

CORROSION

DR. ANUPAMA SAWANT

Definition and classification

- Corrosion is defined as unwanted destruction or deterioration of a metal due to chemical or electrochemical reactions with the surrounding starting at its surface.

Example: Rusting of iron - A layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface of iron metal.

- Classification is based on –

1. Nature of corrodent –

a) Dry corrosion

b) Wet corrosion

2. Mechanism of corrosion –

a) Direct chemical corrosion

b) Electrochemical corrosion

3. Appearance of metal
after corrosion –

a) Uniform corrosion

b) Non uniform/ Localised corrosion

Causes of corrosion

- The metals exist in the earth crust either in free or combined state.
- Except noble metals (Au, Pt), all other metals are highly reactive in nature which undergo 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.
- 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 and 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.

Direct chemical corrosion (Dry corrosion/ Atmospheric corrosion)

Dry corrosion, sometimes also called chemical corrosion, is a type of corrosion that occurs without moisture or water, which are the main drivers of the conventional types of corrosion. In dry corrosion, metal oxidizes with only the atmosphere, in a process sensitive to temperature. Dry corrosion, therefore, refers to an oxidation process sustained by oxygen in the air without a liquid solution.

This type of corrosion is due to the direct chemical attack on 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 on metals by the atmospheric gases present in the environment.

Example:

- (i) Silver materials undergo chemical corrosion by Atmospheric H_2S gas .
- (ii) Iron metal undergo chemical corrosion by HCl gas.

Types of Dry Or Chemical Corrosion:

1. Corrosion by Oxygen or Oxidation corrosion
2. Corrosion by Other gases
3. Liquid Metal Corrosion

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^{n+}



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.

Effect of Nature of Oxide Film on further corrosion

- (i) Stable Oxide film: A Stable film is fine grained in structure and can get adhered tightly to the parent metal surface. It is of two types:
 - a) Nonporous Oxide film: Such film can be of impervious nature (ie., 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 non-porous stable, tightly adhering and impervious in nature.
 - b) Porous Oxide film: The film having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the film, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide. Oxide films on **Li, K, Na, Mg**, are porous in nature.
- (ii) Unstable oxide film: 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 film: The oxide film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. **MoO₃** is volatile in nature.

Effect of Nature of Oxide Film on further corrosion

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

2) Corrosion by other gases (SO₂, H₂S, CO₂, F₂, Cl₂) :

This type of corrosion mainly depends on chemical affinity between metal & the gas involved. The intensity of attack depends on formation of protective or non protective films on metal surface.

If the film is protective or non porous, the volume of metal oxide layer is greater than that of metal. So further corrosion of metal doesn't take place.

eg: Formation of AgCl film by the attack of chlorine on Ag. The intensity of corrosion decreases due to formation AgCl non porous film on its surface which is tightly adherent on Ag.

If the film is non- protective or porous, the volume of metal oxide layer is lesser than that of metal so further corrosion takes place.

eg: SnCl₄ formed by attack of Cl₂ on Sn (tin) which volatiles immediately there by leaving fresh metal surface for further corrosion.

3) Liquid metal corrosion:

This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occur 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.

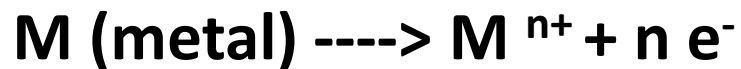
Wet Corrosion (Electrochemical corrosion)

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.



M^{n+} (metal ion) \rightarrow Dissolves in solution
 \rightarrow forms compounds such as oxide

Wet Corrosion/ Electrochemical corrosion (contd...)

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-} , Cl^- , etc.
- Cathodic reaction consumes electrons with either by -
 - (a) evolution of hydrogen or
 - (b) absorption of oxygen, depending on the nature of the corrosive environment

Wet corrosion with Hydrogen evolution

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

At anode:



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

At cathode:

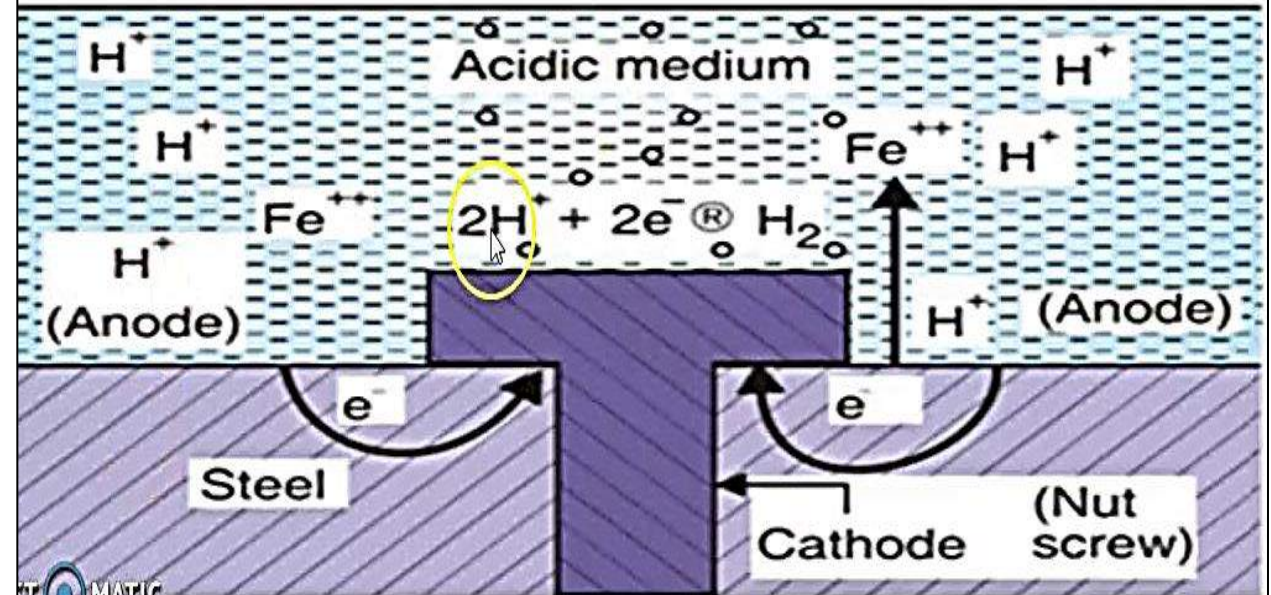


The overall reaction is:



Hydrogen evolution: All metals above H_2 in electrochemical series undergo this type of corrosion

Example: Iron metal in contact with HCl , $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$



Wet corrosion by Oxygen Absorption

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:

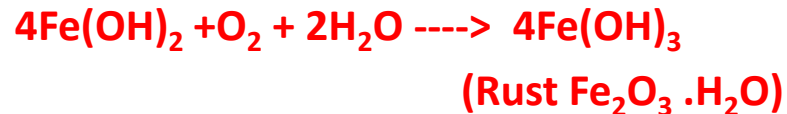
The liberated electrons are intercepted by the dissolved oxygen.



