

# **Corrosion and Its Control**

**"Civilizations, like empire, fall not so much because of the strength of the enemy outside as through the weakness and decay within"**

## **INTRODUCTION**

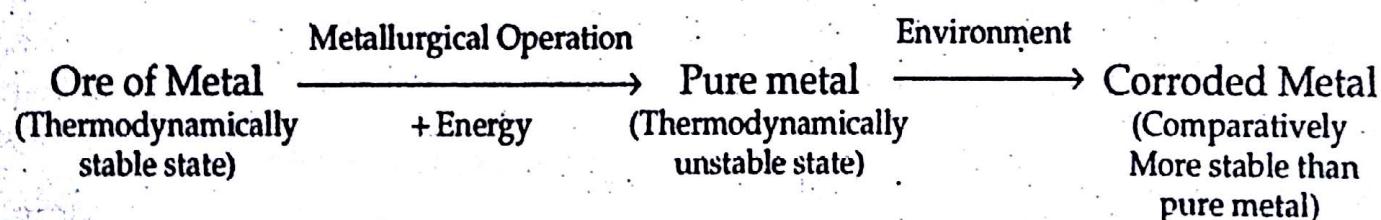
### **1.1 Corrosion**

**Corrosion** is the process of gradual deterioration of a metal from its surface due to the unwanted chemical or electrochemical interaction of metal with its environment.

For example, formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron, also known as "rusting of iron".

### **1.2 Cause of Corrosion**

Metals exist in nature in the form of oxides, sulphides, sulphates and carbonates. These chemically combined states of metal known as 'ore' has low energy and is thus thermodynamically stable state for metal. A considerable amount of energy is required during metallurgy. The extracted metal (in the isolated form) has higher energy and thus it is thermodynamically unstable state. Thus it is the natural tendency of metal to go back to the thermodynamically stable state. Metals do this by interacting chemically or electrochemically with their environment to form surface compound and thus undergo corrosion.



Although corroded metal is thermodynamically more stable than pure metal but due to corrosion useful properties of a metal such as malleability, ductility and electrical conductivity are lost.

### **1.3 Effects of Corrosion**

Effects of corrosion are briefly given below :

- (a) Loss of useful properties of metal and thus loss of efficiency,
- (b) Decrease in production rate, because efficiency is less and replacement of corroded equipment is time-consuming,
- (c) Increase in maintenance and production cost, and
- (d) Contamination of product.

## 2 TYPES AND MECHANISM OF CORROSION

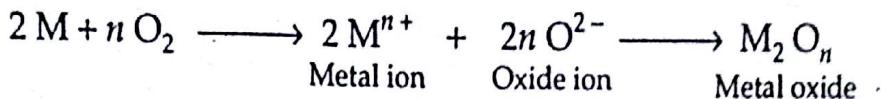
### 2.1 Chemical or Dry Corrosion

When metal surface is in immediate proximity to atmospheric gases or anhydrous liquid, a direct chemical interaction between the two leads to *chemical or dry corrosion*. It is of following three types :

#### (a) Corrosion by O<sub>2</sub> (Oxidation Corrosion)

*only name*

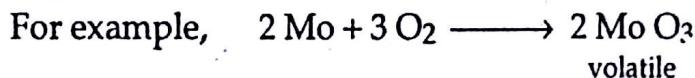
It generally takes place in absence of moisture via



At low temperatures, alkali and alkaline earth metals are oxidised and at high temperatures, except Ag, Au and Pt, all other metals get oxidised.

A thin layer of oxide formed at the surface of metal can be

- (i) **stable**, impervious and tightly-adhering, like the oxide films on Cu or Al, it acts as a protective coating and thus further corrosion is prevented.
- (ii) **unstable** and decomposes back to metal and oxygen. That's why Ag, Au and Pt do not undergo oxidation corrosion.
- (iii) **Volatile**, the moment it is formed it gets volatilized and metal surface again gets exposed for further attack leading to continuous and rapid corrosion.



Hence Mo undergoes excessive corrosion.

- (iv) **Porous**, hence further attack through cracks or pores continues and hence the corrosion continues till the entire metal is converted to metal oxide.

#### Pilling-Bedworth rule

The smaller the specific volume ratio  $\left( = \frac{\text{volume of metal oxide}}{\text{volume of metal}} \right)$ , greater is the oxidation corrosion, because oxide film formed will be porous, through which oxygen can diffuse and bring about further corrosion.

For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently, the rate of corrosion of W is least, even at higher temperatures.

(I) volume of the oxide  $\geq$  volume of the parent metal  $\Rightarrow$  non-porous or

(II) Volume of the oxide  $<$  volume of the parent metal, oxide layer faces stress and strains and hence cracks and pores develop in its structure.

Consequently, rate of oxidation and thus oxidation corrosion decreases to zero in case (I) and rapidly increases in case (II).

Examples of metals which follow case (I) are Al or Cu and

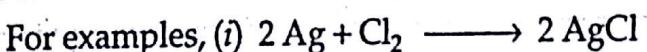
Examples of metals which follow case (II) are Li, Na, K and Mg.

### Mechanism of Oxidation Corrosion

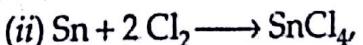
Metal gets oxidized ( $M \longrightarrow M^{n+} + ne^-$ ) and electrons so released lead to the reduction of  $O_2$  ( $\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$ ). Formation of metal oxide ( $M_2 O_n$ ) takes place at the point of meeting of  $M^{n+}$  and  $O^{2-}$ . The resulting metal oxide scale forms a barrier to restrict further oxidation. As the size of  $M^{n+}$  is much smaller than that of  $O^{2-}$ , hence faster outward diffusion of metal through the scale leads to continuation of oxidation, provided metal oxide barrier is sufficiently porous. It is to be noted that slow inward diffusion of  $O^{2-}$  through scale also takes place because size of  $O^{2-}$  is large and hence its mobility is also less.

#### (b) Corrosion by other gases *name only*

Depending on the chemical affinity between metal and gas and the formation of protective or non-protective layer on metal surface, some gases like  $Cl_2$ ,  $H_2 S$  etc. exert corrosive effect to different extent.



$AgCl$  film is protective and thus protects the metal from further attack of chlorine on silver.



$SnCl_4$  film is volatile and hence Sn undergoes excessive corrosion.

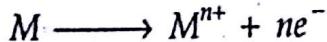
#### (c) Liquid metal Corrosion *name only*

Liquid metal corrosion occurs when liquid metal is allowed to flow over solid metal at high temperature. It leads to weakening of the solid metal due to (i) its dissolution in liquid metal or (ii) penetration of liquid metal into solid metal. For example, coolant (Sodium metal) leads to corrosion of cadmium in nuclear reactor.

**Example 1. Discuss Wagner's theory of oxidation of metals.**

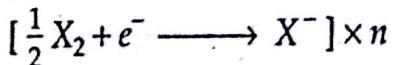
**Solution. Wagner's theory of oxidation of metals :** The oxidation of metals is electrolytic in nature and the rate of oxidation is determined by the electrical properties of the corrosion product. According to Wagner, the steps of the overall oxidation reaction may be visualized as :

**Step 1. Oxidation of the metal (at the anode),**



**Step 2. The electrons liberated in step 1 are transported to the cathode.**

**Step 3. Combination between the electrons and the oxidant,**



**Step 4. Transport of cations to the cathode and anions to the anode to form the compound.**

*The growth of an oxide film can occur as follows :*

Oxides of metals usually form ionic lattices and through this lattice :

- (a) metal ions may migrate outwards ;
- (b) oxide ions may migrate inwards ;
- (c) both processes (a) and (b) may occur simultaneously ; and
- (d) molecular oxygen may penetrate to the metal-oxide interface.

