

*CORROSION  
AND  
CONTROL*

# Contents

- Introduction
- Classification
- Galvanic series
- Factors affecting
- Protection methods
- summary



# Learning Objectives

1. Unfold the practical aspects of metal corrosion with real life examples.
2. Be able to describe the mechanism of corrosion by electrochemical theory
3. Describe different forms of corrosion: galvanic, pitting, inter-granular, stress and microbial influenced corrosion
4. Demonstrate an understanding of the importance of the factors affecting corrosion
5. Know about the different established and modern techniques to control corrosion such as anodic/cathodic protection methods, organic /inorganic coatings
6. Distinguish between dry/wet corrosion, galvanizing/ tinning, electrochemical series/ galvanic series and organic/inorganic coating

# Definition

- Corrosion can be defined as spontaneous destruction or deterioration of a metal by chemical, electrochemical or biochemical reaction.

*Examples:*

Rusting of iron



Tarnishing of silver



Scales on copper

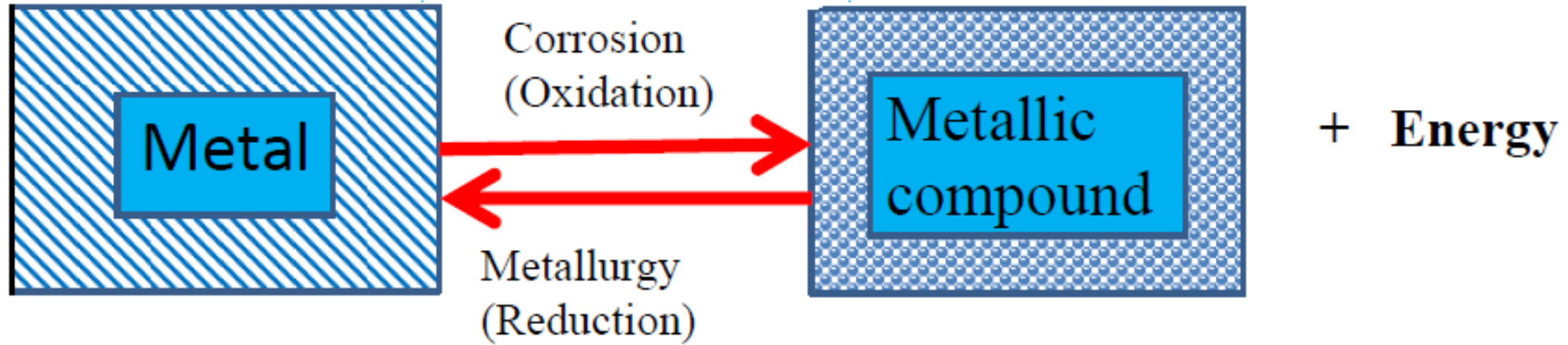




# CORROSION

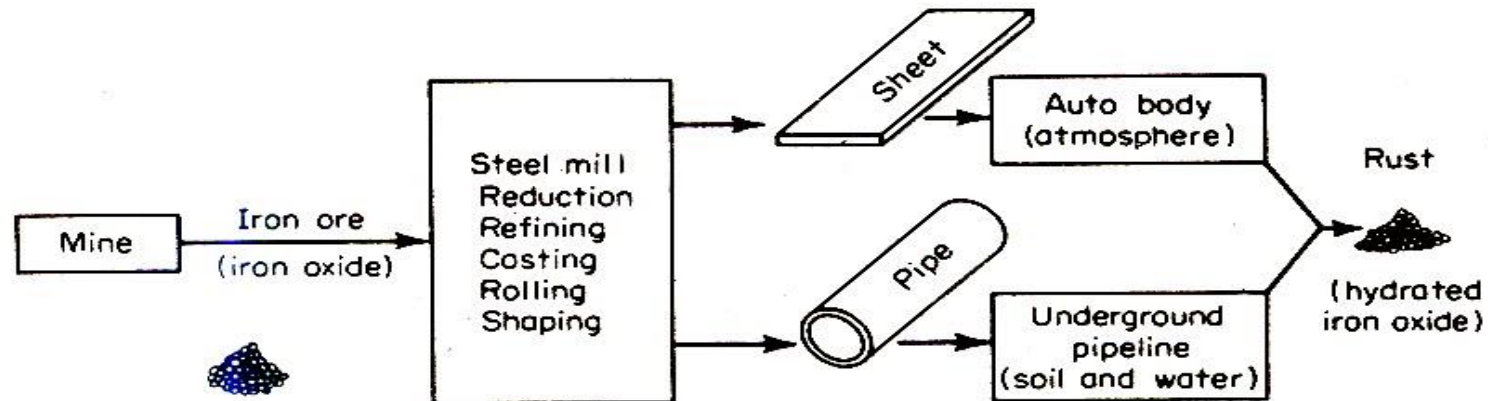
# Corrosion

Corrosion can be viewed as the reverse process of extractive metallurgy.



