

### UNIT- III: Electrochemistry and corrosion

Corrosion: Definition – Theories of Corrosion (chemical & electrochemical) – Formation of galvanic cells by different metals, by concentration cells, by differential aeration and waterline corrosion – Passivity of metals – Pitting corrosion - Galvanic series – Factors which influence the rate of corrosion - Protection from corrosion – Design and material selection – Cathodic protection  
Protective coatings: Surface preparation – Metallic (cathodic and anodic) coatings.

#### **Corrosion-Definition:**

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

“The process of decay metal by environmental attack is known as corrosion. Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.”

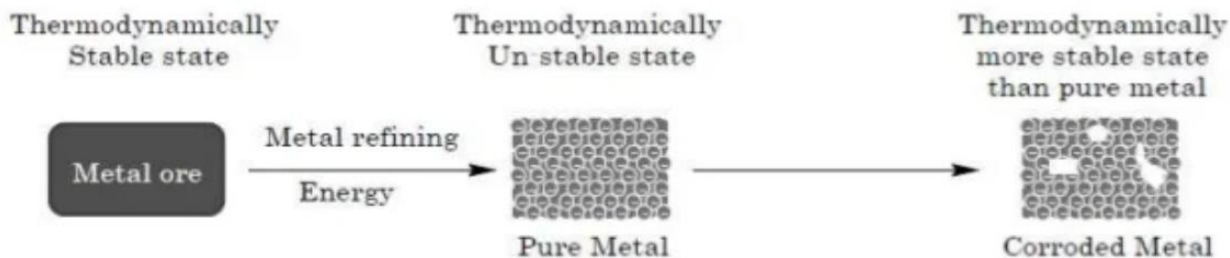
Ex: (1) Iron undergoes corrosion to form reddish brown color rust [ $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ].

(2) A green film of basic carbonate [ $\text{CuCO}_3 + \text{Cu(OH)}_2$ ] is formed on the surface of copper, when it is exposed to moist-air containing carbon dioxide.



#### **Causes of corrosion:**

The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc. During the extraction of metals, these ores are reduced to metallic state. Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores). When metal is exposed to atmospheric gases, moisture, liquids etc., the metal surface reacts and forms more stable compounds.



### Effects of corrosion:

- Wastage of metal in the form of its compounds.
- The valuable metallic properties are lost due to corrosion.
- Life span and efficiency of metallic parts of machinery is reduced.

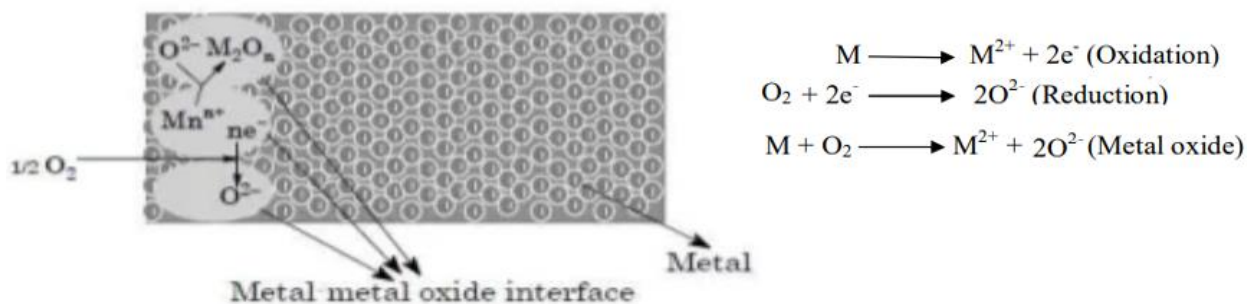
### Theories of corrosion (Chemical & Electrochemical):

#### I. Dry corrosion or Chemical corrosion:

This type of corrosion occurs mainly through the direct chemical action of atmospheric gasses like  $O_2$ , halogens,  $H_2S$ ,  $SO_2$ ,  $N_2$  or anhydrous inorganic liquid with the metal surface. There are three types of chemical corrosion:

1. Oxidation corrosion, 2. Corrosion due to other gases, 3. Liquid metal corrosion

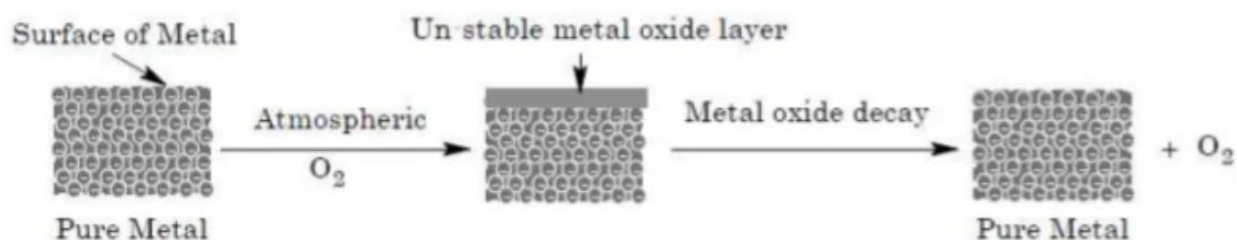
1. **Oxidation corrosion:** This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).



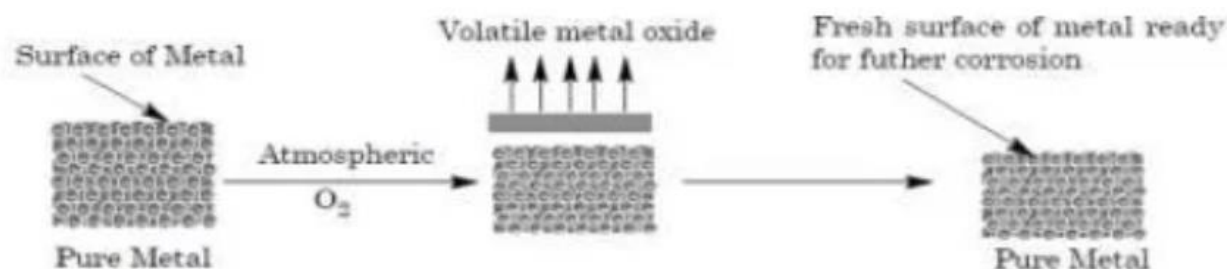
### Mechanism:

- Initially the surface of metal undergoes oxidation and forms metal oxide scale. The extent of corrosion depends upon the nature of metal oxide.

- If the metal oxide is *stable*, it behaves as a protective layer which prevents further corrosion.  
Ex. The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.
- If the metal oxide *unstable*, the oxide layer formed decomposes back into metal and oxygen.  
Oxidation corrosion is not possible.  
Ex. Ag, Au and Pt do not undergo oxidation corrosion.

