

Module 5 : Electrochemistry

Lecture 25 : Corrosion

Objectives

After studying this Lecture, you will be able to

- Outline the electrochemical basis for corrosion.
- Illustrate the use Pourbaix diagrams
- Outline the kinetic features involved in the corrosion process
- List the protective measures against corrosion and highlight the mechanisms involved in the protection.

25.1 Introduction

When common metals such as Fe, Cu and Zn are exposed to the environment, the surface of these materials gets deteriorated due to its interaction with the oxygen, moisture and other substances present in the environment. This process is referred to as corrosion. In the case of iron, the process is referred to as rusting. Due to corrosion, the surface of iron gets covered with brownish ferric oxide, Cu gets coated with a green deposit and Zn is covered with a white deposit. About 20% of production of these metals is to make up for the loss of these metals due to corrosion. The need for environmentally friendly technologies to combat corrosion can not be over emphasized.

The process of corrosion has an electrochemical (thermodynamic) basis. The surfaces of metals such as Fe, Cu, contain impurities and lattice defects and are reactive when they come in contact with air, moisture, acidic and or basic environments. One part of the surface acts as the anode of a galvanic cell and oxidation that occurs in this part results in the formation of $\text{Fe}^{2+}/\text{Cu}^{2+}$ ions. These ions go into the solution formed by the condensed water vapour or the acidic / basic fluids which come into contact with this part of the surface. The electrons released in this oxidation $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$, $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ easily travel through the conducting medium of the metal until they come into contact with H^+ of an acidic neighborhood or $\text{O}_2/\text{H}_2\text{O}$ in a neutral or basic neighborhood and react with them. The reactions involved in these reduction processes are

Table 25.1 : Reduction reactions involved in corrosion

Reaction	Nature of the solution	E° / V
$\text{H}^+ + \text{e}^- \rightleftharpoons 1/2 \text{H}_2 (\text{g})$	acidic	0
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	Acidic	1.23
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$	Neutral / basic	0.40

The movement/migrations of ions in the surrounding medium completes the "circuit" consisting of production of cations, electron flow (inside the metallic medium) and ionic movement.

The extent and the rate of corrosion depends on the presence of active sites (usually “rough” surfaces) on the metallic surface and the availability of O_2 on the metallic surface (for the cathodic reduction). Sharp or pointed ends of the metal are known to act as anodic sites. The oxidation and reduction sites can be demonstrated by the use of suitable indicators on the metallic surfaces. When a metal is in contact with another (a second metal) whose oxidation potential is greater, the second metal gets oxidized in preference to the first. Even if different parts of a metal are exposed to different concentrations/pressures of O_2 , the oxidation of the metal occurs in regions of lower concentrations of oxygen.

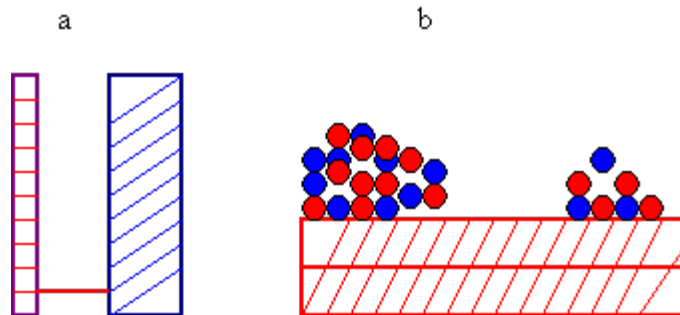


Fig 25.1 a) Two metals in contact, b) Different concentrations of O_2 at different regions of the surface. Some of these aspects will be elaborated and incorporated in the methods for preventing corrosion.

25.2 Pourbaix Diagrams

The electrode potentials of the metal, E and the pH of the surrounding medium are the main factors or parameters that determine the stability of the solid phases and the ionic species produced during redox reactions of metals. When iron metal is exposed to acidic/neutral/basic solutions, several reactions can occur. Some of the reactions involved, their E^0 values (with respect to SHE) and the Nernst equation associated with each of the reactions is given in the following table.

