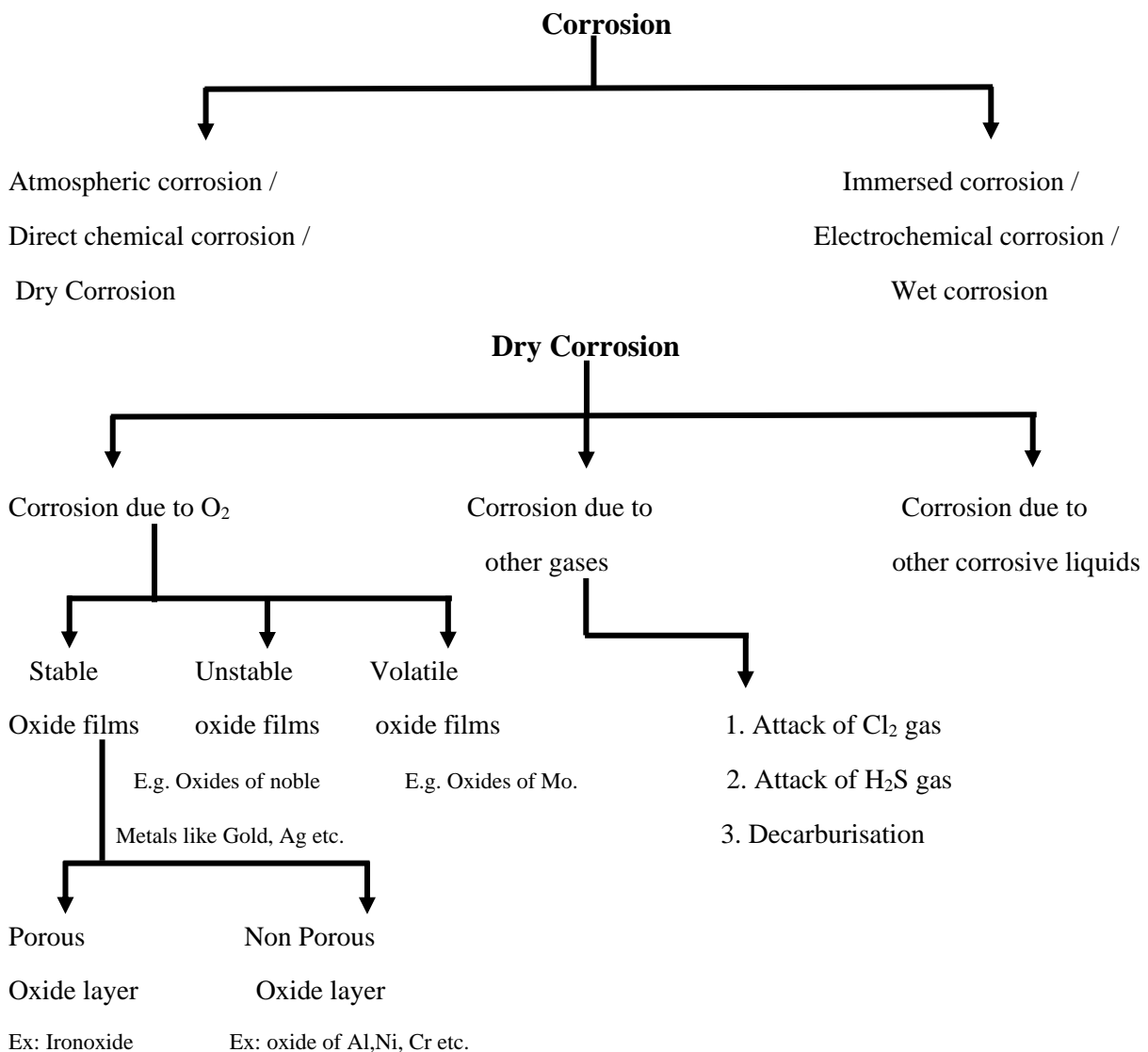


NOTE ON CORROSION

Prof. Ghazala Parveen

Definition of Corrosion: Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide or sulphide. It's a gradual destruction of materials (usually a metal) by chemical and/ or electrochemical reaction with their environment. Corrosion engineering is a field dedicated to controlling and preventing corrosion.

Types of Corrosion:



Atmospheric Corrosion:

The corrosion, which is brought about by atmospheric condition, is called atmospheric corrosion. Metal react with atmospheric gases such as O₂, CO₂, moisture, Cl₂, SO₄, H₂S, etc. To form corresponding compound like oxides, carbonate, chlorides, sulphide etc. on the surface of metal.

This type of corrosion is divided into following classes:

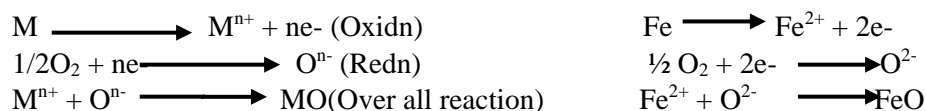
1. Corrosion due to O₂.
2. Corrosion due to other gases.
3. Corrosion due to other corrosive liquids.

1. Corrosion due to O₂ (Oxidation Corrosion):

This type of corrosion occurs when metallic surface are exposed to air.



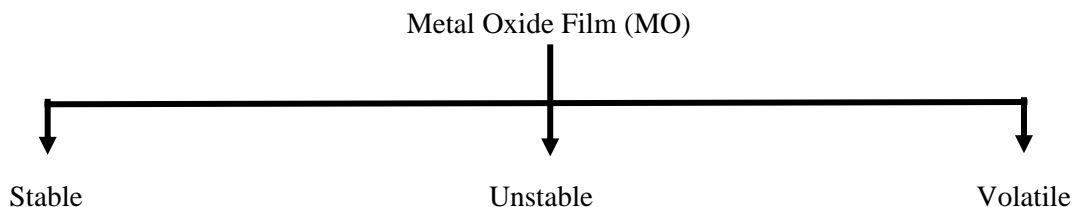
Mechanism:



A thin film of oxide is formed on the surface of the metal.

More active metals get corroded faster than less active metals.eg. Alkali and alkaline earth metals get corroded more as compared to other metals which are less active.

The film so produced is classified into three categories.

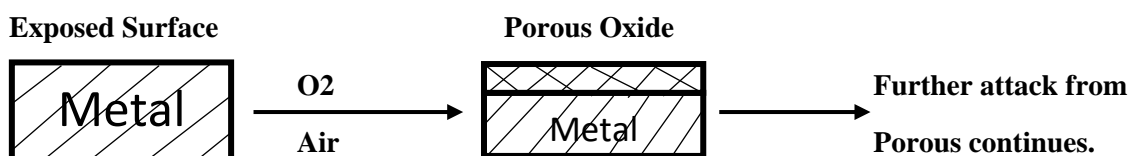


A. Stable Oxide Films:

It gets adhered to the underlying metal surface and hence provide a protective layer on the surface thereby reducing the rate of further corrosion. Extent of further corrosion depends upon the type of stable oxide film formed.

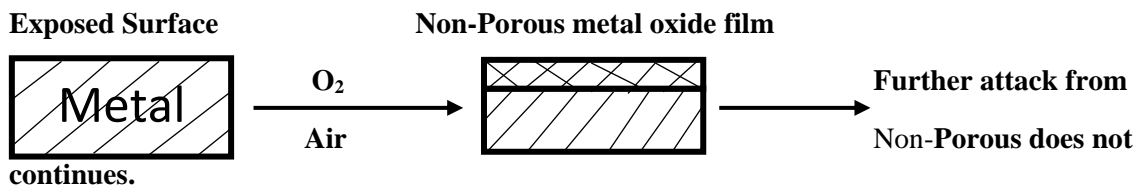
i. Porous Oxide Layer:

This kind of Oxide layer is formed by alkali metal (Li, Na, K, etc.) or alkaline earth metals (Ca, Mg etc.). The metals react with O₂ to form the corresponding oxide where volume of oxide film formed is less than the volume of metal surface. Thus, oxide layer is not able to cover the entire surface of the metal piece, hence pores are developed. These pores give free access to O₂, which attacks the underlying pure metal. Thus, corrosion does not stop until pure metal is available i.e. the rate of further corrosion is not reduced much.



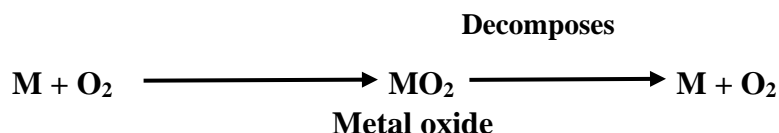
ii. Non-Porous Oxide Layer:

This kind of oxide layer is formed from the metals like Al, Ni, Cr, etc. forming corresponding oxide whose volume is greater than the volume of metals. Hence, the oxide film formed covers the underlying metal surface completely and not leaving any access for further attack thereby stopping further corrosion. Thus, the rate of corrosion reduces considerably in this case.

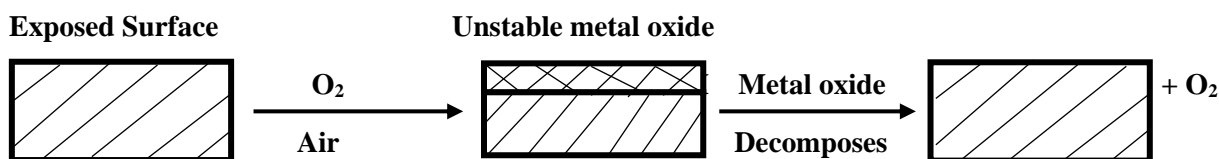


B. Unstable Oxide Film:

This type of oxide film formed by noble metals like Au, Ag, Pt, etc. Where the film formed gets decomposed on the metal surface forming back metal and oxygen.

