

# ENGINEERING

# CHEMISTRY

## UNIT-III

### CORROSION AND CORROSION CONTROL

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#### **CONTENTS:**

a) **Corrosion**: introduction, types of corrosion, mechanism of atmospheric corrosion and wet corrosion. Galvanic series. Factors affecting corrosion: nature of metal and nature of environment. Different types of corrosion: Pitting corrosion, concentration cell corrosion, stress corrosion and soil corrosion.

b) **Corrosion control**: methods of prevention of corrosion - cathodic and anodic protection, metallic coatings and its types - anodic and cathodic coatings. Method to apply metallic coatings - hot dipping, cladding, electroplating and cementation.

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## **INTRODUCTION:**

Corrosion is an undesirable process. Due to corrosion, there is limitation of progress in many areas. The cost of replacement of materials and equipments lost through corrosion is unlimited.

Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment. Thus, it is exactly the reverse of extraction of metals from ores.

Example:

1. Rusting of iron: A layer of reddish scale and powder of oxide ( $Fe_3O_4$ ) is formed on the surface of iron metal.
2. A green film of basic carbonate [ $CuCO_3 + Cu(OH)_2$ ] is formed on the surface of copper, when it is exposed to moist-air containing carbon dioxide.

## **CONSEQUENCES (EFFECTS) OF CORROSION:**

The economic and social consequences of corrosion include

- i) Due to formation of corrosion product over the machinery, the efficiency of the machine gets failure leads to plant shut down.
- ii) The products contamination or loss of products due to corrosion.
- iii) The corroded equipment must be replaced
- iv) Preventive maintenance like metallic coating or organic coating is required.
- v) Corrosion releases the toxic products.
- vi) Health (e.g., from pollution due to a corrosion product or due to the escaping chemical from a corroded equipment)

## **CAUSES OF CORROSION:**

In nature, metals occur in two different forms: Native State and Combined State

### **Native State:**

The metals exist as such in the earth crust then the metals are present in a native state. Native state means free or uncombined state. These metals are non-reactive in nature. They are noble metals which have very good corrosion resistance.

Example: Au, Pt, Ag, etc.

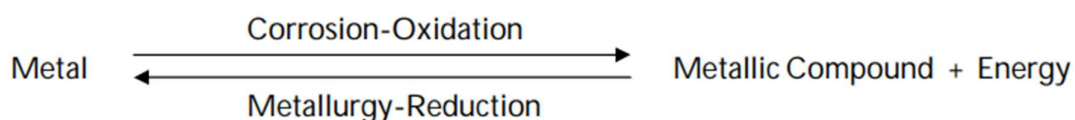
### Combined State:

Except noble metals, all other metals are highly reactive in nature which undergoes reaction with their environment to form stable compounds called ores and minerals. This is the combined state of metals.

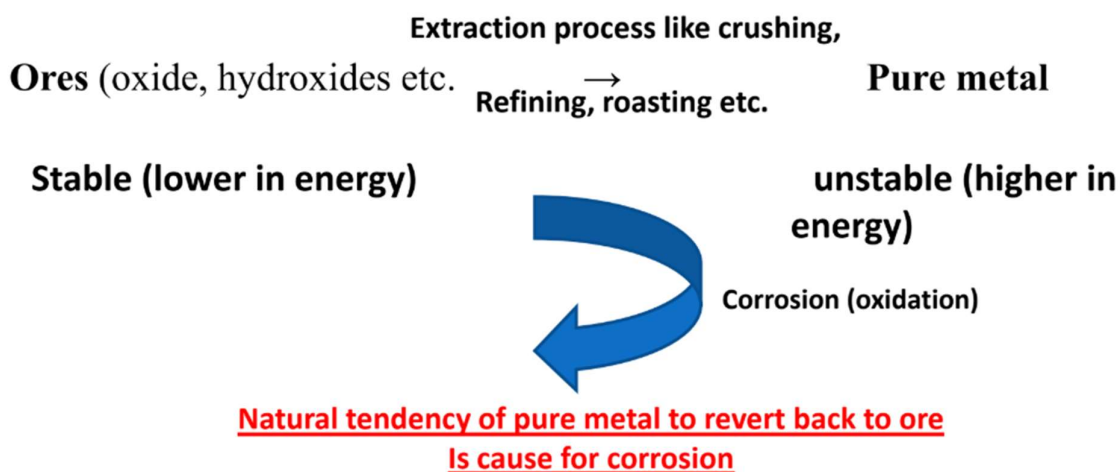
Example:  $Fe_2O_3$ ,  $ZnO$ ,  $PbS$ ,  $CaCO_3$ , etc.,

### Metallic Corrosion:

The metals are extracted from their metallic compounds (ores). During the extraction, ores are reduced to their metallic states by applying energy in the form of various processes. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state). Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form metallic compounds, which are thermodynamically stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, the exposed metal surface begin to decay (conversion to more stable compound). This is the basic reason for metallic corrosion.



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



## CLASSIFICATION OF CORROSION:

Based on the environment, corrosion is classified into:

- (i) Dry or Atmospheric or Chemical Corrosion
- (ii) Wet or Electrochemical Corrosion

## **I. Dry or Atmospheric or Chemical Corrosion:**

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment.

Example: (i) Silver materials undergo chemical corrosion by Atmospheric H<sub>2</sub>S gas.

(ii) Iron metal undergo chemical corrosion by HCl gas.

### **Types of Dry or Atmospheric or Chemical Corrosion:**

- 1) Corrosion by Oxygen or Oxidation corrosion
- 2) Corrosion by Hydrogen
- 3) Liquid Metal Corrosion

#### **1. Corrosion by Oxygen or Oxidation corrosion:**

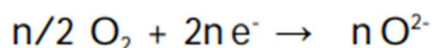
Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

##### **Mechanism:**

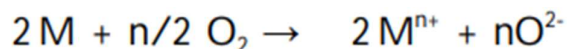
- 1) Oxidation takes place at the surface of the metal forming metal ions  $M^{2+}$



- 2) Oxygen is converted to oxide ion ( $O^{2-}$ ) due to the transfer of electrons from metal.

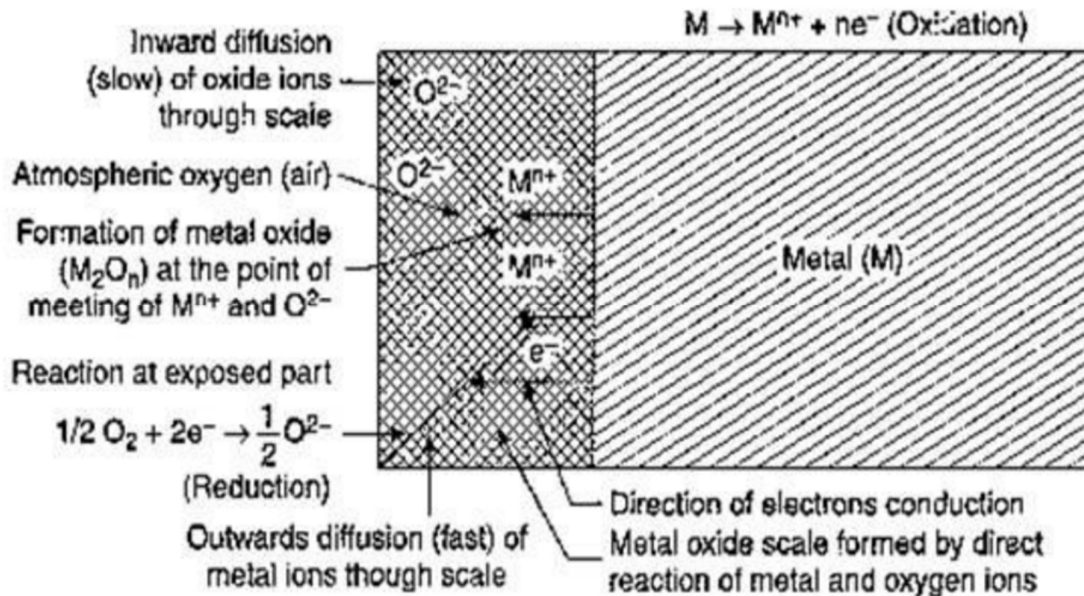


- 3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.



The Nature of the Oxide formed plays an important part in oxidation corrosion process.

Metal + Oxygen  $\rightarrow$  Metal oxide (corrosion product)



When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is

i) **Stable layer:**

A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (i.e., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature.

ii) **Unstable oxide layer:**

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

iii) **Volatile oxide layer:**

The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion.  $MoO_3$  is volatile in nature.

iv) **Porous layer:**

The layer having pores or cracks. In such a case, the atmospheric oxygen has access to the underlying surface of metal (Li, Na, K, Mg), through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

**Pilling-Bedworth rule:**

According to it "an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal from which it is formed". On the other hand, "if the

volume of the oxide is less than the volume of metal, the oxide layer is porous (or non-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below”.

Thus, alkali and alkaline earth metals (like Li, K, Na, Mg) form oxides of volume less than the volume of metals. Consequently, the oxide layer faces stress and strains, thereby developing cracks and pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface (through cracks and pores) for fresh action and thus, corrosion continues non-stop.