Table 25.2 : Reduction reactions, emfs and Nernst equations for redox processes in corrosion.

Reaction	E^0 / V	Nernst Equation $E = E^0 - (2.303RT / nF) * \log \{ [Products] / [Reactants] \}$
1) $Fe^{2+} + 2e = Fe$	-0.440	$-0.440 + 0.0295 \log [a_{Fe^{2+}}]$
2) $Fe_3O_4 + 8H^+ + 8e^- = 3Fe + 4H_2O$	-0.085	$-0.085 - 0.0591 \text{ pH}$
3) $Fe_3O_4 + 8H^+ + 2e^- = 3Fe^{2+} + 4H_2O$	0.980	$0.980 - 0.2364 \text{ pH} - 0.0886 \log (a_{Fe^{3+}})$
4) $Fe^{3+} + e^- = Fe^{2+}$	0.771	$0.771 + 0.0591 \log (a_{Fe^{3+}} / a_{Fe^{2+}})$
5) $2Fe^{3+} + 3H_2O = Fe_2O_3 + 6H^+$	Use $(a_{H^+})^6 / (a_{Fe^{3+}})^2 = 100$ (This is not an electrode reaction)	$\text{pH} = \{ - \log (a_{Fe^{3+}}) - 1 \} / 3$

We wish to plot the data in the above table as E vs pH (Pourbaix diagrams). These diagrams have wide applications in corrosion, electrodeposition, geological processes and hydrometallurgical extraction. These figures help us to analyze the regions where the metal is immune, where it is passive and where it gets corroded.

For each reaction of Table 25.1, lines can be drawn on E vs pH diagrams. For reaction 1, E depends only on $a_{\text{Fe}^{2+}}$ and not on pH as H^+ ions are not involved in the reaction. For each a Fe^{2+} , the graph is a horizontal line (Fig 25.2a). In reaction 4, no electrons are involved (not an electrode reaction) and we get vertical lines for each value of a Fe^{3+} . Reaction 3 involves E, pH and a Fe^{3+} . This yields sloping lines for a given value of a Fe^{3+} . We get negative slopes because of negative pH terms (H^+ on the left side of the reaction). Reaction 2 gives single sloping lines because E and pH are involved, but not a Fe^{2+} . These lines are shown in fig 25.2 (b). Fig 25.2(b) also indicates the stability of water between the dotted lines.