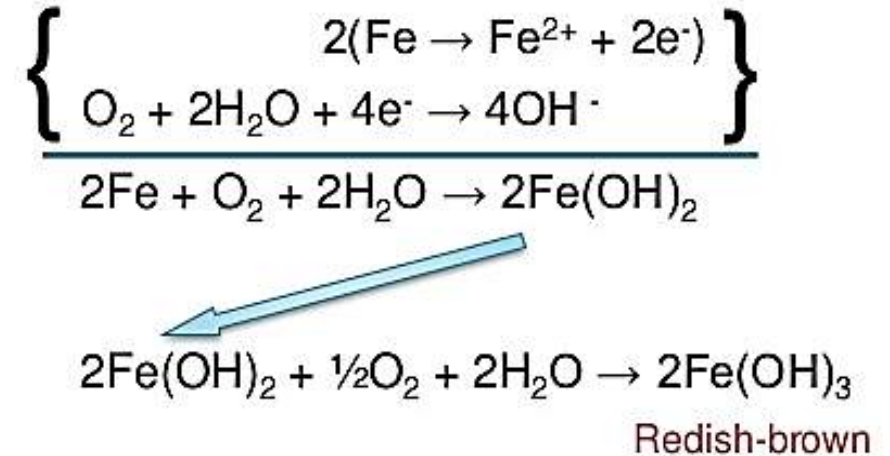
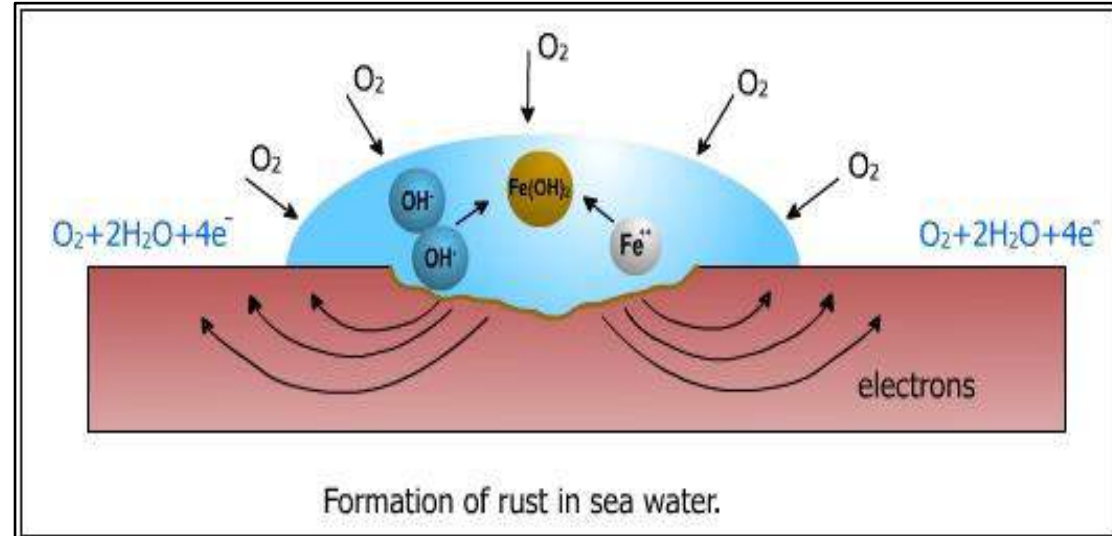
The Fe^{2+} ions and OH^- ions diffuse and when they meet, ferrous hydroxide is precipitated.



- (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 -

Dry Chemical Corrosion	Electrochemical Corrosion
<ul style="list-style-type: none">• It occurs in dry condition.• It is due to the direct chemical attack on the metal by the environment.• Even a homogeneous metal surface gets corroded.• Corrosion products accumulate at the place of corrosion• It is a self controlled process.• It adopts adsorption mechanism.• Formation of mild scale on iron surface is an example.	<ul style="list-style-type: none">• It occurs in the presence of moisture or electrolyte.• It is due to the formation of a large number of anodic and cathodic areas.• Heterogeneous (bimetallic) surface alone gets corroded.• Corrosion occurs at the anode while the products are formed elsewhere.• It is a continuous process• It follows electrochemical reaction• Rusting of iron in moist atmosphere is an example.

CORROSION - 2

DR. ANUPAMA SAWANT

Galvanic corrosion

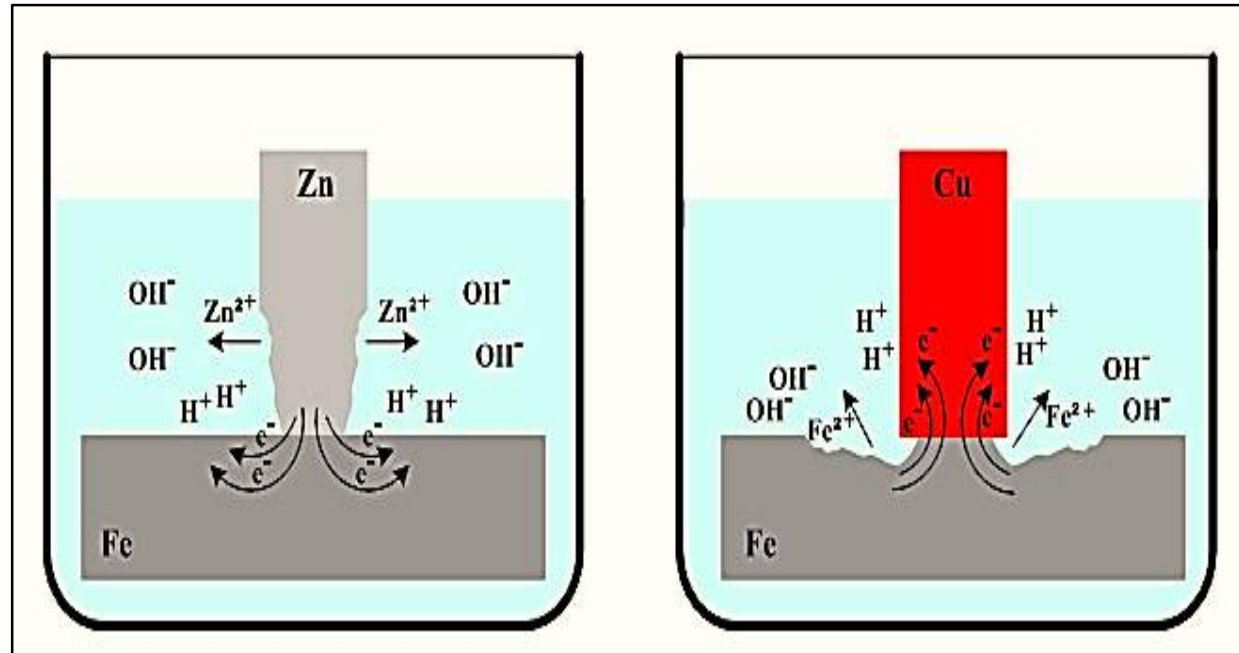
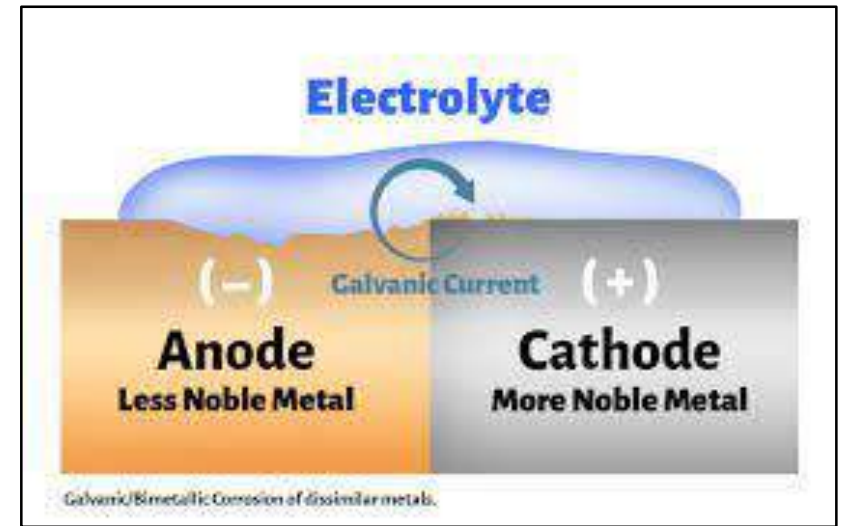
When two dissimilar metals (eg, zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in oxidation potential undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as an anode while the less active metal (with less 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 wire; (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 (**Differential aeration corrosion**). 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. (Corrosion in Ships, Ship-hulls, Large water tanks)

