polarization resistance method

2.18 Electrochemical Aspects of Passivity [1–5, 11, 12]

In the Eh-pH diagrams, stability regions of immunity, corrosion and passivity are indicated for various metals in aqueous solutions. Properties such as immunity and passivity can be effectively used to protect metals form corrosion.

Electrochemical aspects of passivity and methods of corrosion protection utilizing active- passive transition are illustrated below:

Passivity can be defined as follows [5]

(a) A metal active in the EMF series or an alloy constituted of such metals can be defined as passive when its electrochemical behavior or activity becomes same or similar to that of a less active (nobler) metal. Eg: Titanium, Chromium, Stainless steel.

Passive metals such as titanium, chromium, aluminum and alloys such as stainless steel are corrosion resistant due to the formation of very thin, adherent and protective oxidized surface films in the corrosive environment.

(b) A passive metal or alloy effectively resists corrosion in an environment even if there exists a negative free energy change for its conversion from a metallic state to appropriate corrosion products.

Eg: Lead in sulfuric acid, Iron in inhibitor-containing pickling acid.

There are several theories put forward to explain passive behavior of metals and alloys such as oxide film and adsorption theories and appropriate models proposed.

Schematic anodic polarization behavior of a metal exhibiting active-passive transition is illustrated in Fig. 2.27 [1, 2].

Active, passive and transpassive regions are clearly shown. From the anodic polarization curve, the following electrochemical parameters can be deduced.

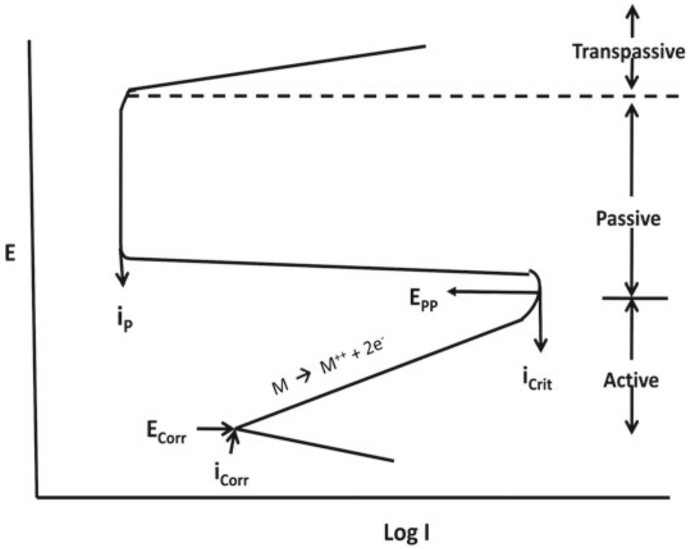


Fig. 2.27 Schematic anodic polarization curve illustrating active-passive transition [1–5]

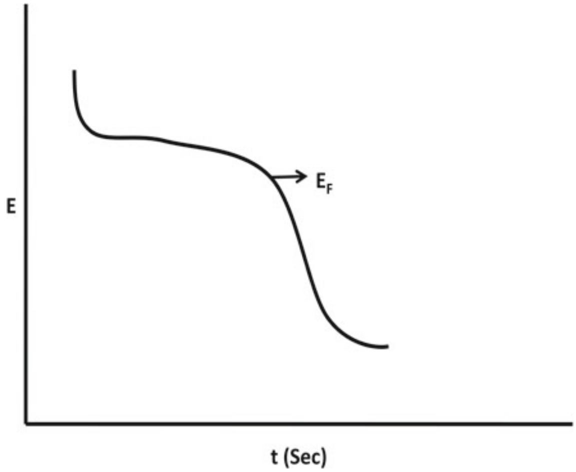
i_{crit}	Critical anodic current density (minimum anodic current density essential to initiate passivation-sudden decrease in corrosion rate from the initial active region)
E_{pp}	Primary passive potential (Above this potential, the passive film becomes stable and corrosion rate decreases drastically to the lower value)
E_F	Flade potential (on interruption of anodic polarization, decay in passivity with time occurs through potential changes in stages. The noble potential exhibited just before rapid potential decay was found to be more noble, the more acid the solution and referred to as Flade potential [5]. See Fig. 2.28.
i_p	Passive current density is the minimum current density required to maintain stable passivity.
E_{pit}	Pitting potential is the potential at which there is sudden increase in current density due to breakdown of passive film. At higher potentials beyond the stable passive region, the passive film is disturbed and breaks down, leading to subsequent increase in anodic corrosion rate in the transpassive region

It is possible to determine, the passive corrosion rate, passive potential region, relative stability of the passive state as well as the essential electrochemical conditions necessary to achieve spontaneous passivity.

Enhancement of temperature and acidity tends to increase the critical anodic current density for passivation. Presence of chlorides is detrimental to passivity.

Mixed potential behavior of active–passive metals and alloys can be understood when cathodic reduction processes are superimposed on the anodic polarization curve. As shown in Fig. 2.29, three different activation controlled reduction

Fig. 2.28 Decay of passivity on interruption of anodic polarization indicating Flade potential (E_F) [5]



processes having varying exchange current densities are superimposed on the anodic polarization curve [2, 12].

Three different conditions are possible, namely [12]

- Case I
  Only one stable potential at C where the mixed potential theory is satisfied. The metal corrodes having i_{corr} and E_{corr} corresponding to point C
  Eg: Fe in dilute H_2SO_4, Ti in dilute H_2SO_4/HCl.