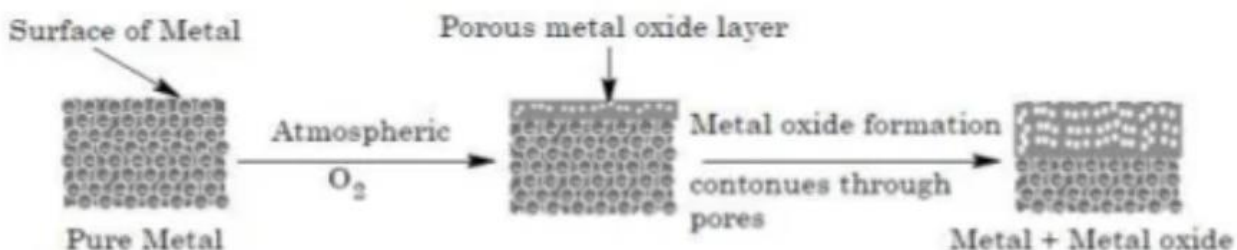


- If the metal oxide layer is *volatile*, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO<sub>3</sub>).



- If the metal oxide layer is *porous*, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This causes continuous corrosion.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.).



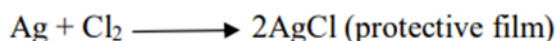
- **Pilling-Bedworth Rule:** The protective or non-protective oxide layer formation in metals is governed by a rule known as Pilling-Bedworth rule. According to this rule, If the volume of the metal-oxide layer is equal to or greater than the volume of the metal from which it is

formed, the oxide layer is non-porous and therefore protective in nature (e.g., Oxides of Cu, In, Al, Ni, Cr) if the volume of the metal-oxide layer is less than the volume of the metal from which it is formed, the oxide layer is porous and therefore non-protective in nature (e.g., alkali or alkaline metal oxides).

**2. Corrosion due to other gases:** This type of corrosion is due to gases like SO<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>S, and other halogens. The extent of corrosion depends upon the affinity between the metal and the gas involved and the type of film formed on the surface of the metal i.e. protective or non-protective.

(i) The extent of corrosion decreases if the layer formed is protective or non-porous.

Ex: Attack of Cl<sub>2</sub> gas on Ag metal forms a non-porous layer of AgCl which protects further corrosion of the Ag metal.



(ii) The corrosion continues if the layer formed is non-protective or porous.

Ex: Attack of Cl<sub>2</sub> gas on Sn (tin) metal forms SnCl<sub>4</sub> which is volatile, so, produces a fresh surface on tin metal for the corrosion to continue.

Ex: In petroleum industry, H<sub>2</sub>S gas at high temperature reacts with steel forming a FeS scale which is porous and corrosion continues.



**3. Liquid metal corrosion:** This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

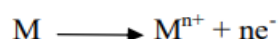
Ex. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

## II. Wet corrosion or Electrochemical corrosion:

- This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs there by destroying the anodic metal. Hence corrosion always occurs at anodic parts.

### Mechanism:

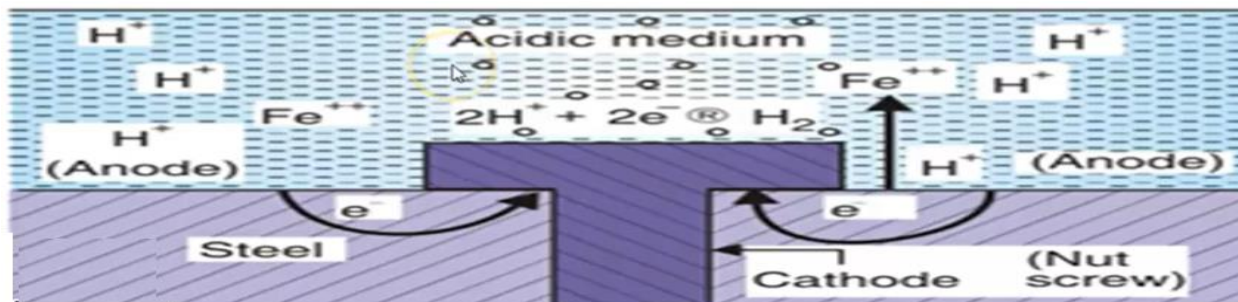
Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



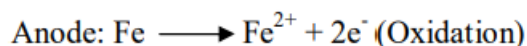
The cathodic reaction consumes electrons (reduction) with either *evolution of hydrogen* or *absorption of oxygen* which depends on the nature of corrosive environment.

**Evolution of hydrogen:** This type of corrosion occurs in acidic medium. All metals above hydrogen in electrochemical series undergo this type of corrosion.

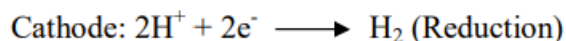
Ex. Considering the Iron metal in contact with HCl



The anodes are large areas, whereas cathodes are small areas. Anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



The electrons released flow through the metal from anode to cathode, whereas  $H^{+}$  ions of acidic solution are eliminated as hydrogen gas.



The overall reaction is:  $Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$

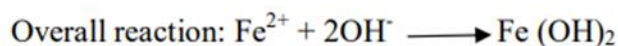
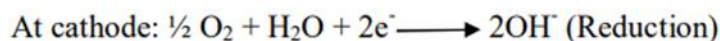
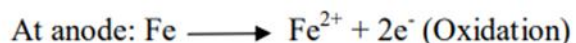
This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H<sub>2</sub> gas.

**Absorption of oxygen:** This type of corrosion occurs in neutral or basic environment. Formation of hydroxide ion type corrosion.

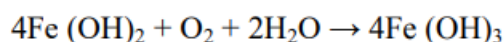


Ex. Rusting of iron in neutral aqueous solution of electrolyte in presence of atmospheric oxygen.

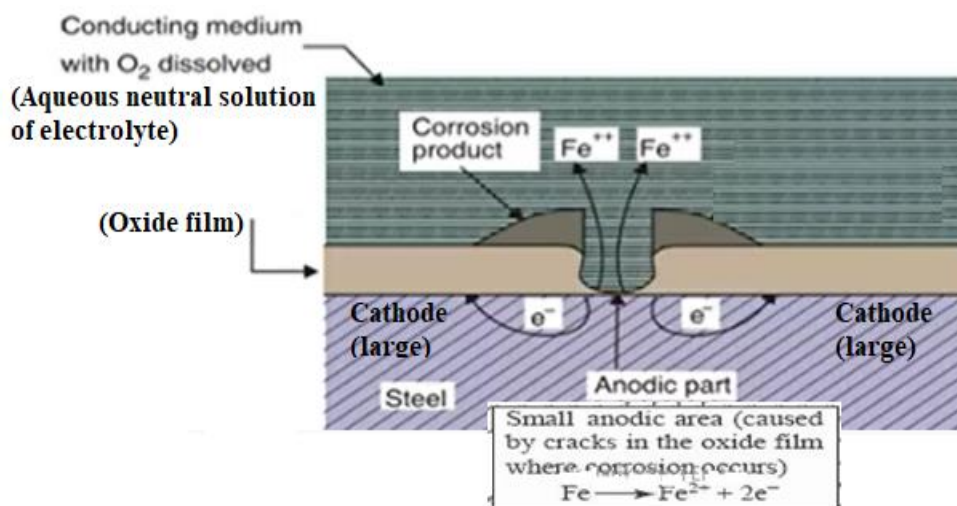
- Usually the surface of iron is coated with a thin film of iron oxide.
- The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area.
- It shows that anodes are small areas, while the rest metallic part forms large cathodes.