State of higher energy

State of lower energy



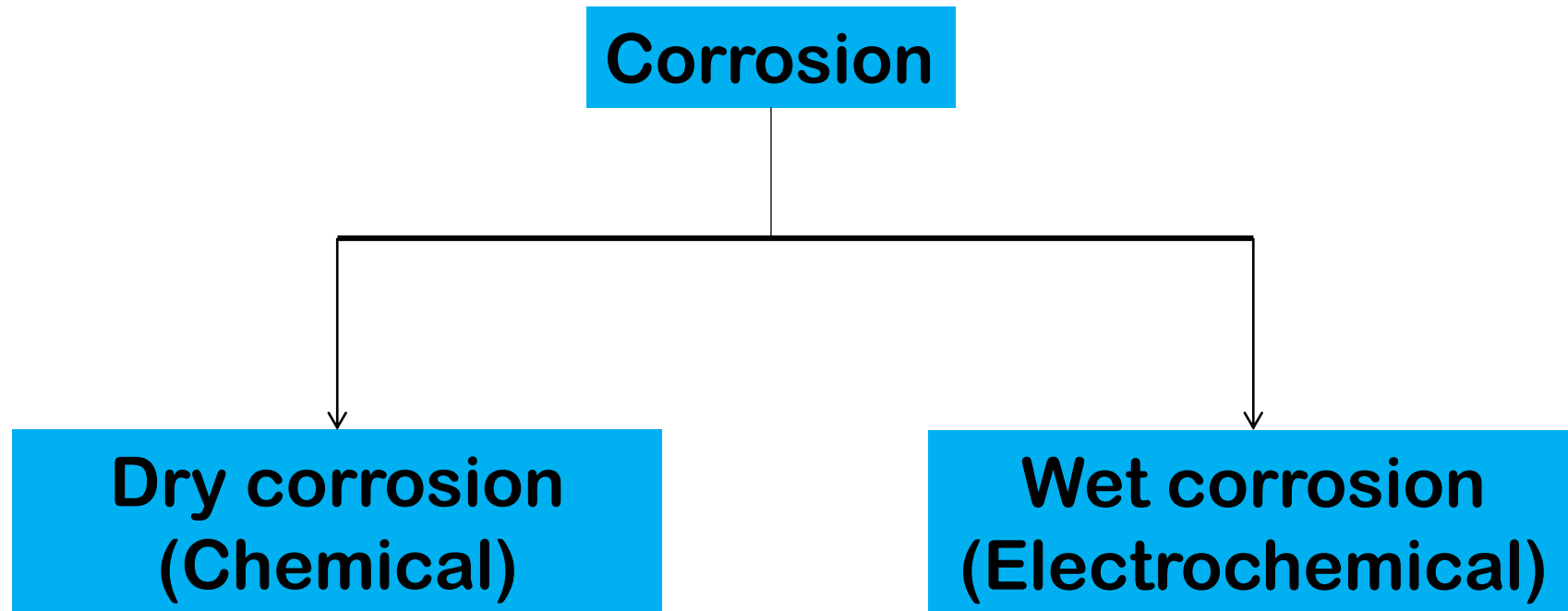
## Importance of Corrosion study

- Human Life and Safety
- Cost of Corrosion
- Conservation of Materials
- Academic interest

## Consequences of Corrosion

- Maintenance and operating costs
- Plant shutdowns, loss of production
- Contamination and loss of valuable products
- Effects on Safety
- Loss of Aesthetic value
- Loss of technically imp. Surface properties
- Loss of efficiency

# Corrosion Classification





# Dry Corrosion

- Occurs due to the direct chemical reactions between the environment and the metals / alloys
- Presence of an electrolyte is not at all essential for the corrosion to occur

## Types:

Oxidation (due to reaction with oxygen)

Other gases ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{X}_2$ , etc.)

Liquid metal

# Oxidation Corrosion

occurs when metals are attacked by dry oxygen

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

Nature of the oxide film decides subsequent corrosion

- If a stable film is formed  
ex. Al, Sn, Pb, and Cu
- Unstable metal film decomposes back into the metal and oxygen.  
ex. Ag, Au, Pt.
- Volatile film layer volatilizes as soon as it is formed, thereby accelerating the corrosion.  
ex.  $\text{MoO}_3$

Non porous  
Adherent  
Stable  
Protective  
continuous

# Dry Corrosion

## *(ii) Corrosion by other gases :*

Due to some gases  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ ,

depends mainly on the chemical affinity between the metal and the gas involved.