**Solution.** The improved corrosion resistance of iron alloyed with chromium is due to a film of oxide, rich in  $\text{Cr}_2\text{O}_3$ , formed in contact with the metal surface. This oxide film has more affinity for oxygen than the host metal.

Similar is the case of alloys of iron with Al. The Al - O bond in aluminium oxide is strong enough to prevent the diffusion of  $\text{Al}^{3+}$  ions through the oxide layer to the surface. Moreover, the structure of the oxide and the metal match so well that the oxide layer is coherent. This explains the protective action of the oxide layer in the case of aluminium.

**Example 5.** Summarize the various laws of oxidation and give examples of metals which obey such laws.

**Solution.** On the metallic surfaces, the growth of an oxide film or scale appears to follow three growth laws, viz.

- (i) a parabolic law ;
- (ii) a linear law, and
- (iii) a logarithmic law.

These laws describe how the thickness of the oxide film varies with time. These laws are briefly summarized below :

*(i) The Parabolic law of oxidation.*

In the sequence of reactions leading to formation of the oxide, if the rate of diffusion of ions through the lattice is the slow step, then the oxidation rate will decrease as the thickness ( $x$ ) of the film increases.

Suppose, the thickness of the film increases by  $dx$  in a time  $dt$ , then the rate of growth is  $dx/dt$ .

In the present case, the rate of growth varies inversely as the thickness, i.e.,

$$dx/dt \propto \frac{1}{x}.$$

This can be solved to give an equation  $x^2 = 2k_1 t$  where  $k_1$  is a diffusion coefficient. From the above equation, if we plot  $x$  against  $t$ , we get a parabola. That's why, this is called as the *parabolic law of oxidation*.

Examples of metals which obey this law are : Co, Fe, Cr, Ni, Cu and alkaline earth metals at elevated temperatures.

*(ii) The linear law.*

When the oxidation rate is constant, i.e.,  $\frac{dx}{dt} = k_2$

$$\text{or } x = k_2 t + \text{constant},$$

oxidation is said to follow the *linear law*.

In this type of oxidation, a very thin protective layer of oxide is probably formed first which maintains constant thickness, being renewed as fast as it breaks down. The film formation and subsequent rupture takes place again and again.

The alkali metals obey this linear law.

*(iii) The logarithmic law.*

It is represented as  $x = k_3 \log(at + 1)$  where  $k_3$  and  $a$  are constants dependent on the temperature and the type of metal.

Metals like Al, Cr, Zn and Be appear to follow this logarithmic law.

**Example 6.** What are the various scales that appear on the surface of iron heated above 575°C ? How is this scale formation useful ?

**Solution.** The iron heated above 575°C is covered with a scale consisting of three layers, as shown below :

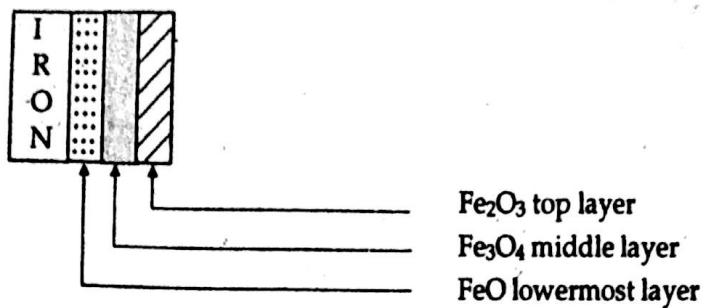


Fig. 3.

The presence of  $\text{FeO}$  in the scale formed at higher temperatures makes the descaling of iron fairly easy. This can be done by pickling in acids, as it decomposes readily into  $\text{Fe}$  and  $\text{Fe}_2\text{O}_4$ .

In contrast, the scales formed at lower temperatures are not easily removed because of the absence of  $\text{FeO}$  layers.

## 2.2 Electrochemical or Wet Corrosion

It takes place mostly under wet or moist conditions through the formation of short-circuited galvanic cells. Wet corrosion is more common than dry corrosion. Electrochemical corrosion involves :

- (i) Separate 'anodic' and 'cathodic' parts/areas between which current flows through the conducting medium.
- (ii) Occurrence of oxidation (corrosion) at anodic areas which generates metallic ions,
- (iii) Non-metallic ions like  $\text{OH}^-$  or  $\text{O}^{2-}$  are formed at cathodic areas, and
- (iv) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

For example, Rusting of iron in neutral aqueous solution of electrolyte in the presence of  $\text{O}_2$  or in acidic environments with the evolution of hydrogen.

$\text{Fe}^{2+}$  ions originate at anode and  $\text{OH}^-$  ions originate from cathode. Smaller  $\text{Fe}^{2+}$  ions diffuse more rapidly than the larger  $\text{OH}^-$  ions, so corrosion occurs at the anode, but rust is deposited near cathode.

The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions such as

- (i) *Oxygen absorption.* In the presence of dissolved oxygen
  - (a) in acidic medium :  $4 \text{H}^+ + \text{O}_2 + 4 e^- \rightarrow 2 \text{H}_2\text{O}$
  - (b) in neutral or weakly alkaline medium :  $2 \text{H}_2\text{O} + \text{O}_2 + 4 e^- \rightarrow 4 \text{OH}^-$
- (ii) *Hydrogen evolution.* In the absence of  $\text{O}_2$ 
  - (a) in acidic medium  $2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2$
  - (b) in neutral or alkaline medium :  $2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^-$

(iii) **Electroplating.** At the cathode, metal ions collect the electrons and get deposited on the cathode surface.



### 2.3 Comparison of Chemical Corrosion with Electrochemical Corrosion

S.No.	Chemical Corrosion	Electrochemical Corrosion
1.	It occurs in dry condition.	It occurs in wet condition (in the presence of electrolyte or moisture)
2.	It involves the direct chemical attack of the metal by environment.	It involves the setting up of a large number of galvanic cells.
3.	It is explained by absorption mechanism.	It is explained by mechanism of electrochemical reactions.
4.	It occurs on both homogeneous and heterogeneous surfaces.	It occurs only on heterogeneous metal surface.
5.	Corrosion is uniform.	Corrosion is not uniform, if the anode area is small, pitting is more frequent.
6.	It is a slow process.	It is a fast process.
7.	Corrosion products accumulate at the same place where corrosion occurs.	Corrosion occurs at the anode, but products accumulate near the cathode.

**Example 1.** What are the various factors that contribute to the rusting of iron?

**Solution.** The various factors which contribute to the rusting of iron are summarized below :

- Both oxygen and water are essential for rusting (This is because iron will not rust in dry air or in water that is completely free from oxygen).
- The rust formation is also accelerated by
  - (i) the presence of acids and electrolytes ;
  - (ii) the contact with less reactive metals like copper and
  - (iii) rust itself.

### 2.4 The Types of Electrochemical Corrosions

#### 2.4.1 Galvanic Corrosion

It takes place when different metals are in contact and jointly exposed to corrosive atmosphere. The metal which is higher up in the electrochemical series, with more negative electrode potential will form anode and undergo corrosion. For examples, Zn and Cu ; Zn and Ag ; Fe and Cu constitute galvanic couples.

In the Zn-Cu galvanic cell, Zn behaves as anode where oxidation and corrosion occurs and Cu behaves as cathode and is protected.