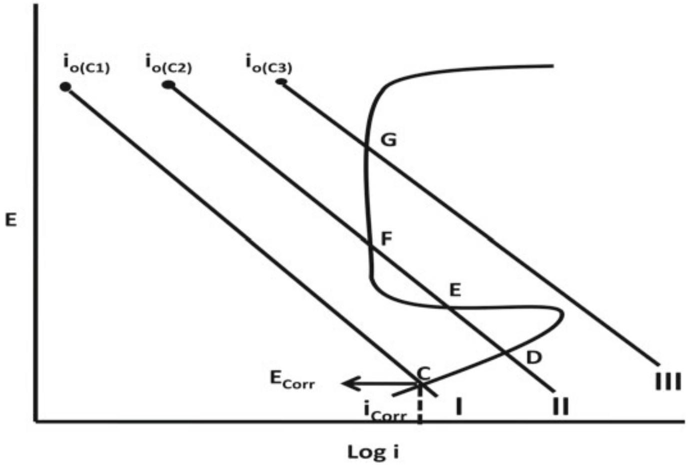


Fig. 2.29 Stability of passivity under different activation—controlled cathodic processes [12]

- Case II

  Three points of intersection D, E and F where rate of oxidation is equal to rate of reduction. Point E is not in stable state, while D is in active region (high corrosion rate) and F in passive state (lowest corrosion rate). This system can exist in active and passive stable states. (Borderline passivity)

  Eg: Cr in dilute HCl or H_2SO_4. Stainless steel in H_2SO_4 (containing oxidizers).
- Case III

  Spontaneous passivation with only stable potential at G in the passive region. This case is the most desirable.

  Eg: Cr—noble metal alloys in H_2SO_4 or HCl.

  Ti—noble metal alloys in dilute H_2SO_4.

  18-8 stainless steel in acid (containing ferric ions).

Achievement of condition as in case III is essential for the development of corrosion resistant alloys. Borderline passivity need to be avoided in which both active and passive states remain stable. At higher oxidizing conditions, passive films break down and transpassivity sets in, leading to initiation of localized corrosion through pitting.

Total cathodic partial current density at E_{pp} should be equal to or greater than i_{crit} to achieve spontaneous passivation.

The electrochemical criterion to achieve spontaneous passivation can be stated as [12]:

$$\text{Passivity Index (PI)} = \frac{i_c(atE_{pp})}{i_{crit}} \tag{2.81}$$

For PI $\geq$ 1, Spontaneous passivation occurs and for PI < 1, no spontaneous passivation occurs, even though as in case II, a stable passive region may exist along with another corrosion region (Borderline passivity).

Spontaneous passivation depends on

(a) Passivation potential
(b) Reversible potential of the oxidant
(c) Passivation current density
(d) Cathodic partial current density of the oxidant at passivation potential.

To achieve stable spontaneous passivation, the following electrochemical conditions need to be satisfied.

- Passive potential to be lower than reversible potential of the oxidant.
- Passive current density to be less than cathodic reduction current density.

The choice of a metal or alloy based on passive corrosion resistance depends on the following factors [12]:

(a) To achieve passive behavior where cathodic reduction is activation controlled, a metal or alloy with an active E_{pp} is superior.

(b) If the reduction process is diffusion controlled, a metal or alloy having a small i_{crit} will passivate faster.

For development of corrosion-resistant alloys based on passivity criterion, two approaches then become possible.

(a) Enhancing ease of passivation by reducing i_{crit} or keeping E_{pp} at more active values.
    Anodic dissolution behavior of the metal/alloy can be changed by appropriate alloy addition in order to decrease i_{crit}.
    Eg: Titanium, chromium
    (alloying additions such as molybdenum, nickel, tantalum and columbium beneficial)
(b) Increase cathodic reduction rates in order to achieve spontaneous passivation—coupling/alloying with noble metals having high exchange current densities for reduction processes.

For example metals with active E_{pp} such as titanium and chromium and alloys containing these metals which possess high exchange current densities for hydrogen reduction can undergo spontaneous passivation.

Rather unusual effects are observed in galvanic contacts between active-passive metals and noble metals such as platinum [4]. For example, titanium when coupled to platinum in an acid solution in the absence of oxidizers exhibits spontaneous passivation. Titanium can exist in passive condition at potentials more active than the reversible hydrogen reduction potentials. The exchange current density for hydrogen reduction on platinum is very high and the reduction current is larger than the critical anodic current density for titanium passivation, under the above conditions. On the other hand, if the passive range for the active-passive metal begins at nobler potentials than the reversible hydrogen potential, the corrosion rate of 'active' titanium will increase when coupled to 'noble' platinum.

Effect of addition of oxidizer (ferric, chromate) on the electrochemical behavior of active-passive alloys can be compared with those of normal metals. Corrosion rate of an active-passive alloy initially increases with oxidizer additions, while still in active state. However, after passive state is reached, the corrosion rate steeply decreases to a lower value and essentially remains at this low corrosion rate thereafter. Corrosion rate however increases due to transpassive behavior on increasing oxidizer levels to very high values [2].

It is interesting to note that, once the passive film has been formed, it can be retained at oxidizer concentrations even lower than that needed for passive film formation.