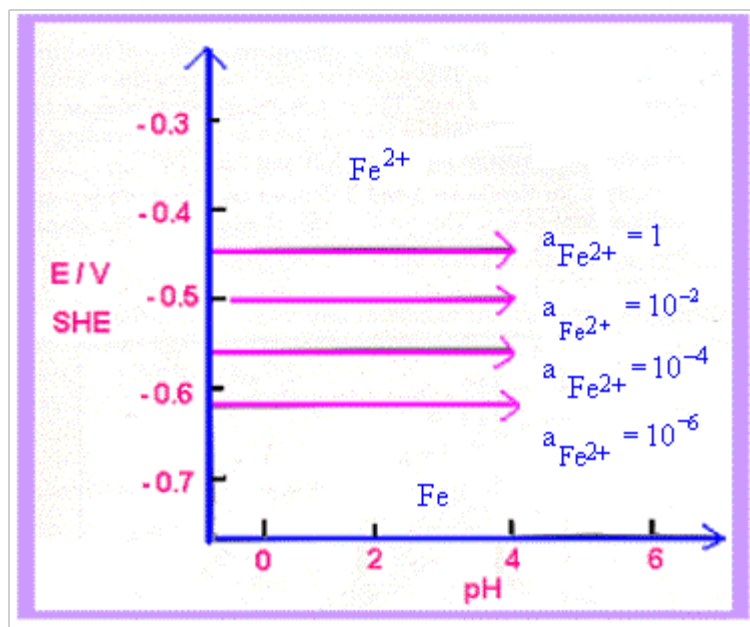
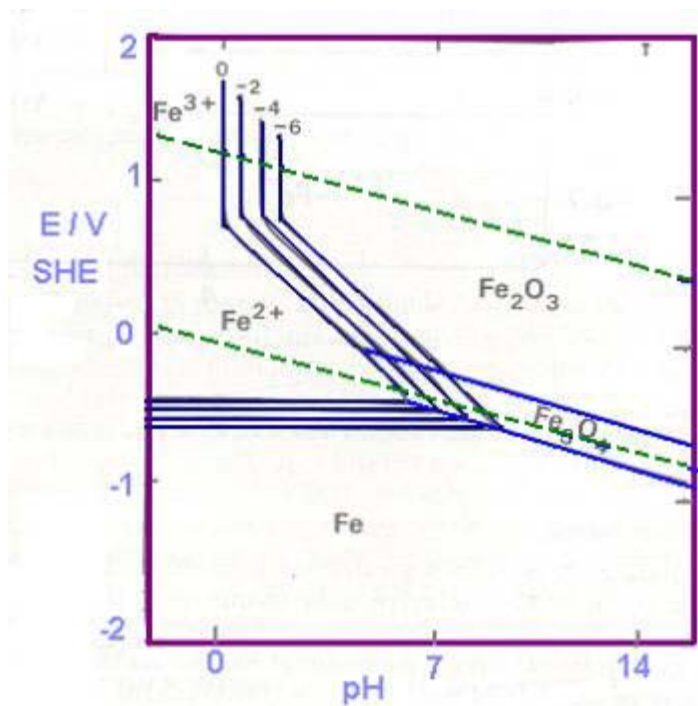


Figure 25.2 a) Potential - pH plots for the equilibrium $\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$ for selected values of $a_{\text{Fe}^{2+}}$



Figures 25.2 (b) Potential - pH plots for the iron water system at 25°C. Domain for the stability of water is bounded by the two bent dotted lines. The labels 0, -2, -4, -6 refer to the concentrations (activities) of ferrous and ferric ions, i.e., -2 refers to $a_{Fe^{2+}} = a_{Fe^{3+}} = 10^{-2}$. Similarly 0 refers to 10^0 , -4 refers to 10^{-4} and -6 refers to 10^{-6} .

Table 25.2 Reactions for the decomposition of water.

Reaction	E^0	Nernst Equation
1) $2H^+ + e = H_2$	0	$E = -0.0591 \text{ pH}$
2) $\frac{1}{2} O_2 + 2H^+ + e^- = H_2O$	1.228	$E = 1.228 - 0.0591 \text{ pH}$

In the region enclosed by the green lines corresponding to reaction 1 (lower dotted line) and reaction 2 (upper dotted line), water is stable. For a combination of pH and potential above the top dotted line, water decomposes evolving oxygen. Below the lower dotted line water decomposes by evolving H_2 . **A widely accepted convention is that a metal is considered to corrode if the activities of ions derived from it (e.g., $a_{Fe^{3+}}$, $a_{Fe^{2+}}$) exceed 10^{-6} .** If the ionic activities/concentrations are less than 10^{-6} , it is considered to be passive. If the ionic concentrations are greater than 10^{-6} and the reaction rates are reasonably fast, these regions correspond to the domain of corrosion. The region of the Pourbaix diagram, wherein the metal can be protected (if the stable species is an insoluble solid which can be made to form an impervious adherent layer covering the metal), it is considered to be immune. The regions of immunity, passivity and corrosivity are shown in fig 25.2c. The limitations of these diagrams are that they do not have any kinetic information, they use an arbitrary value of activity for identifying passivity and that they do not take into account reactions induced or modified by impurities and alloys.