Eg. dry  $\text{Cl}_2$  attacks silver metal and forms  $\text{AgCl}$  as a thin protective and non-porous layer on the metal. As a result of this protective layer on the metal surface, the intensity of corrosion decreases.

## *(iii) Liquid metal corrosion :*

Occurs when a molten liquid is continuously passed on a solid metal surface or on alloy. This behaviour may be either due to the dissolution of the molten liquid or due to penetration of the molten liquid into the metal phase.

# Wet Corrosion

Wet corrosion occurs due to the existence of separate anodic and cathodic areas, between which current flows through the conducting solution

At Anode:



At Cathode:

- (i) Hydrogen evolution
- (ii) Absorption of oxygen depending upon the nature of corrosive environment.

# Wet Corrosion

## Anodic reaction:



## Cathodic reactions:

i) Hydrogen evolution:



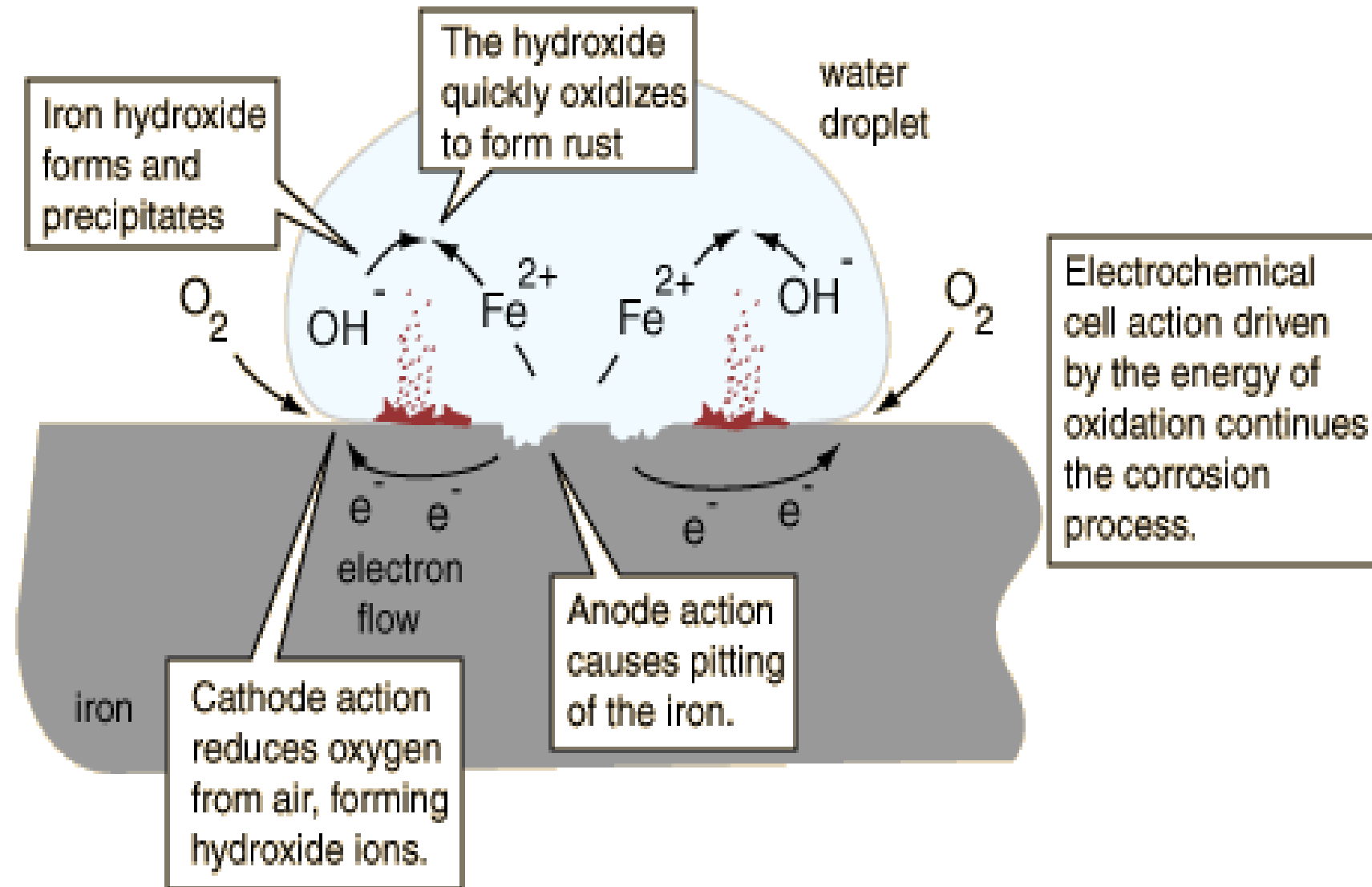
$H_2$  liberation along with  $OH^{-}$  ions formation



ii) Reduction of oxygen in neutral medium:



# Mechanism of rusting



# Mechanism of rusting

Rusting take place when iron is exposed to oxygen in the presence of humidity/moisture.