Oxidizer concentration necessary to maintain passivity should at least be the same or higher than the required minimum to induce spontaneous passivation. There is also a concern of borderline passivity when any surface disturbance (scratching) will destabilize passivity, leading to increase in corrosion rate. The following conditions need to be kept in mind regarding passive behavior of metals and alloys [1, 2, 4]:

- Corrosion rate is proportional to anodic current density in the active state irrespective of whether the metal or alloy exhibits passivity or not.
- Rate of cathodic reduction must exceed i_{crit} to achieve lower corrosion rates.
- Borderline passivity to be avoided while spontaneous passivation is preferred.
- Breakdown of passive films in high oxidizing environments or noble potentials due to transpassivity to be avoided.

2.19 Pitting Behavior of Passive Metals and Alloys

Chloride ions breakdown passivity or even at times prevent passivation of Fe, Cr, Ni, Co and stainless steels, since they can penetrate oxide films through pores and influence exchange current density. Breakdown of passivity by chloride ions is localized leading to pitting corrosion.

Susceptibility for pitting corrosion can be monitored through cyclic anodic polarization as shown in Fig. 2.30. Pitting potential can be experimentally determined. Initiation and propagation of pits occur between E_{pp} and E_{pit}. The potential where the loop closes during reverse scan is the protection potential (E_{prot}). New pits are initiated above E_{pit}. [1, 2, 4].

The following electrochemical aspects with respect to pitting initiation in active-passive metals and alloys may be noted.

- When E_{pit} and E_{prot} are the same, little pitting tendency
- If E_{prot} is more positive than E_{pit}, there will be no pitting.
- Repassivation tendency increases with high E_{prot}.

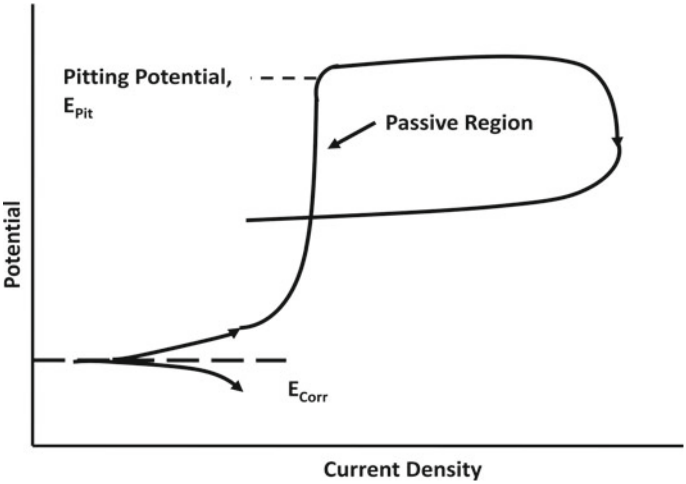


Fig. 2.30 Schematic cyclic anodic polarization of active-passive metal

- Pitting probability higher, if E_{prot} is more negative than E_{pit}.
- When E_{corr} is higher than $E_{pit,}$ spontaneous pitting occurs
- E_{pit} lower, with higher concentration of aggressive anions like Cl^-, which promote pitting.
- E_{pit} increases to nobler values with chromium and molybdenum addition when pitting corrosion is decreased.
- Pitting Resistance Equivalent Number (PREN) is used to measure relative pitting resistance of stainless steels in chloride media. [PREN = % Cr + 3.3% (Mo) + 16% (N)]

2.20 Anodic Protection [1, 2, 13]

Anodic protection through impressed anodic current can be applied to metals and alloys that exhibit active-passive behavior. The interface potential of the protected structure is increased to remain at the stable passive domain.

If an active-passive alloy such as stainless steel is maintained in the passive region through an applied anodic potential (or current), its initial corrosion rate (i_{corr}) can be shifted to a low value at i_p as shown in Fig. 2.31 [1, 2, 4].

Anodic protection unlike cathodic protection is ideally suited for protection of active-passive metals and alloys in aggressive environments such as high acidity and corrosive chemicals.

Typical anodic protection circuit is shown in Fig. 2.32 [2, 4, 13].

Anode is the container material itself (Eg: Stainless steel) Inert cathode materials having large surface area preferred. Recommended cathode materials for acid and

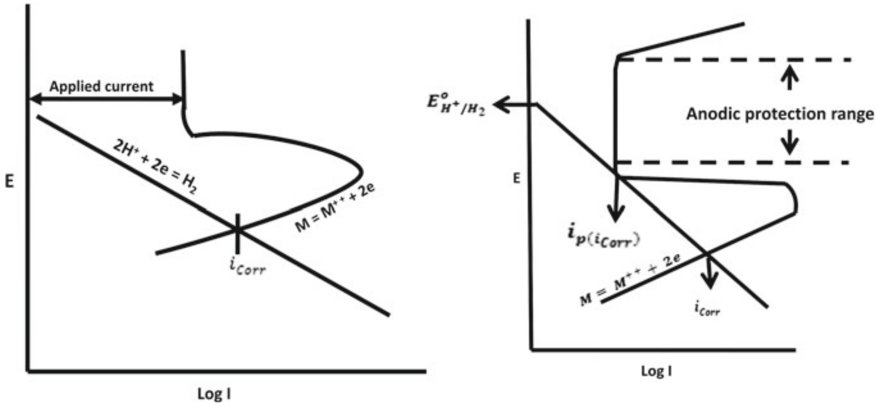


Fig. 2.31 Polarization curves illustrating anodic protection [2, 4]