Galvanic corrosion can be minimised by

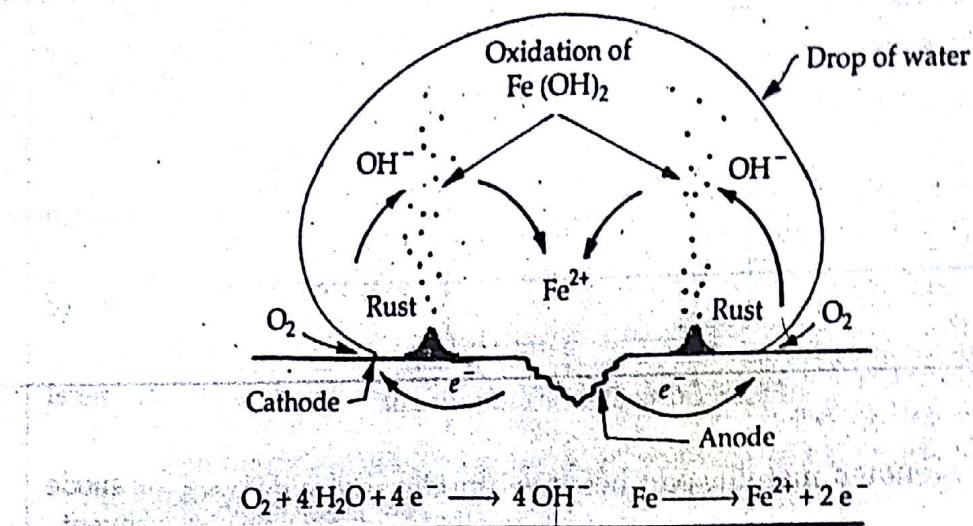
- (i) Avoiding galvanic couple,
- (ii) Providing an insulating material between the two metals.

**Example 1.** Differential metal corrosion (DMC) is also known as galvanic corrosion. True or false ?

**Solution.** True

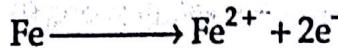
#### 2.4.2 Pitting Corrosion

Consider a drop of water resting on the surface of metal. The metal surface which is covered by the drop has low oxygen concentration ( $[O_2]$ ) and thus acts as an anode and suffers corrosion, the uncovered metal surface, due to high  $[O_2]$  acts as cathode.

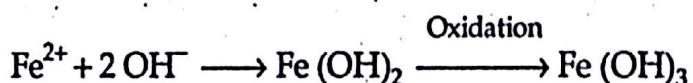
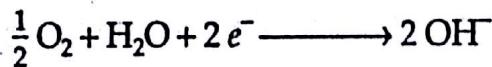


**Fig. 4. Pitting Corrosion.**

At anode :



At cathode :

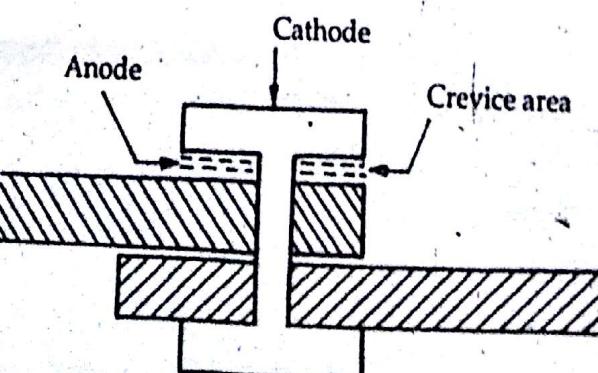


Formation of small anodic and large cathodic areas set up differences of potential at localised spots to pit, this produces corrosion current. Pitting corrosion is a non-uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin-holes in the metal. Once a small pit is formed, the rate of corrosion will be increased.

#### 2.4.3 Crevice Corrosion

Consider a crevice between different metallic objects, e.g., bolts, nuts, rivets, etc., in contact with liquids.

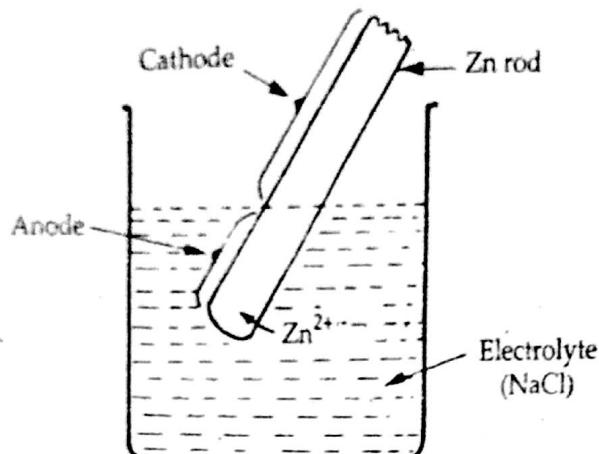
Crevice area has lack of oxygen, and thus becomes anodic region. The exposed areas act as the cathode. Corrosion takes place at anode. Crevice corrosion is thus accelerated attack at the junction of two metals exposed to a corrosive environment.



**Fig. 5. Crevice corrosion**

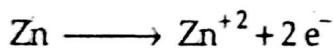
#### **2.4.4 Concentration cell corrosion or Differential aeration corrosion**

It occurs when a metallic surface is partially immersed in an electrolyte and partially exposed to air.



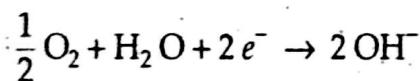
**Fig. 6. Concentration cell corrosion.**

Poorly oxygenated metallic part becomes anodic and undergoes oxidation.



Well oxygenated part becomes cathodic.

At the cathode,  $\text{O}_2$  takes up electrons to form  $\text{OH}^-$  ions.



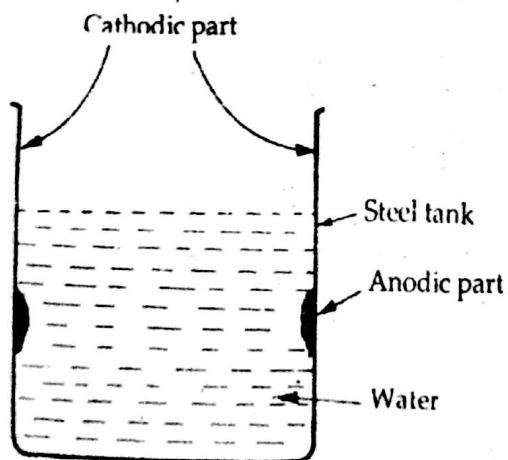
The  $\text{Zn}^{+2}$  and  $\text{OH}^-$  ions interact to give  $\text{Zn}(\text{OH})_2$

Thus, corrosion occurs at anode.

#### **2.4.5 Water-line Corrosion**

The concentration of  $\text{O}_2$  above the water surface is greater than that under the surface, when water is stagnant in a steel tank. This generates an oxygen concentration cell. In this cell the metal just above the water level is cathodic w.r.t. the metal below the water level.

Corrosion occurs at the anodic part, the metal just below the water level. The cathodic area is completely unaffected by corrosion.



**Fig. 7. Water-line corrosion**

(iii) Compared to Fe ; stainless steel, Al and Ni are able to withstand the corrosive action of the atmosphere due to the protective action of the oxide films on their surfaces.

(It is to be noted that, in highly industrialized and urban atmospheres, these Al, Ni and stainless steel are also corroded).

**Example 2. Summarize the various factors for Soil corrosion.**

**Solution.** (i) Soils having high porosity have high corrosivity. This is due to greater degree of aeration,

(ii) Soils having low electrical resistivity (specific resistance) have high corrosivity. This is due to the presence of moisture and dissolved electrolytes.