**At anodic sites**  $[\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-] \times 2$

**At cathodic sites**  $\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq}) + \text{H}_2$

**Overall reaction**  $2\text{Fe} + \text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) \rightarrow 2\text{Fe}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) + \text{H}_2$

Reactions to the formation of hydrated ferric oxide (rust)

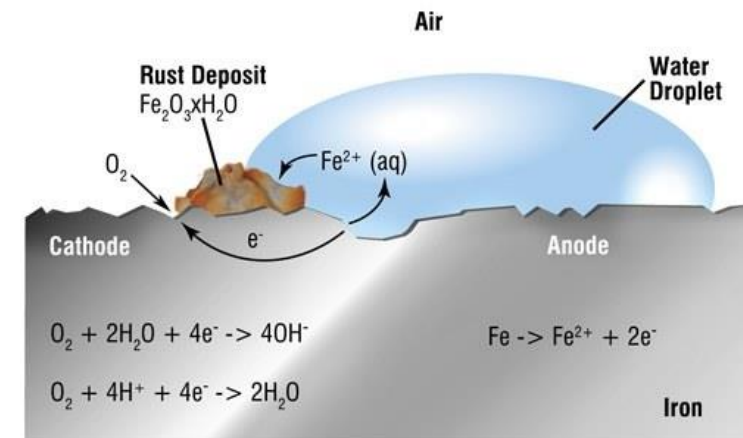
$\text{Fe}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Fe} (\text{OH})_2$

In presence of enough oxygen, ferrous hydroxide reacts with moisture and oxygen to give yellow rust.

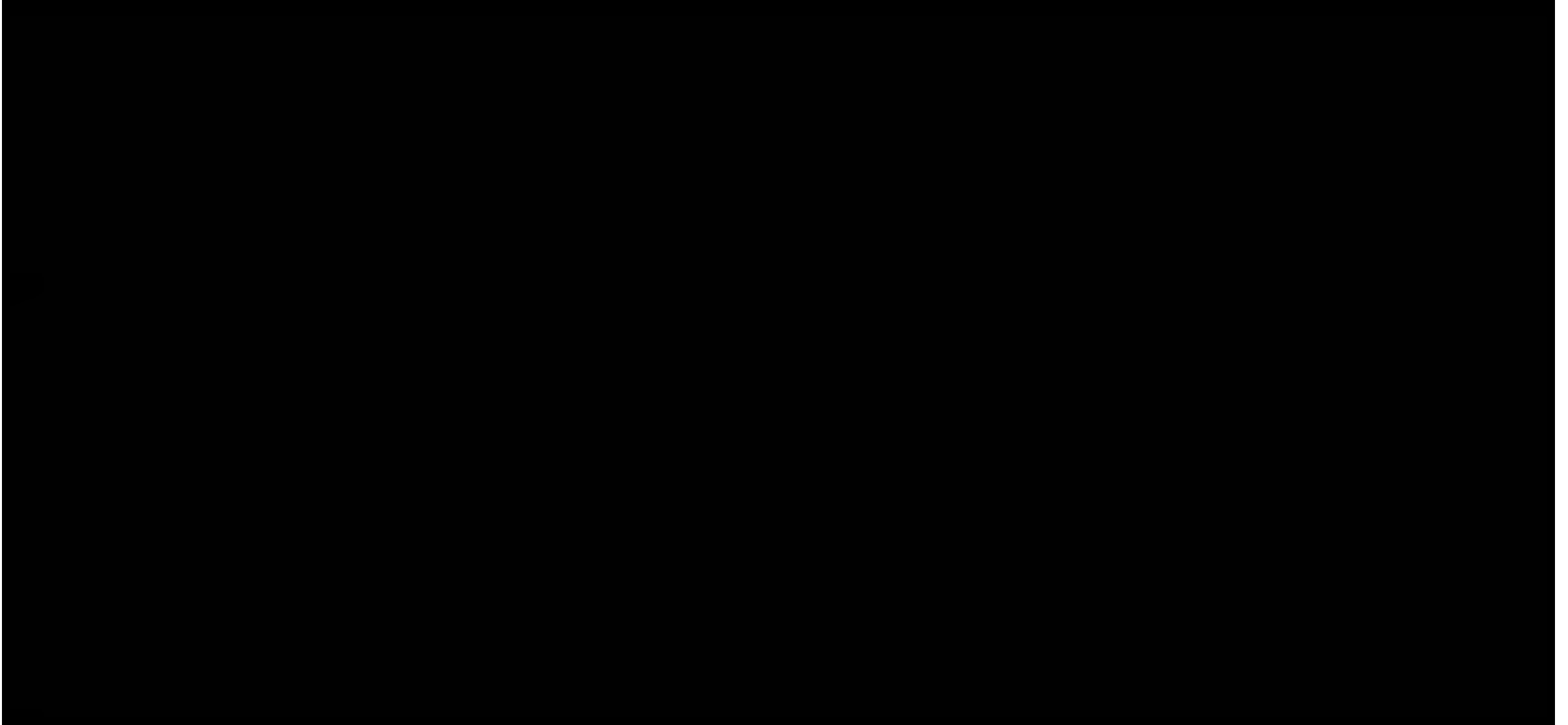
$4 \text{Fe} (\text{OH})_2 + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 2 [\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$  ( Yellow rust)