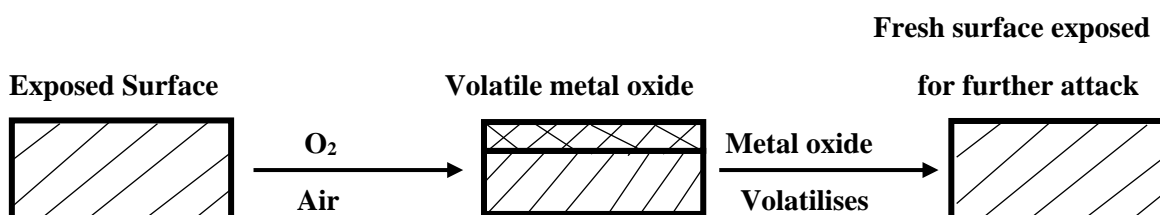


This type of film does not lead to corrosion but loss of metal continues slowly.



C. Volatile Oxide Film:

This type of oxide film is formed by Molybdenum metal. When this metal forms its oxide which is volatile is vaporised from metal surface as soon as they are formed leaving behind the underlying metal surface for further attack of oxygen.



❖ 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”.

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

2. Corrosion due to Other gases:

Gases such as CO_2 , H_2S , SO_2 , Cl_2 , F_2 etc. react on the metal surface resulting in formation of a film of corresponding compound.

Ex: (i) Attack of Cl_2 gas

In case of attack of Cl_2 gas, the nature of product differs from metal to metal.

When it reacts with Ag, to form silver chloride film, which is protective in nature whereas when it reacts with Sn, it forms stannous chloride film, which is volatile in nature.



(ii) Attack of H_2S gas on Fe metal / Hydrogen Embrittlement

- ✓ When H_2 gas attacks the metal at ordinary temperature it is known as hydrogen embrittlement.
- ✓ This action of H_2 is due to nascent $[\text{H}]$ liberated at the surface of iron by the action of H_2S .



- ✓ This nascent H_2 diffuses in the metal and collects there in voids where it combines to form molecular hydrogen.



- ✓ H_2 gas in voids exerts high pressure on metallic structure making it weak and brittle.

(iii) Decarburisation

- ✓ The nascent $[\text{H}]$ is very active at high temperature and it readily combines with C, S, N etc. present in the metal as impurity.
- ✓ C in steel combines with atomic hydrogen at high temperature to form methane gas (CH_4) which creates high pressure in steel.



- ✓ Due to high pressure inter granular cracking and blistering is resulted. It is known as decarburisation.

IMMERSED CORROSION (Electro-chemical corrosion)

Definition

The corrosion, which is brought about by ionic reactions in presence of moisture or solution as a conducting medium when two dissimilar metals are in contact with each other is called as electro-chemical corrosion.

This type of corrosion occurs at a solid-liquid interface when the metals are in contact with the moist air or any other medium.

Principle

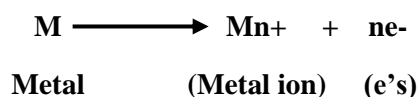
An electrochemical reaction is one, which results in the transfer of e^- 's when metal surface is in contact of aqueous acidic / alkaline / neutral electrolytic solutions.

Theory

- ✓ This type of corrosion occurs under following conditions.
 - (i) Where a conducting liquid is in contact with metal.
 - (ii) Where two dissimilar metals or alloys are either immersed or dipped partially in a solution.
- ✓ At anode, the liberation of e^- 's takes place, i.e. oxidation reaction; therefore, at anode destruction of metal takes place.
- ✓ At cathode the absorption of e^- 's takes place i.e. reduction reaction; therefore, cathode is always protected and corrosion always occurs at anode.

Reaction

- **At anode**



Formation of metal ions at anode causes dissolution of metal and free e^- 's are liberated. These free e^- 's are consumed in cathodic reactions by two different mechanisms depending upon the nature of corrosive environment.

- (a) Evolution of H_2 gas.
- (b) Absorption of O_2 gas.

(a) **H_2 evolution mechanism:**

- ✓ This type of corrosion occurs in acidic environment like industrial waste, acidic solutions like HCl etc.
- ✓ Ex: A steel tank containing acidic industrial waste and a small piece of Cu scrap in contact with the steel.
- ✓ As Cu occupies lower position in electrochemical series Cu scrap acts as a cathode and remains protected.
- ✓ Fe occupies higher position in electrochemical series. Therefore, steel tank acts as an anode and undergoes corrosion in form of Fe^{2+} .
- ✓ There is liberation of H_2 gas at cathode.

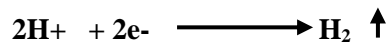
Reaction

- **At Anode**



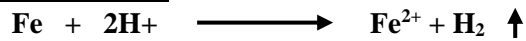
(Part of metal tank)

- At Cathode



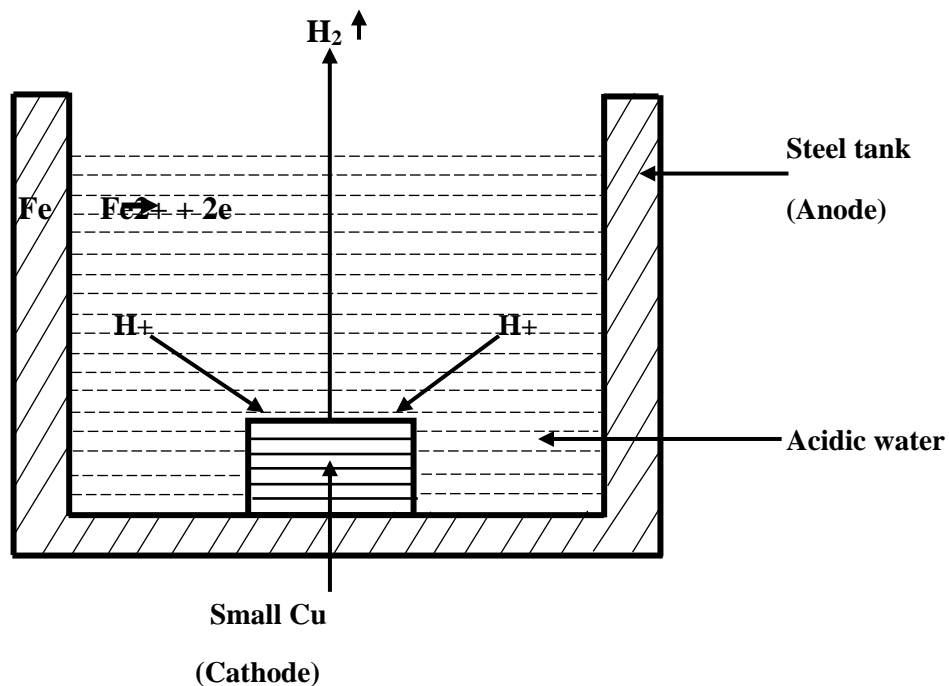
(From acidic Solution) (Liberation of H_2 gas at cathode)

- Net Reaction:

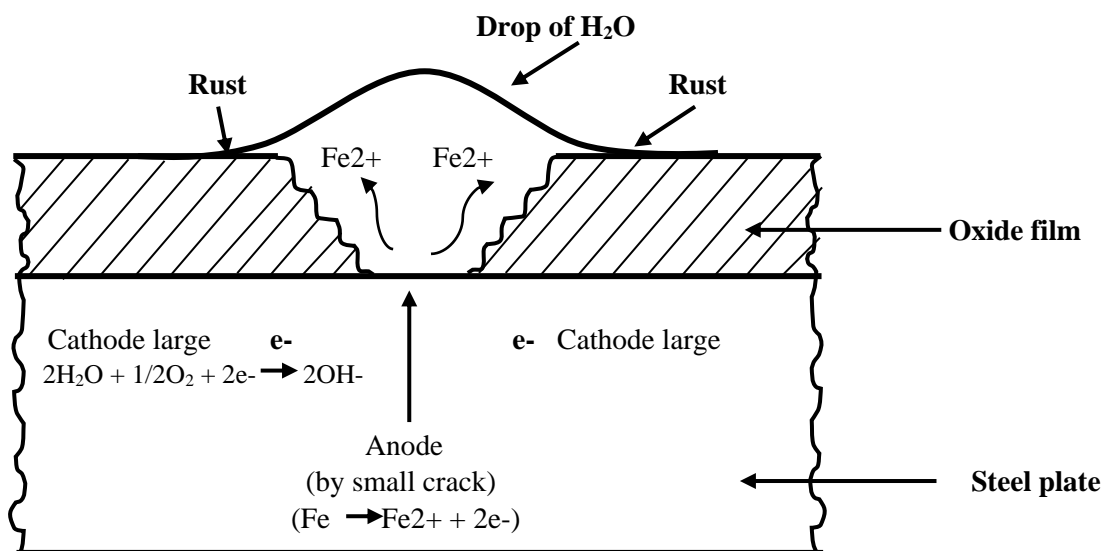


*In this case, anodic area is very large and cathodic area is very small.

Diagram:



(b) O₂ absorption mechanism:



- ✓ This type of corrosion occurs in neutral or slightly alkaline aqueous solution (like NaCl solution) in presence of atmospheric O₂.
- ✓ Ex: Rusting of iron in neutral aq solution of electrolytes in presence of atmospheric oxygen is the most common example of this type of corrosion.
- ✓ The surface of iron is coated with a thin film of iron oxide, which acts as cathode.
- ✓ If some cracks developed in iron oxide film, anodic areas are created on the metal.

Reaction:

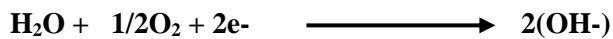
• **At anode:**

Fe dissolves as Fe²⁺ ion with liberation of e⁻s.