Metals like Aluminium forms oxide, whose volume is greater than the volume of metal. Consequently, an extremely tightly-adhering non-porous layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

$$PBR \text{ Ratio} = \frac{\text{Volume of Metal Oxide}}{\text{Volume of Metal Surface}}$$

i) ratio > 1, oxide layer slightly covers the metal surface

ii) ratio < 1, oxide layer not covering the metal surface

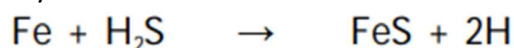
## 2. Corrosion by other gases:

### I. Hydrogen Embrittlement:

Loss in ductility of a material in the presence of hydrogen is known as hydrogen embrittlement.

#### Mechanism:

This type of corrosion occurs when a metal is exposed to hydrogen environment. Iron liberates atomic hydrogen with hydrogen sulphide in the following way.



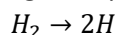
Hydrogen diffuses into the metal matrix in this atomic form and gets collected in the voids present inside the metal. Further, diffusion of atomic hydrogen makes them combine with each other and forms hydrogen gas.



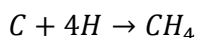
Collection of these gases in the voids develops very high pressure, causing cracking or blistering of metal.

### II. Decarburisation or Hydrogen Attack:

The presence of carbon in steel gives sufficient strength to it. But when steel is exposed to hydrogen environment at high temperature, atomic hydrogen is formed.



Atomic hydrogen reacts with the carbon of the steel and produces methane gas.



Hence, the carbon content in steel is decreases. The process of decrease in carbon content in steel is known as decarburization.

Collection of methane gas in the voids of steel develops high pressure, which causes cracking. Thus, steel loses its strength.

### III. Liquid metal corrosion:

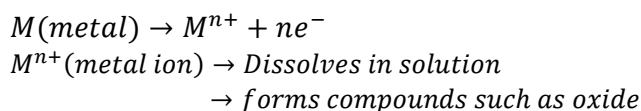
This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either: (i) dissolution of a solid metal by a liquid metal or (ii) internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal.

## II. WET OR ELECTROCHEMICAL CORROSION:

Electrochemical corrosion involves:

- i) The formation of anodic and cathodic areas or parts in contact with each other
- ii) Presence of a conducting medium
- iii) Corrosion of anodic areas only and
- iv) Formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of electron-current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron), so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence corrosion always occurs at anodic areas.



At cathodic area, reduction reaction takes place (gain of electrons), usually cathode reactions do not affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accept the electrons to form some ions like  $OH^{-}$  and  $O_2$

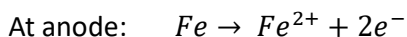
Cathodic reaction consumes electrons with either by

- (a) evolution of hydrogen or
- (b) absorption of oxygen, depending on the nature of the corrosive environment

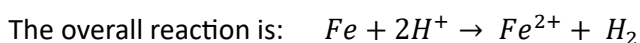
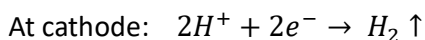
### Hydrogen Evolution Type:

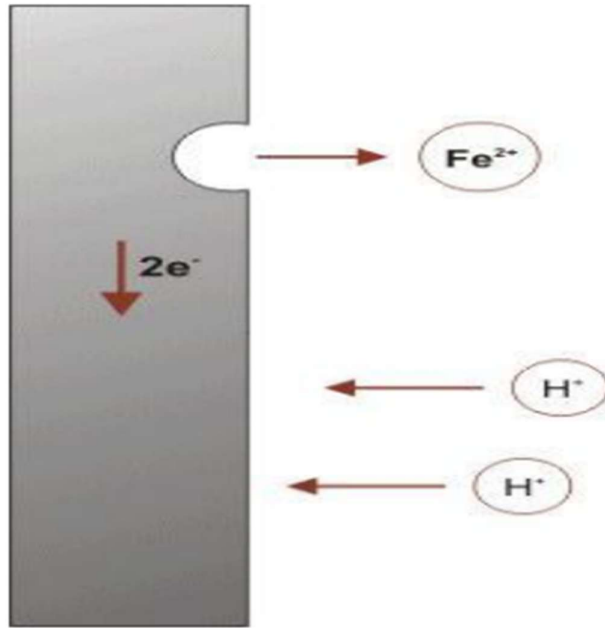
All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

It occurs in acidic environment. Consider the example of iron:



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

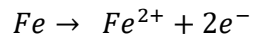




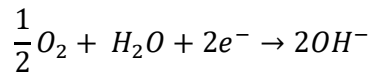
### **Oxygen Absorption Type:**

Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts acts as cathodes.

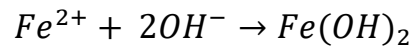
At Anode: Metal dissolves as ferrous ions with liberation of electrons.



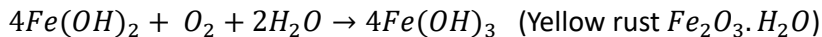
At Cathode: The liberated electrons are intercepted by the dissolved oxygen.



The  $Fe^{2+}$  ions and  $OH^{-}$  ions diffuse and when they meet, ferrous hydroxide is precipitated.

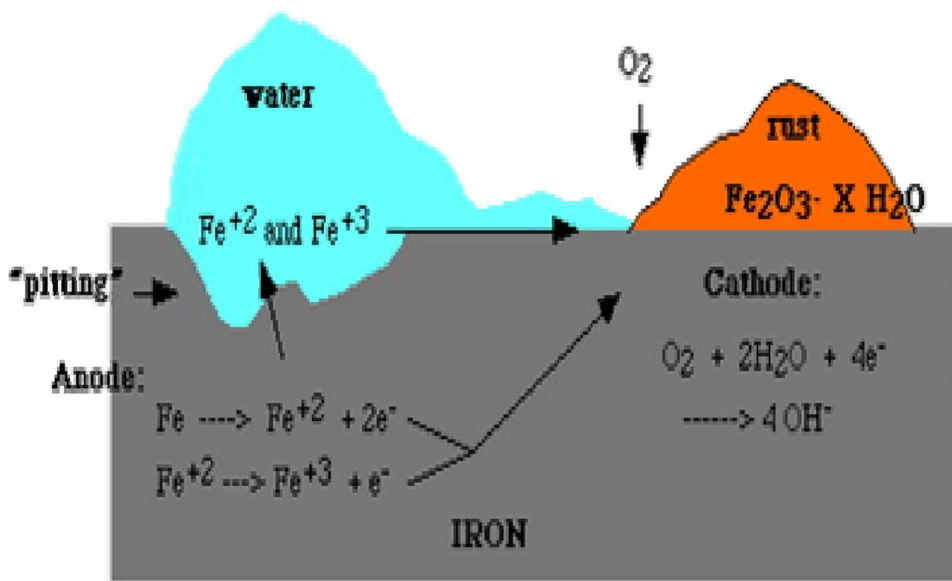


(i) If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite,  $Fe_3O_4$ .





Difference between chemical(dry) and electrochemical(wet) corrosion:

Sr. No.	Chemical Corrosion	Electrochemical Corrosion
1.	It occurs in dry condition.	It occurs in the presence of moisture or electrolyte.
2.	It is due to the direct chemical attack of the metal by the environment.	It is due to the formation of a large number of anodic and cathodic areas.
3.	Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
4.	Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
5.	It is a self-controlled process.	It is a continuous process.
6.	It adopts adsorption mechanism.	It follows electrochemical reaction.
7.	Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.

## **TYPES OF ELECTROCHEMICAL CORROSION:**

The electrochemical corrosion is classified into the following two types:

- (i) Galvanic (or Bimetallic) Corrosion
- (ii) Differential aeration or concentration cell corrosion.

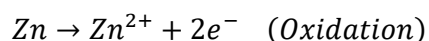
### **Galvanic Corrosion:**

When two dissimilar metals (e.g., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In

this process, the more active metal (with more negative electrode potential) acts as an anode while the less active metal (with less negative electrode potential) acts as cathode.

In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or more noble) acts as cathode.

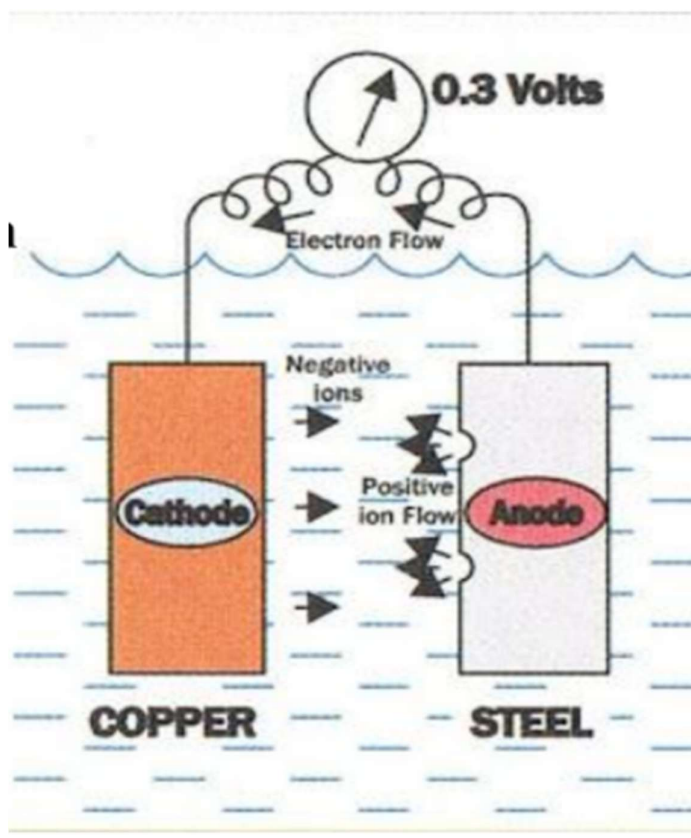
**Mechanism:** In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anode metal, zinc to the cathode metal, copper.