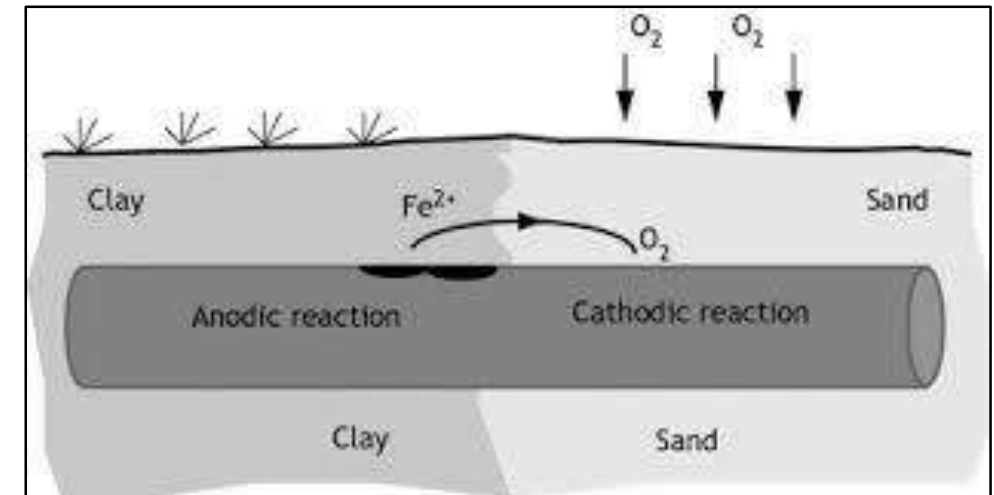
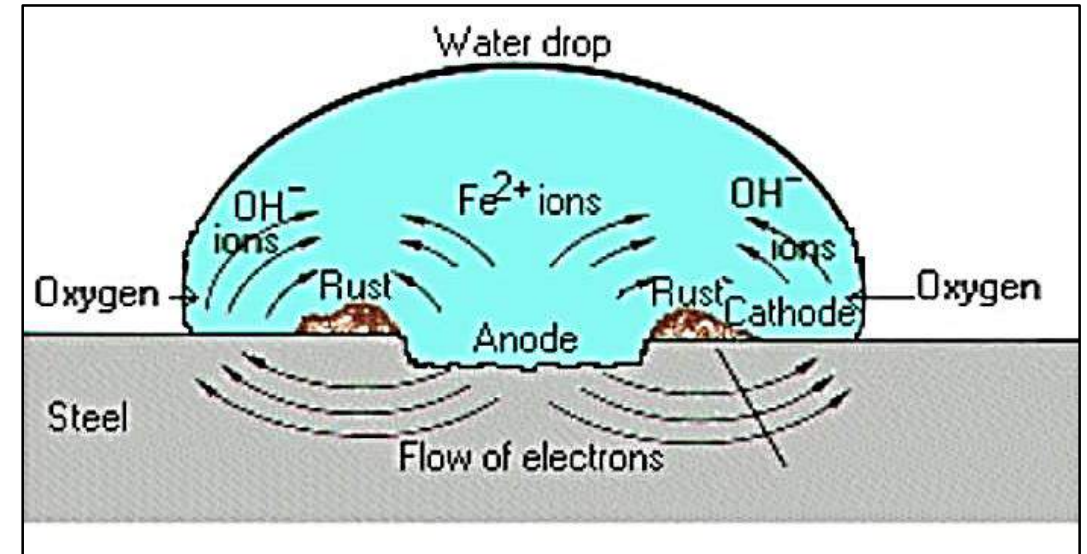
ii) The metal part partially buried in soil. (Underground pipes)

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)



At cathode: OH^{-} ions are produced (more aerated)



Pitting Corrosion

Pitting corrosion 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.

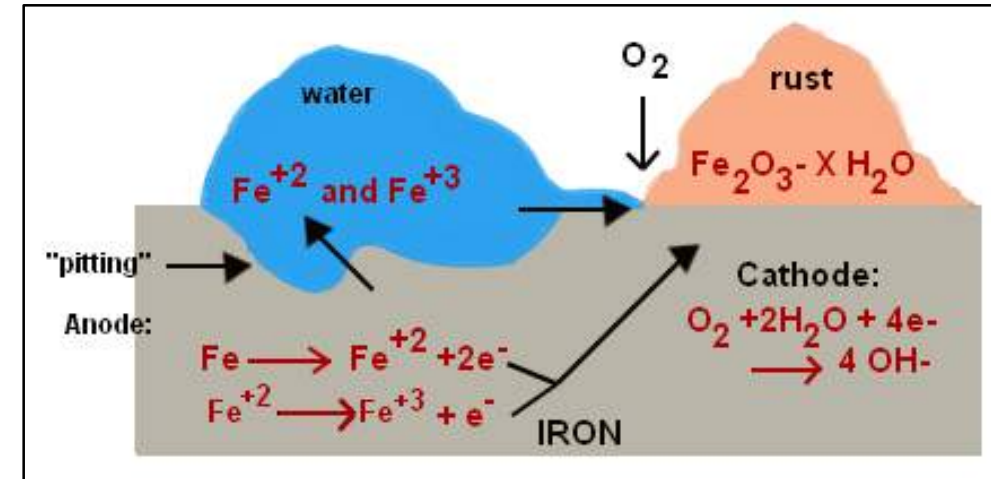
At anode: Fe is oxidized to Fe^{2+} and releases electrons.



At cathode: Oxygen is converted to hydroxide ion



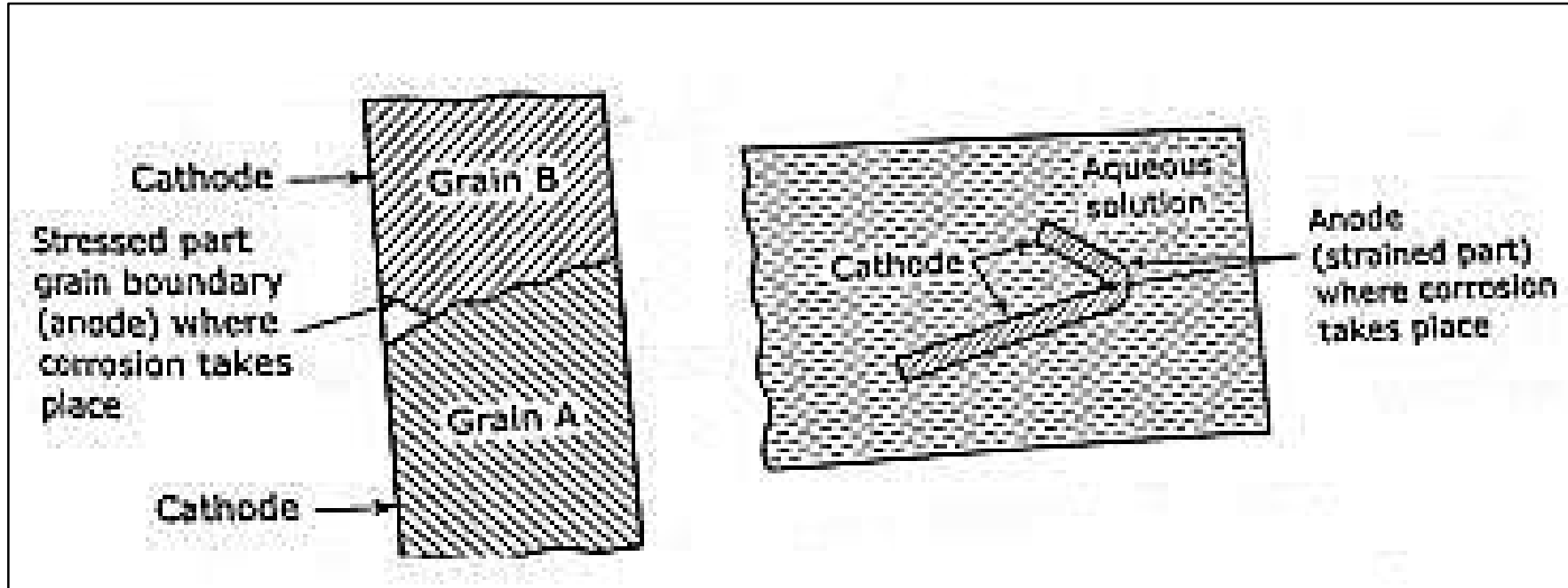
The net reaction is $\text{Fe} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$



Stress Corrosion

- Stress corrosion cracking (SCC) occurs with specific alloys under the following threshold conditions:
 - a) Specific corrosive environment solution composition
 - b) Minimum tensile stress levels
 - c) Temperature
 - d) Metal composition
 - e) Metal structure
- Some examples of Stress Corrosion are the brass and stainless steel alloys.
- Specific brass alloys will crack in ammonia containing environments when a minimum threshold tensile stress is reached.
- Stainless steel alloys do not crack in ammonia environments, but will crack in chloride solutions
- It is believed that the corrosion causes a pit or surface discontinuity to form on the metal which then functions to act as a stress concentrator. The presence of a minimum threshold tensile stress, coupled with the corrosion, causes the crack to propagate. Additionally, during the initial corrosion, the tensile stresses could cause the protective films on the surface to rupture, thereby exposing the metal to the corrosive environment.
- Hydrogen embrittlement – the loss in ductility of a metal due to the saturation of atomic hydrogen in the grain boundaries. It occurs at local cathodic sites and is aggravated by stress and compounds such as hydrogen sulfide
- Caustic Embrittlement in Boilers – Na_2CO_3 decomposes to NaOH & CO_2 at high temp. This reaches the hot boiler wall through crevices and water gets evaporated leaving behind conc NaOH which attacks iron body and makes it brittle. This is a very dangerous type of corrosion which sometimes may lead to explosion.