(iii) At greater depths, the corrosion rate also depends on the diffusion of dissolved oxygen in soil water and sometimes on sulphate-reducing bacteria.

**Example 3. What is stray-current corrosion ?**

**Solution.** Electric current from electric traction systems such as electric trains can leak into adjacent conducting structures. The point at which the current leaves the structure is the seat of corrosion as it is anodic. This is known as stray-current corrosion and is aided by dissolved electrolytes. This corrosion can lead to pitting and serious damage to underground structures.

**Example 4. Oil, gas and water are transported through cast-iron pipelines buried underground. (i) How these cast-iron pipelines get corroded ? (ii) Discuss some prevention methods.**

**Solution.** (i) Underground corrosion is possible. Graphitic corrosion of cast iron is believed to be due to

- (a) Anaerobic microbiological corrosion of iron,
- (b) Stray-current corrosion and
- (c) Electrochemical action in which the ferrite of the cast iron is anode and graphite is the cathode.

(ii) Microbiological corrosion is avoided by choosing a location where the soil is well aerated, and avoiding water-logged and clayey locations.

Bituminous materials are extensively used for coating metals to be used for underground usage. This coating is reinforced with fiberglass cloth over which another bituminous coating is applied.

### **3 / PASSIVITY OR PASSIVATION**

**Passivation** is the phenomenon by which a metal or alloy shows high corrosion resistance due to the formation of a highly protective, very thin (about 0.0004 mm thick) and quite invisible surface film.

Passivation of metal takes place only in certain environments, which tend to maintain protective film on the surface. For example, Ti, Cr, Al and Cr containing stainless steel alloys exhibit outstanding corrosion resistance in the presence of oxygen. This is due to the formation of thin, protective oxide film on their surfaces. Whenever any damage occurs, this film is automatically repaired in oxidising environments. But in reducing environments, the passive metals and alloys become chemically active and are rapidly corroded.

**Examples :** Aluminium is not attacked by dilute HNO<sub>3</sub>, but iron gets rapidly corroded even by dilute HNO<sub>3</sub>. In contrast, stainless steel, due to the presence of Cr in it, maintains protective oxide film so exhibits high corrosion resistance in HNO<sub>3</sub> solution over a wide range of concentrations.

#### 4 GALVANIC SERIES

Passivation makes effective electrode potentials of some metals more positive so they act cathodic and exhibit noble behaviour. This behaviour is exactly opposite to that predicted by the *electrochemical series*. Consequently, a more practical series, called *galvanic series* have been prepared which gives real and useful information regarding the corrosion behaviour of metals and alloys in a given environment.

##### *Galvanic series :*

Mg, Mg alloys, Zn, Al, Cd, Mild steel, Cast iron, Solder, Pb, Sn,

Anodic  
(Easily corroded)

Brass,  
Cu,  
Ni,

Cathodic (Protected)

Pt, Au, Ti, Ag, Cr, Stainless steel

The following points should be noted regarding galvanic series :

*Galvanic series* predicts the corrosion tendencies of both metals and non-metals in actual environments. But *electrochemical series* predicts the relative displacement tendencies of metals and non-metals in electrolytes containing particular concentrations of salts of the same metal that was being studied. In Galvanic series, electrode potentials are measured by using calomel electrode as reference electrode. In contrast, in electrochemical series, electrode potentials are measured by using standard hydrogen electrode as reference electrode. In galvanic series, the position of metal alloy is different than that of pure metal.

#### 5 FACTORS INFLUENCING CORROSION

Rate and Extent of Corrosion Depends on

S. No.	Nature of the metal	Nature of the environment
1.	Purity of metal,	Temperature,
2.	Physical state of the metal,	Humidity,
3.	Nature of the oxide film,	Effect of pH,
4.	Position in the Galvanic series,	Nature of electrolyte,
5.	Relative areas of the anode and cathode	Conductance of the corroding medium,
6.	Solubilities of the product of corrosion,	Formation of oxygen concentration cell,
7.	Volatility of corrosion products,	Presence of suspended particles in atmosphere , Presence of impurities in atmosphere

##### **5.1 Nature of the Metal**

Let us discuss first, how rate and extent of corrosion depends on the nature of the metal :

(i) *Purity of metal*. Lesser is the percentage purity of a metal, faster is the rate of corrosion. For example, in the case of Zinc metal

% Purity	99.999	99.99	99.95	99.0
Corrosion rate	1	2650	5000	7,200

(vi) *Presence of impurities in atmosphere.* Corrosion of metals is more in areas near to the industry and sea. This is due to the fact that corrosive gases like  $H_2S$ ,  $SO_2$ ,  $CO_2$  and fumes of  $H_2SO_4$  and  $HCl$  in industrial areas and  $NaCl$  of sea water leads to increased conductivity of the liquid layer in contact with the metal surface, thereby increase the corrosion rate.

(vii) *Presence of suspended particles in atmosphere.* Atmospheric suspended particles can be classified into two types :

- (a) Active like  $NaCl$ ,  $(NH_4)_2SO_4$  etc. and
- (b) Inactive like charcoal.

Suspended particles of type (a) enhance atmospheric corrosion because they absorb moisture and act as strong electrolytes.

Suspended particles of type (b) also slowly enhance corrosion rate because they can absorb moisture and sulphur gases although they are not electrolytes hence by their own cannot increase the conductivity of the medium.

## 6 PROTECTIVE MEASURES AGAINST CORROSION

The methods used to protect a metal from corrosion mainly operate by preventing corrosion reactions from taking place. One of the best ways of doing this is to protect the metal from water and oxygen.

The various protective measures include modification of the environment ; modification of the properties of the metal ; use of protective coatings and cathodic protection.

Before protecting measures are adopted, the metal should be cleaned or 'descaled' by degreasing and descaling.

Oily and greasy surface films are dissolved out by exposure to trichloroethylene  $\left( \begin{array}{c} H \\ | \\ Cl-C=C-Cl \\ | \\ Cl \end{array} \right)$ , tetrachloroethylene  $\left( \begin{array}{c} Cl \\ | \\ Cl-C=C-Cl \\ | \\ Cl \end{array} \right)$  and other volatile organic solvents.

Mechanical or chemical methods can be used for Descaling.

The various protective measures are summarized below :

### 6.1 Modification of the Environment

In this category, the metals are protected from corrosion either by removal of corrosion stimulants or by the use of inhibitors (*i.e.*, the substances which effectively decrease the corrosion rate).

These are briefly discussed below :

(a) *Removal of corrosion stimulants.*

- To prevent corrosion due to the oxygen, dissolved oxygen from water is removed by physical or chemical means. Either Deaeration is done or reducing substances are added like  $N_2H_4$ ,  $Na_2SO_3$  etc.
- To prevent corrosion by acids, they are neutralized with lime.
- To prevent corrosion by salts, they are removed by using ion-exchange resins,
- To prevent corrosion by moisture, moisture from air is removed by dehumidification using silica gel.

(b) Use of corrosion inhibitors. Inhibitors are inorganic or organic substances which when added to the environment are able to reduce the rate of corrosion.