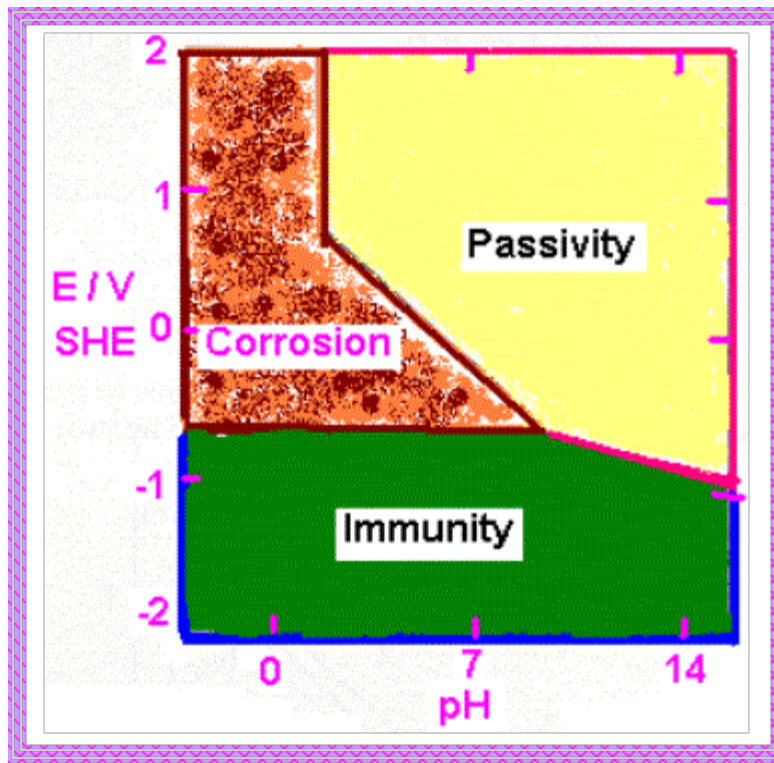


Figure 25.2 c) Pourbaix diagram for the iron water system showing zones of immunity, corrosion and passivity at 25°C.

25.3 Kinetics of corrosion

The degradation of metals and alloys is eventually inevitable and the “prevention” of corrosion mainly deals with slowing down the rate of corrosion. In this section we shall deal with some elementary aspects of corrosion kinetics. The concepts involved herein are overpotential, exchange current density, polarization, corrosion velocities and breakdown of passivity.

The electrode potentials of electrodes that were discussed in the earlier chapters/lectures were the potential differences between a point in the bulk metal of the electrode and a point in the bulk solution in contact with the electrode. When the cell is not in equilibrium and is producing a current (net flow of electrons into the solution or into the electrode), the dynamical processes at the electrode surface become important. Since the solvent surface immediately in contact with the metal is different from the bulk solvent, the charge transfer across a metal surface is an activated process. The rate (k) of charge transfer may be written as

$$k_{\text{charge transfer}} = B \exp \left[- \frac{\Delta G_m^\#}{RT} \right] \quad (25.1)$$

Where B is a coefficient and $\Delta G_m^\#$ is the molar free energy of activation. The net flow of current depends on the difference of the actual electrode potential ($\Delta \phi$) and the equilibrium electrode potential $\Delta \phi_e$, denoted by η (called overpotential). (In this section, we shall only emphasize these aspects which are necessary to understand the concept of corrosion current)

$$\eta = \Delta \phi - \Delta \phi_e \quad (25.2)$$

Larger the overpotential, larger the current density j , which measures the number of charges (electrons) transferred at the electrode per unit area per unit time. The anodic and the cathodic current densities (J_a and J_b) can be written as

$$J_a = F B_a \exp \left(- \frac{\Delta G_{m,a}^\#}{RT} \right) \exp \left\{ (1 - \alpha) F \frac{\Delta \phi}{RT} \right\} \quad (25.3)$$