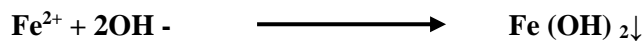
• **At cathode:**

The liberated e⁻s flow from anodic to cathodic areas through iron metal where e⁻s are accepted by the dissolved O₂ which in presence of water drop to form OH⁻ ions

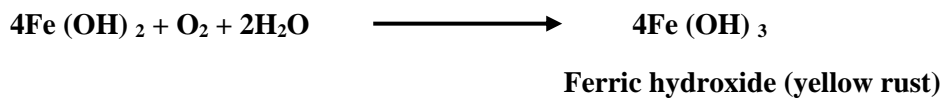


• **Net Reaction:**

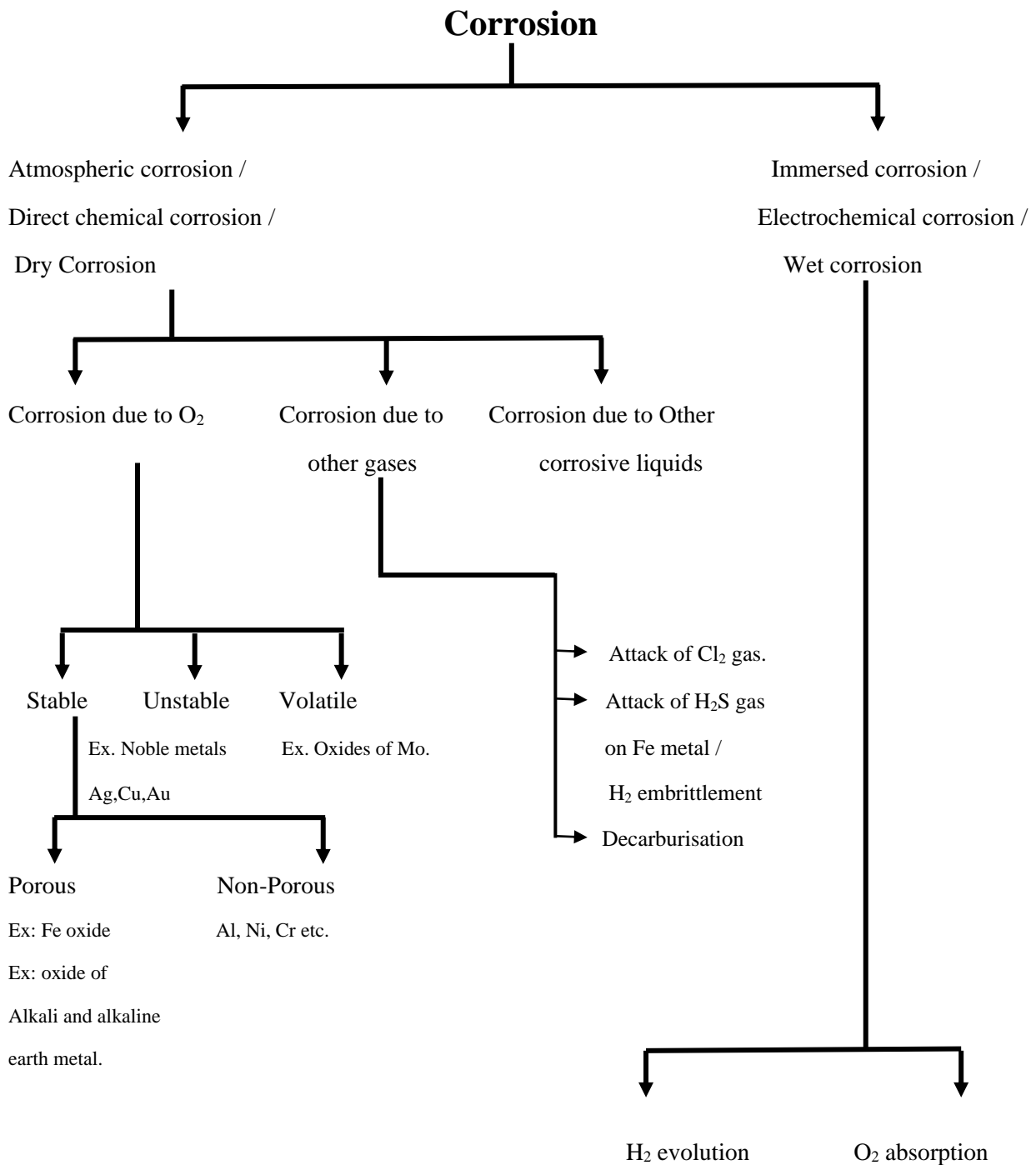
The Fe²⁺ ions at anode and OH⁻ ions at cathode reacts to form ferrous hydroxide precipitate.



If enough O₂ is present Fe(OH)₂ is oxidised to ferric hydroxide.



- In this case, iron oxide film acts as cathode and remains protected.
- Metallic part, which acts as an anode undergoes corrosion in the form of Fe²⁺ ions.
- In this case, anodic area is very small and cathodic area is very large.



Factors Affecting Rate of Corrosion

The rate and extent of corrosion depends mainly on the following factors:

- (1) Nature of Metal**
- (2) Nature of environment**

(1) Nature of metal

(a) Position of metal in galvanic series

If two dissimilar metals are in corrosive environment, then the metal having higher position in the galvanic series acts as an anode and undergoes more corrosion.

Thus, **corrosion rate \propto higher position of metal**

(b) Over Voltage

Overvoltage is defined as the difference between the theoretical reversible electrode potential and the actual potential at which evolution of gas occurs.

Example: If pure Zn metal is placed in 1N H_2SO_4 , it undergoes corrosion forming a film and evolving hydrogen gas. The initial rate of the reaction is slow because of the high overvoltage (0.7 V) of Zn metal, which reduces the effective electrode potential to a small value. However, if a few drops of CuSO_4 are added the corrosion rate of Zn is accelerated because some Cu gets deposited on the Zn metal forming minute cathode. At copper hydrogen overvoltage drops to 0.33 V. Hence corrosion is faster.

Thus, **corrosion $\propto \frac{1}{\text{Overvoltage}}$**

(c) Relative areas of the anodic and cathodic parts

When 2 dissimilar metals are in contact, the corrosion part is directly proportional to the ratio of areas of the cathodic part and anodic part.

Thus mathematically, **Rate of corrosion $\propto \frac{A_{\text{cathodic}}}{A_{\text{anodic}}}$**

This is because when the cathodic area is larger than the anodic area, then the demand for electrons by the cathodic area will be more which can only be met by the anodic area by undergoing faster corrosion. Thus, **smaller the area of the anode, faster is the rate of corrosion.**

Thus, **Corrosion $\propto \frac{1}{\text{anodic area}}$**

(d) Purity of the metal

Impurities in a metal generally cause heterogeneity, and due to the impurities present in them, small galvanic cells are produced at the sites where the metal is exposed to corrosive environment and the anodic part gets corroded

The rate and extent of corrosion increases with the increasing exposure and extent of the impurities.

Thus , **Rate of corrosion \propto impurity.**

(e) Physical state of the metal

The rate of corrosion is influenced by physical state of the metal such as grain size, orientation of crystals, stress etc.

- (i) **Grain size:** The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion.
- (ii) **Orientation of crystal:** The corrosion rate of a metal may be influenced by orientation of crystals at the metal surface e.g. corrosion rate of copper ions was found to be different on different faces of pure copper crystal.
- (iii) **Stress:** Even in a pure metal, areas under stress tend to be anodic and corrosion may be taking place at these areas.

(f) Nature of Corrosion product i.e Oxide film

- (i) **Stable oxide film:** It get adhered to the underlying metal surface and hence provides a protective layer on the surface, thereby reducing the rate of further corrosion which depend upon the type of the stable film formed.
Case I: Porous Oxide layer: In this the pore are developed in the film, which give access to O₂. Thus corrosion does not stop till pure metal is available.
Case II: Non-porous oxide layer: Here the rate of corrosion reduces considerably and mostly the corrosion stops.
- (ii) **Unstable oxide film :** Here, there is no corrosion but loss of metal continues slowly.
- (iii) **Volatile oxide film :** Here, corrosion continues till the metal is available.

(g) Solubility of corrosion products

In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate. On the contrary, if the corrosion product is insoluble in the medium or it interact with the medium to form another insoluble product (e.g. PbSO₄ formation in case of Pb in H₂SO₄ medium), then the corrosion product functions as physical barrier, thereby suppressing further corrosion.

(h) Volatility of corrosion products

If the corrosion product is volatile, it volatilises as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion. For example, molybdenum oxide (MoO₃), the oxidation corrosion product of molybdenum, is volatile.

(i) Passitivity of the metal / Passive character of metal

Passivity is the characteristics of a metal due to which the metal exhibits a much higher corrosion resistance than that at its position in the electrochemical series. The metals like Cr, Ni, Ag, Al and Co have a higher passivity.

Thus, mathematically

Corrosion rate $\propto \frac{1}{\text{Passivity}}$

(2) Nature of environment

(a) Temperature

As temperature increases, the rate of corrosion increases, diffusion of gases increases with the rise in temperature.

Thus, **corrosion rate \propto temperature.**

(b) Moisture or Humidity of air

Humid air has tendency to dissolve gases like O_2 , CO_2 etc and also the acidic vapours. Due to this, electrochemical cells are set up on the metal surface causing corrosion some metals like Mn, Cr, Fe, Mg etc get corroded in the moist air even in the absence of O_2 . Therefore, as moisture increases, rate of corrosion increases.

Thus, **Corrosion rate \propto moisture.**

(c) Influence of pH

Generally acidic media (i.e. $pH < 7$) are more corrosive than alkaline and neutral media. So as a pH value decreases, rate of corrosion increases.