For the proper selection of inhibitors, Evans polarization diagrams are quite helpful. These are discussed below :

### 6.1.1 Evans Polarization Diagrams

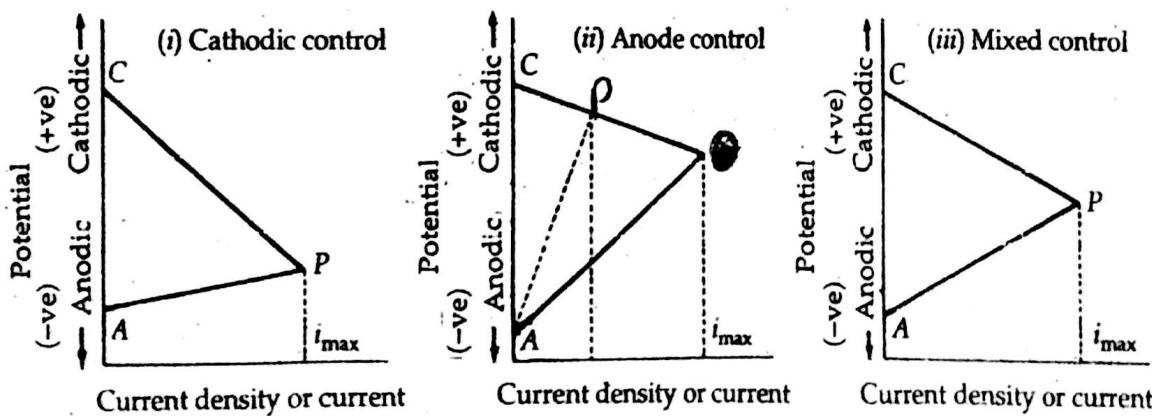
Either the anodic or the cathodic reaction rate principally governs the overall rate of electrochemical corrosion. The difference in potential between the anode and the cathode is the driving force of an electrochemical corrosion process. However the current flowing in the circuit determines the corrosion rate. Any factor that decreases the resistance of the circuit or increases the potential difference between the two electrodes will lead to an increase in the flow of current. When a current is drawn from a cell, certain irreversible changes occurring near the electrodes tend to oppose the direction of the current flow. The potential of each electrode is changed from the equilibrium value. (Equilibrium potential of the electrode is that potential when no current is drawn from, or applied to, the electrode). The electrode is then known as polarized electrode and the phenomenon is called polarization.

Polarization at the electrodes is due to

- (i) the presence of surface film on the electrode,
- (ii) overvoltage, or
- (iii) concentration changes in the electrode region.

The polarization of an electrode increases with the current flowing ; the cathode (electrode with a more positive standard electrode potential) assuming an increasingly negative electrode potential, and the anode (electrode with a more negative standard electrode potential) assuming an increasingly positive electrode potential.

'Evans diagrams' result when the potentials of polarized anode and cathode are plotted against the current in the circuit.



AP = Polarization line for anode ;

P = Corrosion potential ;

CP = Polarization line for cathode

$i_{\max}$  = Maximum Corrosion current

Fig. 9. Evans Polarization Diagrams (schematic—not to scale).

Evans diagrams represent the polarization curves for corrosion processes proceeding by (i) cathodic control, (ii) anodic control and (iii) mixed control.

In this diagram, for the electrode that is polarised to a greater extent, the polarization curve has a steeper slope. The point, P, is called corrosion potential and at this point of intersection of two curves, the electrodes will be at the same potential.

The current ( $i$ ) that flows between anodic and cathodic areas is given by

$$i = \frac{(E_c' - E_a')}{R}$$

where  $E_c'$  is polarized potential of cathode.

$E_a'$  is polarized potential of anode and

$R$  is total resistance of the corrosion circuit.

$R$  is small when the anodic and cathodic areas are close enough and under this condition  $i = i_{max}$ .

The magnitude of the corrosion current will depend on the slope of the polarization curve.

When only the anode undergoes polarization, its curve will be steeper, the point of intersection will be  $P$ , and thus the corrosion current ( $i_1$ ) decreases. This is shown in Fig. 9(ii). Under such conditions, the corrosion process is under anodic control.

The corrosion rate (i.e., the weight of the metal lost ( $m$ ) in time ( $t$ )) is given by

$$\frac{m}{t} = \frac{ie}{F}$$

where  $i$  = current,

$e$  = the number of electrons involved in the corrosion process and

$F$  = Faraday constant.

Thus the corrosion rate is related to corrosion current.

Similarly, the system is under cathodic control when only the cathode undergoes polarization.

The system is under mixed control when both the electrodes get polarized.

From the Evans diagrams, it can be concluded that if a metal is to corrode at an extremely slow rate, the cathodic and anodic polarization curves must intersect at a very low value of current, i.e., the anodic and/or cathodic processes must be significantly polarized.

By retarding the anodic or cathodic or both processes, the inhibitors retard the corrosion rate.

### 6.1.2 Corrosion Inhibitor

Inhibitors are chemical substances which reduce the corrosion rate when added in small quantities to the corrosive environment.

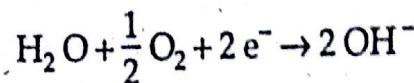
*Corrosion inhibitors are of following three types :*

(a) *Anodic inhibitors* like alkalis, molybdates, phosphates, chromates, etc. They react with the ions of the anode and produce insoluble precipitates. The precipitates so formed are adsorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate.

(b) *Cathodic inhibitors*. In an acidic solution, the cathodic reaction is  $2 H^+ + 2e^- \longrightarrow H_2$ , the corrosion can be controlled by slowing down the diffusion of  $H^+$  ions through the cathode. It can be done by using organic inhibitors like

amines, mercaptans, heavy metal soaps, substituted ureas and thioureas. They absorb over the cathodic metal surface and act as a protective layer. Antimony and arsenic oxides deposit adherent film of metallic antimony or arsenic at the cathodic areas, thereby increasing considerably the overvoltage for hydrogen evolution.

In a neutral solution, the cathodic reaction is



The formation of  $\text{OH}^-$  ions is only due to the presence of oxygen. Therefore, corrosion can be controlled either by eliminating  $\text{O}_2$  from the corroding medium (by adding reducing agents like  $\text{Na}_2\text{SO}_3$  or by deaeration) or by retarding diffusion of  $\text{O}_2$  to the cathodic areas. It can be done by adding Zn, Ni or Mg salts which react with  $\text{OH}^-$  at cathode to form insoluble hydroxides which are deposited on the cathode. These deposits are impermeable barriers hence retard diffusion of  $\text{O}_2$  to cathode.

(c) *Vapour Phase inhibitors* are organic inhibitors which readily sublime and form a protective layer on the surface of metal.

e.g., dicyclohexylammonium nitrite is used for the protection of machineries and sophisticated equipments.

**Example 1. Why are the anodic inhibitors not considered to be satisfactory ?**

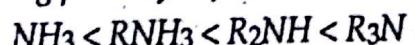
**Solution.** This is because, for each inhibitor, there is a certain critical concentration of solution above which inhibition may be expected.

When an insufficient concentration is used, all the anodic areas may not be covered. The resulting combination (small anodic and large cathodic areas) leads to considerable increase in the current density (current flowing per unit area of the surface) at the few anodic sites. This causes rapid localized perforation of the metal (pitting). For cathodically controlled reactions, anodic inhibitors are especially dangerous, unless used in excess of the critical concentration.

**Example 2. (i) What are Organic inhibitors ?**

(ii) Give reasons.

(a) *The inhibiting power of aliphatic amines increases as*



*where R is an alkyl group.*

(b) *Inhibitors containing S are usually more effective than N compounds.*

**Solution.** (i) *Organic Inhibitors* are S – or N – containing Organic compounds which retard corrosion processes even in acid solutions by getting adsorbed all over the metal surface.

*Examples :* Amines, organic nitrites, Substituted thiocarbamides and heterocyclic compounds.