Thus, it is evident that the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

Example:

- (i) Steel screws in a brass marine hardware;
- (ii) Lead-antimony solder around copper wise;
- (iii) a steel propeller shaft in bronze bearing (iv) Steel pipe connected to copper plumbing.



## Concentration Cell Corrosion:

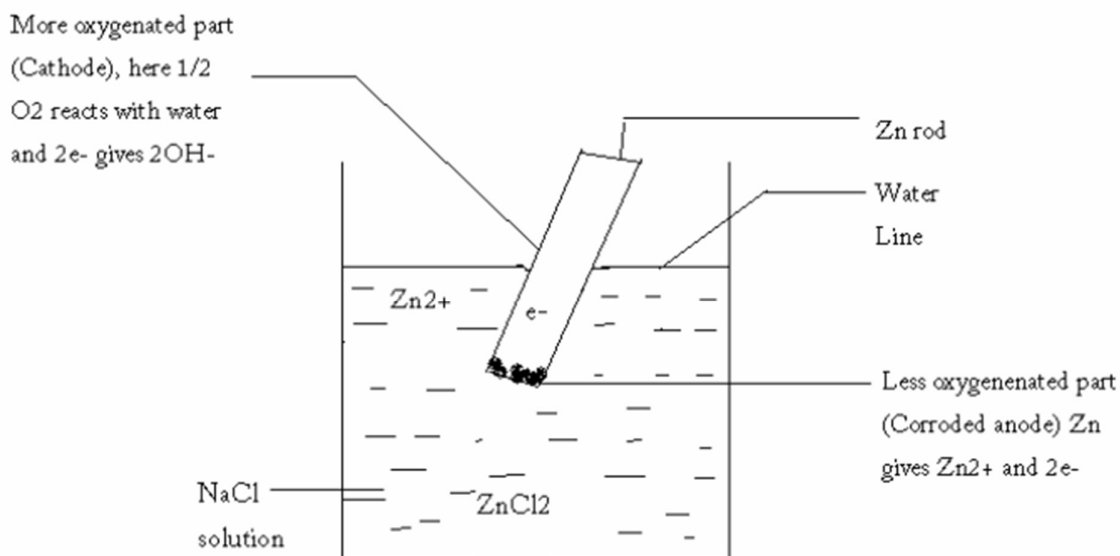
It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration.

It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that poor-oxygenated parts are anodic.

Examples:

- i) The metal part immersed in water or in a conducting liquid is called water line corrosion.
- ii) The metal part partially buried in soil.

**Explanation:** If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.



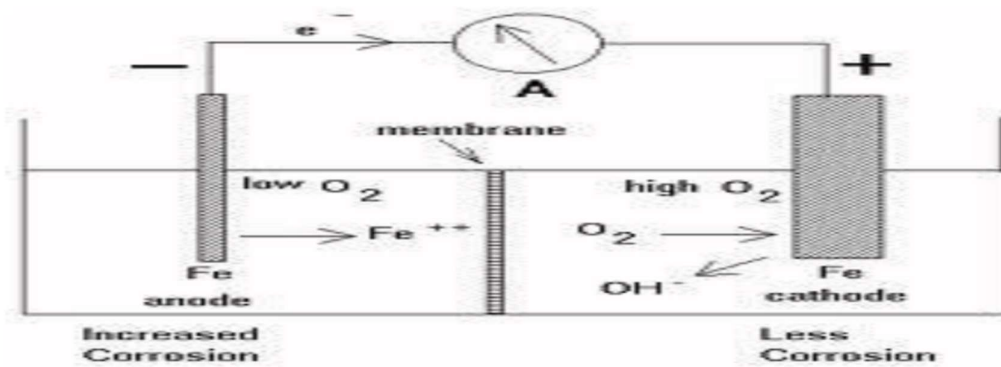
At anode: Corrosion occurs (less aerated)  $M \rightarrow M^{2+} + 2e^{-}$

At cathode:  $OH^{-}$  ions are produced (more aerated)  $\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$

Examples for this type of corrosion are

- 1) Pitting or localized corrosion
- 2) Crevice corrosion
- 3) Pipeline corrosion
- 4) Corrosion on wire fence

For oxygen concentration cell corrosion: When different parts of metal are exposed to different aeration, the potential difference is developed. Less Aerated metal part behaves as anode and more aerated part as cathode.



### Pitting Corrosion:

Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively unattacked.

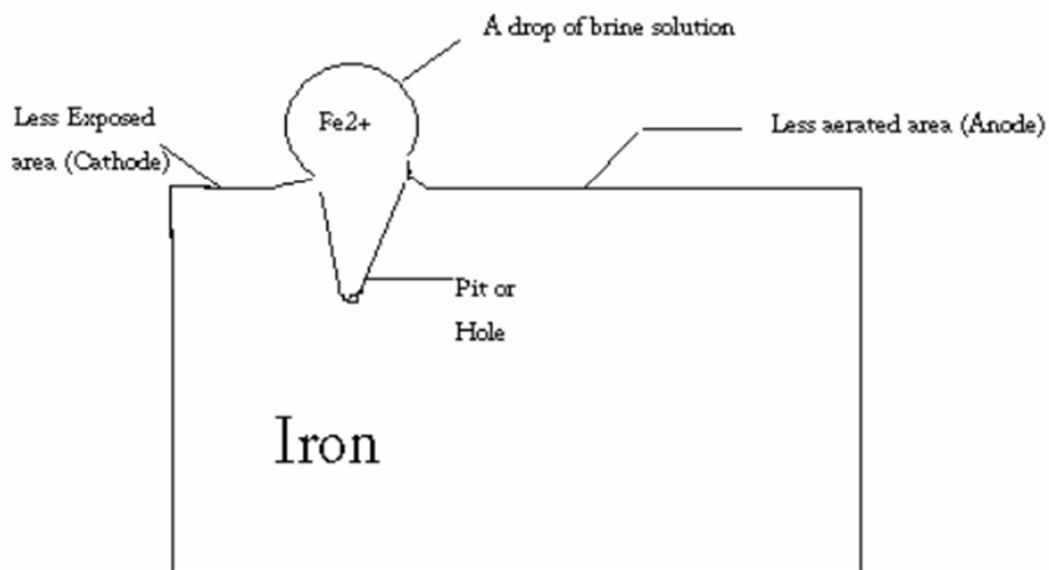
The mechanism of this corrosion involves setting up of differential aeration or concentration cell.

Metal area covered by a drop of water, dust, sand, scale etc. is the aeration or concentration cell.

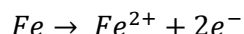
Pitting corrosion is explained by considering a drop of water or brine solution (aqueous solution of NaCl) on a metal surface, (especially iron).

The area covered by the drop of salt solution as less oxygen and acts as anode. This area suffers corrosion, the uncovered area acts as cathode due to high oxygen content.

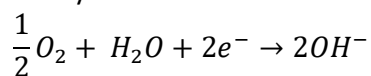
It has been found that the rate of corrosion will be more when the area of cathode is larger and the area of the anode is smaller. Hence there is more material around the small anodic area results in the formation hole or pit.



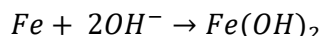
At anode: Fe is oxidized to  $Fe^{2+}$  and releases electrons.



At cathode: Oxygen is converted to hydroxide ion



The net reaction is



The above mechanisms can be confirmed by using ferroxyl indicator (a mixture containing phenolphthalein and potassium ferricyanide). Since  $OH^{-}$  ions are formed at the cathode, this area imparts pink colour with phenolphthalein indicator. At the anode, iron is oxidized to  $Fe^{2+}$  which combines with ferricyanide and shows blue colour.

### Stress Corrosion:

Stress corrosion cracking (SCC) is a localized form of corrosion that leads to the cracking of materials due to the combined effects of tensile stress and a specific corrosive environment. It is one of the most dangerous forms of corrosion because it can lead to sudden and catastrophic failures in materials that otherwise appear sound.

SCC occurs when three critical factors come together: Tensile stress, Corrosive environment, Susceptible material.