$$J_c = F B_c \exp \left(- \frac{\Delta G^\#_{m, c}}{RT} \right) \exp \left\{ \alpha F \frac{\Delta \phi}{RT} \right\} \quad (25.4)$$

and the net current density $J = J_a - J_c$ is given by the Butler volmer equation shown below . The value of α , the transfer coefficient, is usually $\frac{1}{2}$. Here, F is the Farady constant and $\Delta G^\#_{m, a}$ and $\Delta G^\#_{m, c}$ are the activation energies for the anodic and cathodic current densities respectively. The equations (25.3) and (25.4) indicate that current densities result from activated processes. Free energy of activation and overpotential determine the current densities and our emphasis in this section are not these mathematical expressions but the relation between current density and over voltage (Figure 25.3). The total current density is given by

$$J = J_a - J_c = J_0 \left\{ e^{(1-\alpha) \frac{\eta F}{RT}} - e^{-\alpha \frac{\eta F}{RT}} \right\} \quad (25.5)$$

J_0 is called the exchange current density and it is the extrapolated value (at either of the electrodes) of J_a or J_b vs η when $\eta \rightarrow 0$. For small over potentials $J = J_0 \frac{\eta F}{RT}$. This shows that current density is proportional to the overpotential for small values of the overpotentials. Dynamic electrochemistry is quite complex and we have given here some of the most basic equations to introduce you to this subject which is of great technological importance. You may refer to reference books for further details.

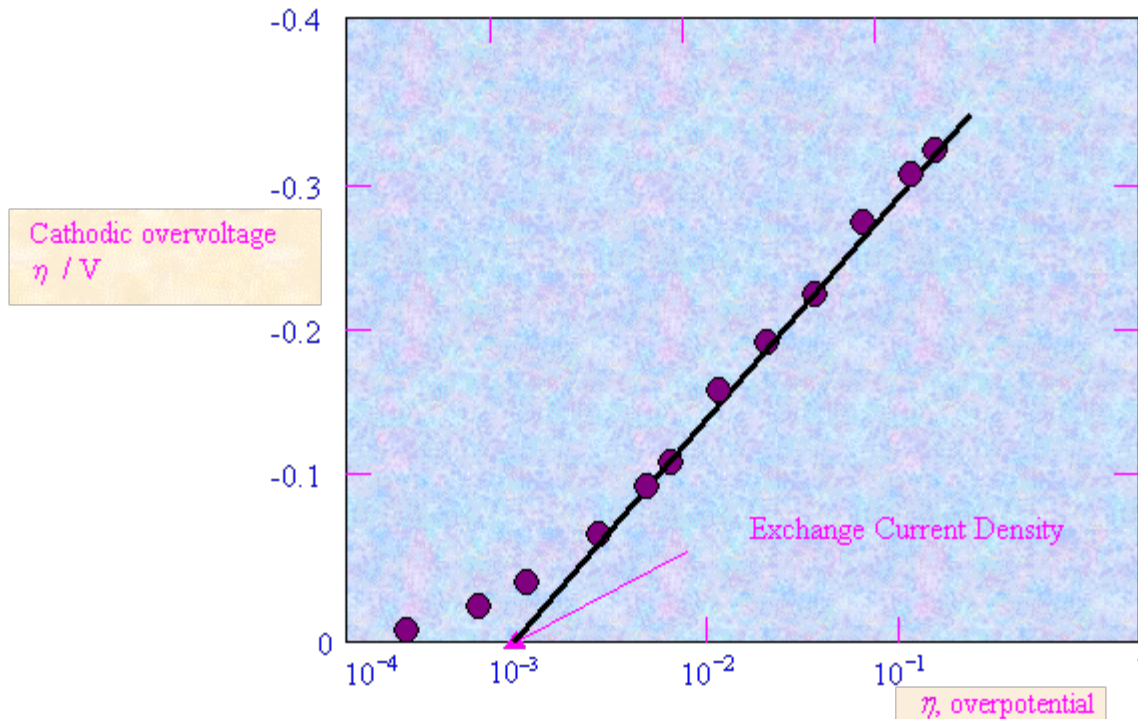


Figure 25.3 Overpotential vs current density (J/cm^{-2}). This is called the Tafel plot. The process studied is hydrogen evolution on platinum in a 0.1 M hydrochloric acid at 25°C .