Thus, **Rate of corrosion $\propto \frac{1}{pH}$**

(d) Presence of impurities in atmosphere

Atmosphere in the vicinity of industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 and fume 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. This consequently results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces. Similarly, in the marine atmosphere, the presence of sodium and other chlorides leads to increased conductivity of the liquid layer in contact with the metal surface.

Thus, **corrosion \propto impurities.**

(e) Presence of suspended particles in atmosphere

In case of atmospheric corrosion:

- (i) If the suspended particles are chemically active in nature like $NaCl$, $(NH_4)_2SO_4$, they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.
- (j) If the suspended particles are chemically inactive in nature like charcoal which absorb sulphur gases (SO_2 , SO_3) and moisture and slowly enhance the corrosion rate.

(f) Nature of ions present

Anions: Presence of anions like silicate may form an insoluble reaction product (silica gel) which inhibits corrosion. On the contrary, chloride ions if present in medium destroy the protective and passive surface film and corrode metal alloy.

Cations: Many metals corrode rapidly in the presence of ammonium (NH_4^+) salts than in sodium (Na^+) salts of same concentration. Presence of even traces of copper or any noble metal in mine water accelerate the corrosion of the iron pipe used for carrying such water.

(g) Conductance of corroding medium

In corrosion of underground or submerged structures, the conductance of the medium is of prime importance. Conductance of dry, sandy soils is lower than those of clayey and mineralized soils. Consequently, stray currents from power leakage will cause more severe damage to the metallic structures, buried under clayey and mineralized soils than those under dry sandy soils.

(h) Formation of oxygen concentration cell

The rate of corrosion increases with increasing supply of oxygen or air to the moist metal surface. Poorly oxygenated part becomes anodic where the corrosion occurs. The highly oxygenated part becomes cathodic and does not corrode. Both anodic and cathodic areas lead to the formation of oxygen concentration cell.

At anodic area $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation takes place)

At cathodic area $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$ (Reduction takes place)

Thus, oxygen concentration cell promotes corrosion at anode where oxygen concentration is lower. Waterline corrosion of buried pipeline and cables passing from one type of soil to another and crevice corrosion are due to differential oxygen concentration cells.

Types of Corrosion:

Different forms of corrosion are as follows

- 1) Galvanic Cell Corrosion
- 2) Concentration Cell Corrosion
- 3) Pitting Corrosion
- 4) Intergranular Corrosion
- 5) Stress Corrosion
- 6) Water Line Corrosion

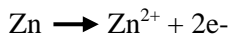
1) Galvanic Cell Corrosion:

It is a wet type of Corrosion. When two dissimilar metals are in electrical contact with each other and are exposed to an electrolyte, a potential difference is created between two dissimilar metals. The less noble metals dissolve and act as anode while more noble metal acts as cathode. This type of Corrosion is called Galvanic cell Corrosion.

Ex: If two dissimilar metal Zn and Cu plates are in electrical contact with each other and are immersed into a solution of electrolyte. The more electropositive metal Zn placed higher in electrochemical series acts as Anode, is attacked, and gets dissolved. Cu lowered in series acts as Cathode and remains protected.

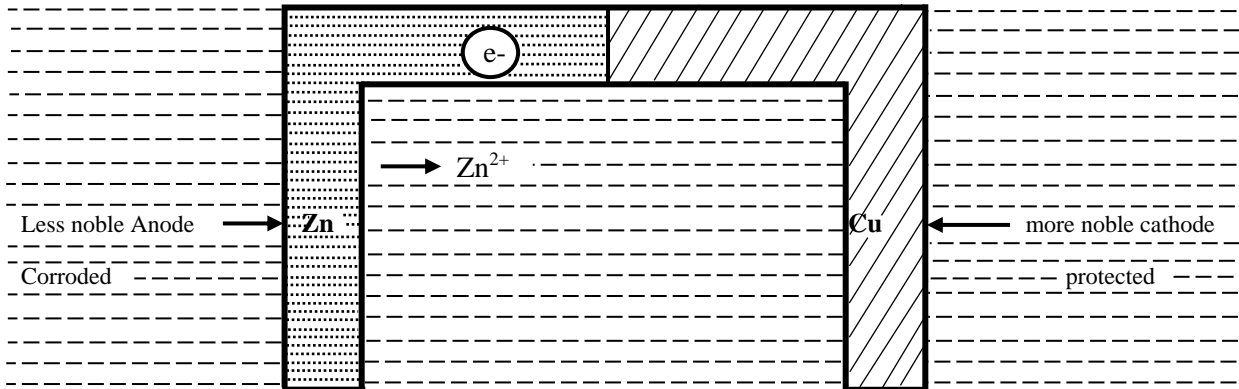
In Galvanic Corrosion cathode is always protected.

If the electrolyte is acidic in nature, Corrosion take place by hydrogen evolution mechanism while in neutral or slightly alkaline solution, Corrosion take place by oxygen absorption mechanism.



→ electronic current

Electrolyte



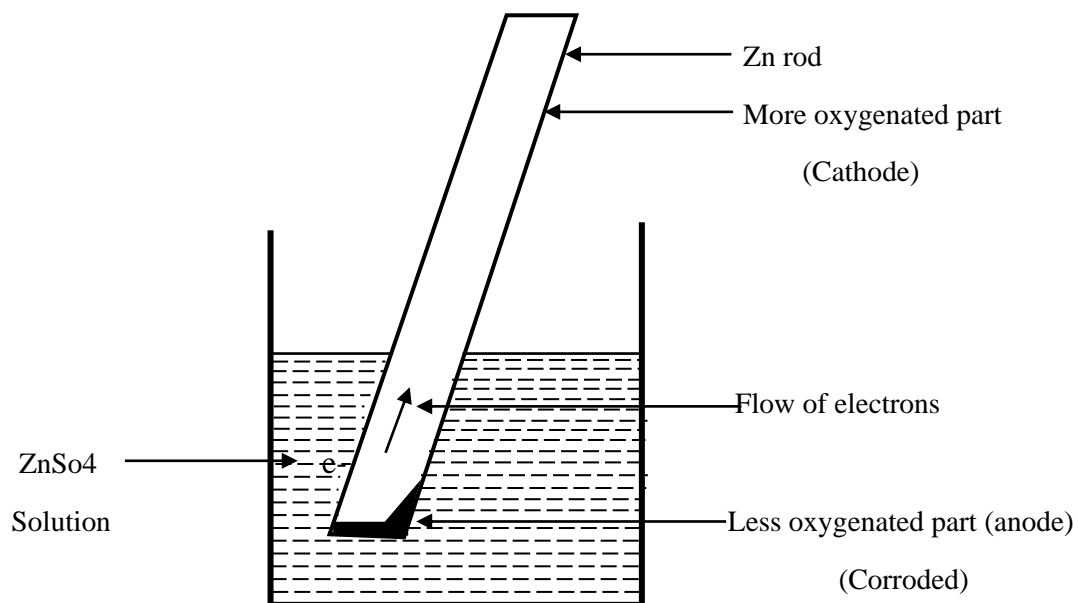
Various examples of Galvanic Cell Corrosion are:

- 1) Steel screws in a brass marine hardware.
- 2) Lead- Antimony solder around Cu wire.
- 3) Steel pipe connected to copper plumbing.

2) Concentration cell Corrosion:

Differential aeration is most important type of concentration cell corrosion. It occurs when metal faces different concentration of air at different places. This causes difference in potentials between aerated areas. Poor oxygenated part of the metal acts as an anode and it is this part of the metal, which undergoes corrosion. Highly oxygenated part of the metal acts as a cathode and it remains unaffected. A differential aeration of metal causes a flow of current called differential aeration current.

Ex: A Zn rod partially immersed in a dilute solution of ZnSO_4 .



- **Anode**

Immersed part of Zn rod is less oxygenated hence it acts as an anode and undergoes corrosion.



- **Cathode**

The part of the Zn rod above the solution is more oxygenated and hence it acts as a cathode and remains unaffected.



- **Net Reaction**



Ex: Corrosion of iron under drop of water.

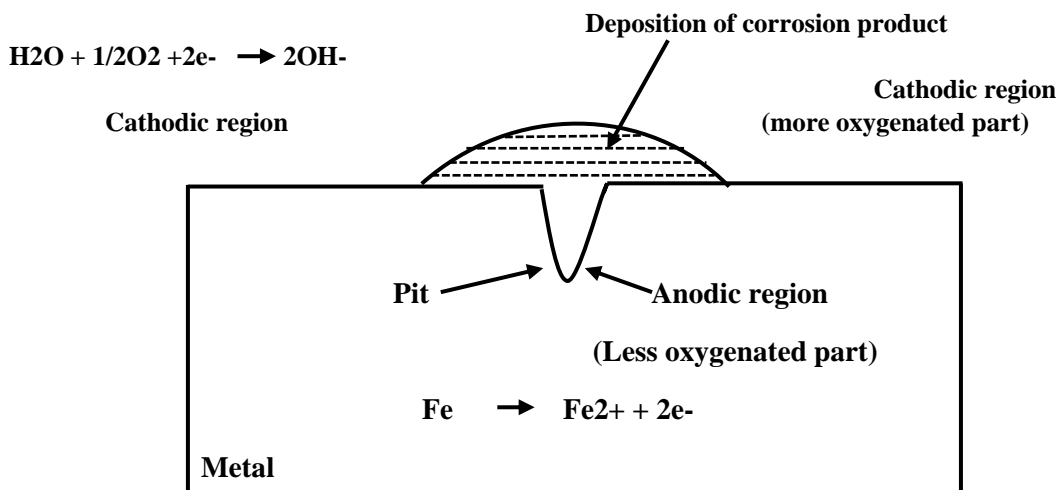
3) **Pitting Corrosion:**

Pitting corrosion is extremely localized attack resulting in the formation of cavities or holes in the metal. Pitting may penetrate deep into the metal; it is very destructive and can ruin the metal. It grows in the direction of gravity.