If the supply of oxygen is limited, the corrosion product may be black anhydrous magnetite.

$6 \text{Fe} (\text{OH})_2 + \text{O}_2 \rightarrow 2 [\text{Fe}_3\text{O}_4 \cdot 3\text{H}_2\text{O}]$  ( Black Rust)



# Mechanism of rusting





# Comparison between Dry & Wet Corrosion

Dry Corrosion	Wet Corrosion
Involves direct attack of atmospheric gases	Occurs due to the existence of separate anodic and cathodic areas between which current flows through the medium
Do not need a corrosive medium	Needs corrosive medium
Types include oxidation corrosion, liquid metal corrosion and corrosion by gases	Types include galvanic, pitting, stress and intergranular
Less prevailing	More common

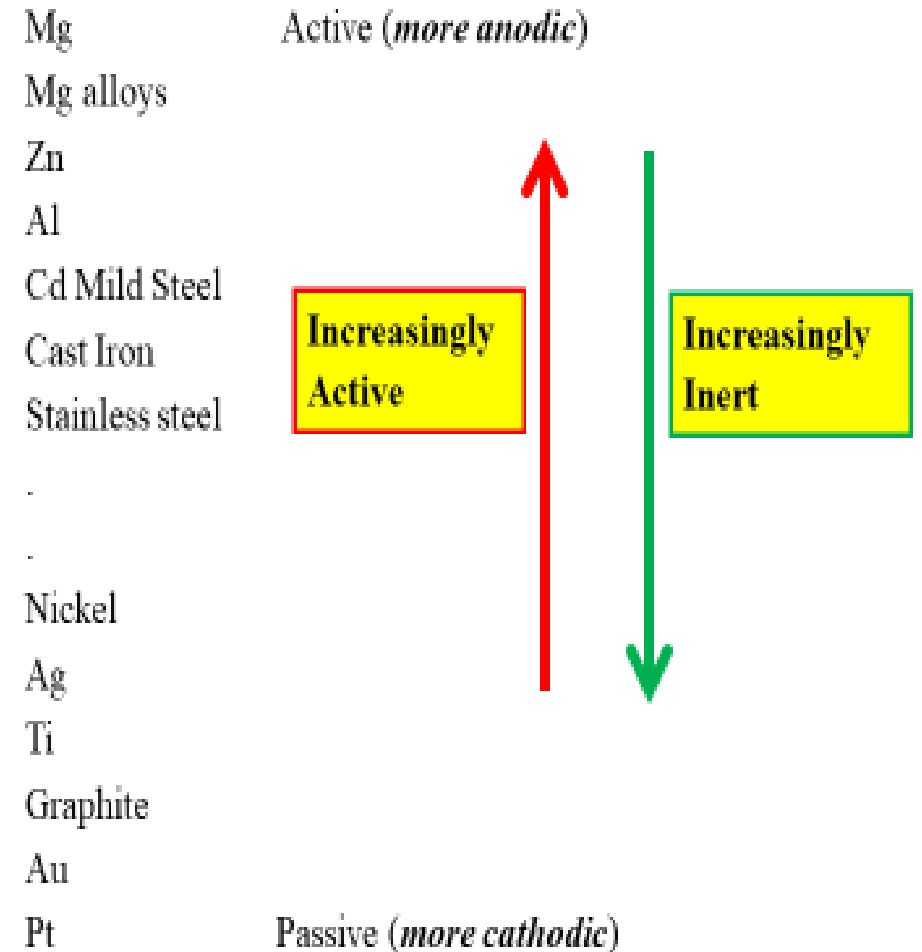
# Galvanic Series

## Need for galvanic series

The electrochemical series does not take passivity into account.