The kinetics of corrosion is measured by the corrosion current I_{corr} . The final expression for the corrosion current is

$$I_{\text{corr}} = A J_0 \exp \left(\frac{\eta F}{4RT} \right) \quad (25.6)$$

where A and J_0 are the geometric means of the areas and the exchange current densities in the anodic and cathodic regions respectively.

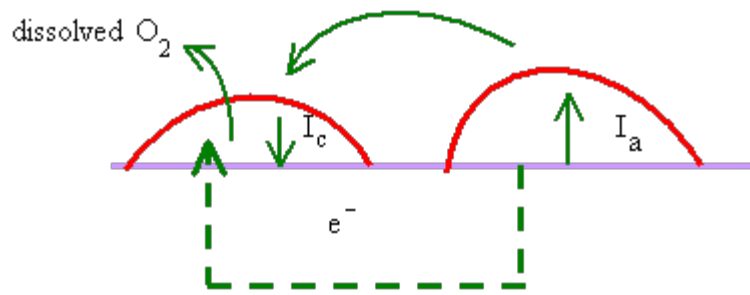


Figure 25.4 Figure showing anodic and cathodic currents.

Anodic reaction $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathodic reactions: (a) $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$, (b) $4\text{H}^+ + \text{O}_2 + 4\text{e}^- = 2\text{H}_2\text{O}$

It is seen that larger the values of A , J_0 and η , faster the corrosion rate. Even if the emf is smaller, the process with larger J_0 will occur more rapidly. E.g., the J_0 for reaction (a) in the figure is $10^{-6} \text{ A cm}^{-2}$ and for (b) it is $10^{-14} \text{ A cm}^{-2}$ and kinetically, the hydrogen evolution dominates the corrosion process.