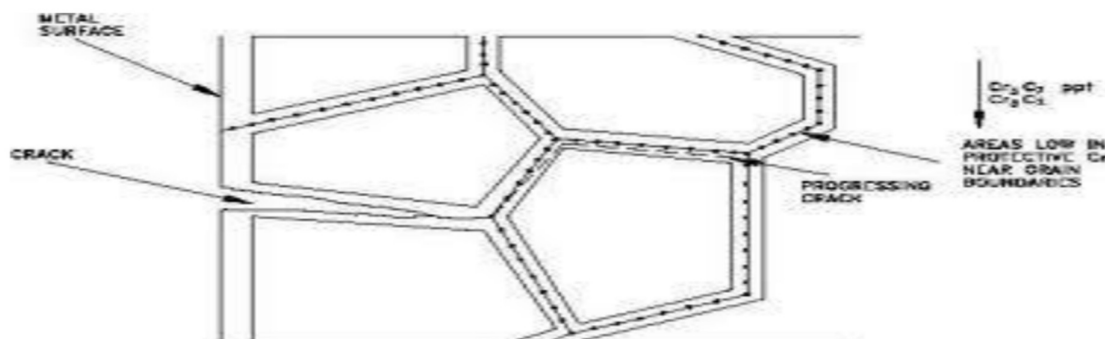
Areas under stress act as anode, other areas act as cathode in presence of corrosive environment.

### Inter-granular Corrosion:

Occurs in granular metals and homogenous alloys.

Occurs along grain boundaries which contain material which has more anodic nature than grain centre in corroding liquid.

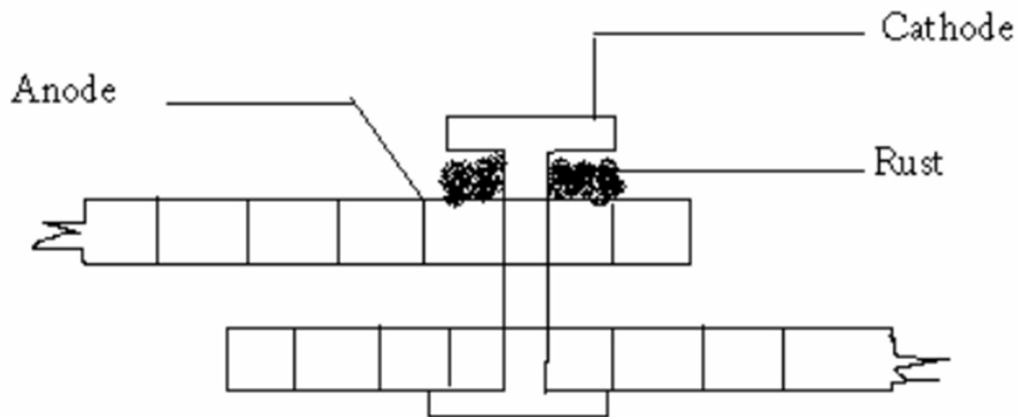
The centre is untouched and ppt of corrosion happen at boundary only.



### Crevice corrosion:

If a crevice (a crack forming a narrow opening) between metallic and non-metallic material is in contact with a liquid, the crevice becomes anodic region and undergoes corrosion. Hence,

oxygen supply to the crevice is less. The exposed area has high oxygen supply and acts as cathode.



## Crevice Corrosion

Bolts, nuts, rivets, joints are examples for this type of corrosion.

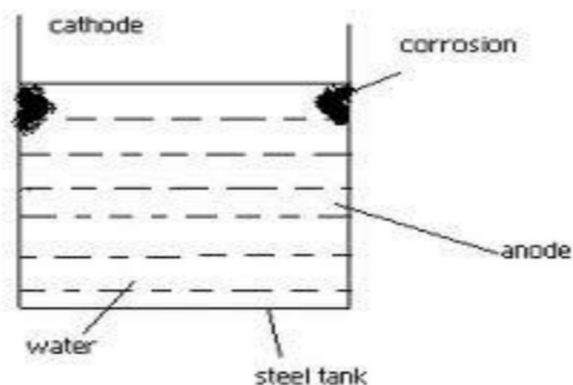
### Erosion Corrosion:

This happens when gases or vapours or liquid strike side-walls with high velocity. The effect of abrading action of turbulent flow and mechanical rubbing of particles with metal surface which leads to formation of differential cells. The localized corrosion at anode is then set up.

### Water Line corrosion:

In a tank with stagnant water, Oxygen concentration is greater above the water surface than oxygen under the surface. This leads to Oxygen concentration cells. In this cell, metal above water line is cathode and metal below water line is anode corrosion occurs at this are i.e. below water level.

Water Line Corrosion



### Soil corrosion:

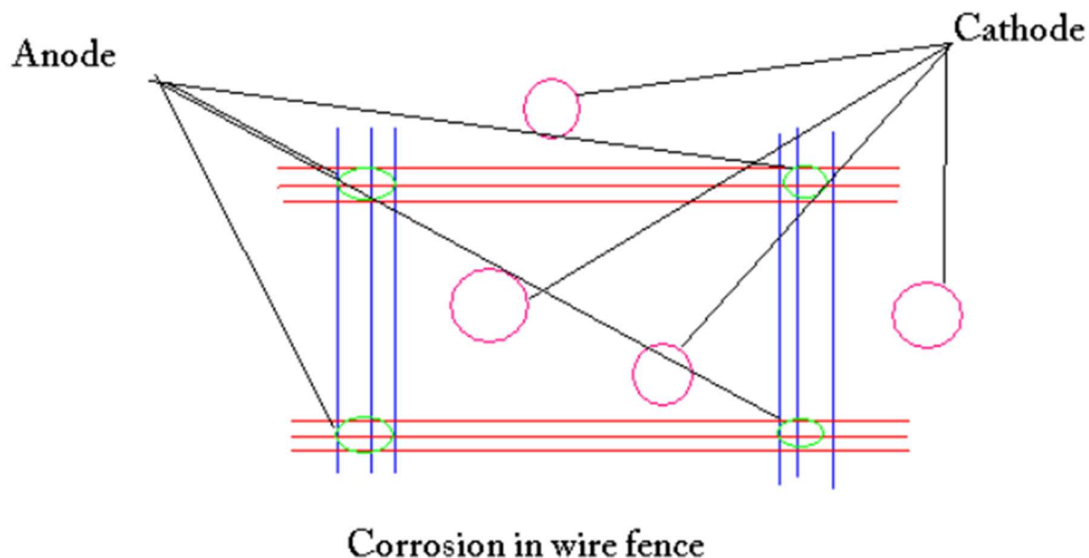
Moisture, bacteria, micro-organisms and electrolyte present in soil are responsible for soil corrosion. Differential aeration is also the other factor responsible for soil corrosion. It happens for pipe lines and cables passing from one type of soil to another.

Lead pipe passing from clay (less aerated) to sand (more aerated). Which portion of pipeline will corrode? The pipe which is in clay will corrode. In water-logged soil, the aeration is less and microbes are more, which corrodes the metal.

### Corrosion in wire fence:

A wire fence is one in which the areas where the wires cross (anodic) are less aerated than the rest of the fence (cathodic). Hence corrosion takes place at the wire crossing.

Corrosion occurring under metal washers and lead pipeline passing through clay to cinders(ash) are other examples.



### **GALVANIC SERIES:**

Anode (Most Active)	Magnesium
	Zinc
	Aluminum (2S)
	Cadmium
	Aluminum (175T)
	Steel or Iron
	Cast Iron
	Lead - Tin solder
	Lead
	Nickel
	Brass
	Copper
	Bronze
	Stainless Steel (304)
	Monel Metal
	Stainless Steel (316)
	Silver
	Graphite
Cathode (Least Active)	Gold

Sr. No.	Electrochemical series	Galvanic series
1.	Series of metals and non metals.	Series of metals and alloys.
2.	The position of a metal in the series is permanently fixed.	Position of metal and alloy is different.
3.	It predicts relative displacement.	It predicts relative corrosion tendencies.
4.	Electrode potential measured by dipping pure metal into ionic solution.	Measured in common electrolyte like sea water without any oxide film.
5.	Electrode potential is measured using SHE.	It is measured using standard Calomel electrode.

- ❖ Metal higher in series act as an anode. Less active metal act as a cathode. Oxidation occurs at anode and is corroded. Reduction occurs at cathode and is protected. More the difference between the two, faster the corrosion of anodic metal.



## **FACTORS INFLUENCING CORROSION:**

Rate of corrosion depends on

1. Nature of metal
2. Nature of environment

### **Nature of the metal:**

#### **a. Physical State:**

The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

#### **b. Purity of Metal:**

The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

% purity of aluminium	99.99	99.97	99.2
Relative rate of corrosion	1	1000	30000

#### **c. Over Voltage:**

The voltage or potential at which  $H_2$  gas liberated at cathode in Hydrogen evolution mechanism is called decomposition potential. The difference between theoretical and actual potential is called over-voltage. Higher the over-voltage, slower and lesser is the corrosion.

E.g. *Pb*, *Sn*, *Cd* do not corrode in acidic solution due to higher voltage.

Zn (over-voltage = 0.7V) slow corroding in 1N  $H_2SO_4$  can be made to corrode fast by adding  $CuSO_4$  (over-voltage = 0.33V) and  $PtCl_2$  (over-voltage = 0.2V).