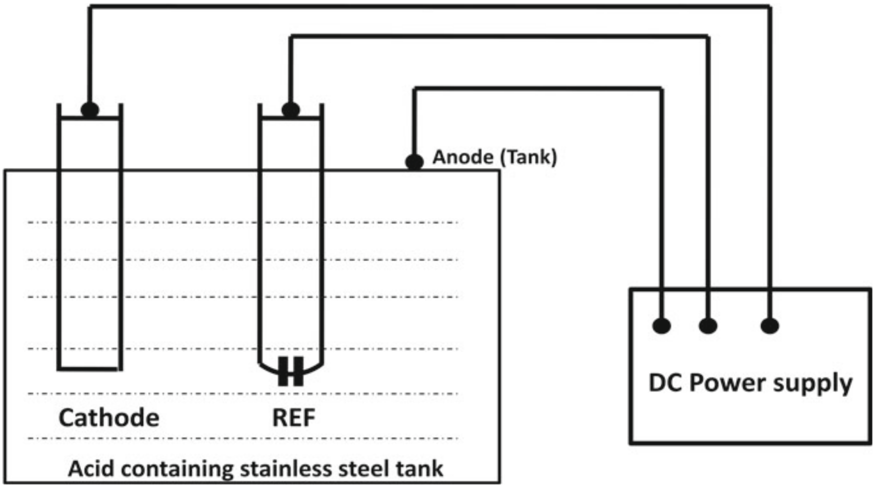


Fig. 2.32 Schematic illustration of anodic protection of acid containing stainless steel tank

corrosive industrial liquids include platinum-clad brass, chromium-nickel steel, silicon cast iron, copper, Hastelloy C and nickel-plated steel. Various types of reference electrodes such as Calomel, Ag/AgCl, $Hg/HgSO_4$ and platinum are used depending on the chemical environment.

Anodic protection can substantially reduce corrosion rate of active-passive alloys in very aggressive environments. For example, anodic protection of 304 stainless steels exposed to aerated sulfuric acid (5 M) containing about 0.1 M chlorides could reduce corrosion rate from an unprotected value of about 2000 μm/year, to about 5 μm/year. It has been widely applied to protect chemical storage tanks, reactors, heat exchangers and even transportation vessels.

A comparison between anodic and cathodic protection is given in Table 2.4.

Table 2.4 Comparison of anodic and cathodic protection methods [2–5]

Major factors	Anodic protection	Cathodic protection
Environmental conditions	For aggressive chemical corrosives	Moderate corrosion environments only
Suitability	Only for active-passive metals and alloys	Applicable to all metals in general
Operational features	Electrochemical estimation of appropriate protection range possible	Protective cathodic currents to be established through initial design and field trials
Cost aspects	Higher investment, but low operational costs	Low investment and higher operational costs

2.21 Cathodic Protection [1–5, 14, 15]

From potential—pH diagrams for metal—H_2O–O_2 equilibria, stability regions for metal immunity (state where the metal remains in its thermodynamically neutral form without oxidation) can be predicted. If the metal potential is maintained at its reversible equilibrium value where its remains in its neutral metallic state, corrosion can be eliminated.

Corrosion occurs due to differing potentials (anodic and cathodic areas) on a metal surface. When the potential differences are narrowed down and eventually eliminated with the entire surface converted to equipotential region (cathodic zone), corrosion can be arrested. Cathodic protection is based on the principle of corrosion control by making the metal surface cathodic (through cathodic polarization). This can be achieved either by attaching to a sacrificial anode or by an impressed DC current (potential). The entire corroding structure in forced to collect current (electrons) from the environment. Cathodic protection is defined as elimination or reduction of corrosion by making the entire metal a cathode by means of an impressed current or attachment to a sacrificial (more anodic) electrode. Basic electrochemical concepts involved in cathodic protection are illustrated in Fig. 2.33.

If the cathode ($E_{cathode}$) is polarized by an external current, the anodic reaction would be retarded, while the catholic reduction is enhanced. At the region, where the rates of cathodic and anodic reactions are equal, $E_{corr,}$ and I_{corr} are indicated defining the corrosion rate of the metal. If the corrosion potential is moved from E_{Corr} (B) to a lower value E through an applied current (C-D), rate of corrosion would decrease to (D-E) from I_{Corr}. If the applied current is further increased, corrosion current further deceases, as the potential moves to more active values. At

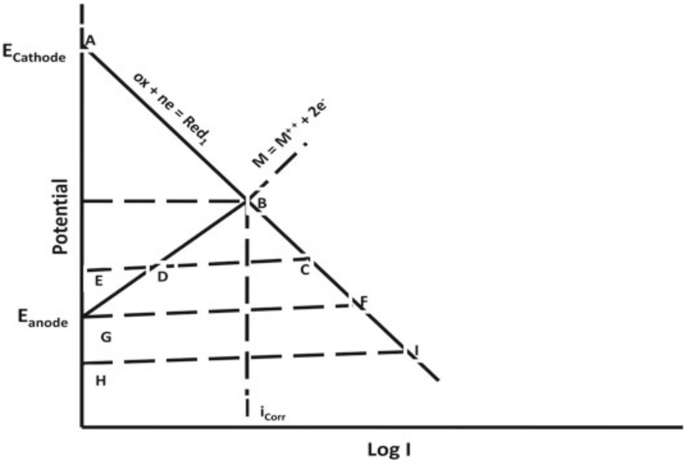


Fig. 2.33 Electrochemical illustration of cathodic protection [5]

an applied current equal to G-F, corrosion is nullified completely as the potential coincides with $E_{anode.}$ Still higher applied currents (H-I) do not help (over-protection).