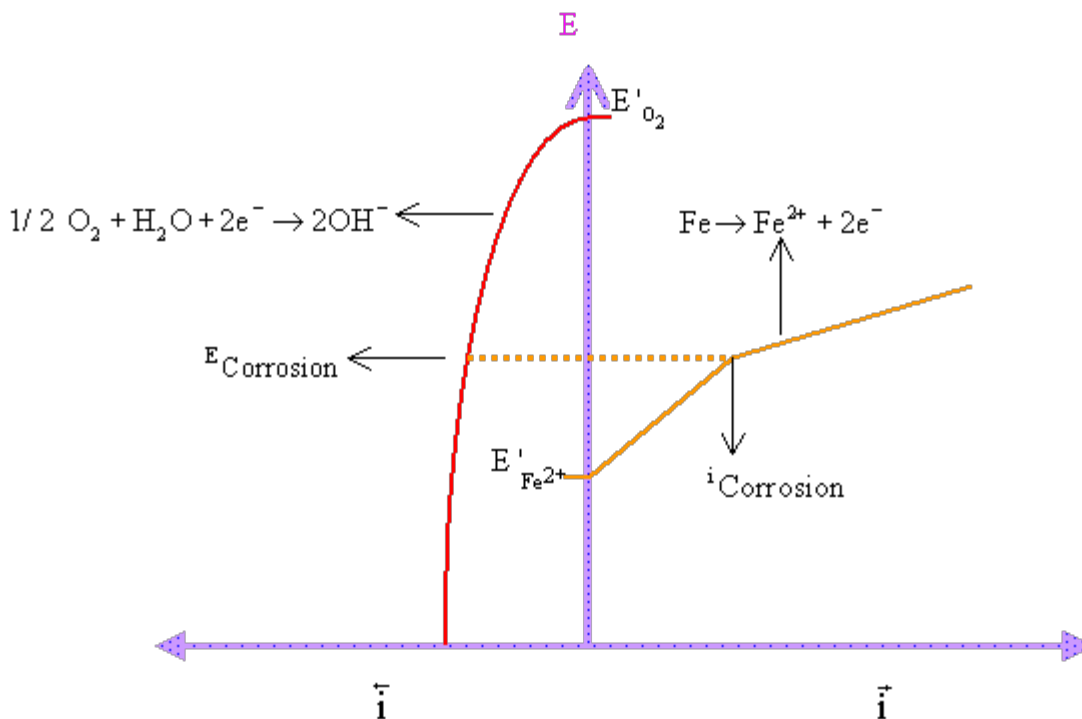


Figure 25.5 Corrosion velocity diagram. In the figure, \vec{i}^+ refers to anodic current density and \vec{i}^- refers to cathodic current density. This figure is for iron being corroded by aerated water. At the corrosion potential, the total anodic current is equal to the total cathodic current.

A corrosion velocity diagram graphically indicates the regions of the corrosion potentials ($E_{\text{corrosion}}$) (at which the anodic and cathodic currents are equal) and the values of corrosion currents ($I_{\text{corrosion}} = I_{\text{anodic}}$).

25.4 Prevention of Corrosion

Billions of tons of iron products and other metallic products are produced every year. Prevention of corrosion through protective coatings of polymer films, coating with other metals (galvanizing), passivation (by an adhering oxide layer), cathodic protection, use of sacrificial anodes, and so on, constitute a “mini” industry in itself. We will outline the principles involved in these processes.

a) Paint Coatings :

Paints obstruct the mechanisms that sustain corrosion and provide protection against mechanical forces as well as natural ultraviolet radiation. They also provide aesthetically pleasing coloured and glossy appearances. The major components of paints are the binding media (that control the physical and chemical properties of hardened coating), pigments (insoluble filters ground and mixed with binding media) and solvent for application on the metal surface. The binding media have structural units that contain functional groups that can be used for linear as well as cross linking of the chains. The common ones are alkyd resins (polyesters), amino resins (urea or melamine) with formaldehyde and epoxy resins (whose structural units contain hydroxyl and epoxide groups at two ends). Typical pigments (of particle size range of 0.1 to 50 μ m) are white pigments (containing TiO_2), black pigments (carbon black), red pigments (Fe(III) oxide), yellow pigments (hydrated Fe(III) oxide) and inhibiting pigments (Pb_3O_4 , CaPbO_3 , ZnCrO_4 and metallic zinc dust). Common solvents are white spirit, toluene, xylene, alcohols, ketones, esters as well as water for solubilization of especially cationic species. If the paint comes off or has defects, the consequences will be disastrous.

b) Galvanizing:

Galvanizing iron is done by coating its surface with zinc. The electrode potential of zinc is -0.76 V which is more negative than Fe/Fe^{2+} (-0.44 V). Therefore, oxidation of zinc is thermodynamically more favoured than that of Fe. Fe survives over Zn and zinc too survives as it gets coated with a protective layer of a hydrated oxide. Tin can not be used as a galvanizing material as its reduction potential (-0.14 V) is higher and if the tin surface is scratched, it oxidizes iron and corrodes it. Protective layers of oxides protect the metal surface, especially in the case of Al where the reduction potential is very low, -1.66 V. This is also a form of passivation. We can use the Pourbaix diagram to find out the most suitable conditions for electrodepositing Ni on metal surfaces. The pH range of 4.2 to 6 is most suitable. At lower pH, there is too much hydrogen evolution and at higher pH, $\text{Ni}(\text{OH})_2$ gets incorporated into the deposit.

c) Cathodic Protection:

In this method, corrosion of a metal is prevented by a constant supply of electrons and the reduction of oxygen is carried out by electrons provided by a sacrificial anode. E.g., magnesium whose reduction potential is -2.36 V. When a Mg rod is connected to Fe, Mg gets oxidized to Mg^{2+} without affecting Fe. Although Mg is more expensive than Fe, it is used as a sacrificial anode in ships, buildings, etc which are more "valuable" than the loss caused by the corrosion of the sacrificial anode.