#### d. Nature of surface film:

In aerated atmosphere, practically all metals get covered with a thin surface film (thickness=a few angstroms) of metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. The specific volume ratios of *Ni*, *Cr* and *W* are 1.6, 2.0 and 3.6 respectively. Consequently, the rate of oxidation of tungsten is least, even at elevated temperatures...

For Li, Na, K, Ca, Mg specific volume is less, therefore nature of film is porous and less protective and so more corrosion.

For Al, Cr, Ni greater specific volume hence film is nonporous, protective and not much corrosion.

#### e. Relative areas of the anodic and cathodic parts:

When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part. Corrosion is more rapid and severe, and highly localized, if the anodic area is small (e.g., a small steel pipe fitted in a large copper tank), because the current density at a smaller anodic area is much greater and the demand for electrons can be met by smaller anodic areas only by undergoing corrosion more briskly.

#### f. Position in galvanic series:

In the **galvanic series**, metals higher (anodic) corrode when paired with metals lower (cathodic) in the presence of an electrolyte. The **anodic metal** loses electrons (oxidizes), while the **cathodic metal** is protected. The further apart the metals are in the series, the faster the anodic metal corrodes.

For example:

**Zinc** (higher) corrodes when in contact with **steel** (lower).

Using similar-position metals reduces galvanic corrosion.

#### g. Passive character of metal:

The **passive character** of a metal refers to its ability to form a thin, protective oxide film on its surface that significantly reduces its corrosion rate. This phenomenon is called **passivation**.

This layer prevents the metal from reacting with its environment (i.e. minimizing chemical reactions) and can often regenerate if damaged (re-passivation). Examples include stainless steel and aluminium.

#### h. Solubility of corrosion products:

The **solubility of corrosion products** affects metal corrosion as follows:

Low solubility: Corrosion products form a protective layer, slowing further corrosion (e.g., rust on steel).

High solubility: Corrosion products dissolve, leaving the surface exposed, which accelerates corrosion (e.g., in acids).

#### i. Volatility of corrosion products:

The volatility of corrosion products affects metal corrosion by:

**High volatility:** Corrosion products evaporate, leaving the metal surface exposed and

increasing corrosion (e.g., in high-temperature environments).

**Low volatility:** Corrosion products remain on the surface, potentially forming a protective layer that slows corrosion.

Volatility determines the product's ability to protect the metal surface.

## **Nature of Environment:**

### **Temperature:**

The rate of corrosion is directly proportional to temperature i.e., rise in temperature increases the rate of corrosion. This is because the rate of diffusion of ions increases with rise in temperature.

### **Humidity of air:**

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 a corrosion cell or a galvanic cell. Even in absence of gases, water corrodes *Mg, Al, Zn, Cr, Fe*.

### **Presence of impurities in atmosphere:**

Atmosphere in industrial areas contains corrosive gases like  $CO_2$ ,  $H_2S$ ,  $SO_2$  and fumes of  $HCl$ ,  $H_2SO_4$  etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

### **Presence of suspended particles in atmosphere:**

In case of atmospheric corrosion:

- (i) if the suspended particles are chemically active in nature (like  $NaCl$ , Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion;
- (ii) if the suspended particles are chemically inactive in nature (e.g., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.

### **Influence of pH of the medium:**

Generally acidic media (i.e.,  $pH < 7$ ) are more corrosive than alkaline and neutral media. However, amphoteric metals (like *Al, Zn, Pb*, etc.) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5. The corresponding corrosion rate in presence of oxygen is much higher. Consequently, corrosion of metals, readily attacked by acid, can be reduced by increasing the pH of the attacking environment, e.g., *Zn* (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at  $pH=11$ ).

### **Nature of ions present:**

Silicate anion form insoluble products which form scale and inhibit further corrosion. If  $Cl^-$  is present, it destroys protective film, expose metal surface and causes fresh rapid corrosion.

### **Conductance of the corroding medium:**

In case of corrosion of underground or submerged structure, the conductance of medium i.e. Soil affects the rate of corrosion as corrosion current depends on it.

Clay and mineralized soil is more conducting thus causing more corrosion than sandy soil.

### **Formation of Oxygen concentration cell:**

If two different portions of the same metal are exposed to different aeration and get different amount of oxygen, then Oxygen Concentration cell is formed.

Such differential aeration leads to the corrosion of less oxygenated part, which acts as an anode.

### **Flow velocity of a process stream:**

The flow velocity of a process stream affects metal corrosion as follows:

Low velocity: Corrosion products may accumulate, forming a protective layer that slows corrosion.

High velocity: Increased flow can remove protective layers, expose fresh metal surfaces, and accelerate corrosion (e.g., erosion-corrosion).

Optimal flow rates are critical to managing corrosion.

### **Polarization of electrodes:**

Polarization of electrodes affects metal corrosion by altering the electrochemical reactions:

Anodic polarization: Slows metal dissolution, reducing corrosion.

Cathodic polarization: Slows the reduction reactions (e.g., oxygen or hydrogen), reducing overall corrosion.



## **CORROSION CONTROL (PROTECTION AGAINST CORROSION):**

As the corrosion process is very harmful and losses incurred are tremendous, 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. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. As the corrosion is a reaction between the metal or alloy and the environment, any method of corrosion control must be aimed at either modifying the metal or the environment.

### **a. Choice of metals and alloys:**

1. 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.
2. 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.
3. Thus, the next choice is the use of corrosion resistant alloys. Several corrosion

resistant alloys have been developed for specific purposes and environment. For example,

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

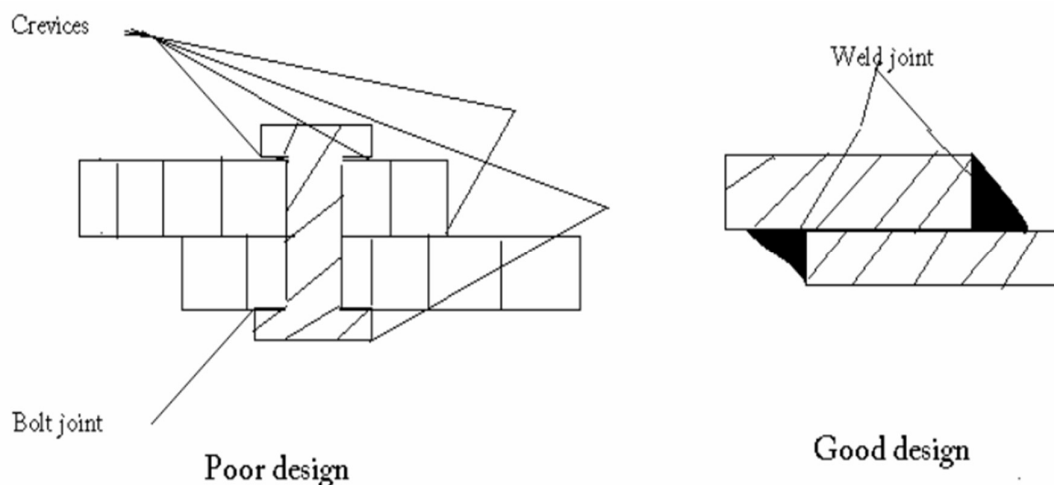
b) Cupro-nickel (70% *Cu* + 30% *Ni*) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries.

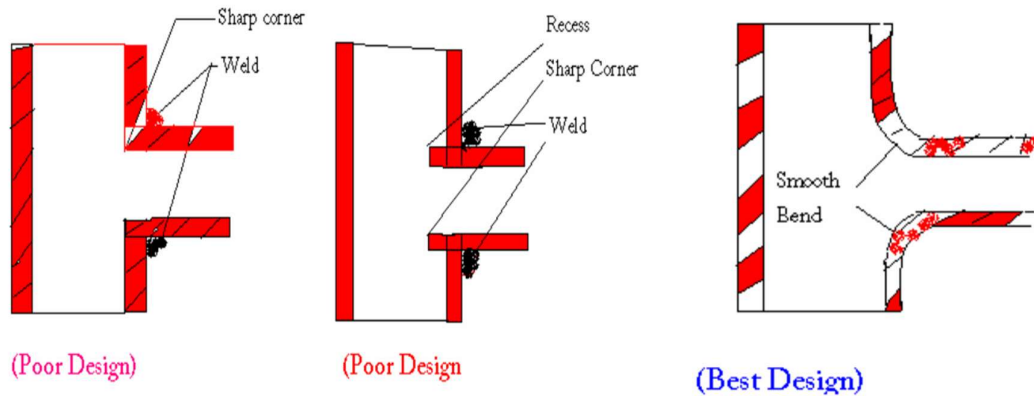
c) Highly stressed Nimonic alloys (*Ni – Cr – Mo* alloys) used in gas turbines are very resistant to hot gases.

## b. Proper Designing:

Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following:

- a. Use always simple design and structure
- b. The design must avoid more complicated shapes having more angles, edges, corners etc.
- c. Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion. To overcome this, insulation can be used.
- d. 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.
- e. As far as possible, crevices (gap or crack) should be avoided between adjacent parts of a structure.
- f. Bolts and rivets should be replaced by proper welding
- g. Metal washers should be replaced by rubber or plastic washers as they do not adsorb water. They also act as insulation.
- h. Corrosion in pipelines can be prevented by using smooth bends.
- i. Heat treatment like annealing minimizes the stress corrosion.
- j. 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.