- If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



- The product called yellow rust corresponds to Fe<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O.





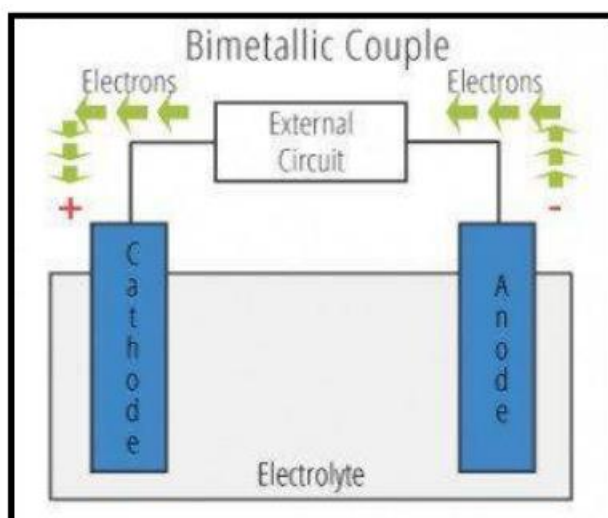
## Galvanic corrosion:

There are two primary types of galvanic cells that cause corrosion:

**1. Bi-metallic couple/Formation of galvanic cells by different metals:** A bi-metallic couple is like a battery, consisting of two dissimilar metals immersed in an electrolyte solution.

**2. Concentration cell:** A concentration cell consists of an anode and cathode of the same metal or alloy.

### Bi-metallic couple:



- Any two metals can be used to make a galvanic cell.
- Whether a metal will behave as an anode or a cathode in combination with another metal can usually be determined by its relative position on the galvanic series.
- The metal which appears higher up on the list (more negative on the potential scale) will be the anode and will thus corrode.
- The metal lower down on the list (more positive on the potential scale) will be the cathode and thus will not corrode.

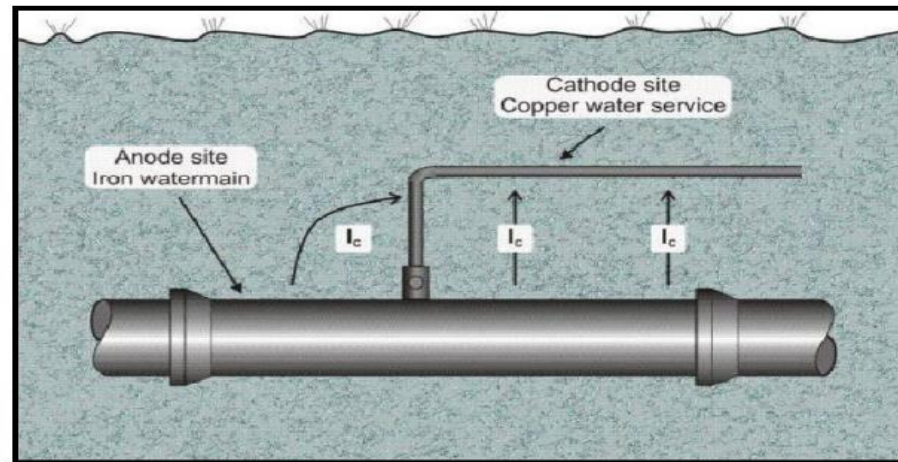
**Ex 1.** Two dissimilar metals, zinc and copper, are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion.

Zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series) acts as cathode. Thus, the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

**Ex.2** When a copper pipe service line is directly connected to a cast iron main water line, a galvanic cell such as shown in the Figure is formed.

The soil is the electrolyte, the copper service line is the cathode, the iron (or steel) main is the anode, and the connecting circuit is completed by attaching the line to the main.

Normally, such cells do not do any great amount of damage, because the anode (corroding metal) is so much larger than the cathode that the attack is spread out over a large area.



#### Corrosion by concentration cells:

- Concentration cell corrosion is the deterioration of parts of a metal surface.
- Concentration cells occur when the concentration of electrolyte in contact with the metal is different in two contact locations.
- The extent of this corrosion reaction is proportionate to the difference in concentrations at the contact points. It also varies with the type of electrolyte.
- If a region of the metal exposed to lower concentration electrolyte, the region has to turn anodic in comparison to different portions of metal surface. Thus, this part of the metal corrodes faster.





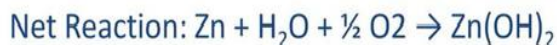
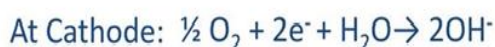
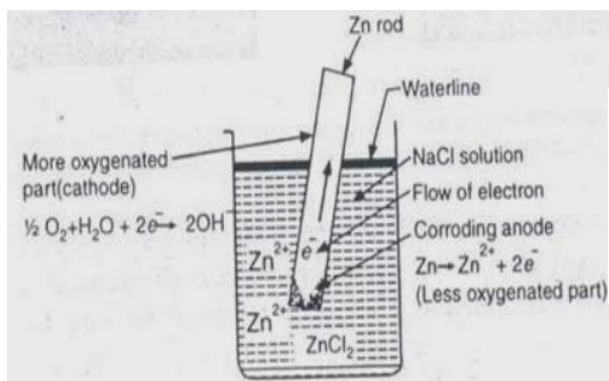
### Differential aeration corrosion:

Corrosion of metals arising as a result of the formation of an oxygen concentration cell due to the uneven supply of air on the metal surface is known as differential aeration corrosion.

- The difference in the availability of air or oxygen over a metallic surface leads to formation of oxygen concentration cells.
- It occurs when one part of metal is exposed to a different air concentration from the other part.
- The less oxygenated part behaves anodic while the more oxygenated part cathodic.
- It is believed that aeration causes the formation of an oxide film on the metal surface resulting in the development of a metal-metal oxide cell.
- Most of the common types of corrosion are due to differential aeration.

Ex. Corrosion of metals partly immersed in solutions

- When a metal piece is partly immersed in a solution or water, the part of the metal piece above the surface of the solution is more aerated and behaves cathodic while the part immersed in interior has less accessibility to oxygen and behaves anodic.
- The extent of this corrosion reaction is proportionate to the difference in concentrations at the contact points. It also varies with the type of electrolyte.