The electrochemical series does not account for corrosion behavior of alloys.

- The series prepared by studying the corrosion of metals and alloys in a given environment like sea water.



# Characteristics of galvanic series

- Galvanic series include both metals and alloys.
- Metals and alloys are arranged in the increasing order of their corrosion resistance in seawater.
- Metals and alloys having almost same corrosion characteristics are grouped within a square bracket.
- Same metal can occupy two positions in the galvanic series; For example, aluminum occurs both active and noble region depending upon its active and passive states.

# Comparison between ES & GS

## Electrochemical series

- EPs are measured by dipping pure metals in their salt solution of 1M conc. without any oxide film.
- Position of a given metal in is fixed.
- Gives no information regarding the position of alloys.
- Metals & non- metals are included.

## Galvanic series

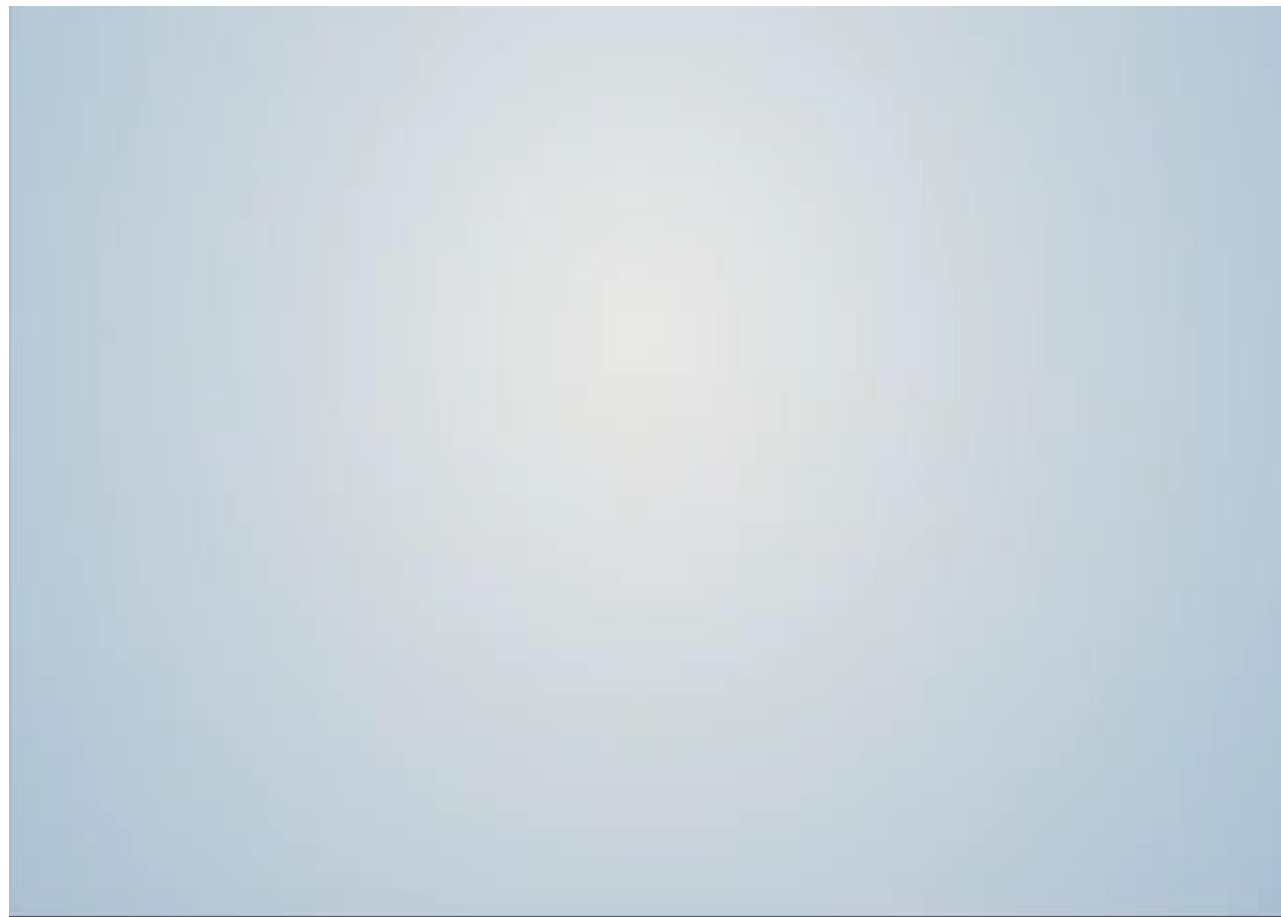
- Series developed by studying corrosion of metals & alloys in unpolluted sea water, without their oxide films.
- The position of a given metal may shift as it takes active & passive states.
- Alloys are included based on their corrosion behavior
- Metals and alloys are included