Pitting corrosion is due to:

- Roughness of surface
- Scratches or cut edges.
- Impurities.
- Stress.
- Chemical attack.
- Sliding under load.
- Corrosion product may be insoluble etc.

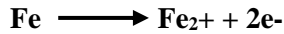
Ex: Pitting corrosion due to dirt, dust or scale deposited on metal surface.



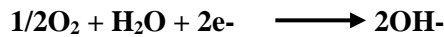
The portion covered by the dust will not be well aerated as compared to rest of the area. As a result, concentration cells are set up. Covered portion acts as an anode with respect to the exposed surface, which acts as cathode.

Reaction:

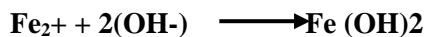
- **At anode**



- **At cathode**



- **Net reaction**



Once pit is formed the rate of corrosion increases because of the formation of small anodic area compared to large cathodic area. This type of corrosion is highly dangerous and cause damage and destruction of pipes, tubes and reaction vessels.

Prevention from pitting corrosion:

A pure and homogeneous metal with a highly polished surface will be resistant to pitting.

Cleanliness and selection of proper material will also resist the pitting corrosion.

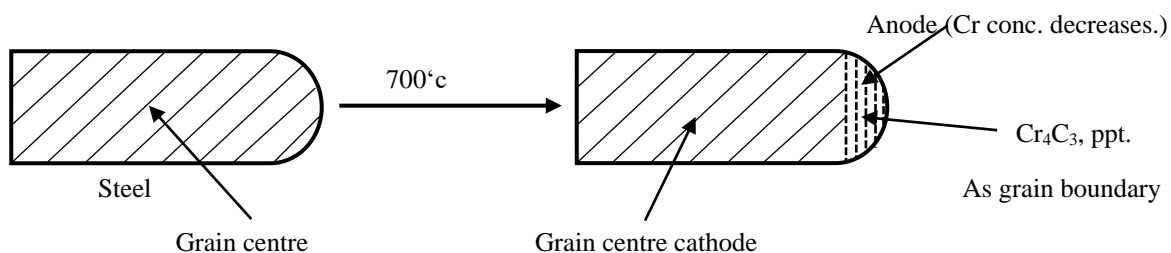
4) Intergranular Corrosion / Grain Boundary Corrosion :

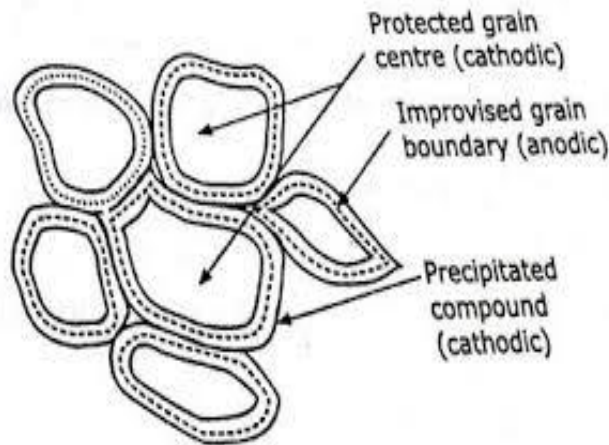
This type of corrosion is normally observed in case of alloys when grain boundaries are depleted by the formation of a compound that changes the concentration of the metal. This type of corrosion is due to the fact that the grain boundaries contain material which shows electrode potential more anodic than that of the grain centre in the particular corroding medium. This is due to the precipitation of certain compounds at the grain boundaries.

Ex: Stainless Steel – Corrosion resistant alloy containing about 12% Cr which forms thin invisible layer of oxide film on steel that prevents corrosion.

However, this Cr forms a compound like chromium carbide (Cr_4C_3) which depletes the concentration of chromium at grain boundary leads to corrosion.

When stainless steel is heated to 700°C for a long time during welding leads to the formation of Cr_4C_3 and is precipitated at the grain boundaries. This results in decrease in concentration of Cr at the grain boundary and hence it acts as anode with respect to grain centre where Cr concentration is more and corrosion takes place at grain boundaries.



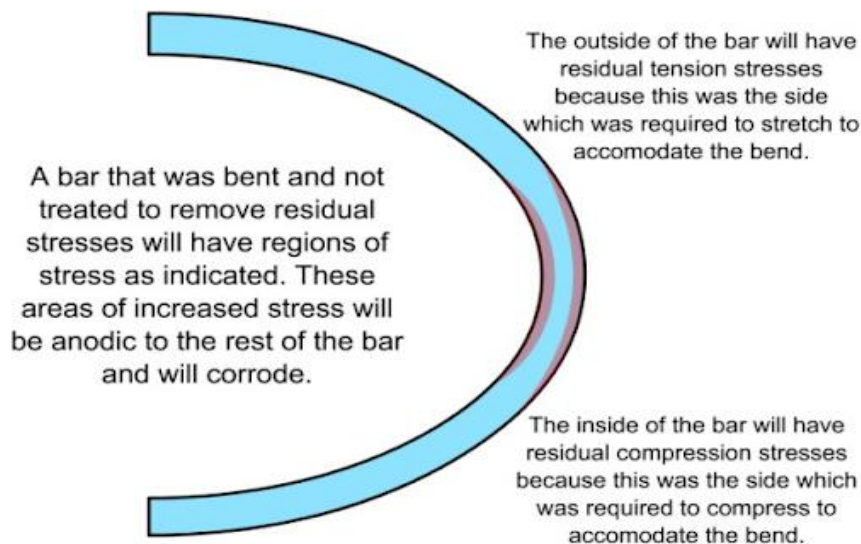


Prevention of Grain boundary Corrosion:

- ✓ It can be prevented by addition of **Ti, niobium and tantalum** that forms resp. Carbides preferentially to chromium carbide.
- ✓ By lowering the carbon content in the steel.
- ✓ By heating entire specimen to 1000°C and quenching it in water that leads to dissolution of the Cr_4C_3 in the grains and then preventing its precipitation.
- ✓ Hold steel at elevated temperature for a long time just to prevent Cr_4C_3 precipitation. This type of corrosion is termed as weld decay.

5) Stress Corrosion:

When the metal and alloy are subjected to metallurgical operations such as welding, bending, riveting and quenching, a part of the metal or alloy undergoes stress.



At the stress portion, the atoms are somewhat displaced and as a result, it becomes anodic site and corrosion takes place.

Examples of Stress Corrosion

A) Seasonal Cracking:

It is a term applied to stress corrosion of Cu alloy mainly brasses. Pure Cu is immune to Stress corrosion, but presence of small amount of alloying elements like (P,As,Sb,Zn,Al and Si) result in marked sensitivity. Ex: Alpha brass (which when highly stressed) undergo intergranular cracking in an atmosphere containing traces of ammonia or amines.

B) Caustic Embrittlement :

This type of corrosion is observed in boilers.

Boilers feed water contains a certain amount of Na_2CO_3 for hardening purpose.

In high-pressure boilers, i.e. at high temperature and pressure it breaks up to give sodium hydroxide and CO_2 .



NaOH makes boiler water alkaline.

This dilute alkaline boiler water flows through the minute hair cracks and crevices (by capillary action).

The water evaporates and caustic soda concentration builds up in the crevices.

This concentrated alkali reacts with Fe to form sodium ferroate, which gets deposited in crevices, cracks. Hence, the metal is stressed.

The sodium ferroate decomposes like this



A galvanic cell is formed between iron and dilute NaOH, iron and conc. NaOH and corrosion takes place leading to explosion of boilers.

Prevention of boiler Corrosion:

- 1) By addition of Sodium Sulphate to the boiler water.
- 2) By addition of Lignin and Tanin as additive to the boiler water.

Prevention of Stress Corrosion:

- 1) Care should be taken to see that the stressed portion is not formed.
- 2) This can be achieved by proper heat treatment and annealing.

Methods to Decrease/Prevent the rate of Corrosion:

The method to prevent the corrosion are as follows

- 1) Selection of the material.
- 2) Proper designing
- 3) Use of alloys/pure metal.
- 4) Modifying the environment.
- 5) Use of inhibitions.

6) Cathodic and Anodic protection methods.

7) Application of protective coatings.

1) Selection of material:

- a) The materials should be selected in such a way that the contact of dissimilar metals should be avoided especially in corrosive environment.
- b) If two dissimilar metals are to be selected, then metal should be chosen in such a way that they are as close as possible in the electrochemical series.
- c) If two dissimilar metals are to be chosen then area of anodic metal should be larger than that of cathodic metal.
- d) If two dissimilar metals are to be used, the current flow should be reduced by introducing an insulation between these metals.

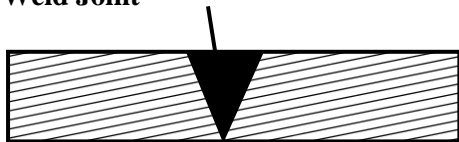
2) Proper designing / Improvement of designing:

The following points should be taken care of while designing

- a) If two dissimilar metals are in contact, they should be as close as possible to each other in the electrochemical series.
- b) For two dissimilar metals in contact, the anodic part should have as large area as possible.
- c) The local stresses should be completely avoided.
- d) A proper design should avoid sharp bends, joints, projected parts and presence of crevices.