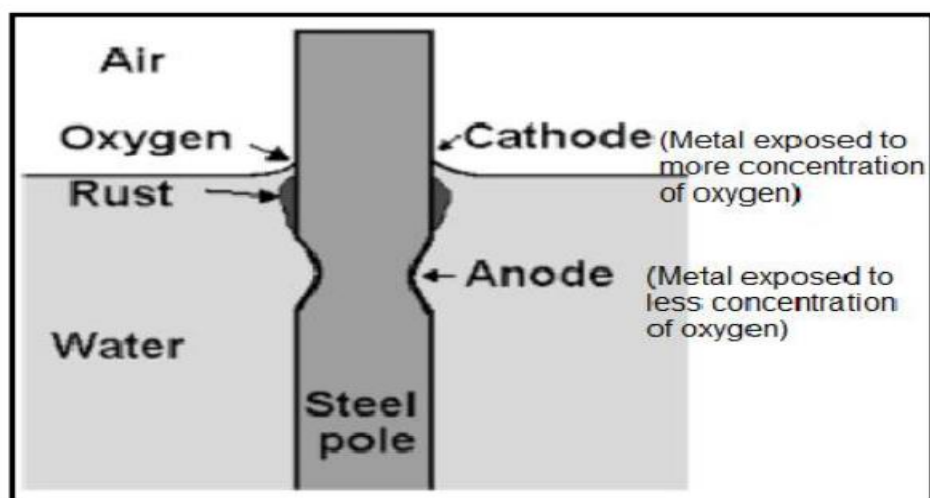


### Waterline corrosion:

This type of corrosion is observed in the water tanks where water remains collected for a long time. It is found just below the line of water, so called waterline corrosion.

- Waterline corrosion is a case of differential aeration corrosion (differential oxygen concentration cells). It is more predominant in cases such as ocean going ships, water storage steel tanks, etc., in which a portion of the metal is always under water.

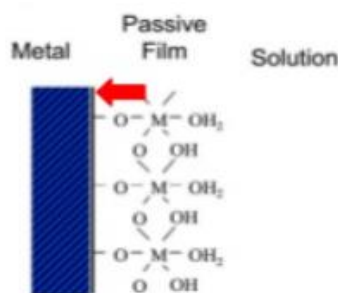
- The part of the metal below the water line is exposed only to dissolved oxygen while the part above the water is exposed to higher oxygen concentration of the atmosphere.
- Thus, part of the metal below the water acts as anode and undergoes corrosion and part above the waterline is free from corrosion.
- A distinct brown line is formed just below the water line due to the deposition of rust.



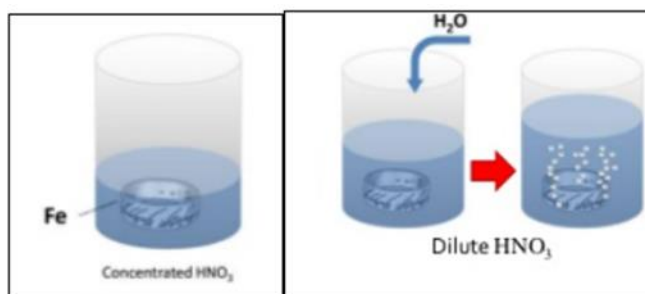
### Passivity of metals:

- A metal which shows lower corrosion rate is called passive metal whereas a metal which shows a higher corrosion rate is called active metal.
- Passivity or passivation of metals is defined as, “a state in which metal or alloy exhibits much higher corrosion resistance than expected from its position in the electrochemical series”.
- Passivity is due to reduction in the anodic rate of reaction because of the formation of a protective film of oxide.

- Passivity is the result of formation of a highly protective but (thickness 0.0004 mm) quite invisible, thin film on the surface of metal or alloy, thus making it nobler.
- The film formed during passivation is insoluble, non-porous and of such a “self-healing nature”, that when broken, it will repair itself on re-exposure to oxidizing conditions.
- The common examples of passive metals and alloys are Ti, Al, Cr and a wide variety of stainless steel alloys containing Cr. These exhibit outstanding corrosion resistance in oxidizing environments.
- Passivators: Passivators are inorganic oxidizing agents that form a thin protective oxide layer on a metal surface that prevents further oxidation (corrosion).
- They are the solution of chromate ( $\text{CrO}_4^{2-}$ ), molybdates ( $\text{MoO}_4^{2-}$ ), tungstates ( $\text{WO}_4^{2-}$ ), ferrates ( $\text{FeO}_4^{2-}$ ). They act as anodic inhibitors.



- A same metal can act as active as well as passive depending on the situation.



Fe in concentrated  $\text{HNO}_3 \rightarrow$  No reaction.

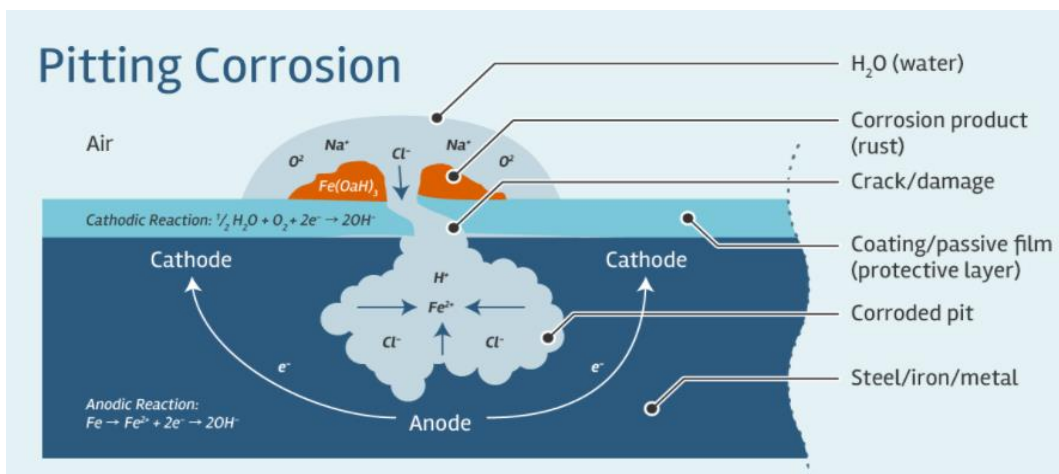
Insulative film is formed on the surface of Fe. As concentrated nitric acid is strong oxidizing agent,  $\text{Fe}_3\text{O}_4$  layer forms on the surface and protects it from further corrosion.

Fe in dil.  $\text{HNO}_3 \rightarrow$  Rapid corrosion reaction.

Diluted nitric acid is not a strong oxidizing agent and hence,  $\text{Fe}_3\text{O}_4$  layer does not form on the surface. In this case, the Fe freely corrodes ( $\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ).