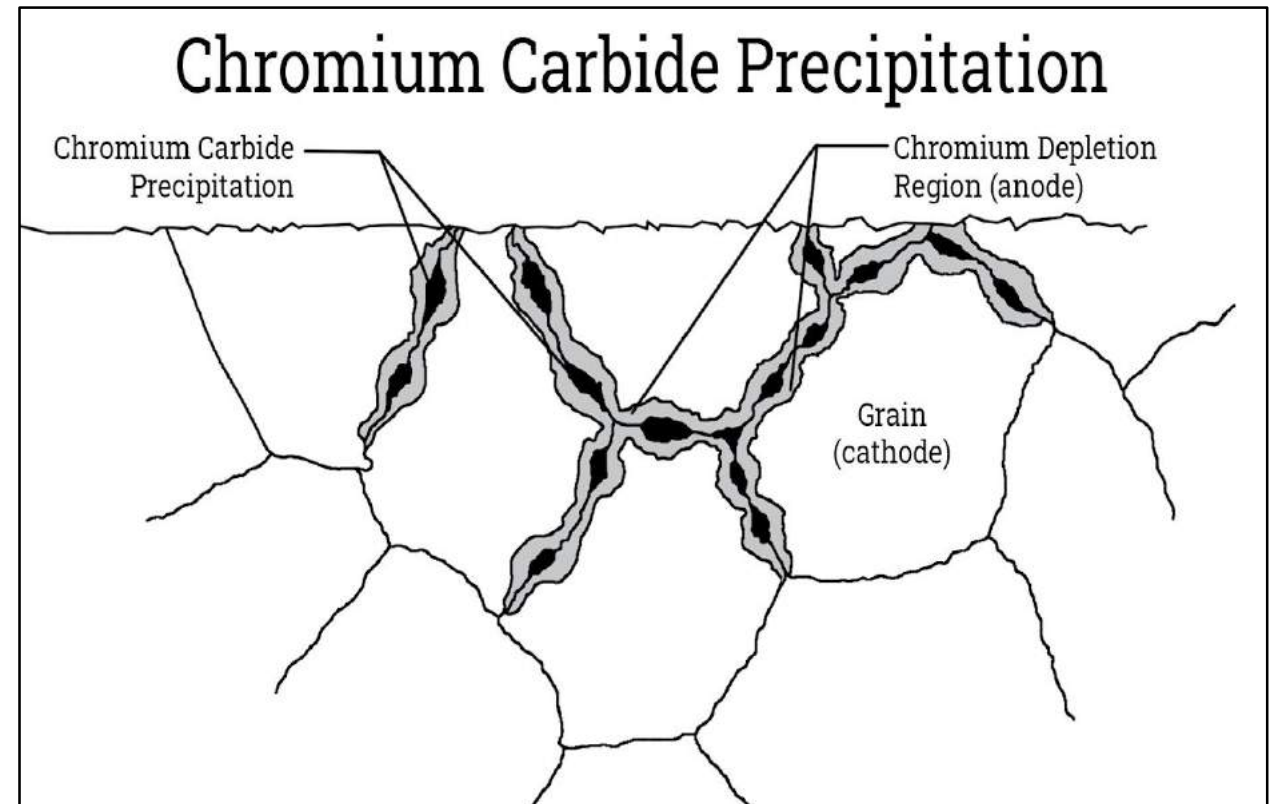
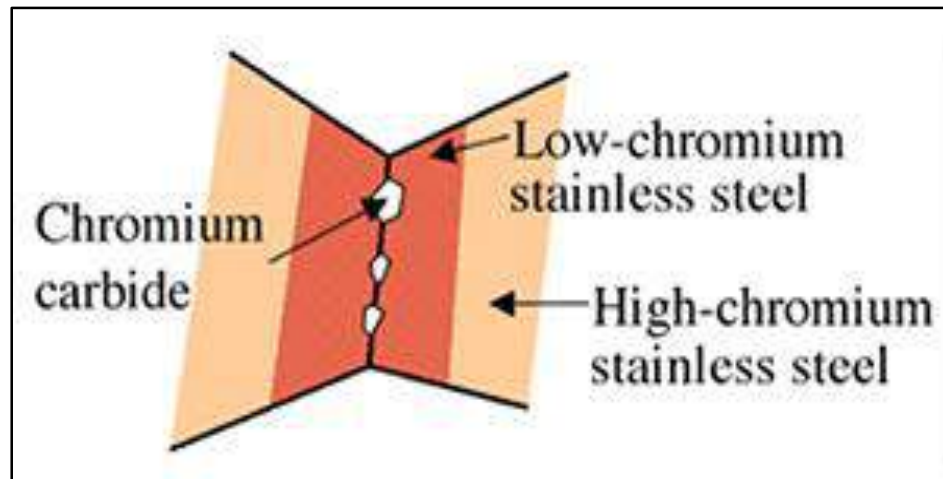
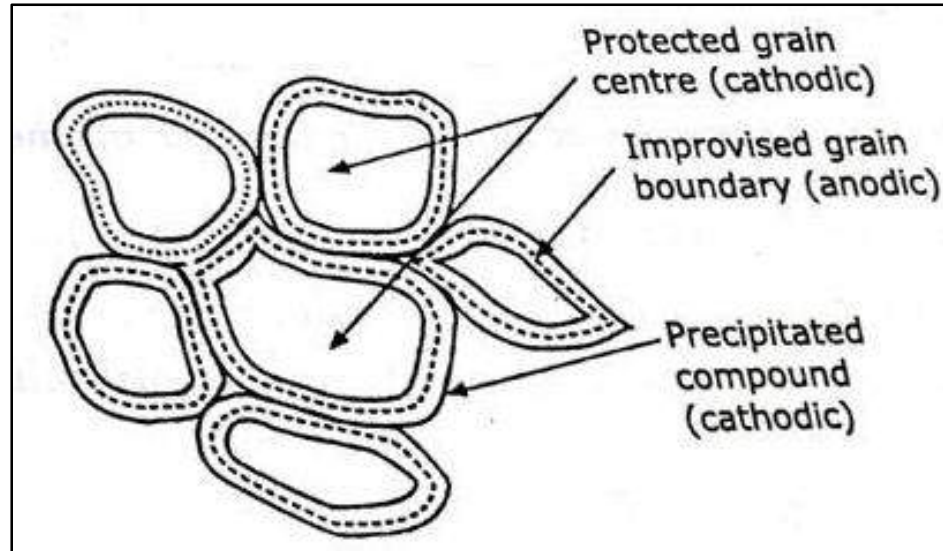
Stress Corrosion



Intergranular Corrosion

- On a microscopic level, metals and their alloys have small, distinguishable regions called grains. Within an individual grain the orientation of the atomic arrangement (called a lattice) is the same. Individual grains have different orientations and the boundary between the grains is called the grain boundary. Normally, grain boundaries are no more reactive in corrosion than the grain itself.
- Under certain conditions, however, the grain boundaries are altered from the grain itself by impurities and/or enrichment (or depletion) of one of the alloying elements.
- Heat treatment and welding can lead to changes in metal composition which may initiate intergranular corrosion.
- In severe cases, intergranular corrosion can lead to a marked decrease in mechanical properties and in extreme cases, turn the metal into a pile of individual grains.
- One of the most common examples of intergranular corrosion occurs in stainless steels. During welding of the alloy, or heating in the temperature range of 950°F to 1450°F, the alloy becomes sensitized or susceptible to intergranular corrosion as illustrated in Figure. The chromium carbide is not soluble at this temperature range and precipitates out of the grain into the grain boundary. As a result, the area of the grain adjacent to the grain boundary is depleted of the chromium and becomes anodic to the rest of the grain and to the grain boundary. The corrosion of this depleted grain boundary area is very severe and occurs in environments and acids where the alloy would not normally corrode. The simplest solution to the stainless steel intergranular corrosion problem is to cast alloys with carbon contents below 0.03%. (This prevents the formation of the chromium carbide and the chromium stays in solution).