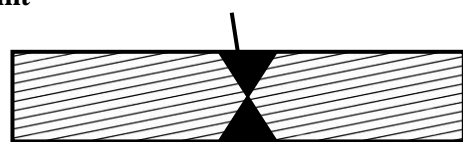
Different Types of joints:

Weld Joint



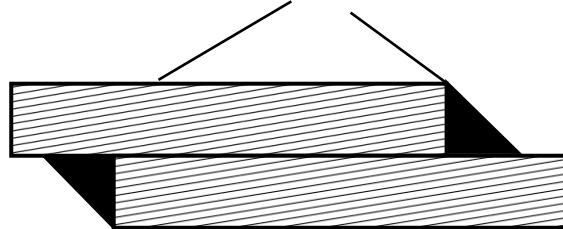
Best Design

Weld joint



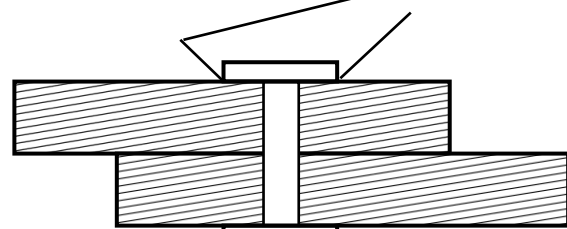
Best Design

Weld Joint



Good design

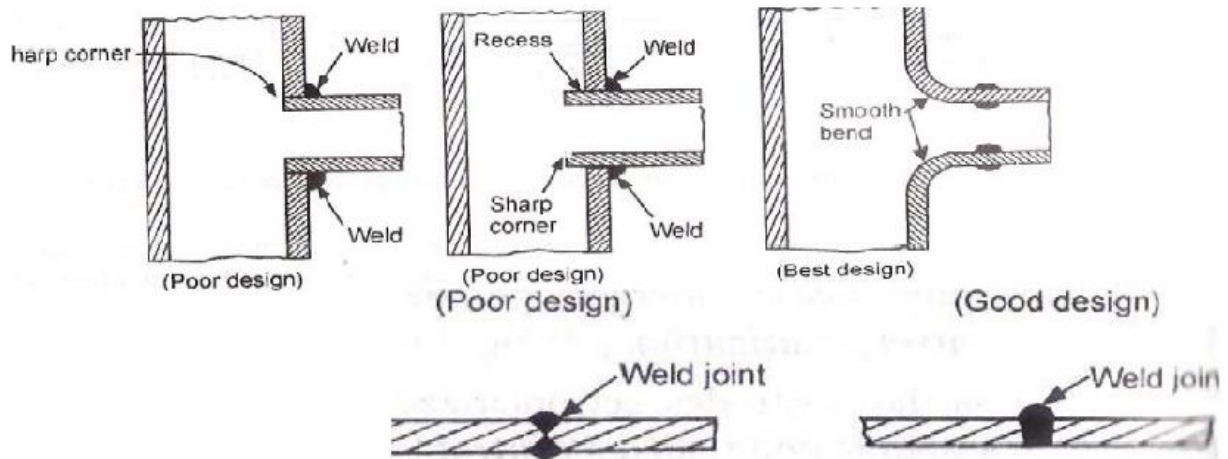
Crevices



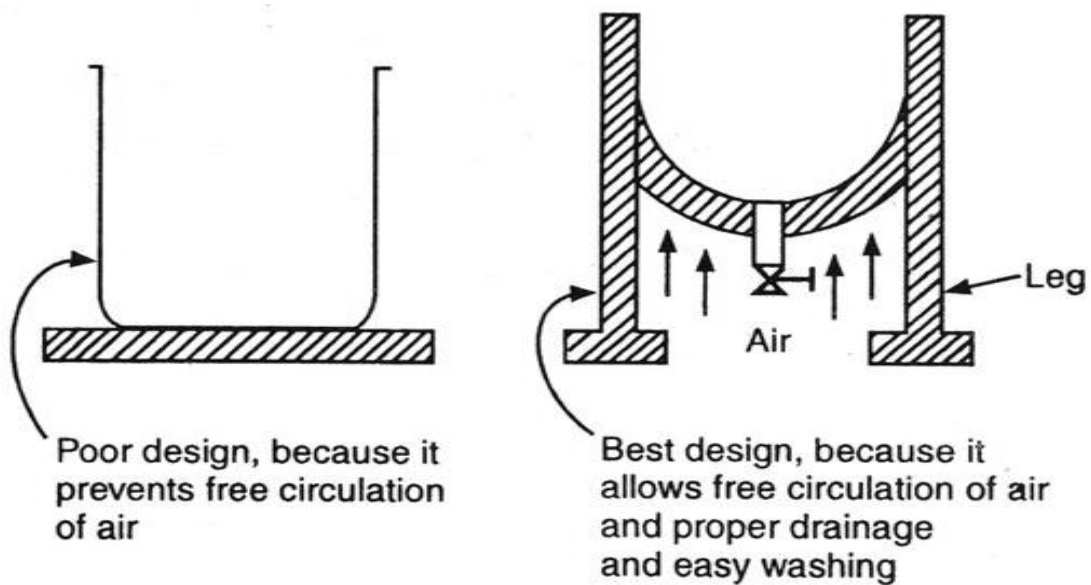
Poor design

e) The designing should allow adequate cleaning and flushing of the critical parts especially those which are highly susceptible for the deposition of dirt, dust etc.

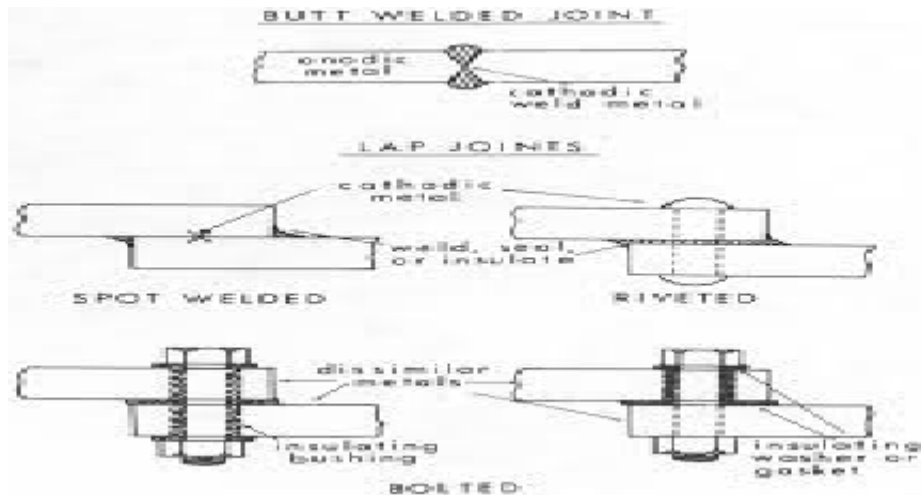
Thus, sharp corners should be avoided as they favour the formation of stagnant areas and accumulation of solids.



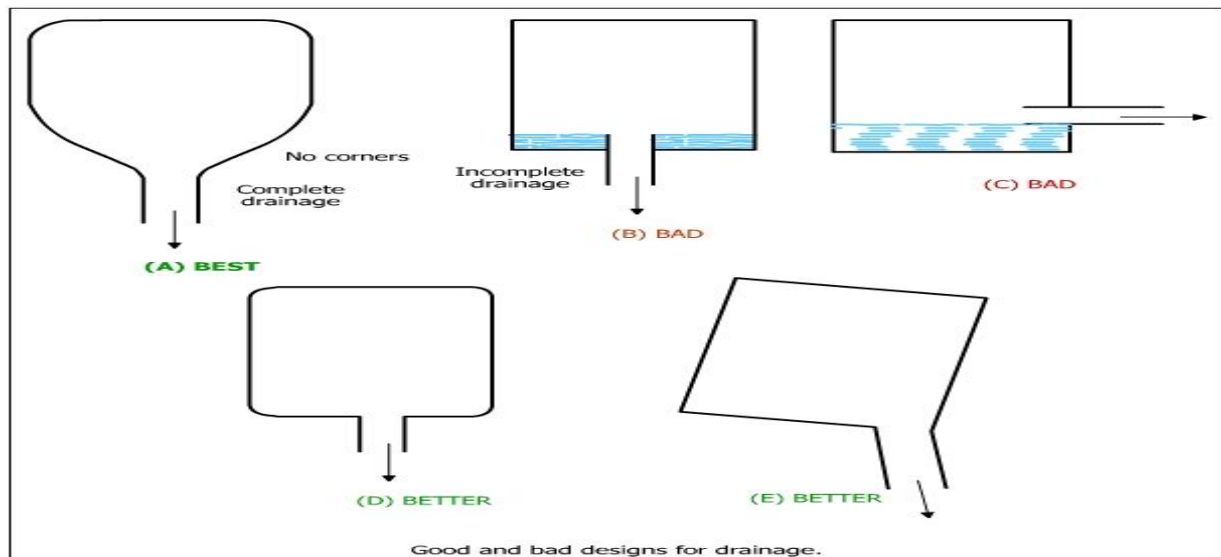
- e) Equipment like storage tanks on reaction should be supported on legs to allow free circulation of air. This prevents formation of stagnant areas.



- f) Whenever there is direct joining of dissimilar metals is there, an insulating fitting should be applied in between them to avoid direct metal-metal electrical contact.



g) Uniform flow of corrosion liquid is desirable .Drainage affects corrosion.



- h) The use of screws, nuts, bolts, etc. should be avoided and rather welding should be preferred.
- i) The surface of two joining parts should be as smooth as possible.

3) Use of alloys/Purification of metals:

Use of alloys: In this method, metal is protected from corrosion by alloying it with suitable elements. Alloys of steel containing Si, Ni, Cr, etc. offers very good resistance to corrosion.

Purification of Metal: Generally less active impurities present in metal or dust /dirt particles on the metal becomes cathode, while metal becomes anode and undergoes corrosion. Hence, metal is protected from corrosion by keeping it pure.

4) Modifying The Environment:

In this method, metal is protected from corrosion by keeping metal away from acids, stray currents, circulating water, sea water.