## Pitting corrosion:

- In pitting corrosion cavities or "holes" are produced in the material. Pitting corrosion is one of the most damaging forms of corrosion.
- Pitting corrosion occurs when a metal is exposed to water droplets and dust particles.
- The area below the droplet is insufficiently oxygenated while the surrounding areas are well oxygenated. This results in differential aeration corrosion where surrounding areas are cathodic and the small area below the droplets and dust particles become anodic.
- Electrons flow through the metal and are met by water and oxygen to produce rust. Pits, cracks and gaps develop in the metal as the rust is produced.
- Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect.
- Corrosion products often cover the pits.
- A small, narrow pit can lead to the failure of an entire engineering system. The bulk of the surface remains un-attacked.

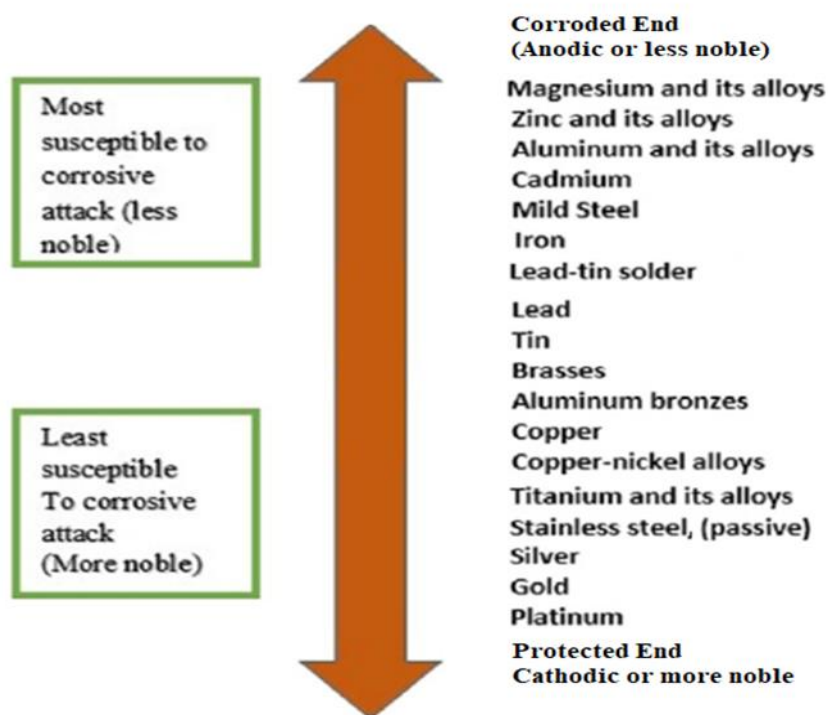


Corrosion Pits are the primary source of leaks in **water handling systems**

- Pitting is vigorous when the solution on the metal surface contains halide ions. Sulphides and water are also known to enhance the pitting process.
- Metals responsible to pitting corrosion are: Stainless steel, chromium, passive iron, mercury, cobalt, aluminum, copper.

### Galvanic series:

- The galvanic series (or electro potential series) determines the nobility of metals and semi-metals.
- When two metals are submerged in an electrolyte, while also electrically connected by some external conductor, the less noble metal will experience galvanic corrosion.
- The rate of corrosion is determined by the electrolyte, the difference in nobility, and the relative areas of the anode and cathode exposed to the electrolyte.
- The less noble metal is the one with a lower electrode potential than the nobler one, and will function as the anode.



- The Galvanic series of metals lists metals and alloys in decreasing order of electrical activity.
- Metals nearer the top of the table are less noble metals and have a greater tendency to lose electrons than the more noble metals found lower on the list.

**Factors which influence the rate of corrosion:** The rate and extent of corrosion depends upon various factors such as:

*Factors due to nature of metal:*

1. Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.
2. Metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (eg. Zn, Mg, Al etc.).
3. Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.
4. When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.
5. The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.  
Ex. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn.
6. If the metal has small anodic and large cathodic area, the rate of corrosion is very high. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.
7. In aerated atmosphere, practically all metals get covered with a thin surface film of metal oxide. If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Ex: Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

*Factors due to nature corroding environment:*

1. The rate of corrosion is directly proportional to temperature. The rate of corrosion reactions increases with increase in temperature. This is because the rate of diffusion of ions increases with rise in temperature.



2. The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up an electrochemical cell.
3. Atmosphere is contaminated with gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ; fumes of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  etc. in the vicinity of industrial areas. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases, thereby the rate of corrosion increases.
4. As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell.

#### **Protection from corrosion:**

- Corrosion is the gradual destruction of materials, (usually metals). As the corrosion process is very harmful, it becomes necessary to minimize or control corrosion of metals.
- Corrosion can be stopped completely only under ideal conditions. But the attainment of ideal conditions is not possible. However, it is possible only to minimize corrosion considerably.
- Any method of corrosion control must be aimed at either modifying the metal or the environment.

#### **Design and material selection:**

Choice of metals:

- The most common method of preventing corrosion is the selection of the proper metal.
- The first choice is to use noble metals such as gold and platinum. They are most resistant to corrosion. As they are precious, they cannot be used for general purposes.
- The next choice is to use purest possible metal. But in many cases, it is not possible to produce a metal of high chemical purity. Hence, even a trace amount of impurity leads to corrosion.
- Thus, the next choice is the use of corrosion resistant alloys. Several corrosion resistant alloys have been developed for specific purposes and environment.

Ex. (a) Stainless steel containing chromium produce an exceptionally coherent oxide film which protects the steel from further attack.

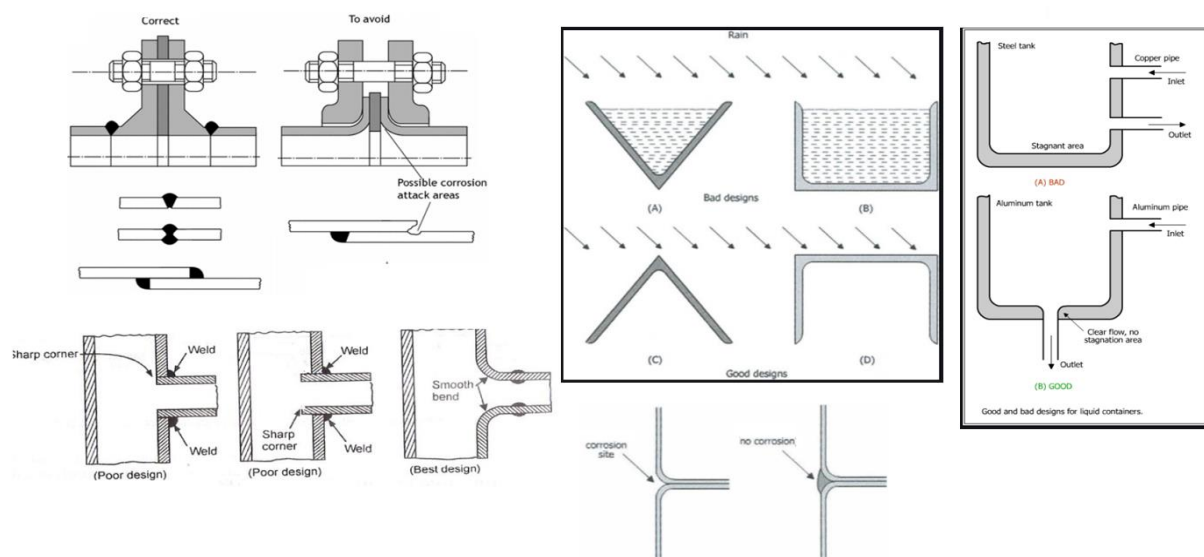
(b) Cupro-nickel (70% Cu + 30% Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries.