**Similarity:** In both, base metals are placed higher & noble metals lower in the series

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# Types of Corrosion

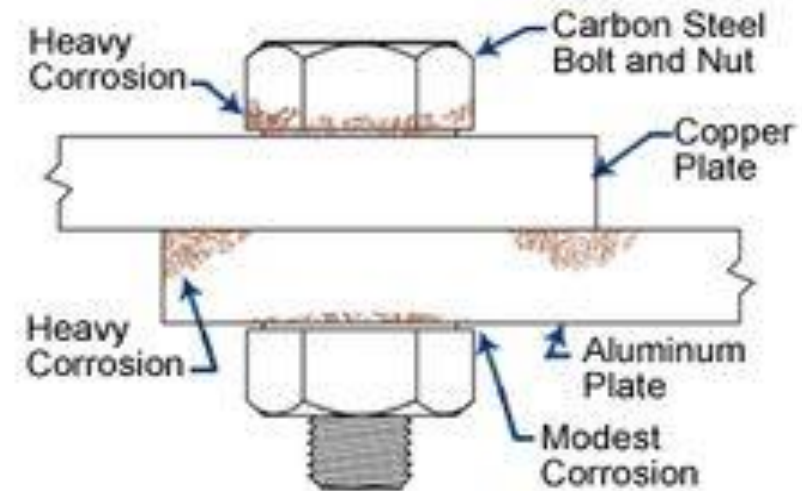
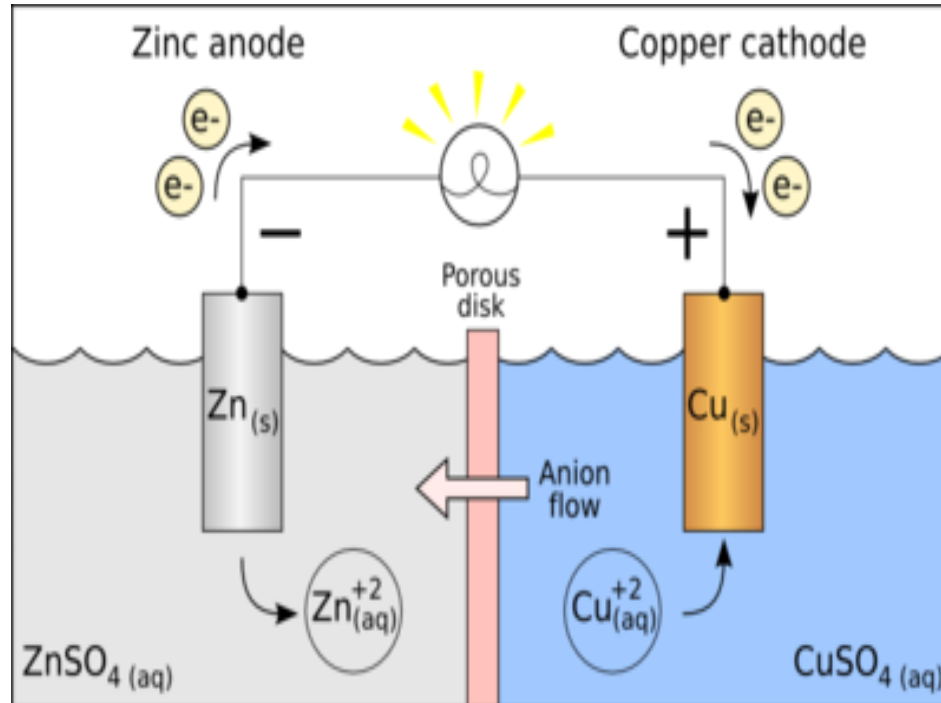
- Galvanic corrosion
- Pitting corrosion
- Inter-granular corrosion
- Stress corrosion



# Galvanic Corrosion

- Occurs when two dissimilar metals are in contact with an electrolyte.
- Anode:  
Metal with lower standard electrode potential value.
- Cathode:  
Metal with higher standard electrode potential.
- Examples:
  - Copper piping connected to steel tanks
  - Steel screws in a brass marine hardware.
  - Lead antimony solder around the copper wire.
  - A steel propeller shaft in bronze bearing
  - Steel pipe connected to copper plumbing