## **I. CATHODIC PROTECTION:**

The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur. There are two methods of applying cathodic protection to metallic structures.

- a) Sacrificial anodic protection (galvanic protection)
- b) Impressed current cathodic protection

### **SACRIFICIAL ANODIC PROTECTION METHOD:**

In this method, the metallic structure to be protected is made cathode by connection it with more active metal (anodic metal). Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.

#### **Applications:**

1. Protection as buried pipelines, underground cables from soil corrosion.
2. Protection from marine corrosion of cables, ship hulls, piers etc.
3. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
4. Calcium metal is employed to minimize engine corrosion.

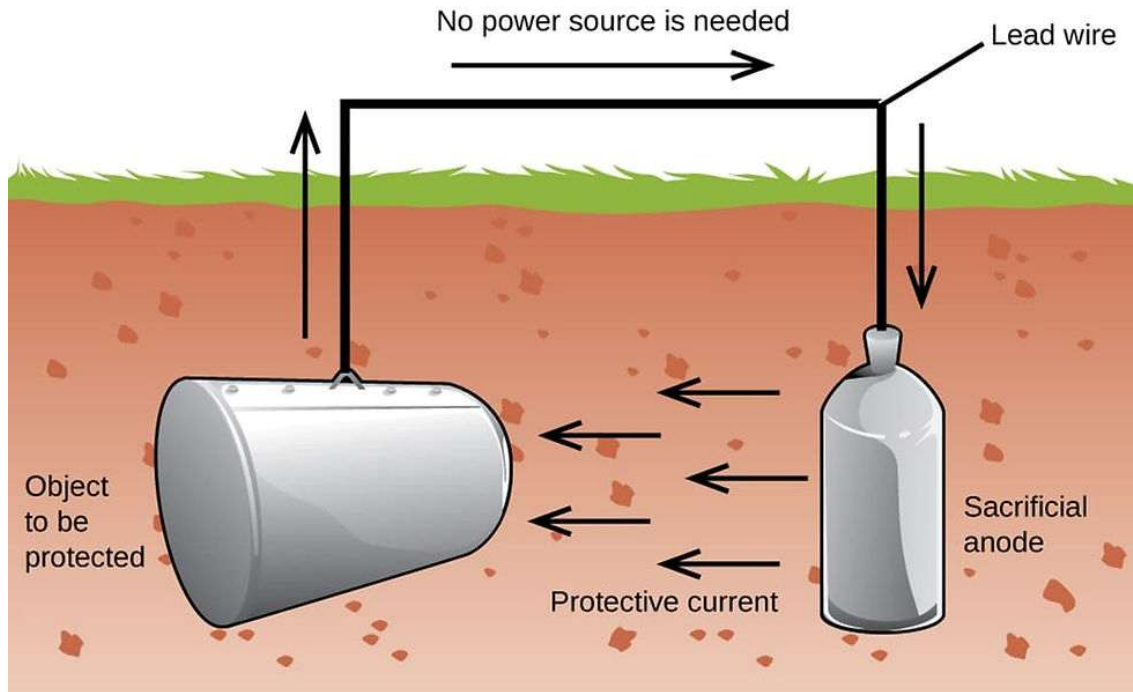
#### **Advantages:**

1. Low installation and operating cost.
2. Capacity to protect complex structures.
3. Applied to wide range of severe corrodents.
4. No external power needed.

#### **Limitations:**

1. High starting current is required and lower current output.

2. Uncoated parts cannot be protected and poorly coated cathode may require many anodes.
3. Limited driving potential, hence, not applicable for large objects.
4. Installation expensive after construction.
5. Ineffective in high resistivity environment.



## **IMPRESSED CURRENT CATHODIC PROTECTION**

### **METHOD:**

In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

Usually, the impressed current is derived from a direct current source (like battery or rectifier on AC line) with an insoluble, inert anode (like graphite, scrap iron, stainless steel, platinum or high silica iron).

A sufficient DC current is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is, usually, a back fill, composed of coke breeze or gypsum, so as to increase the electrical contact with the surrounding soil.

### **Applications:**

Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid up ships etc.

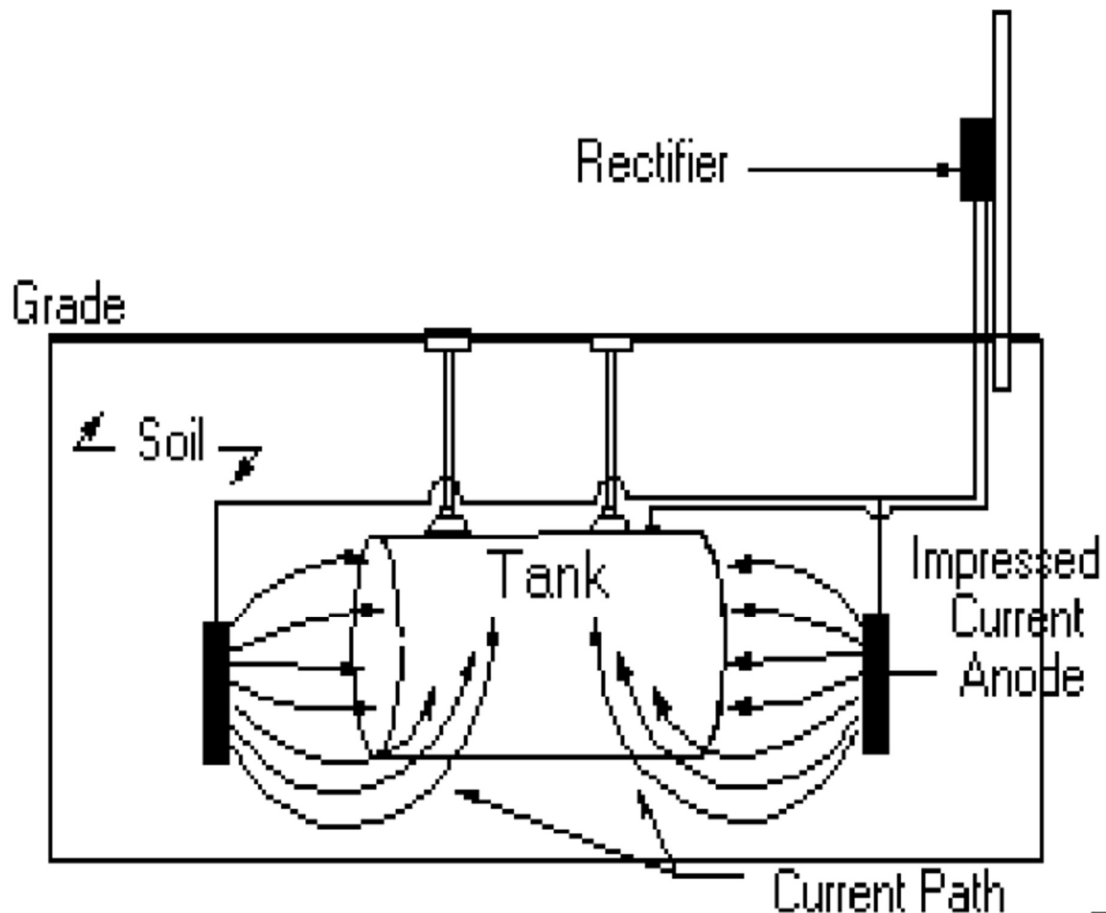
### **Advantages:**

1. Large structures can be protected for long term operations.
2. It can be designed for a wide range of voltage and current.

3. Can be applied in high resistivity environment.
4. Effective in protecting uncoated and poorly coated material.

**Limitations:**

1. Require periodic maintenance.
2. Require external power, therefore more cost.
3. Over protection cause coating damage.
4. Are subject to power failure.



**Comparison of Sacrificial anode method with Impressed current cathodic method:**

Sr. No.	Sacrificial Anode method	Impressed Current method
1.	External power supply is not required.	External power supply is required.
2.	The cost of investment is low.	The cost of investment is high.
3.	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4.	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.