### Proper designing:

Proper geometrical design plays a vital role in the control of corrosion of equipment and structures.

The general guidelines of the design of materials and components to control corrosion are:

- Use always simple design and structure
- The design must avoid more complicated shapes having more angles, edges, corners etc.
- Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion. So insulating material between the two metals should be inserted.
- When two dissimilar metals are to be in contact, the anodic area must be as large as possible and the cathodic area should be as small as possible.
- As far as possible, gaps or cracks should be avoided between adjacent parts of a structure or they should be filled using fillers.
- Bolts and rivets should be replaced by proper welding
- Metal washers should be replaced by rubber or plastic washers as they do not adsorb water.
- Corrosion in pipelines can be prevented by using smooth bends.
- A good design of water storage container is the one from which water can be drained and cleaned easily. Such a design avoids accumulation of dirt etc.



### Cathodic protection:

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection. There are two types of cathodic protection.

### *Sacrificial anode method:*

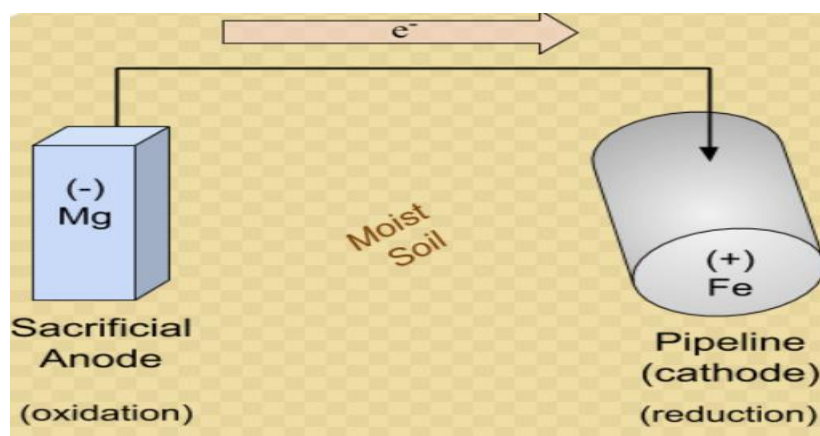
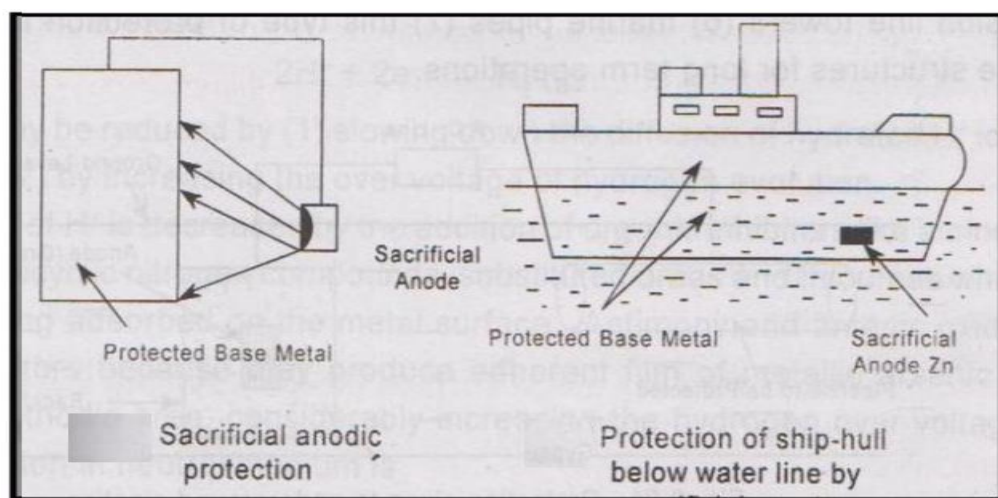
- In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The most active metal becomes the anode to the others, and sacrifices itself by corroding to protect the cathode. Hence, the term sacrificial anode.
- The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

Ex: Mg, Zn, Al and their alloys

- By referring to the electrochemical series, the metal with low reduction potential and occupies higher end in electrochemical series is connected to the base metal which acts as anode.

Ex. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

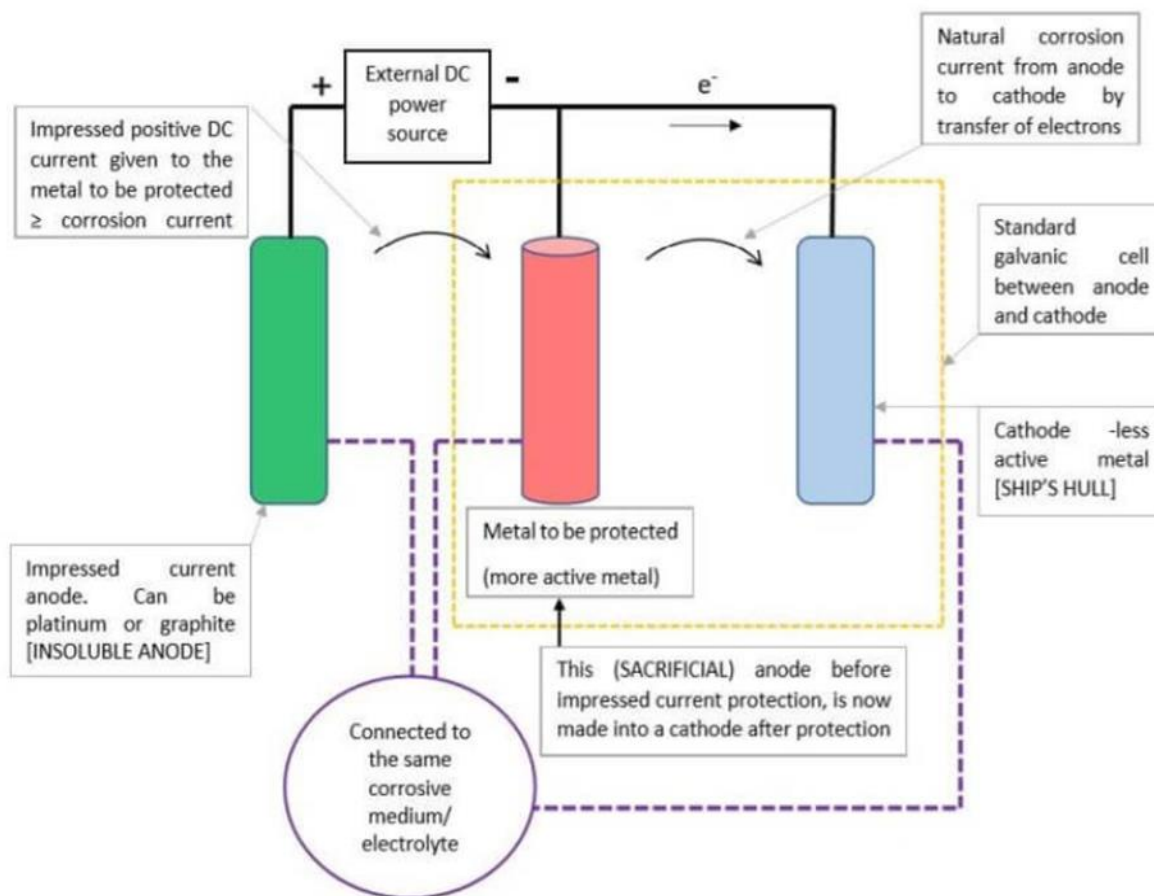
Ex. The underground water pipelines and water tanks are also protected by sacrificial anode method.