(ii)

(a) *This is because adsorption of amines increases with the basic strength of the N atom i.e., with the greater availability of the lone pair of electrons on the N atom.*

(b) *This is because S (being less electronegative) is a better electron donor.*

**Example 3.** Enlist one or two applications where volatile inhibitors are used.

**Solution.** Volatile inhibitors [vapour-phase inhibitors (VPI) or volatile corrosion inhibitors (VCI)] like dicyclohexyl ammonium nitrite (DCHAN) are used for protection against corrosion of metallic parts in small closed containers (such as machine parts packed and sent by ship). These are also used in compressors and condensers.

### **6.2 Modification of the Properties of the Metal**

The properties of the metal can be modified to decrease the effects of corrosion. The following methods are used to modify the properties of metals :

#### **6.2.1 Alloying**

The alloying additions for increasing corrosion resistance may be for

**Passivating.** Al, Cr, Ti, Ni and Mo ; as protective oxide layers make steel less corrosive.

**Inhibiting.** As or Sb in brass prevents dezincification.

**Neutralizing.** Ta, Nb and Ti combine with carbon to form respective carbides and thus make the stainless steel, corrosion resistant.

Mn and Cu combine with S in steels.

Provided the [oxygen] is low, alloy containing much Ni, like monel metal (Ni = 67%, Cu = 30%, Mn = Fe = 1.2% rest C and Si) have good corrosion resistance in acid solution.

#### **6.2.2 Refining**

It is done to lower the content of S and P in steels and C in stainless steels.

#### **6.2.3 Annealing**

It is a heat treatment given to metals to remove the residual stresses.

### **6.3 Use of Protective Coatings**

For protection against corrosion, the metal surface may be coated with metallic or non-metallic coatings.

#### **6.3.1 Metallic Coatings**

Iron and steel are the most commonly used construction metals due to their low cost, easy availability and ease of fabrication into desired structures. Iron and steel can be protected from corrosion by covering their surface with metallic coatings. Surface coatings made up of metals are known as *metallic coatings*. The metallic coatings often used are of zinc, tin, nickel, chromium, aluminium, copper etc. These coatings separate the base metal from the corrosive environment and also function as an effective barrier for the protection of base metals.

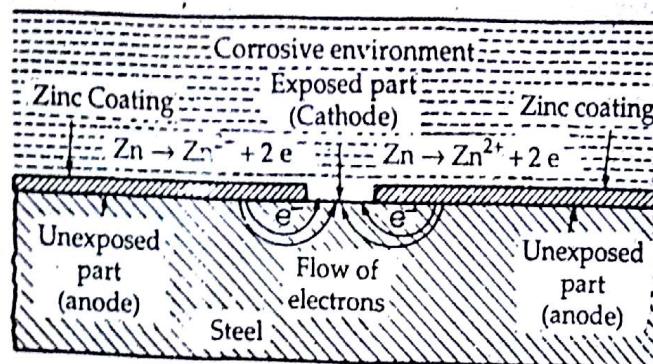
#### **Types of Metallic coatings** *Only name*

There are two types of metallic coatings :

(i) **Anodic coatings.** In these coatings, the metal which is used for coating is more "anodic" than the metal which is to be protected (*i.e.*, the base metal). Anodic coatings protect the underlying base metal sacrificially.

*For example,* Coating of Al, Cd and Zn on steel surface. Let us discuss, how galvanised steel is protected from corrosion. Here Zn is coating metal and steel is

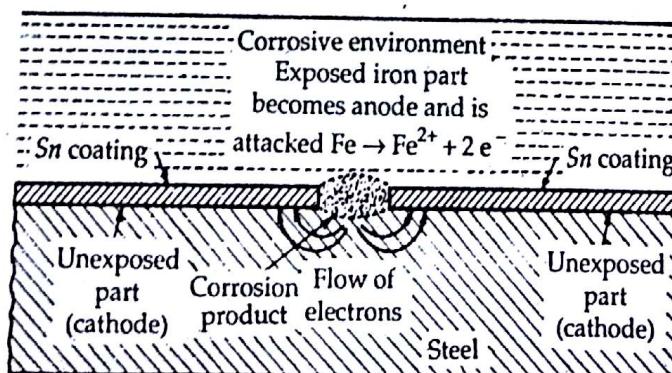
base metal. Zn being anodic is attacked; leaving the underlying cathodic (iron/steel) unattacked, even if it is exposed when pores, breaks or discontinuities occur in such an anodic coating. Iron or steel is not corroded, till all the coating metal (Zn) is consumed.



**Fig. 10:** Functioning of anodic coating. In galvanized steel, Zn serves an anode; while iron of steel serves as the cathode. Therefore, the iron is protected, even if it is exposed.

(ii) **Cathodic coatings.** These coatings protect the underlying base metal, due to their noble character and higher corrosion resistance. In such coatings, effective protection is possible only when they are completely continuous and free from pores, breaks or discontinuities. If pores, breaks or discontinuities occur in such a coating, the corrosion of the base metal is speeded up. This is due to the fact that exposed metal acts as anode and coating becomes the cathode. A galvanic cell is set up and an intense localized attack at the small exposed part occurs. This results in severe pitting and perforation of the base metal.

Coating of tin on iron is an example.



**Fig. 11.** Tin-plated steel. The tin protects the iron, when the coating is uniform. When the coating is broken, the iron of the steel becomes the anode and is subjected to intense local corrosion.

### 6.3.2 Inorganic Coatings

The inorganic coatings are non-metallic protective coatings. Important inorganic coatings are :

- (i) Surface conversion or chemical Dip coatings,
- (ii) Anodised oxide coating,
- (iii) Vitreous or Porcelain enamel coating.

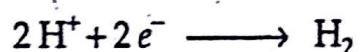
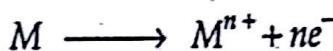
### Uses of Lacquers :

Lacquers are used in

- (i) preparing artificial leathers by coating cotton fabrics,
- (ii) giving finishing coat to automobile bodies, due to their resistance to abrasion, cracking and chalking etc.
- (iii) interior decoration like paintings of furniture or any other wood work.

### 6.4 Cathodic Protection (or Electrochemical Protection)

Let us consider the corrosion of a metal ( $M$ ) in an acidic environment. Metal ( $M$ ) undergoes corrosion by its oxidation (i.e., when metal behaves like an anode). This reaction is simultaneously accompanied by a reduction reaction viz., evolution of hydrogen gas



As is clear from the above reactions, we can prevent the dissolution of metal (its corrosion) by forcing the metal to behave like a cathode. This is the principle of cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur.

### Types of Cathodic Protection *Only name*

There are following two types of cathodic protection :

(i) *Sacrificial anodic protection*. The metal structure can be saved from corrosion by connecting it with wire to a more active (i.e., more anodic) metal, so that all the corrosion is concentrated at the more active metal. As the more active metal is sacrificed in the process of saving metal from corrosion, hence it is known as sacrificial anode. Metals commonly used as sacrificial anodes are Zn, Al, Mg and their alloys. Zinc is used as sacrificial anode in good electrolytes such as sea water.

Magnesium is used in high resistivity electrolytes such as soils due to its most negative potential and it can provide highest current output.

*Applications.* Important applications of this technique are :

- (a) Protection of underground cables and pipelines from soil corrosion [Fig. 12(a)].
- (b) Protection of ships and boat hulls from marine corrosion. Sheets of Mg or Zn are hung around the ship hull, these sheets being anodic to iron so these sheets get corroded. When consumed completely, these are replaced by fresh ones [Fig. 12(b)].
- (c) The formation of rusty water is prevented by the insertion of Mg sheets or rods into domestic water boilers or tanks [Fig. 12(c)].