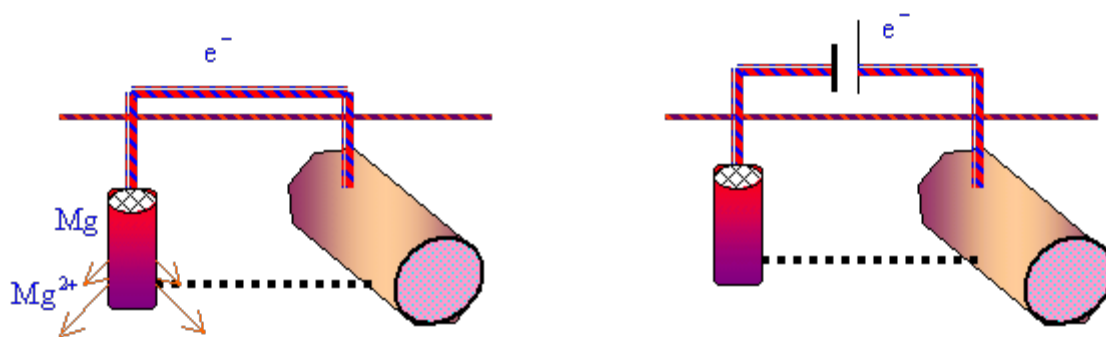


Figure 25.6 a) Cathodic protection by sacrificial cathode, b) Cathodic protection by impressed current

d) Cathodic protection by impressed current :

If the surface of the metal is kept at a more negative potential than the equilibrium value by impressing a current at its surface by a DC supply, then, the electrons required for reducing the O_2 of surrounding air or water are supplied by this generator or rectifier, preventing Fe from going into solution as Fe^{2+} . For this purpose, current is supplied to the Fe metal by inert anodes mounted on the surface. The choice between methods (c) and (d) is determined by costs and maneuverability. In food processing wherein contamination by sacrificial anode can not be tolerated, and in ocean going ships and pipe-lines, impressed current protection is favoured over cathodic protection.

25.5 Problems

25.1) Verify the Nernst equations given in the third column of table 25.2.

25.2) Rationalize the slopes of the curves of figures 25.1 (a) and (b).

25.3) What is the difference between passivity and immunity in systems undergoing corrosion?

25.4) Define overvoltage and exchange current density. What are the physical reasons for the existence of overvoltage?

25.5) How is the electrochemical circuit completed in a corrosion process?

25.6) What do we learn from corrosion velocity diagram?

25.7) What are the advantages and drawbacks of Pourbaix diagrams?

25.8) In addition to the standard methods for the prevention of corrosion, can you think of some new alternatives?

Recap

In this Lecture you have learnt the following

Summary :

In this lecture, you have been introduced to the thermodynamics and kinetics of corrosion and also to some of the common methods for preventing corrosion. Due to the constant contact of the metal surfaces with the environment and due to the fluctuating differences in the electrode potentials at various regions of the metal surface, regions of low reduction potentials readily get oxidized. The metal easily provides mobility to the electrons which move around until they can reduce H^+ or O_2 . The plots of E vs pH (Pourbaix diagrams) have wide applications in corrosion, electrodeposition, geological processes and hydrometallurgical extraction. These diagrams help us to analyze the regions where the metal is immune, where it is passive and where it gets corroded.

The kinetics of corrosion is governed by overpotentials, exchange current densities and corrosion currents. Prevention of corrosion is commonly achieved by protective coatings of polymer films, coating with other metals /galvanizing, passivation (by an adhering oxide layer), cathodic protection and the use of sacrificial anodes.