### *Impressed current method:*

- Impressed Current Cathodic Protection Systems (ICCP) are regarded as a superior alternative to sacrificial anode systems.
- In the ICCP, the metal to be protected is connected to an insoluble anode and current is passed using a DC source opposite to the corrosion current, so that the corroding metal gets converted from anode to cathode and is protected from corrosion.
- This insoluble anode can be either platinum, platinized titanium or any other inert elements.
- Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers, ships, buried pipelines etc.
- The below diagram is a similar galvanic cell of an anode (more active metal) and a cathode (less active metal) with some modifications.

### IMPRESSED CURRENT CATHODIC PROTECTION BASIC CELL DIAGRAM



- Under normal circumstances, a corrosion current is set up which corrodes the anode.
- Here, an impressed current anode which is insoluble is added in the system.
- In this case, a DC current is pass opposite to the natural corrosion current between the anode and cathode.
- In impressed current method, a DC current is provided to the metal to be protected in order to make it the cathode.
- This DC current has to be equal to or slightly greater than the natural corrosion current so that the anode is now protected and does not corrode.

### **Protective coatings: Surface preparation**

- In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings.
- A protective coating is a layer of material applied to the surface of another material to prevent the corrosion.
- Surface preparation is essential before a paint or other protective coating is applied.
- A solvent is used to remove all visible compounds or other soluble contaminants.  
Solvents: steam, emulsifying agents or other cleaning compounds.
- The surface preparation process not only cleans metal, but also introduces a suitable profile to receive the protective coating.
- The coatings may be sprayed on, plated on, or applied using hand tools.
- Protective coatings can be broadly classified into two types. They are

*Inorganic coatings* are further classified into two types. They are

- a. Metallic coatings
  - Hot dipping-Galvanizing, Tinning
  - Electroplating
- b. Non-metallic coatings
  - Phosphate coating and Oxide coating
  - Porcelain coating

*Organic coatings* consist of Paints, Varnishes, Polishes and Enamels.

*Paints:* Paint is a viscous, opaque (not clear), dispersion mixture of one or more pigments (dye) in a vehicle (drying oil). A good paint should have the following properties.

- form a good and uniform film on the metal surface
- the film should not crack on drying
- give a glossy film
- the film produced should be washable
- give a stable and decent color on the metal surface
- have good resistance to the atmospheric conditions
- be fluid enough to spread easily over the surface
- possess high adhesion capacity to the material over which it is proposed to be used
- dry quickly or in a reasonable duration
- the color of the paint should not fade

Constituents of paint: Pigment, Vehicle or medium or drying oil, Thinner, Driers. Fillers, Plasticizers, Anti-skinning agents

*Pigment:* It is a solid substance which imparts color to the paint. It is an essential constituent of a paint. The most commonly used pigments in paints are:

White pigments - White lead,  $\text{ZnO}$ ,  $\text{BaSO}_4$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$

Blue pigments - Prussian blue, ultramarine blue

Black pigments - Graphite, carbon black, lamp black

Red pigments - Red lead,  $\text{Fe}_3\text{O}_4$

Green pigments - Chromium oxide, chrome green

Brown pigments - Burnt umber, yellowish-brown

Yellow pigments - Chrome yellow, lead chromate

*Vehicle or drying oil or medium:* Vehicle is a liquid substance and film forming material. It holds all the ingredients of a paint in liquid suspension. Ex. Linseed oil, Tung oil

*Thinners:* Thinners are volatile substances which evaporate easily after application of the paint. They are added to the paints for reducing the viscosity of the paints so that they can be easily applied to the metal surface. Ex. Dipentene, turpentine, toluol, xylol etc.



*Driers:* These are the substances used to accelerate the process of drying. Ex. Naphthenates, borates etc.

*Fillers:* These are the inert materials which improve the properties of the paint. These are used to fill the voids in the film. Ex. Gypsum, chalk, silica, talc, clay,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$

*Plasticizers:* These are added to the paint to provide elasticity to the film and to minimize its crack. Ex. Triphenyl phosphate, dibutyl tartarate, tributyl phthalate, tricresyl phosphate, diamyl phthalate

*Anti-skinning agents:* These are sometimes added to some paints to prevent crystalizing and skinning (peeling) of the finished product. Ex. Polyhydroxy phenols

### **Metallic (cathodic and anodic) coatings:**

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

#### **Anodic coating:**

- The metal used for the surface coating is more anodic than the base metal which is to be protected. Thus, anodic coatings protect the underlying base metal sacrificially.  
Ex. Coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron.

#### **Cathodic coating:**

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) on the base metal.  
Ex: Coating of Sn on Fe because Sn is lower in electrochemical series than Fe.

### **Methods of application of metallic coatings:**

#### **Hot dipping:**

- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a molten flux layer (usually  $\text{ZnCl}_2$ ,  $\text{NH}_4\text{Cl}$  etc.).