In natural aqueous environments at neutral pH as in sea water, reduction of oxygen ($O_2 + 2H_2O + 4e = 4OH^-$) is the cathodic reaction which is diffusion controlled. Polarization diagram representing cathodic protection under the above conditions is illustrated in Fig. 2.34. Corrosion rate under the conditions is dictated by limiting (diffusion) current for oxygen reduction and therefore, the applied cathodic current for corrosion protection is substantially lower.

The cathodic current density required to maintain the correct protection potential will vary depending on environmental conditions. The protection potential which is equal to the equilibrium potential for different metals can be calculated. For example, for iron,

$$\mathrm{Fe} = \mathrm{Fe}^{++} + 2\mathrm{e}, \mathrm{E}^0 = -0.44\mathrm{V} \tag{2.27}$$

Depending on the pH and from a knowledge of the solubility product (K_{sp}) of the reaction product ($Fe(OH)_2$ for example), concentration of Fe^{++} can be estimated and the corresponding equilibrium potential calculated. For neutral pH, the protective potential for iron works out to be about −0.62 V (NHE) or −0.85 to 0.90 V ($Cu–CuSO_4$).

Major applications of cathodic protection include external surfaces of pipelines, ship hulls, storage tank, jetties and harbor structures, steel sheets and piles, off shore platforms, floating subsea structures, reinforced concrete structures as well as water storage and circulating systems. Generally, exterior of pipelines and other structures

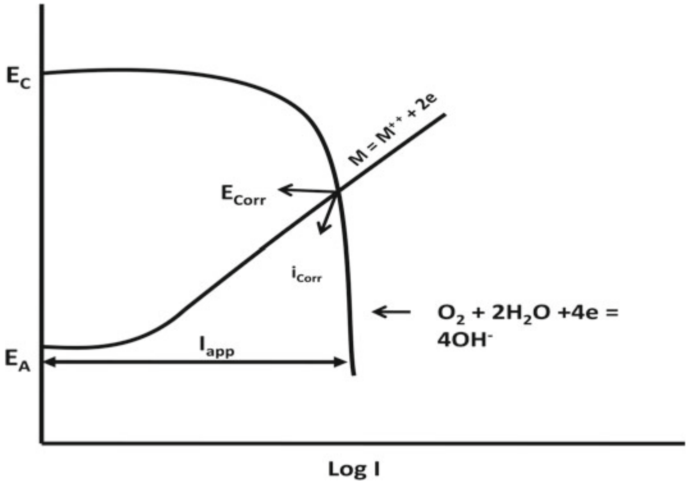


Fig. 2.34 Cathodic protection for systems under cathodic diffusion control [2]

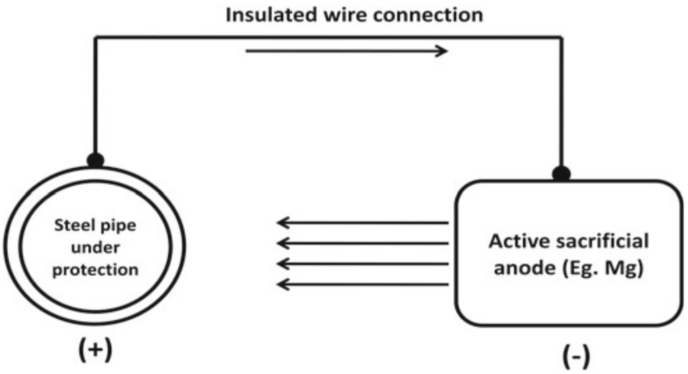


Fig. 2.35 Sacrificial anode cathodic protection

are initially well coated and cathodic protection is applied only to coating defects/holidays (5–10% of the damaged coatings).

Two methods of cathodic protection are:

(a) Sacrificial anode protection where the structure to be protected is connected directly to a more active metal/alloy (Fig. 2.35).
(b) Impressed current method, where the protected structure is connected to an auxiliary anode through a DC power supply (Fig. 2.36).

In sacrificial anode protection no external power source is used. More active anodes such as magnesium, aluminum and zinc can be used to protect steel structures which require only lower currents for protection in soils having low resistivity.

The following factors need to be ascertained in the choice of an appropriate galvanic anode.

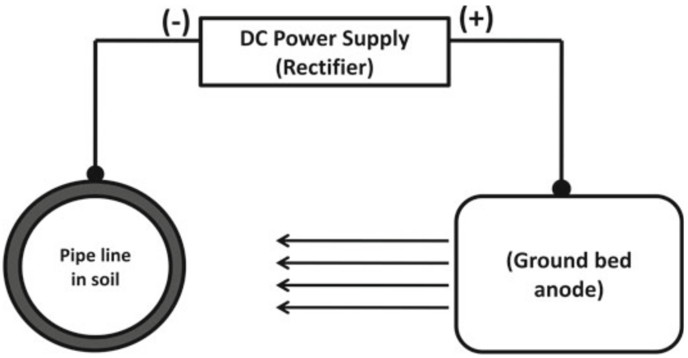


Fig. 2.36 Impressed current cathodic protection’

(a) Electrical energy content or anode capacity which is a measure of electric energy per weight provided by the sacrificial anode as dictated by Faraday's laws. Electrical energy content (EEC) for zinc anode is estimated to be 820 A hours/Kg which means that if a zinc anode were to discharge one ampere continuously, one Kg will be consumed in 820 h. The EEC output will be proportional to the anode efficiency and practical energy output will be actually dictated by the anode efficiency of the chosen galvanic anode.
(b) Solution potential
(c) Driving potential which is the difference between solution potential and the potential of the polarized structure.
(d) Anode bed—number of anodes in the back-fill.