5) Cathodic and Anodic Protection Method:

Cathodic Protection:

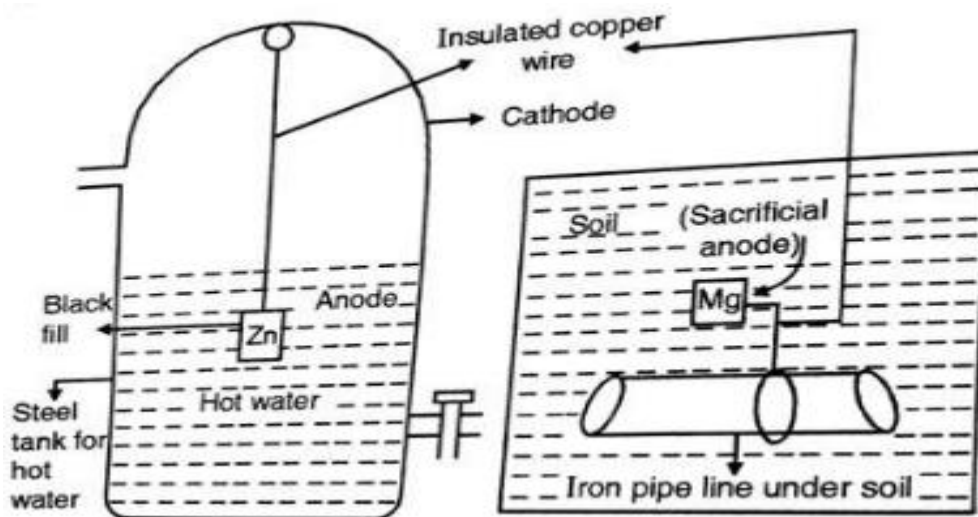
In any type of corrosion, anode gets corroded. However, if the anode is forced to act as cathode by using another active metal that is more reactive than anode, then the active metal supplies e's and gets corroded. thus, the base metal is saved.

Methods of Cathodic Protection:

- By using sacrificial anode.
- By using impressed current method.

a) Sacrificial Anode method:

The method is named as sacrificial anode method auxiliary anode method because more active metal sacrifices itself by undergoing corrosion and saving the base metal.



- ✓ To achieve this kind of protection by sacrificial anode the metal to be protected from corrosion is connected by a wire to another piece of metal, which is more reactive than the base metal.
- ✓ When the piece of more active metal gets corroded completely, it is replaced by new piece.
- ✓ The metals normally used are Mg, Zn, or Al.

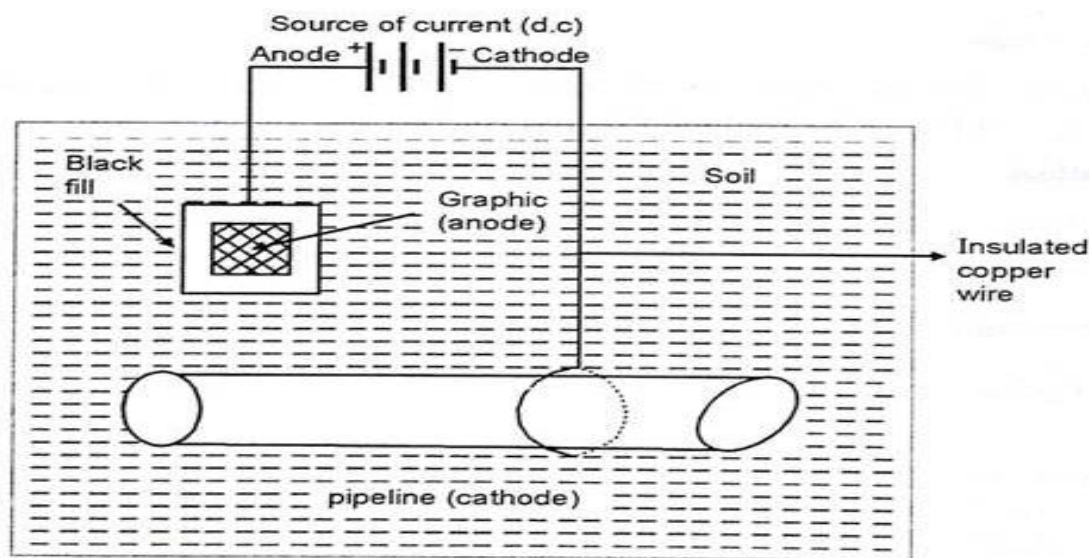
Application:

- ✓ It is normally used to protect pipelines carrying water, oil or industrial waste, which are buried under the soil.
- ✓ Protection of cables or iron pipelines by connecting them to Mg – blocks.
- ✓ Marine structures, ships are protected by using Zn - plates.
- ✓ Water, boilers are protected by Zn - metals.

b) Use Of Impressed Current:

In this method a current is applied in the opposite direction to that of corrosion current thereby nullifying the effect of latter one on the base metal i.e. connecting the base metals to cathode from anode.

This type of impressed current can be obtained by using D.C source such as battery or dry cell along with an insoluble anode such as Pt, molybdenum, stainless steel, graphite etc.



- ✓ In the diagram the insoluble anodic metal (graphite) is embedded underground. To this, with the help of D.C current source, the impressed current is applied and the whole assembly is connected to the metallic str. to be protected.
- ✓ Connections are done by using wires.
- ✓ Insoluble anode is kept inside back fill made up of gypsum, which Inc. the electrical contact with the soil.
- ✓ If the metal to be protected is small in area, then this kind of signal anode is used. However, if the area is very large, then many such anodes connected in series can be used.

Advantages:

- 1) It is very useful because it can protect the metal for a long term reducing the frequency of monitoring and maintenance cost.
- 2) Protection provided by both method is long term and maintenances is easy.

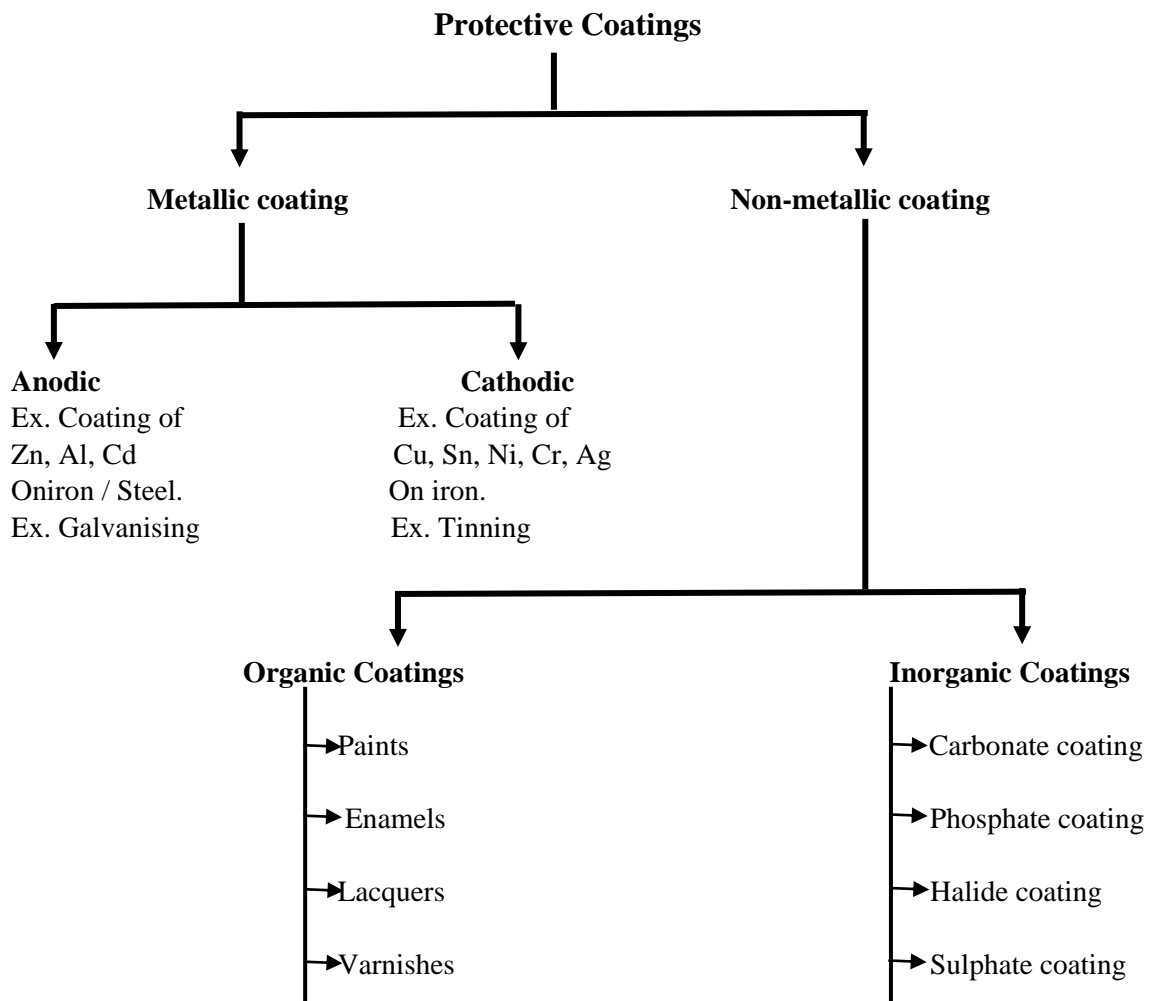
Disadvantage:

- 1) Due to application of impressed current, the anode deteriorates and hence it has to be replaced from time to time.

Application:

- a) Water tanks
- b) Buried pipe lines carrying water or oil.
- c) Condensers
- d) Transmission line towers.
- e) Ships etc.

6) Application of Protective Coatings:



- From this chart we have to only do Metallic coating i.e. Anodic and Cathodic method.