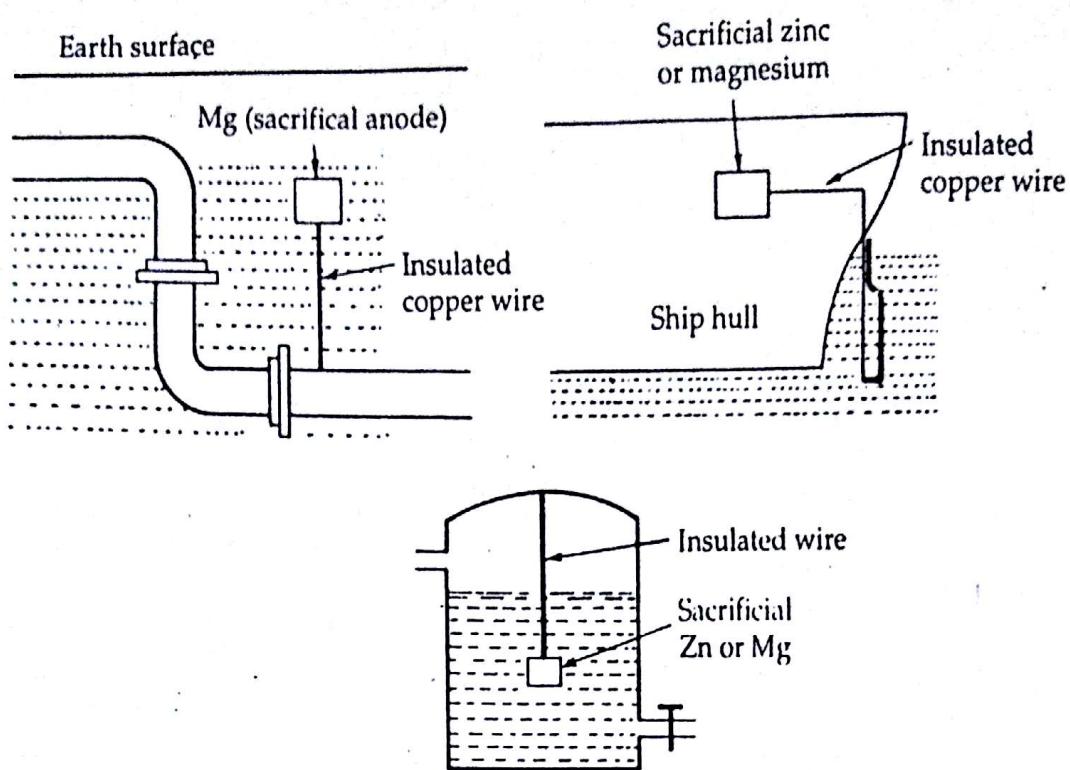


Fig. 12. Sacrificial anodic protection.

(ii) **Impressed current cathodic protection.** In this method, current from an external source is impressed (applied in the opposite direction) to nullify the corrosion current. This is done to convert corroding metal from anode to cathode. Once the metal becomes cathodic, it is protected from corrosion. The anode may be either an inert material or one which deteriorates and will have to be replaced periodically. The commonly used anodic materials are graphite, carbon, stainless steel, scrap iron, high silica iron and platinum. The anode is buried in back fill such as gypsum to increase the electrical contact between itself and the surrounding soil.

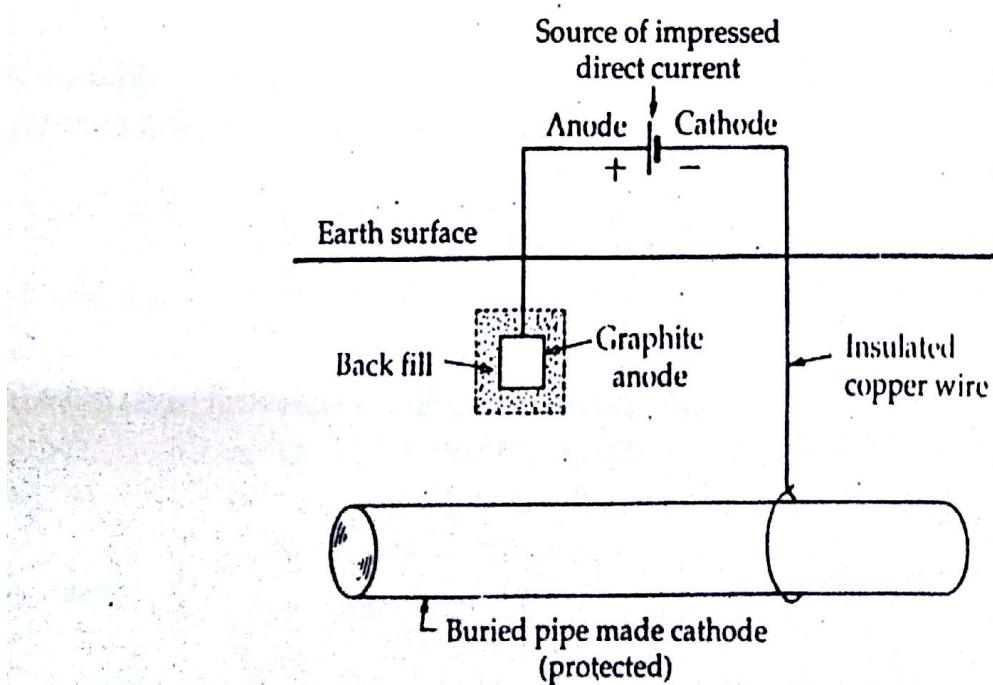


Fig. 13. Impressed current cathodic protection.

**Applications.** This protection method is useful when electrolyte resistivity and current requirements are high. It is well-suited for large structures and long-term applications. Maintenance and operating costs can be reduced by employing automatic impressed current cathodic protection.

This protection technique is employed in the case of buried structures such as pipe-lines, tanks, marine piers, transmission line towers, laid-up ships etc.

### 8.5 Prevention of Corrosion by Material Selection and Design

Design is the initial stage for protection against corrosion. Before a suitable design is made, careful consideration of constructional material ; atmospheric and environmental conditions ; and accessibility for maintenance and repair is required.

#### Design and Material Selection Principles

(a) Avoid L, T and U shaped profiles in constructions as far as possible [Fig. 14(a)]. This is because, the greater the number of angles, corners, edges and internal surfaces in any design, it becomes more difficult for efficient surface treatment.