The following parameters need to be predetermined for the application of impressed current protection.

(a) Source of DC Current.
(b) Estimation of current necessary for complete protection.
(c) Auxiliary anodes—choice, size, number, installation.
(d) Installation, design, erection and maintenance.

For large structures such as underground pipe lines, impressed current cathodic protection is used, while for smaller structures such as house-hold water tanks, ship's hull etc., sacrificial anodes can be effectively used. Initial coating of steel pipe lines and tubes can significantly reduce protection current requirements and thus save cost.

Approximate current requirements for cathodic protection of steel pipes are indicated below:

Uncoated structures in flowing sea water	10–15 mA/ft^2
Well-coated pipes in water	0.01–0.003 mA/ft^2
Excellently coated and exposed to water or under soil	0.0003 or less mA/ft^2

Some anode materials that could be used as ground-beds in impressed current cathodic protection are indicated in Table 2.5.

Design considerations for both impressed current and sacrificial anode systems have some common steps such as.

Table 2.5 Anode materials for impressed current cathodic protection

Anode material	Average consumption, kg/A-year
Cast iron	5–8
Steel scrap	5–10
Aluminum	4–6
Graphite	0.5–1.0
Lead	–
Platinum	–

(a) Exposed areas to be protected—exposed area at breaks and deteriorated coatings in case of coated structures.
(b) Polarized potential—Current density.
(c) Current demand—depend on the environment and nature of surface coating.
(d) Anode consumption—Numbers and weights of anode materials required to be determined from known consumption rates for the desired current demand. Anode number and distribution can be thus estimated. Anode resistance and design output current to be estimated.

Monitoring the effectiveness of cathodic protection of a structure is important. Potential measurements of a cathodically polarized structure with reference to a standard electrode can be periodically made. A potential of −0.85 V ($Cu/CuSO_4$) is sufficient for protection of steel in soil and natural water environments. The above criterion is not optimum and situations may arise when more negative potentials (up to −1.0 V) may be required for protection. Interference from IR components needs to be taken into account. Close Interval Potential Survey (CIPS) is an intensive monitoring technique. Direct Current Voltage Gradient (DCVG) method enables evaluation of protection and defects in insulation. Corrosion coupons (probes) can be used for monitoring of cathodic protection.

Controlled potential cathodic protection can be adapted to suit specific environments. For example, in sea-going vessels, the hull is subjected to variations in flow velocities which can alter limiting current density (for oxygen reduction), influencing cathodic protection current requirements from time to time. In such cases, controlling the potential (rather than current) would be more beneficial. **Controlled potential protection** can be used incorporating auxiliary anode—reference electrode attachment along with automatically—controlled power supply unit [2].

2.22 Stray Current Corrosion [1–5]

Stray-current corrosion is caused by several impressed current cathodic protection systems. In industrial protected systems, such as oil production industries having innumerable buried pipe lines, current leakage from impressed current anodes installed with cathodic protection systems can unintentionally enter a near-by unprotected structure (such as water pipelines) and leave from the surfaces creating severe corrosion (see Fig. 2.37).

Other sources of stray currents include DC electric power rail traction, welding units, electroplating cells and ground electric DC power.

Leaking stray currents from the above installations take a low resistance pathway to enter nearby unprotected structures before returning to the source. Regions from where current leaves are susceptible to stray-current corrosion, while areas receiving currents are protected!.

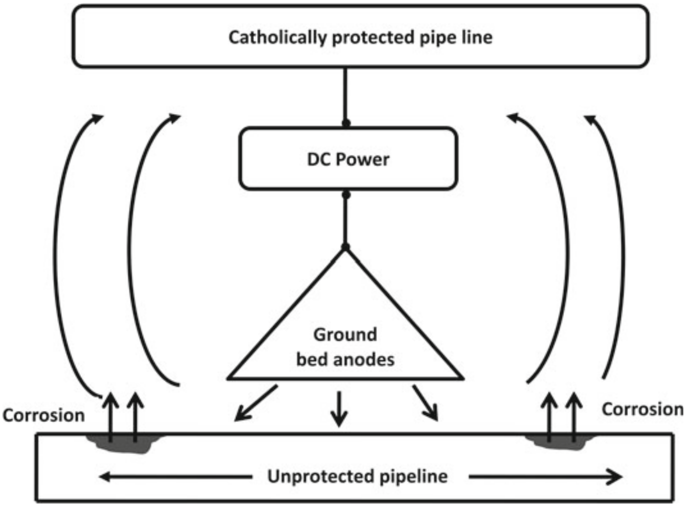


Fig. 2.37 Illustration of stray current corrosion [1]

Solutions to stray current corrosion include electrical bonding of the near-by unprotected structure. Simultaneously, additional anodes and increasing DC power capacity can accord full protection to all structures in the vicinity. Properly insulated couplings can also help reduce the problem (see Fig. 2.38). When impressed current protection systems are installed, anode ground beds should be so located to ensure that stray currents cannot leak to enter into other near-by structures.