5.	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.
6.	This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

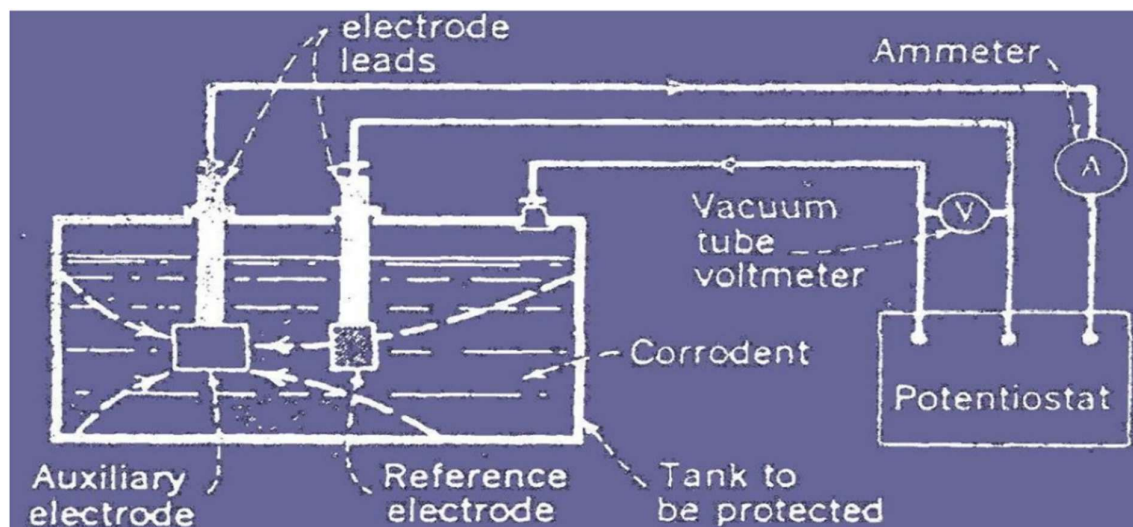
## II. ANODIC PROTECTION:

This is an electrochemical method of corrosion control in which an external potential control system, called potentiostat, is used to produce and maintain a thin non corroding, passive film on a metal or an alloy. The use of potentiostat is to shift corrosion potential into passive potential so that the corrosion of the metal is stopped.

The potential of the object (say acid storage tank) to be protected is controlled by potential controller (potentiostat) so that under certain potential range, the object becomes passive and prevents further corrosion. This potential range depends upon the relationship between the metal and the environment.

**In short (for better understanding),**

In anodic protection method, the metal to be protected is made more anodic by applying impressed external current in the same direction as corrosion current thus making metal more anodic which forms thin protective oxide film for further protection from corrosion.



### Applications:

1. Used in acid coolers in dilute sulphuric acid plants.
2. Used in storage tanks for sulphuric acid.
3. Used in chromium in contact with hydrofluoric acid.
4. Stainless steel containers used for transporting corrosive chemicals like concentrated acids.
5. Pipes carrying corrosive liquids.
6. Chemical reactors, tanks.



### **Advantages:**

1. Here complex structures can be protected.
2. Method can be applied to severely corroding medium like acids.
3. Low current density, hence operational cost is low.

### **Limitations:**

1. This method cannot be applied in the case of corrosive medium containing aggressive chloride.
2. This cannot be applied if protection breaks down at any point, it is difficult to reestablish.
3. The method is applicable only to those metals and alloys which exhibit passivity.
4. During anodic protection, corrosion though slow takes place therefore corrosion not stopped completely.

Sr. No.	Cathodic Protection	Anodic Protection
1.	Applicable to all metals	Applicable to only passive metals
2.	Metal to be protected is forced to behave like cathode	Metal to be protected is made more anodic
3.	Installation cost low	Installation cost is high, operational cost low.
4.	Can be used when there is no source of power	External power is required
5.	Used for protecting standard shape	Complex structure can be protected



## **PROTECTIVE COATINGS:**

In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings. These coatings act as a physical barrier between the coated metal surface and the environment. They afford decorative appeal and impart special properties like hardness, oxidation resistance and thermal insulation.

Surface treatment: before applying coating, surface should be clean-

- a) removal of grease
- b) removal of oxide layer, rust etc
- c) etching treatment for better adhesion of coat.

The metal to be coated is called base metal and protective layer called Coating.

### **Classification:**

Protective coatings can be broadly classified into two types. They are-

1. Inorganic Coatings
- and 2. Organic Coatings

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

1. Metallic Coating
- and 2. Non-Metallic Coating

Organic coatings consist of Paints, Varnishes, Lacquers and Enamels.

Here, we are going to focus on metallic coating, its types and methods to apply metallic coatings.

## **METALLIC COATINGS:**

Metallic coating is of two types:

- i) Anodic Coating/ sacrificial coating
- ii) Cathodic coating/ noble coating

### **I. Anodic Coating/ Sacrificial coating:**

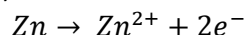
An anodic coating is a type of protective layer applied to metals where the coating material is more anodic (less noble) than the base metal. This means the coating will corrode preferentially, protecting the underlying metal through galvanic action.

#### **Working Mechanism:**

##### **1. Galvanic Protection:**

When exposed to a corrosive environment, the anodic coating acts as the sacrificial anode. The coating corrodes instead of the base metal, protecting it from damage.

Example Reaction (Zinc-coated steel):



The electrons flow to the base metal, reducing its tendency to corrode.

##### **2. Barrier Effect:**

The coating also serves as a physical barrier, reducing exposure of the base metal to corrosive elements like moisture and oxygen.

#### **Common Examples:**

- 1. Galvanizing: Steel is coated with zinc, a more anodic metal.
- 2. Aluminium Coating: Aluminium coatings on steel provide anodic protection in environments with chloride exposure.

#### **Advantages:**

- 1. Long-lasting protection due to sacrificial action.
- 2. Can self-heal minor scratches or damage because the anodic metal corrodes to protect exposed areas.

#### **Disadvantages:**

- 1. The coating depletes over time and requires reapplication.
- 2. Ineffective in environments where the coating cannot corrode (e.g., non-conductive mediums).

### **Applications:**

1. Infrastructure (bridges, poles, pipelines).
2. Automotive parts (galvanized steel in cars).
3. Marine environments (ships, docks).

Anodic coatings are essential for protecting metals, especially steel, in harsh environments, extending their lifespan and reducing maintenance costs.

## **II. Cathodic Coating/ Noble Coating:**

A cathodic coating is a protective layer applied to a metal where the coating material is more cathodic (noble or less reactive) than the base metal. This coating prevents corrosion of the underlying metal by making the base metal the cathode in a galvanic cell. As a result, corrosion is inhibited on the protected metal, while the coating remains largely unaffected.

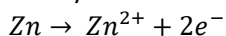
### **Working Mechanism:**

#### 1. Galvanic Protection:

In a corrosive environment, the metal substrate (base metal) becomes the cathode of an electrochemical cell, while the coating acts as the anode. The base metal is protected from corrosion because it does not undergo oxidation; instead, the coating, which is anodic, corrodes in its place.

Example Reaction (for a zinc-coated steel as cathodic coating):

The metal substrate (steel) remains protected because it does not undergo corrosion. Instead, zinc, being more anodic, corrodes preferentially:



This prevents the base metal from being exposed to corrosive agents.

#### 2. Physical Barrier:

The coating also serves as a barrier to physical elements such as moisture, salts, and oxygen, which are necessary for corrosion to occur.

### **Common Examples:**

1. Galvanization (Zinc Coating): Zinc is used as a cathodic coating on steel (commonly known as galvanized steel).
2. Plating with Nickel, Chromium, or Tin: These metals, being more cathodic than steel, are often used to coat steel or other base metals to prevent rust and corrosion.

### **Advantages:**

1. Extended Life of base metal
2. Protection in Harsh Environments
3. The coating itself is typically hard and resistant to wear, scratches, and abrasion.

### **Disadvantages:**

1. The cathodic coating can wear down over time, particularly in environments with high mechanical abrasion, which can expose the underlying metal.
2. Cathodic coatings like nickel, chromium, or zinc can add cost to the manufacturing process, particularly in the case of complex shapes.

3. Once the coating is depleted or damaged, it needs to be re-applied, which might be costly or impractical in some applications.

### **Applications:**

1. Automotive Industry: Zinc or nickel plating is used on parts like bumpers, exhausts, and wheel rims.
2. Construction: Steel reinforcement bars in concrete are often coated with zinc to prevent corrosion.
3. Marine: Zinc and aluminium coatings are used to protect steel in ships and offshore platforms.
4. Electronics: Tin plating is common on connectors and electronic components to avoid corrosion.

### **Methods to apply metallic coating:**

Corrosion of metals can be prevented or controlled by using methods like galvanization, tinning, metal cladding, electroplating, cementation, anodizing, phosphate coating, enamelling, electroless plating. Some of the methods are

#### **A] Hot Dipping:**

It is used for producing a coating of low-melting metals such as  $Zn$  (m.p.=419 °C),  $Sn$  (m.p.=232 °C),  $Pb$ ,  $Al$  etc., on iron, steel and copper which have relatively higher melting points. The process is immersing the base metal in a bath of the molten coating-metal, covered by a molten flux layer (usually zinc chloride).

e.g. Coating of  $Zn$  (m.p. = 419°C) on iron called as Galvanizing of steel

Coating of  $Sn$  (m.p. = 232°C) on iron called as Tinning

##### **a. Galvanizing:**

The process of coating iron or steel (base metal) with a thin coat of  $Zn$  by hot dipping for prevention of corrosion is called as Galvanizing.

##### **Process:**

- 1) The metal article is cleaned and degreased by using organic solvents.
- 2) It is treated with dil.  $H_2SO_4$  for 20 min at 90°C to remove rust.
- 3) Then, it is washed with water, dried and dipped in  $Zn$  bath at 430°C. Surface is covered with Flux ( $NH_4Cl$ ) for better adhesion.
- 4) It is passed through pair of hot rollers to remove excess zinc and to form thin coating.
- 5) And then, it is heated at 650°C and cooled to room temperature slowly.