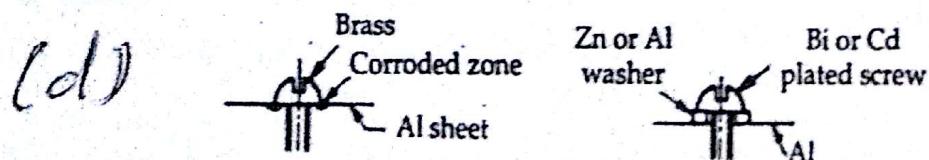
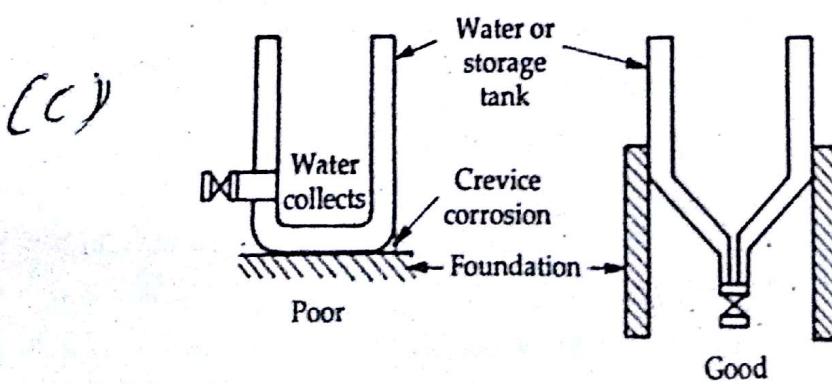
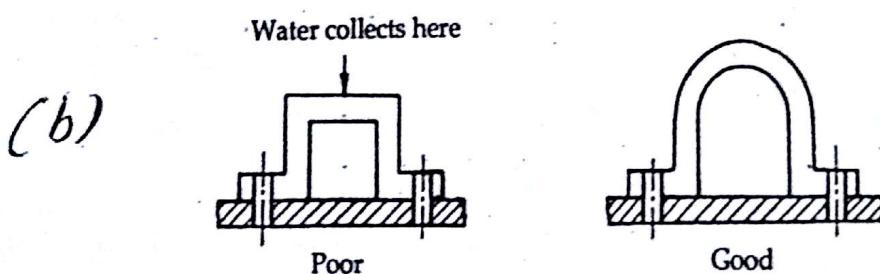
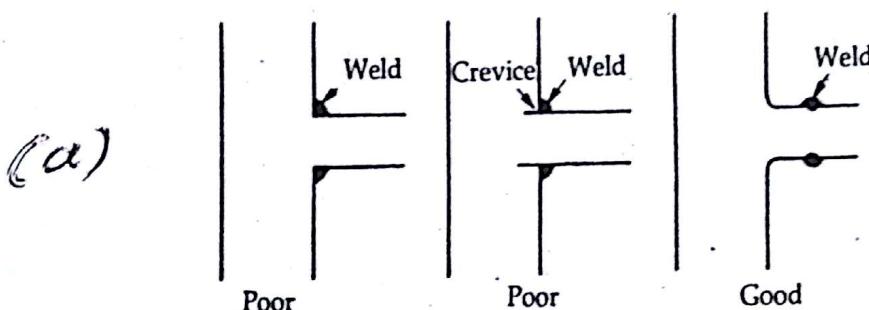


Fig. 14. Control of Corrosion by design and material selection.

(b) Avoid Galvanic corrosion by following methods :

- Never join different metals and alloys, especially if they are far apart in the galvanic series. If at all they have to be used together, insulate them with efficient moisture resistant electrical insulator, Fig. 14(d). (d)
- Never use a design in which relative sizes of the cathode and anode are widely different.
- Screws, bolts, nuts and welds must be made from a more noble material than the joined materials.
- Continuous welds should be preferable. The intermittent welds are unsuitable both from the mechanical and corrosion points of view. The smaller side of weld should be turned toward the corrosive medium. 14(c)

(c) Avoid improper insulation otherwise leakage of current takes place. Such stray currents cause anodic corrosion, especially in areas where electric traction is used.

(d) Avoid the contact of metallic object with moisture.

- The design of a structure should be such that retention of moisture should be as low as possible.
- Design the storage containers in such a manner that they can be completely drained and cleaned, Fig. 14(c).
- Arrange profiles in such a manner that water is completely drained and as far as possible, avoid crevice corrosion. For example, Design electrical boxes (exposed to atmosphere) in such a manner that water does not collect at the top or in the crevices, Fig. 14(b). (b)

## 6.6 Other Corrosion Prevention Methods

### 6.6.1 Metal Cladding

*Metal cladding* is the process of coating of base metal by a dense, homogeneous layer of cladding materials. Cladding materials can be pure metals (which are corrosion-resisting like Ni, Pb, Ag, Pt or Cu) or alloys (like stainless steel, or alloys of Ni, Cu or Pb). The choice depends on the environment in which corrosion-resistance is required.

Generally, a base metal (e.g., duralumin) is sandwiched between two layers of cladding materials (e.g. 99.5 % pure Al), which are then passed through rollers, under the action of heat and pressure to form say 'aclad' sheeting which is very widely used in the air-craft industry.

### 6.6.2 Electroplating

*Electroplating* is the process of deposition of coating metal on the base metal by passing a direct current through an electrolytic solution which contains the soluble salt of the coating metal.

Apart from increasing the resistance of metal to corrosion and chemical attack, electroplating also improves physical appearance, hardness, surface properties and aesthetics.

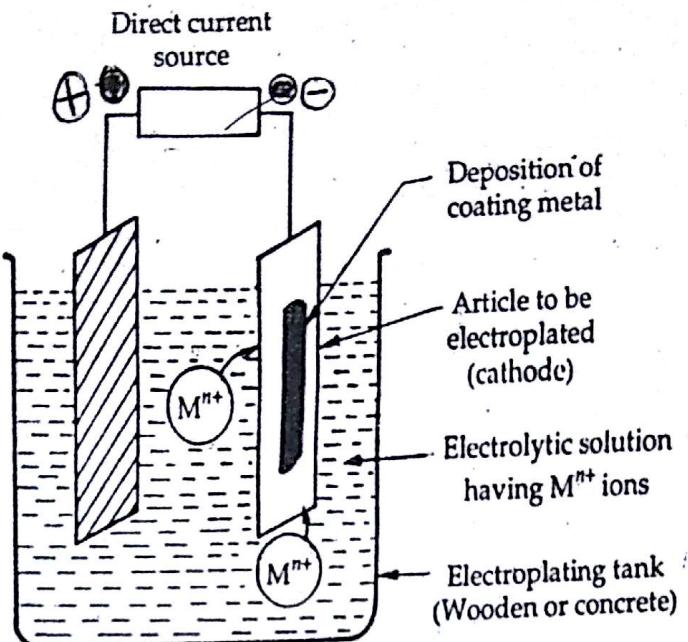


Fig. 15. Electroplating.

Oils, greases, etc. are first removed from the surface of metal to be electroplated by treatment with organic solvent like tetrachloroethylene. Surface scales, oxides etc. are then removed by treating with HCl (for Ni and Cu plating) or  $H_2SO_4$  (for chromium plating). The cleaned metal is then made cathode of an electrolytic cell. The anode is either an inert material of good electrical conductivity (like graphite) or coating metal (pure) itself. The electrolyte is a solution of a soluble salt of a metal (to be deposited). The anode and cathode are dipped in an electrolytic solution kept in an electroplating tank.

When direct current is passed, coating metal ions migrate to the cathode and get deposited there in the form of thin-layer.

### 6.6.3 Painting

The paint is essentially a suspension of fine opaque particles of pigment in a fluid vehicle. The main types are briefly discussed below :

S.No.	Type of paint	Properties and Applications
(a)	Silicon paint	Because heat resistant, hence prevent corrosion of surfaces exposed to high temperatures like exhaust pipes and chimneys etc.
(b)	Aluminium paint	Corrosion protection for iron and steel surface is better than all other paints hence used for corrosion resistance painting of electric and telegraph poles and towers.
(c)	Antifouling paint	Retard the fouling of ships by marine worm, fungi, etc. and this helps in controlling their corrosion.
(d)	Coal-tar paint	Used for protecting iron and steel surfaces used under the ground.

### 6.6.4 Plastic Coating

It is applied on costly components like verniers, micrometers, tools and gauges. The metal is firstly thoroughly cleaned and dried. It is then dipped in liquid plastic. Once the plastic layer adheres to metal, it is removed, cooled and then dried. Plastic coated surface isolates the underlying metal from the corroding environment and prevent the penetration of the environment to the material, which they protect.