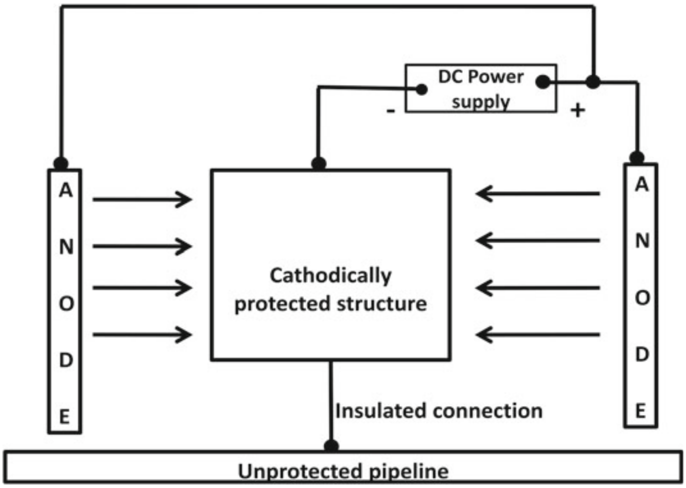


Fig. 2.38 Prevention of stray current corrosion by proper design

Direct stray currents can be classified as anodic, cathodic or a combined interference. Anodic interference occurs in close proximity to a buried anode. On the other hand, cathodic interference is encountered in close proximity to a polarized cathode, the potential shifting in a positive direction where current leaves the structure (causing corrosion damage). In combined interference, stray current pick-up occurs close to anode and discharge closer to cathodically polarized areas. The corrosion damage could be severe in this case since current pickup (overprotection) and discharge (corrosion) are both detrimental.

2.23 Biofouling and Microbially Influenced Corrosion [1, 16–22]

Biofouling and microbially influenced corrosion (MIC) brought about by various microorganisms has assumed great industrial significance in recent years. While biofouling involving attachment of microorganisms onto metals and alloys promotes MIC, electrochemical principles govern biological catalysis of oxidation/reduction reactions. The role of microorganisms in metallic corrosion can be seen as a biological catalyst influencing anodic or cathodic reactions along with generation of biogenic corrodants.

Various microorganisms as listed below are implicated in various MIC processes.

Sulfur/sulfide oxidizing bacteria	*Acidithiobacillus thiooxidans* *Acidithiobacillus ferrooxidans*
Sulfate reducing bacteria (SRB)	*Desulfovibrio* spp. *Desulfobacter* spp. *Desulfotomaculum* spp.
Iron/manganese oxidizing bacteria	*Gallionella* *Crenothrix* *Leptothrix*
Metal-reducing bacteria } Slime producing bacteria }	*Pseuclomonas* spp. *Bacillus* spp.

Fungi such as *Cladosporium resinae*, *Aspergillus niger*

Microorganisms can promote corrosion through changes in electrochemical conditions at the metal-solution interface which is modified and conditioned by prior biofilm formation. Microbial adhesion to metal surfaces as well as interaction with extracellular polymeric substances (EPS) promote MIC.

The sulfur-bacteria cycle in nature is closely linked to MIC. Sulfur- Sulfide-iron oxidizing aerobic *Acidithiobacillus* bacteria bring about oxidation of sulfur, ferrous ions and various sulfides to ferric-ion containing sulfuric acid, while anaerobic sulfate-reducing bacteria such as *Desulfovibrio* sp. reduce sulfates to sulfides promoting formation of H_2S and metallic sulfides. Fungi such as *Aspergillus niger* and *Cladosporium resinae* produce organic acids such as citric acid which can dissolve many ferrous and non ferrous metals and alloys. Potential-pH diagrams can be used to demarcate stability and activity regions of various microorganisms as well as to understand metal corrosion behavior induced by bacterial activity. While anodic reaction is oxidation of the metal, the cathodic reactions could be reduction of hydrogen or oxygen depending on pH of the environment.

Corrosion-promoting microbiological functions are listed below:

- Production of organic and inorganic acids, sulfides, phosphides and ammonia.
- Biodegradation of surface coatings, passive films and inhibitors.
- Formation of oxygen concentrations cells due to heterogeneous biofilm formation, generating localized anodes and cathodes promoting pitting and crevice corrosion.
- Direct participation in anodic and/or cathodic electrochemical reactions, influencing corrosion kinetics.

Microorganisms thus do have both direct and indirect roles in causing metallic corrosion.

MIC of various steels brought about by Sulfate Reducing Bacteria (SRB) such as *Desulfovibrio sulfuricans, Desulfovibrio vulgaris* and *Desulfotomaclum nigrificans* has been extensively studied. SRB are the most widely implicated anaerobe causing corrosion in oil and gas, nuclear power, water treatment, mining and chemical-based industries. Pipe line internal corrosion and corrosion of sea-going vessels and marine installations are caused by the presence of these anaerobes.