Metallic Coatings:

In this method, the metal surface has to be prepared for coating by cleaning. The methods of cleaning and preparation of metal surfaces are-

- 1) Solvent cleaning
- 2) Acid cleaning
- 3) Chemical cleaning
- 4) Alkali cleaning
- 5) Mechanical cleaning
- 6) Flame cleaning
- 7) Sand blasting
- 8) Acid pickling and etching

(I) Anodic Coating:

- In anodic coatings a coating of more reactive elements are applied on the base metal.
- Metals like Zn, Al or Cd if coated on iron or steel serve as anodic coating because their electrode potentials are higher than the base metal.

- As long as the coated layer is intact, the corrosion of base metal is totally under control, but in case any pores, cuts or breaks occur, there is formation of galvanic cell between the coated metal portion and the exposed base metal portion.
- Ex. Galvanised Steel: where Zn is coated on iron (steel). Here Zn is anodic to iron, it dissolves and iron is protected.

(II) Cathodic Coating:

- In Cathodic coating, a coating of more noble metal is applied on the base metal.
- Application of Cu, Sn, Ni, Cr, Ag coating on iron surface.
- Cathodic coating provides complete protection to the base metal until the coat layer is intact. But the moment this layer is broken, the base metal is exposed.
- Since the electrode potential of base metal is higher than that of the coated metal, a galvanic cell is formed, where anode is small (exposed base metal) and cathode is larger (coated metal). This gives rise to severe corrosion of base metal.
- Ex. Tinning: Tin coating on iron surface.

Difference between Anodic and Cathodic coating

<u>Sl. No</u>	<u>Anodic Coating</u>	<u>Cathodic Coating</u>
1.	Protects the underlying base metal sacrificially.	Protects the underlying base metal due to its noble nature.
2.	Electrode potential of coating metal is lower than that of the base metal.	Electrode potential of coating metal is higher than that of the base metal.
3.	If pores, breaks or discontinuities occur in such a coating, the base metal is not corroded till all the coating metal is consumed.	If pores, breaks or discontinuities occur in such a coating, the corrosion of the base metal is speeded up.
4.	Coating of Zn on iron is an example.	Coating of Sn on iron is an example.

Methods of Application of Metallic Coatings:

The following methods are used for applying the metallic coatings on the base metals.

1) **Hot dipping**

- a) Coating Zn on Fe i.e. galvanizing (Anodic coating)
- b) Coating Sn on Fe i.e. tinning (Cathodic coating)

2) **Metal Spraying**

3) **Diffusion or Cementation**

- a) Coating of Zn by diffusion i.e. Sherardizing.
- b) Coating of Al by diffusion i.e. Calorizing.
- c) Coating of Cr by diffusion i.e. Chromising.
- d) Coating of Si by diffusion i.e. siliconizing.

4) **Metal Cladding**

5) **Electroplating**

- Out of these 5 different methods of metallic coating only we have to study Hot dipping process.

1) Hot dipping:

In this method, the coating metal is of low M.P as compared to the base metal.

Ex. Zn (M.P – 410°C) which is less than M.P of Fe.

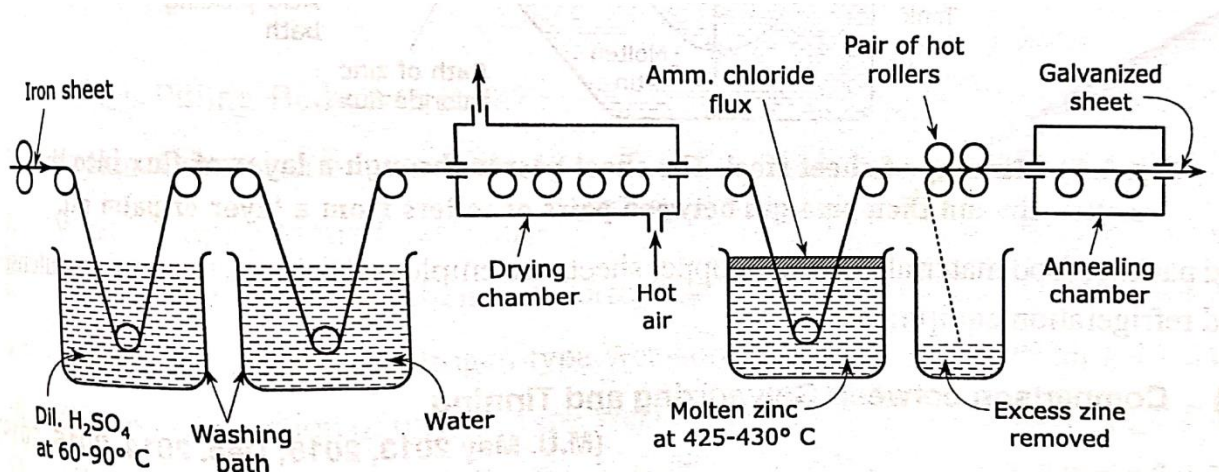
Sn (M.P – 232°C) which is again less than M.P of Fe.

a) Galvanising (Coating of Zn on Fe)

It is anodic coating obtained by coating of Zn on Fe or sheets to prevent them from rusting.

Process:

1. The iron or steel articles like sheet, pipe, wire is first cleaned by picking with dilute H_2SO_4 solution for 15-20 minutes at 60-90°C. This treatment removes scales, rusts (Oxide layer) and impurities from the surface of article.
2. The article is then washed properly and dried. It is then dipped in bath of molten zinc maintained at 425-430°C.
3. The surface of the bath is kept covered with a flux (*ammonium chloride*) to prevent its oxide formation.
4. When the article is taken out, it is found to have been coated with a thin layer of zinc. It is then passed through a pair of hot roller.
5. This process removes any excess of zinc and produces a thin film of uniform thickness.
6. Then it is annealed at a temperature of 650°C and finally, cooled slowly, which is shown below.



Application:

Galvanised sheets are used for making water pipelines, roofing sheets, wires, nails, screws, bolts, nuts, tubes etc.

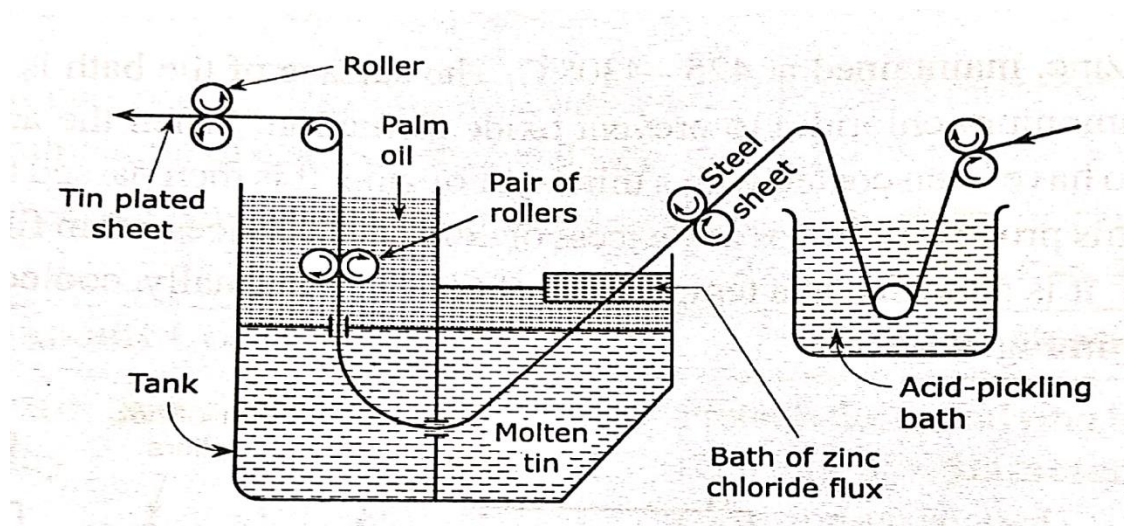
Disadvantage:

Galvanised iron sheet containers cannot be used for storing foodstuffs (especially acidic food items like pickles, cold drinks, lassi etc.) because coated metal (Zn) gets dissolved in acidic medium forming Zn compounds, which are highly poisonous if consumed.

b) Tinning (Coating of Sn on Fe)

It is cathodic coating obtained by coating of Sn on Fe or steel to prevent them from rusting.

Process: Steel sheet is first treated with dilute Sulphuric Acid (Pickling) to remove any kind of oxide film. The molten tin bath is covered with Zinc Chloride as a flux. The function of flux is to avoid the oxidation of molten tin. The sheet then passes through a tank of molten tin and finally through a series of hot rollers. The roller removes excess tin from the surface and produces a thin film of uniform thickness on the steel sheet.



Application:

- ✓ Tinned sheets are used for manufacturing containers to store foodstuffs, oils, ghee, pickles and pharmaceuticals.
- ✓ Used to cover Cu wire.
- ✓ Tinned Cu wire is used for soldering.

Disadvantages:

As it is cathodic coating, if the coat is broken the corrosion is initiated due to formation of small anode of Fe.

Q) Distinguish between galvanising and tinning.

Sl. No	Galvanising	Tinning
1.	Covering of Fe or steel with thin coat of Zn.	Covering of Fe or steel with thin coat of Sn.
2.	Zn protects Fe sacrificially therefore; it is more electropositive than Fe.	Sn protects Fe due to its noble nature.
3.	Zn continues to protect the base metal Fe by galvanic cell action even if Zn coating is broken at some place.	Sn protects the base metal Fe until the coat is perfect. Any break in the coating causes rapid corrosion of Fe.
4.	Galvanised containers cannot be used for storing acidic foodstuffs because with acid Zn forms highly toxic and poisonous Zn compounds.	Tinned containers can be used for any food storing even acidic.
5.	Used to protect roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc.	Used for coating steel, Cu and brass sheets, food containers, cookware's etc.