Intergranular corrosion



Factors affecting Rate of Corrosion

There are two factors that influence the rate of corrosion. Hence a knowledge of these factors and the mechanism with which they affect the corrosion rate is essential because the rate of corrosion is different in different atmosphere.

- 1. Nature of the metal**
- 2. Nature of the corroding environment**

Nature of 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.

b) Purity of metal:

Impurities in a metal cause heterogeneity and form minute/tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded. For example, the rate of corrosion of aluminium in hydrochloric acid with increase in the percentage impurity is noted.

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

Nature of Metal (Contd...)

c) Over voltage:

The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 V when zinc metal is placed in dil sulphuric acid and the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal.

d) Nature of surface (Oxide) 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..

Nature of metal (Contd...)

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

Rate of Corrosion \propto Cathodic Area / Anodic Area

e.g. a small steel pipe fitted in a large copper tank, because the demand for electrons can be met by smaller anodic areas only by undergoing corrosion more briskly.

F) Position of metal in galvanic series:

- Higher the position of metal in galvanic series (based on oxidation potential) higher is the tendency of metal to undergo corrosion. If Na, Zn and Cu are kept in electrolyte of same concentration for same period it is found that Na (highest Oxidation potential) undergoes corrosion to the greater extent than Zn whereas Cu (Lowest Oxidation Potential) gets corroded the least.
- When two metals are in electrical contact in presence of an electrolyte the one with the higher oxidation potential becomes anode and undergoes corrosion.
- When difference in the Oxidation potential of two metals in contact is more the extent of corrosion in anodic metal is more.

Nature of metal (Contd...)

g) Passive character of metal:

Certain metals like Cr, Ni, Mg, Ti, Al, Ag, Co are passive and show much higher corrosion resistance than expected from their position in Galvanic series due to formation of 'protective' and 'self-healing' thin film of their oxides.

e.g. Corrosion resistance of stainless steel is due to Cr present in it.

h) Solubility and Volatility of corrosion products:

- If corrosion product (oxide or hydroxide) is soluble in corroding medium rate of corrosion is faster
- If corrosion product(oxide and hydroxide) is insoluble in corroding medium or forms insoluble product with corroding medium (PbSO_4) it creates barrier for further corrosion
- If corrosion product is volatile (MoO_3) metal surface gets exposed for further corrosion and rate of corrosion is faster

Nature of Corroding Environment

a) 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. Dissolved Oxygen is exception for this as with increase in temperature the amount of dissolved oxygen decreases and thus the rate of corrosion also decreases.

b) 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.

Nature of Corroding Environment(Contd...)

c) 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.

d) 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 (eg., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.

Nature of Corroding Environment (contd...)

e) Influence of pH:

Generally acidic media (ie., $\text{pH} < 7$) are more corrosive than alkaline and neutral media. (H_2 gas is the corrosion product which shifts the equilibrium to right)) 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, eg., Zn (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at $\text{pH} = 11$).

f) Nature of ions present

g) Conductance of the corroding medium

h) Formation of oxygen concentration cell

Corrosion Control

- **As the corrosion process is very harmful and losses incurred are tremendous, it becomes necessary to minimize or control corrosion of metals.**
- **Corrosion can not be stopped completely, 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.**

Corrosion Control (contd...)

A) Selection of material:

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 Ni-Cr-Mo alloys used in gas turbines are very resistant to hot gases.

Corrosion Control (Contd...)

B) Proper Designing:

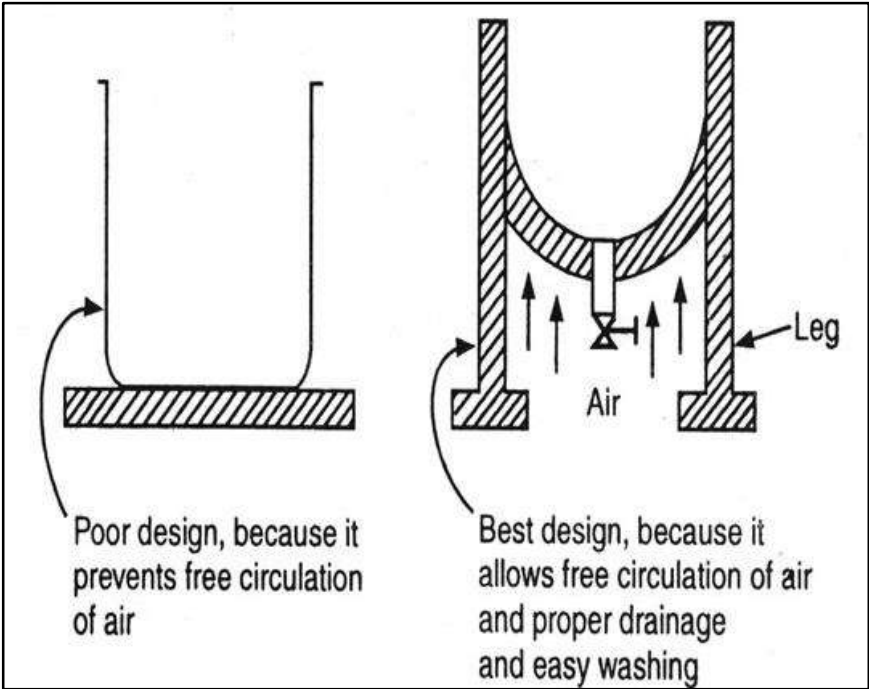
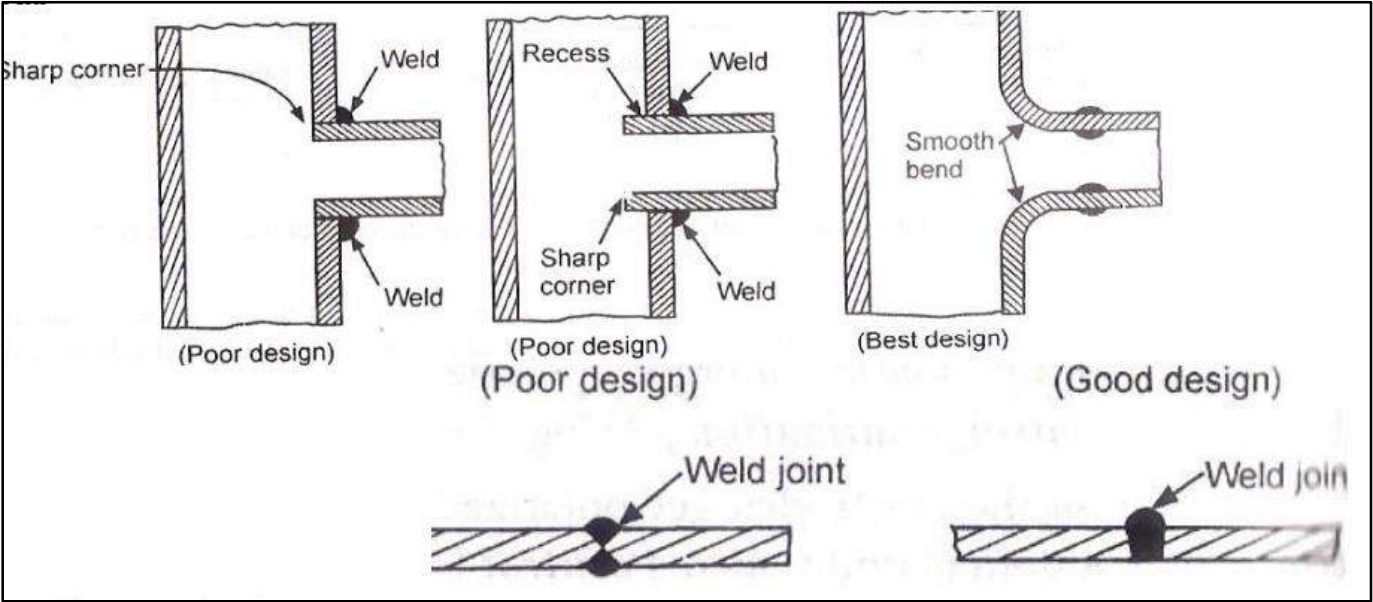
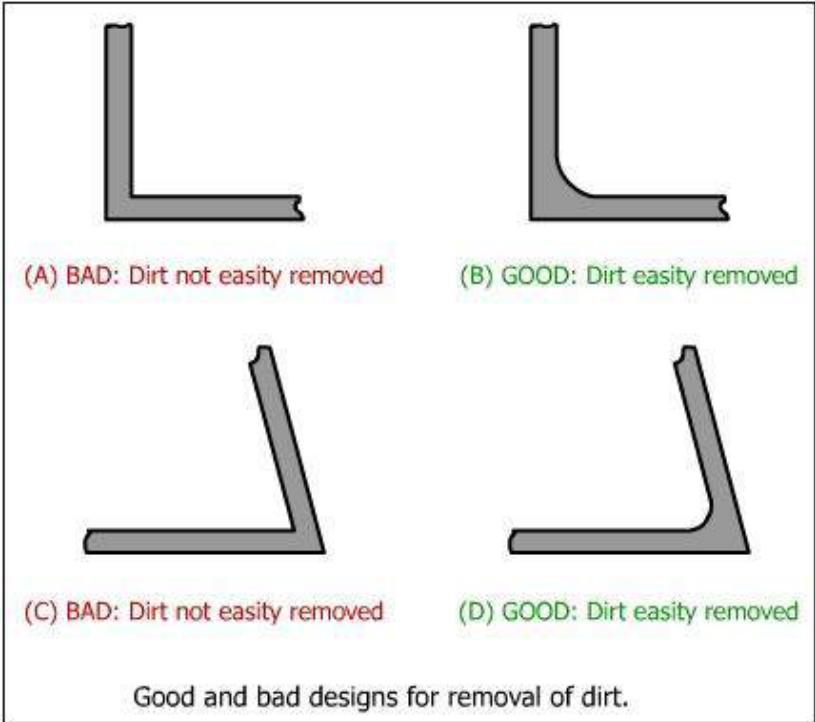
Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following:

- a. **Avoid the contact of dissimilar metals** as they may lead to galvanic type corrosion.
- b. 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.
- c. When two dissimilar metals are to be in contact, they should be **as close as possible to each other in electrochemical series**.
- d. Whenever direct joining of dissimilar metals is unavoidable, **insulation can be used**.
- e. Use always **simple design and structure**
- f. The design must **avoid more complicated shapes** having more angles, edges, corners etc.

Corrosion Control (Contd...)

- g. As far as possible, **crevices (gap or crack) should be avoided** between adjacent parts of a structure.
- h. Bolts and rivets should be **replaced by proper welding**
- i. Metal washers should be **replaced by rubber or plastic** washers as they do not adsorb water. They also act as insulation.
- j. Corrosion in pipelines can be prevented by **using smooth bends**.
- k. Heat treatment like **annealing** minimizes the stress corrosion.
- l. 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.

Corrosion Control (Proper Designing)



Corrosion Control (contd...)

C) Cathodic Protection

- The reduction or prevention of corrosion by forcing metal to behave like a cathode 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 anode Cathodic protection (galvanic protection)
 - b) Impressed current cathodic protection

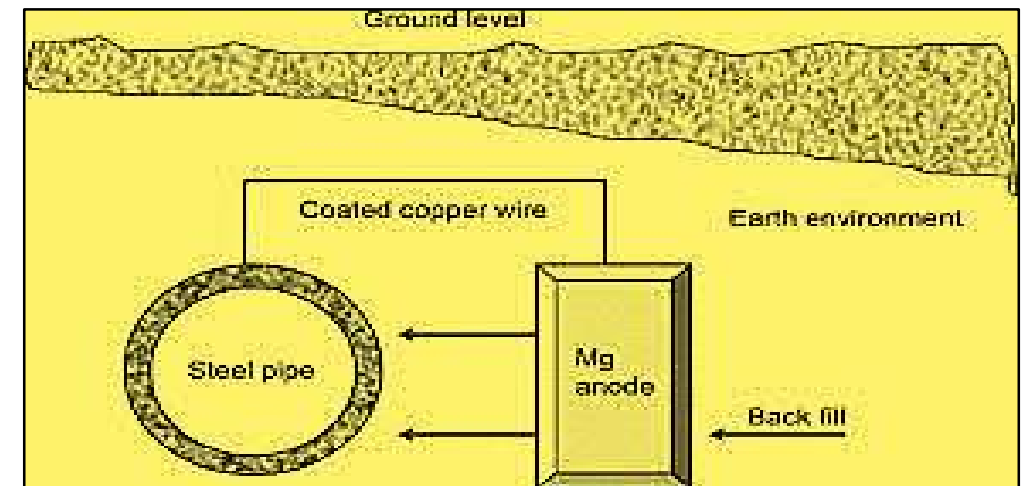
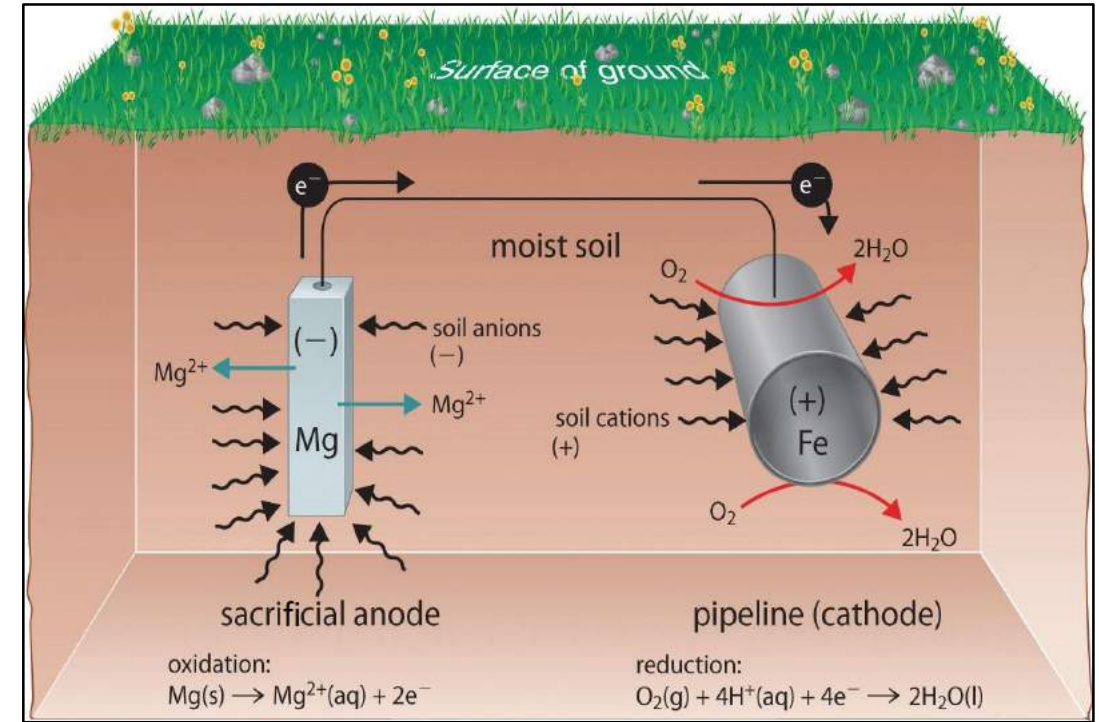
Sacrificial Anode Cathodic Protection Method

In this method, the metallic structure to be protected is made cathode by connecting 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, etc.

Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.

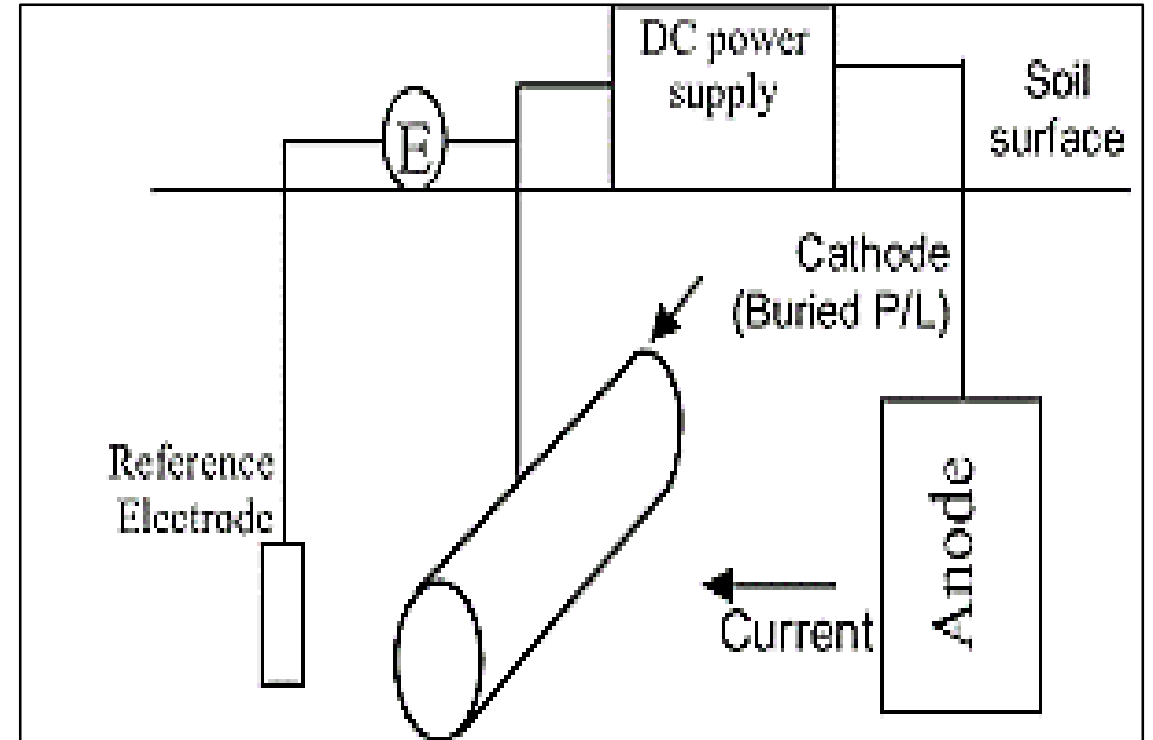
Applications:

1. Protection as buried pipelines, underground cables from soil corrosion.
2. Protection from marine corrosion of cables, ship hulls, etc.
3. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.



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 sources (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. 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. This kind of protection technique is particularly useful for large structures for long term operations.



Comparision

Sacrificial Anode Method	Impressed Current Method
<ul style="list-style-type: none">• External power supply is not required.• The cost of investment is low.• This requires periodic replacement of sacrificial anode.• Soil and microbiological corrosion effects are not considered.• This is the most economical method especially when short term protection is required.• This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	<ul style="list-style-type: none">• External power supply is required.• The cost of investment is high.• Replacement is not required as anodes are stable.• Soil and microbiological corrosion effects are taken into account• This is well suited for large structures and long term operations.• This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

Use of 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.

- Classification:

Protective coatings can be broadly classified into two types.

1. Inorganic coatings

2. Organic coatings

Inorganic coatings are further classified into two types.

A) Metallic coating:

1. Hot dipping – Galvanising, Tinning
2. Metal cladding
3. Cementation – Sherardising, Chromising, Calorising
4. Electroplating.

B) Non-metallic coating:

1. Surface coating or chemical conversion coating – Chromate coating, Phosphate coating and Oxide coating.
2. Anodising
3. Enamel coating or Vitreous or Porcelain coating.

Metallic Coatings

Corrosion of metals can be prevented or controlled by using methods like galvanization, tinning, metal cladding, electroplating, cementation. Some of the methods are

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).

A) Galvanizing

It is the process of coating iron or steel sheets with a thin coat of zinc.

B) Tinning

It is a method of coating tin over the iron or steel articles.

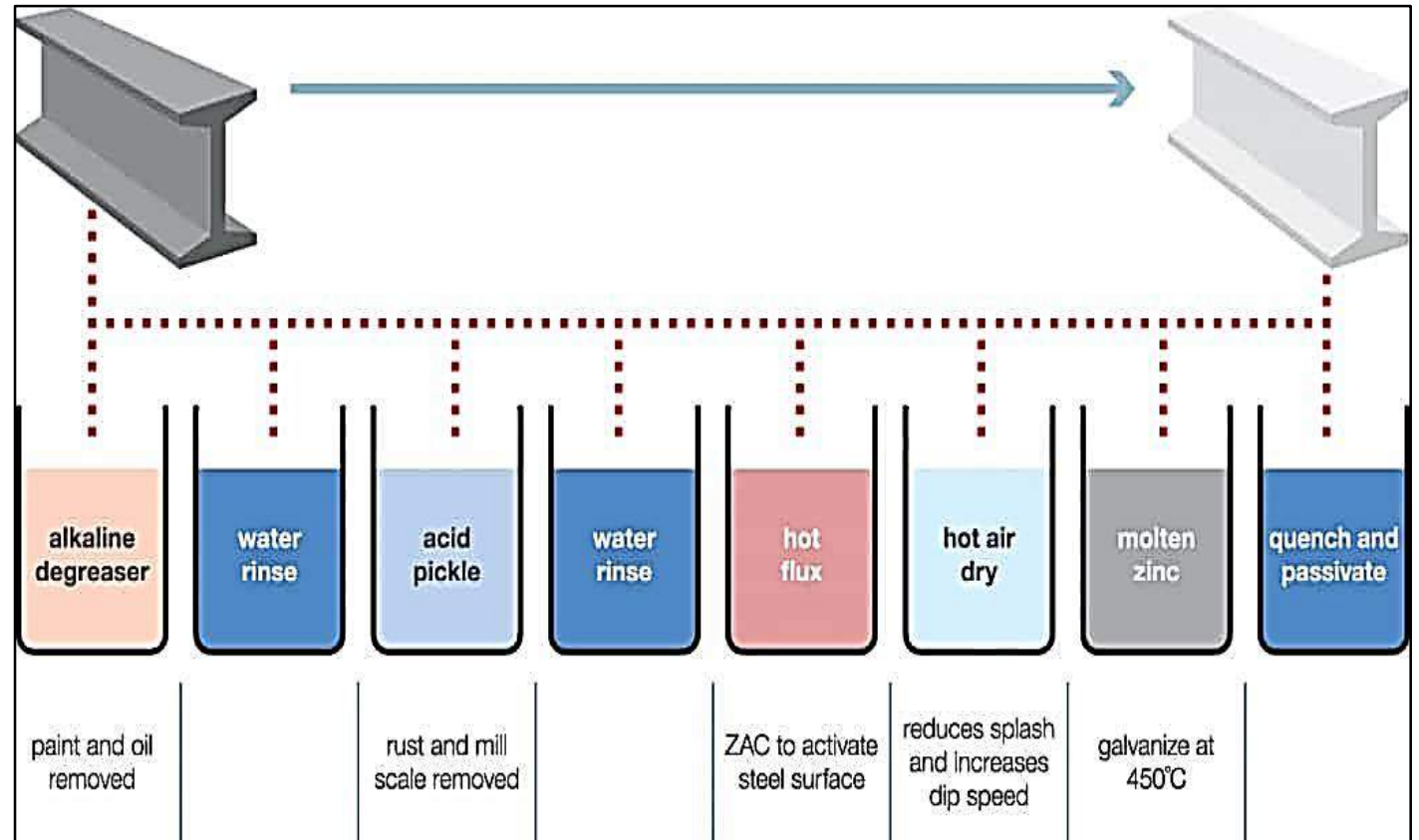
Galvanising

It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. During the process the iron or steel article is first cleaned with dil. Sulphuric acid (pickling). This removes any scale, rust and impurities. Then it is washed with distilled water and dried. The dried metal is dipped in bath of molten zinc maintained at 425-430°C. The surface of bath is covered with NH_4Cl flux to prevent oxidation. Now the thin layer of zinc is coated on the iron or steel article. It is then passed through a pair of hot rollers to remove excess of zinc and produce thin uniform film. Finally it is annealed at 650°C and cooled.