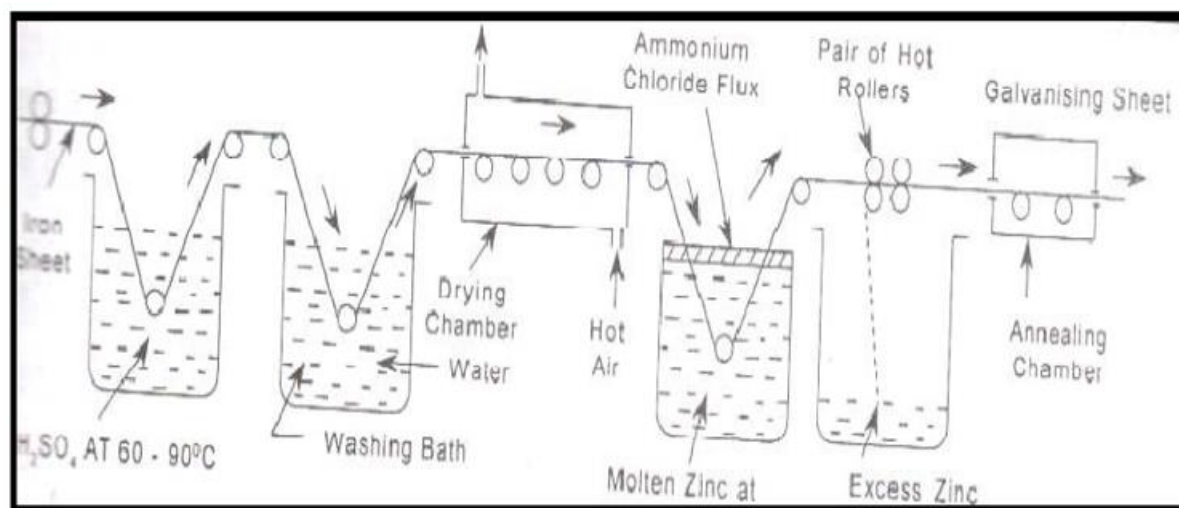
- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Ex. Coating of low-melting metals such as Zn, Sn, Pb, Al etc., on iron, steel and copper surfaces which have relatively higher melting points.

The most widely used hot dipping processes are galvanizing and tinning.

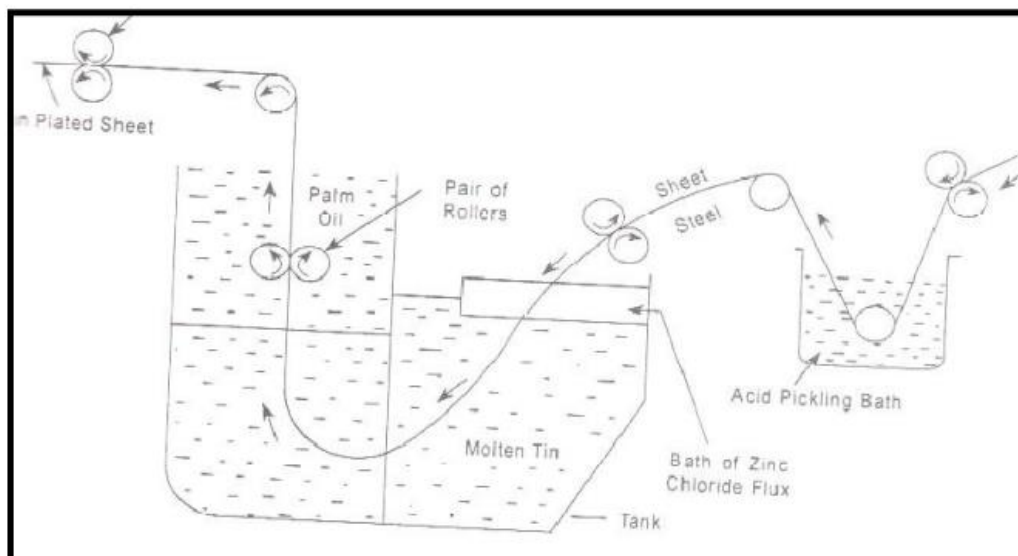
### Galvanizing:

- Galvanizing is an anodic coating process. Coating of more active metal over less active metal.  
Ex. Coating zinc over copper, iron, steel etc.
- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc (Zn).
- In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 min. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried.
- Then, dipped in the bath containing molten zinc which is at 425-450°C. The surface of bath is covered with ammonium chloride flux, to prevent it from oxide formation.
- When the iron sheet is taken out it is coated with a thin layer of zinc.
- To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at temperature of 450°C followed by cooling.
- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.)
- Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.



## Tinning:

- Tinning is a cathodic coating process. Coating of less active metal over more active metal.  
Ex. Coating tin over iron, steel etc.
- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.
- Tin is a noble metal and therefore it possesses more resistance to chemical attack.
- It is the cathodic protection offered by the tin.
- In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath  $\text{ZnCl}_2$  molten flux followed by molten tin and finally through a suitable vegetable oil.
- The  $\text{ZnCl}_2$  flux helps the molten metal to adhere to the base metallic surface.
- Palm oil protects the tin coated surface against oxidation.
- Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.



## Electroplating:

- Electroplating is a process of coating a less active metal over the more active base metal by passing direct current through the electrolyte containing the soluble salt of the coating material.
- Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc.

- The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- The two electrodes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.

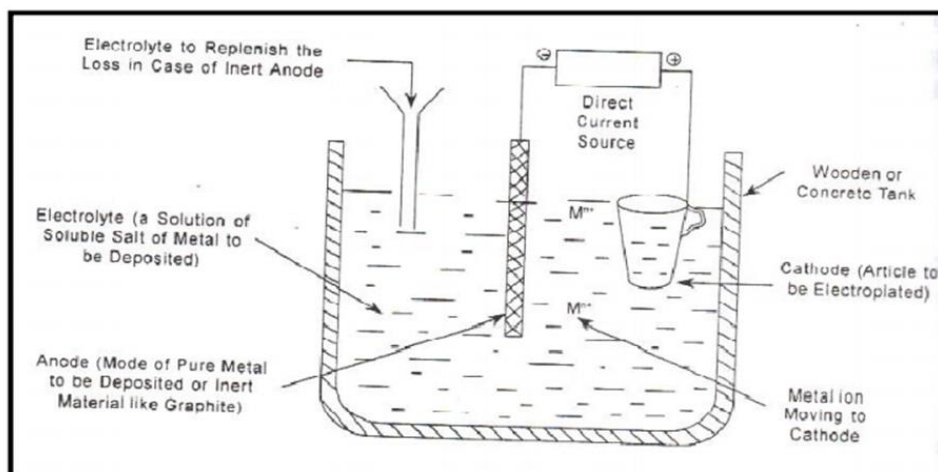
Objectives of the electroplating:

- To improve the corrosion resistance of the metal.
- To increase the thermal conductivity of the metal

Ex: Copper bottomed vessels

- For the aesthetic appearance of metals.

Ex: Gold covering ornaments



- Ex: Coating of copper on objects