##### **Uses:**

For roofing sheets, wires, pipes, bolts, screws, tubes, buckets.

Not good for storing acidic food stuff.

### **b. Tinning:**

The process of coating iron or steel with thin coat of tin by hot dipping for prevention of corrosion.

#### **Process:**

1. Clean the metal surface by treating it with dilute  $H_2SO_4$ .
2. It is passed through the flux ( $ZnCl_2$ ).
3. Next, the steel passes through a tank of molten tin ( $Sn$ ) at  $240^\circ C$ .
4. Finally, it is passed through a series of rollers from underneath (bottom of) the surface of a layer of palm oil. Rollers remove excess of  $Sn$  to produce thin, uniform coating. Palm oil protect coating against oxidation.

#### **Uses:**

It is non-toxic, hence used for storing food stuffs, oils, ghee.

Used for making utensil and refrigeration equipment.

#### **Comparison between Galvanizing and Tinning:**

Sr. No.	Galvanizing	Tinning
1.	It is process of covering $Fe$ with a thin coat of $Zn$ .	It is a process of covering steel with a thin coat of $Sn$ .
2.	$Zn$ is anode and protects steel sacrificially.	$Sn$ protects the base metal due to its noble nature.
3.	Even if coating ruptured, $Zn$ still protects the base sacrificially.	Protection only when coating is intact. If holes develop in the coating, base metal starts corroding fast.
4.	Galvanized steel not used for storing acidic food stuff.	Safe to store food stuff since tin is non-toxic.

### **B] Metal Cladding:**

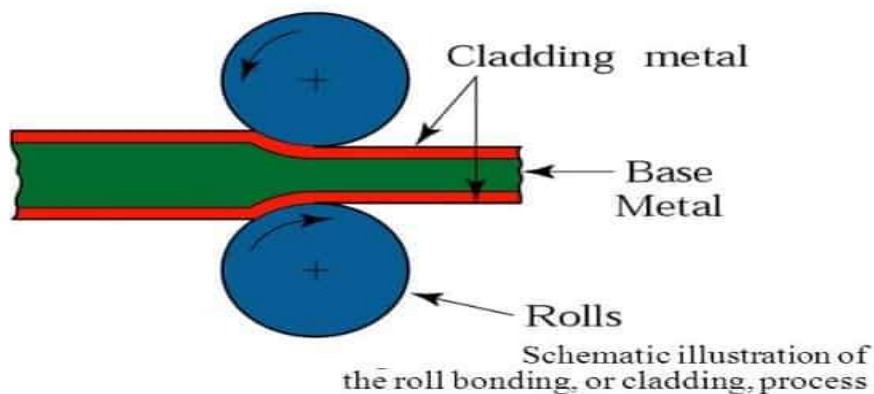
It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides. Corrosion resistant metals like nickel, copper, lead, silver, platinum and alloys like stainless steel, nickel alloys, copper alloys, lead alloys can be used as cladding materials.

Done by performing sandwich of cladding metal and base metal by passing through rollers under the action of heat and pressure.

#### **Uses:**

1.  $Al$  cladding: used in aircraft industry
2.  $Ni$  clad steel in storing chemicals, petroleum, rubber industries.
3.  $Cu$  clad in electrical industries.

# Roll Bonding

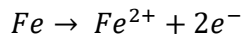


## **C] Cementation/ Diffusion coating:**

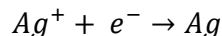
Cementation is a metallurgical process in which a metal is coated or plated onto another metal through a chemical reaction. It involves the displacement of a more noble metal from its solution by a less noble metal, which acts as a sacrificial material.

### **Working Mechanism:**

1. A metal salt solution (e.g., silver nitrate) comes into contact with a less noble metal (e.g., iron).
2. The less noble metal dissolves and releases electrons:



3. The more noble metal is deposited as it gains these electrons:



### **Key Features:**

1. Involves redox reactions.
2. Commonly used for metal recovery from solutions (e.g., recovering silver or copper).

### **Applications:**

1. Metal Recovery: Extracting precious metals (silver, copper) from waste solutions.
2. Anti-corrosion Coating: Protecting metals by forming a noble metal layer.
3. Chemical Industry: Used in processes requiring selective deposition of metals.

Cementation is a simple and cost-effective method for metal deposition and recovery.

### **a) Sherardizing (developed by Sherard Cowper-Coles in 1890):**

It is the process of cementation, using  $Zn$  powder as coating metal.

In this process iron particles are cleaned and rotated with  $Zn$  dust in drum at  $370^{\circ}\text{C}$  for 2-3 hrs.

During this process,  $Zn$  diffuses into iron and form  $Fe - Zn$  alloy on surface.

It is good for small articles like bolts, screws, nuts and gives uniform coating.

**b) Colorizing:**

By heating metal objects having rough surface with  $Al$  powder in a packed drum at  $840 - 930^{\circ}C$  in reductive atmosphere where  $H_2$  is used.

This method is good for coating furnace parts, valves, condensers in refinery and appliances where protection from oxidation is required.

**c) Chromizing:**

Carried out by heating base metal with mixture of  $Cr$  powder and alumina at  $1300^{\circ}C$  for 3-4 hrs.

It is extensively used for protection of gas turbine blades.

Chromized steel is also used in appliances where corrosion by salt, spray, steam or dilute  $HNO_3$  occurs.

**D] ELECTROPLATING OR ELECTRODEPOSITION:**

Electroplating is a coating technique. It is the most important and most frequently applied industrial method of producing metallic coating.

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

The base metal to be plated is made cathode whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

**Objectives:**

Electroplating is carried out for

- 1) Decoration or better appearance of both metal and non-metal.
- 2) Increasing the resistance to corrosion of the coated metal.
- 3) Improving the hardness of the metal.
- 4) Increasing the resistance to chemical attack (i.e., chemical resistivity).
- 5) Electro refining.
- 6) Makes surface of a non-metal conductive.
- 7) Increases the strength of non-metal.
- 8) Preservation of non-metal.

**Cleaning and surface preparation of metal before electroplating:**

i) Solvent cleaning: Done with solvents like,  $CCl_4$ , toluene, xylene, acetone etc. for removing oils, greasy substances which is followed by cleaning with steam.

ii) Alkali cleaning: For removing old paint coating with trisodium phosphate along with soaps and caustic soda. Followed by mild rinsing with water and acidic water to neutralise alkali.

iii) Mechanical cleaning: To remove loose rust by using chisels, scrapers, brushes, etc.

iv) Flame cleaning: Metal surface is heated with hot flame to remove moisture and scales.

v) Sand blasting: To remove oxide scales and for getting rough surface. Sand is introduced into air stream at 100 atm. Then it is pressurized and blasted with high impact on metal surface.

vi) Pickling: Immersing metal in acidic or alkaline solution to provide clean, smooth surface.

Acid pickling is easier as compared with mechanical cleaning and sand blasting. Except *Al*, all other metals are dipped in dilute *HCl*.

**Process of Electroplating:**

1. Base metal to be coated is cleaned to remove oils, grease etc. using above methods.
2. Electroplating is carried out in electroplating bath.
3. Metal to be protected is made the cathode of the electrolytic cell.
4. The anode is either the coating metal itself or an inert material of good electrical conductivity.
5. Number of cathodes and anodes are suspended alternately for getting uniform deposition.
6. They are dipped in the electrolyte which is a solution of soluble salt of the coating metal.
7. pH of electrolyte is adjusted and suitable current density is chosen for electrolysis.
8. As electrolysis proceeds, the anode metal gets oxidized and enters electrolyte solution. The metal ions get reduced and deposit on cathode to give uniform coating on metal.
9. The metal ions getting reduced and deposited at cathode are reformed by oxidation of anode, so concentration of metal ions in the electrolyte remains unchanged.

**EXTRAS!**

10. In order to get a strong, adherent and smooth deposit, certain types of additives (glue, gelatine, boric acid) are added to the electrolytic bath.
11. In order to improve the brightness of the deposit, brightening agents are added in the electrolytic bath.

**For Nickel plating,**

Anode reaction:  $Ni \rightarrow Ni^{2+} + 2e^{-}$

Cathode reaction:  $Ni^{2+} + 2e^{-} \rightarrow Ni$

Salt:  $NiCl_2$

**For Copper plating,**

Anode reaction:  $Cu \rightarrow Cu^{2+} + 2e^{-}$

Cathode reaction:  $Cu^{2+} + 2e^{-} \rightarrow Cu$

Salt:  $CuSO_4$

**The favourable conditions for a good electrodeposit are**

- i) Optimum temperature.
- ii) Optimum current density.
- iii) Low metal ion concentrations.
- iv) Control of rate of deposition.
- v) Control of anode surface area and position.
- vi) Control of pH of electrolyte.

**Advantages:**

1. Coating thickness can be controlled.
2. Coating of metals having high melting points like *Cr*, *Ni*, *Ag*, etc. can be done.
3. Process is not expensive.
4. Fine coatings can be obtained with improved hardness.