Uses:

Most widely used for protection of many iron articles from atmospheric corrosion.

E.g. Roofing sheets, pipes, wires, nails, buckets, tubes, etc.



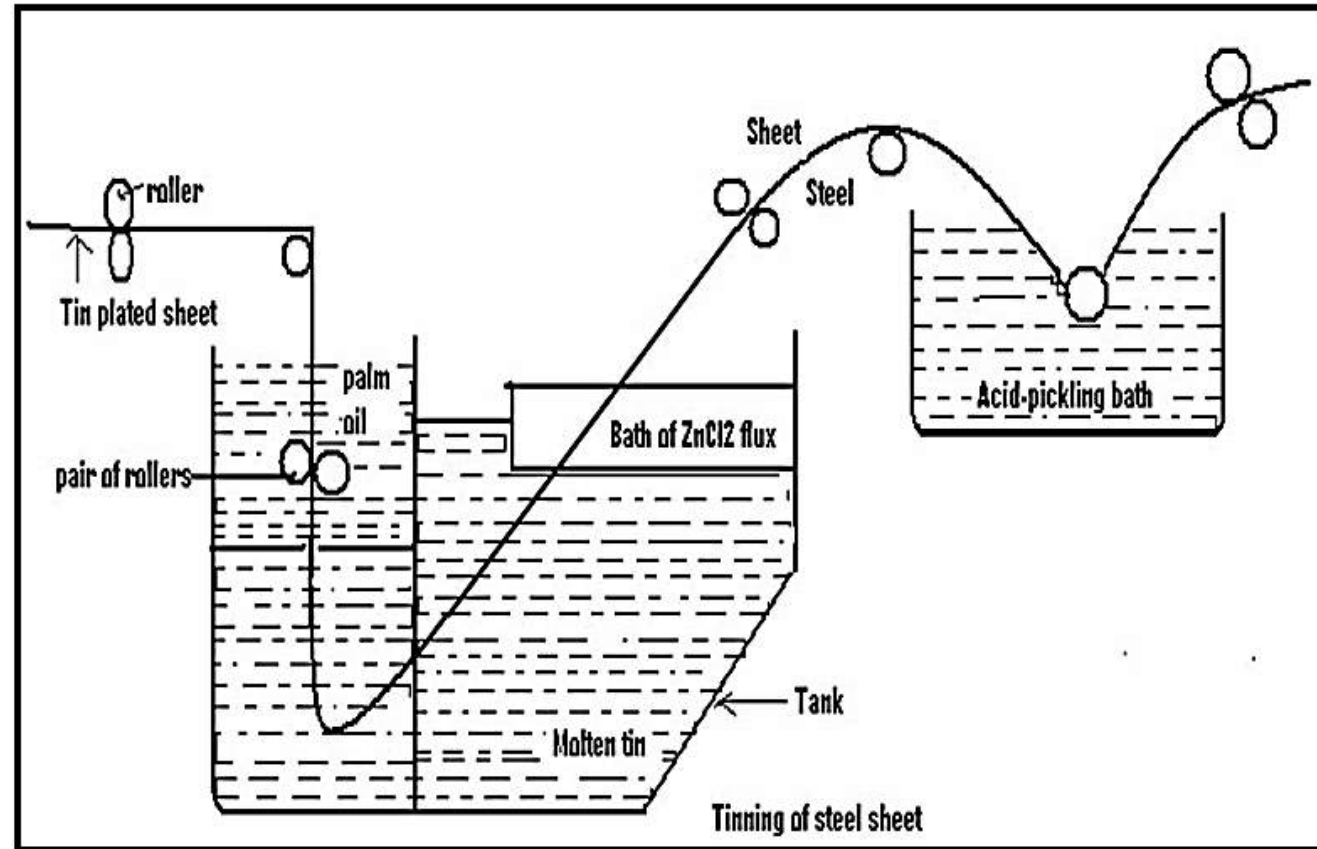
Tinning

It is a method of coating tin over the iron or steel articles. The process is first treating steel sheet in dilute sulphuric acid (pickling) to remove any oxide film and it is passed through a flux (ZnCl_2). The flux helps the molten metal to adhere to the metal sheet. Next the sheet passes through a tank of molten tin and finally through a series of rollers from underneath (bottom of) the surface of a layer of palm oil. The palm oil protects the hot tin-coated surface against the oxidation. The rollers remove any excess of tin and produce a thin uniform film on steel sheet.

Uses:

1. Has considerable resistance against atmospheric corrosion
2. Widely used for coating steel, copper, brass containers for storing food stuff, oil, etc.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipments.

TINNING OF STEEL SHEET



Comparision

Galvanising	Tinning
<ul style="list-style-type: none">• Process of covering iron or steel with a thin coat of ZINC to prevent it from rusting.• Zinc protects iron sacrificially since it is more electro-positive than iron and does not permit iron to pass into the solution.• In galvanized articles, zinc continues to protect the underlying iron by galvanic cell action, even if the coating of zinc is broken at any place• Galvanized containers cannot be used for storing acidic foodstuffs as zinc reacts with food acid forming poisonous compounds• Ideal temperature is around 450 degree C• Ammonium chloride is used as flux	<ul style="list-style-type: none">• Process of coating steel with a thin coat of TIN to prevent it from corrosion• Tin protects the base metal iron from corrosion due to its noble nature and higher corrosion resistance.• Tin protects underlying iron till the coat is intact. Any break in coating causes rapid corrosion of iron.• Tin coated containers and utensils can be used for storing any food stuff as tin is non-toxic and protects metal from corrosion• Ideal temperature is around 250 degree C• Zinc chloride is used as flux

Hydrogen Overvoltage (Not in syllabus)

- Hydrogen overvoltage is the potential difference that can be found between an electrode and a reversible hydrogen electrode within a single solution. This is where hydrogen (H_2) undergoes formation from ions of hydrogen.
- Overvoltage typically occurs when equilibrium within a reaction does not take place. This is the case when more powerful currents pass across the boundaries of metals and electrolytes.
- In terms of hydrogen overvoltage, there is a difference in potential between the gas hydrogen or metal and an electrode in two conditions:
 - When placed in a certain solution and corrosion does not occur
 - When corrosion begins
- When a metal or electrode is put into a solution such as water, the solution presumes a potential. If the metal begins to undergo corrosion, the metal's potential alters in value. The difference in this value of potential is referred to as overpotential.
- The same thing applies to hydrogen, since hydrogen overvoltage can be described as the difference between the hydrogen's equilibrium reactions in a solution and the hydrogen itself present in the solution when it begins to form a corrosive reaction with metal.
- Understanding this particular reaction makes it possible to control corrosion rates and the effects of corrosion reactions due to hydrogen overvoltage. Hydrogen evolves into gas and reacts at different rates for each type of metal. Thus, it can be said that the rate of corrosion varies in every kind of metal.
- The key here is to elevate the hydrogen overvoltage in order to slow down or halt the corrosion reaction. For instance, there are corrosion inhibitors that can make hydrogen overvoltage increase and at the same time make dissolution current decrease as it inhibits both cathodic and anodic processes.