There are several proposed mechanisms illustrating the role of SRB in steel corrosion

The cathodic depolarization hypothesis proposed in 1934 [23] dealt with bacterially-induced depolarization of hydrogen reduction reaction by hydrogenase-positive SRB as per the following reaction pathways.

$$\mathrm{Fe} = \mathrm{Fe}^{++} + 2\mathrm{e}(\text{corrosion of iron}) \tag{2.27}$$

$$\mathrm{H_2O} = \mathrm{H}^{+} + \mathrm{OH}^{-} \tag{2.82}$$

$$\mathrm{H}^{+} + \mathrm{e} = \mathrm{H_{ads}} \tag{2.83}$$

$$2\mathrm{H_{ads}} = \mathrm{H_2} = 2\mathrm{H}^{+} + 2\mathrm{e}\ (\text{cathodic reaction}) \tag{2.84}$$

$$\mathrm{SO_4^{--}} + 8\mathrm{H}^{+} + 8\mathrm{e} = \mathrm{S}^{--} + 4\mathrm{H_2O}\ (\text{Bacterial sulfate reduction}) \tag{2.85}$$

$$\mathrm{Fe}^{++} + \mathrm{S}^{--} = \mathrm{FeS}\ (\text{Biogenic reaction product}) \tag{2.86}$$

Iron hydroxide and iron sulfide precipitates coat the corroded steel surfaces.

The above hypothesis has since been questioned and many alternative mechanisms proposed. The role FeS formed during MIC has been highlighted as a potential promoter of corrosion through galvanic interaction (Fe–FeS couple), cathodic depolarization and stress initiation.

Corrosion fatigue and hydrogen embrittlement of steel could be caused by SRB activity. H_2S—produced by the bacteria can decrease pH at the metal-biofilm interface (causing acidification) and promote hydrogen permeation into the metal. Even anodic depolarization by iron-reducing and sulfate-reducing bacteria can be caused in the MIC of steels Electrical Microbially influenced Corrosion (EMIC) was proposed to substantiate metallic iron as an electron donor, while biogenic H_2S aggravates the corrosive effect [19]. Anodic iron oxidation can be enhanced by electron consumption through bacterial sulfate reduction. Another deleterious role of marine and soil sulfate reducing bacteria is their ability to destabilize passive films present on active-passive alloys such as stainless steels. Corrosion behavior of stainless steels is significantly influenced by biofilms. Ennoblement of stainless steels has been reported in the presence of biofilms containing iron-and manganese-oxidizing bacteria [1, 16–22].

Tubercle formation in oil and water pipelines is a serious problem, mainly brought about by iron-oxidizing bacteria. Massive tubercles can seriously impede mass and heat transfer in pipes and heat exchangers. In various fuel systems, microbial growth can create problems such as clogging of valves, filters and pipes, sludge accumulation, corrosion of storage tanks, biodegradation of hydrocarbon oils and breakage of engine parts.

Microbial corrosion in aircraft components has now been well established. Various bacterial and fungal species can grow and proliferate in fuel tanks. Bacteria like *Pseudomonas* and fungi such as *Cladosporium resinae* have been isolated from aircraft aluminum alloy fuel tanks.

Intergranular cracking and extensive pitting of aluminum alloys can occur due to microbial activity.

Biofouling and microbial corrosion are extensively observed in reinforced concrete structures and in human body implants. MIC of reinforced steels in concrete is a serious problem since integrity of bridges, buildings, terrestrial and marine environment-structures could be compromised. Formation of biogenic corrosion products inside concrete components induce internal stresses causing catastrophic fracture.

Human body environment has been proved to be corrosive, especially with respect to various implant biomaterials such as stainless steels and titanium alloys. An oxygenated saline electrolyte at neutral pH containing water, chlorides, calcium, phosphates, amino acids and various organic polymers present a corrosive environment promoting anodic and cathodic electrochemical reactions. Various bacterial species inhabiting human body organs and circulatory systems interact with implanted metals and alloys. Corrosion forms such as pitting, crevice corrosion, galvanic attack, stress corrosion and intergranular attack are known to be prevalent in different locations of the human body. Some examples are given below:

(a) Austenitic stainless steels used in cranial plates, orthopaedic and spinal implants undergo pitting and crevice corrosion. Stress corrosion and corrosion fatigue has been observed in orthopedic joint implants.
(b) Cobalt-chromium alloys used in dental implants, orthopaedic fracture plates and joint replacements undergo dissolution in presence of serum proteins causing metal toxicity.
(c) Titanium alloys used as cranial and orthopaedic fracture plates undergo fracture.

2.24 Summary

Various corrosion processes can be explained with respect to electrochemical and microbiological mechanisms. Thermodynamic and kinetic aspects of corrosion are explained with reference to galvanic and concentration cells, electrochemical polarization, electrode kinetics and mixed potential theory. Mass and electron transport processes at a metal-solution interface can be understood in terms of concentration and activation over-potentials and kinetic equations derived to estimate corrosion rates. Cathodic protection, the extensively used protection method is based on principles of immunity and cathodic polarization. Principles of passivity find application in anodic protection of active-passive metals and alloys exposed to aggressive acid environments. Corrosion processes are catalyzed by various soil and marine microorganisms. Electrochemical mechanisms control microbially influenced corrosion, promoted by formation of biofilms. Biomaterials used in human body implants are exposed to corrosive environments prevailing in the human body.

Most of the types of corrosion occurring in industrial environments can be effectively explained in terms of electrochemical and microbiological principles.

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