# Galvanic Corrosion



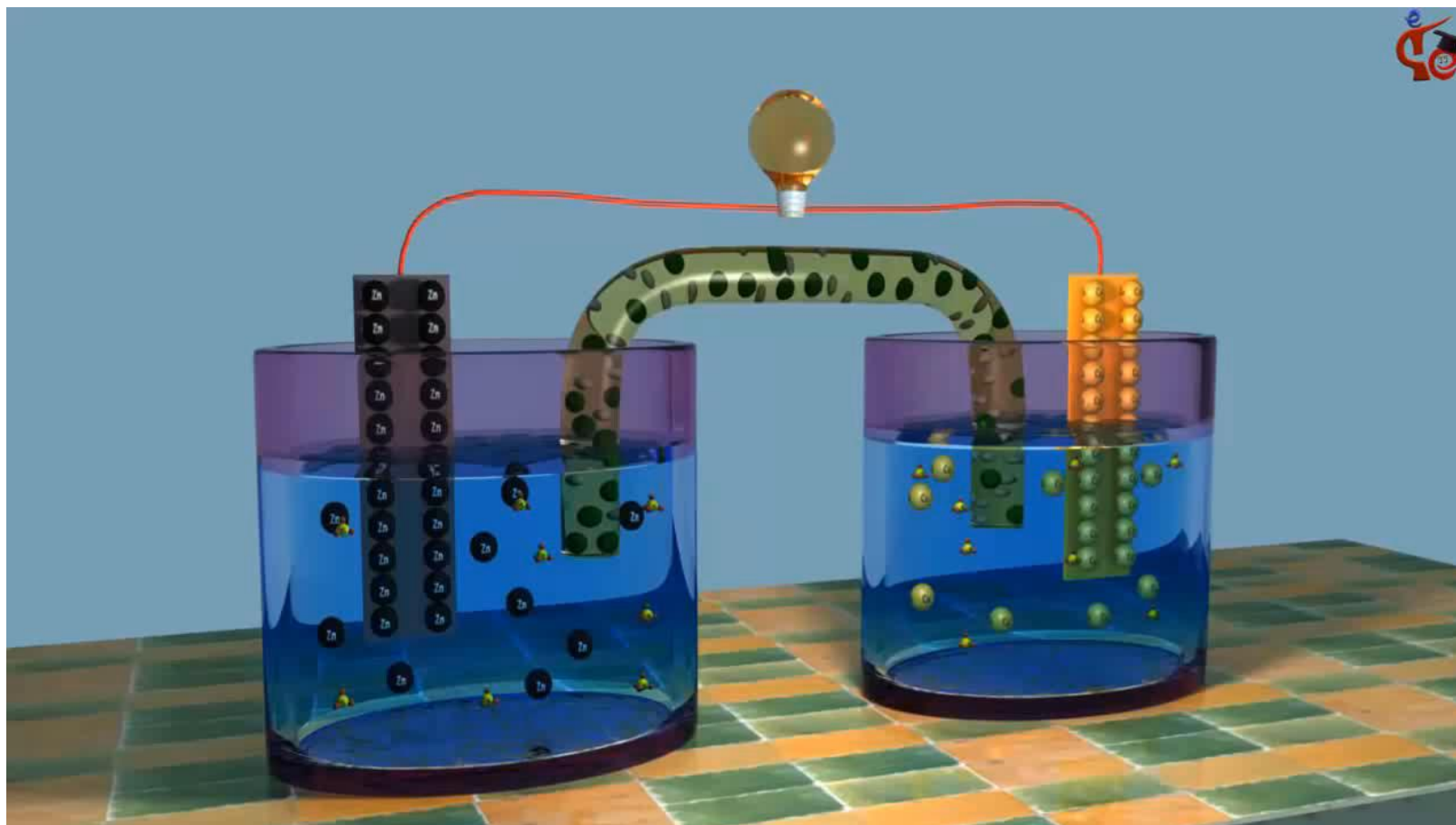
Effects of Galvanic Corrosion



# Galvanic Corrosion



This rainwater guttering is made of aluminium and would normally resist corrosion well. Someone tied a copper aerial wire around it, and the localised bimetallic cell led to a “knife-cut” effect.



# Pitting Corrosion

A pit may be described as a cavity or hole with the surface diameter about the same length as or less than the depth.

The **important reasons** for the pitting corrosion are:

- Surface roughness or non uniform finish
- Scratches or cut edges
- Local straining of metal, due to non uniform stress
- Depositions of extraneous matter such as sand, scale, water drop, dust etc.

# Pitting Corrosion

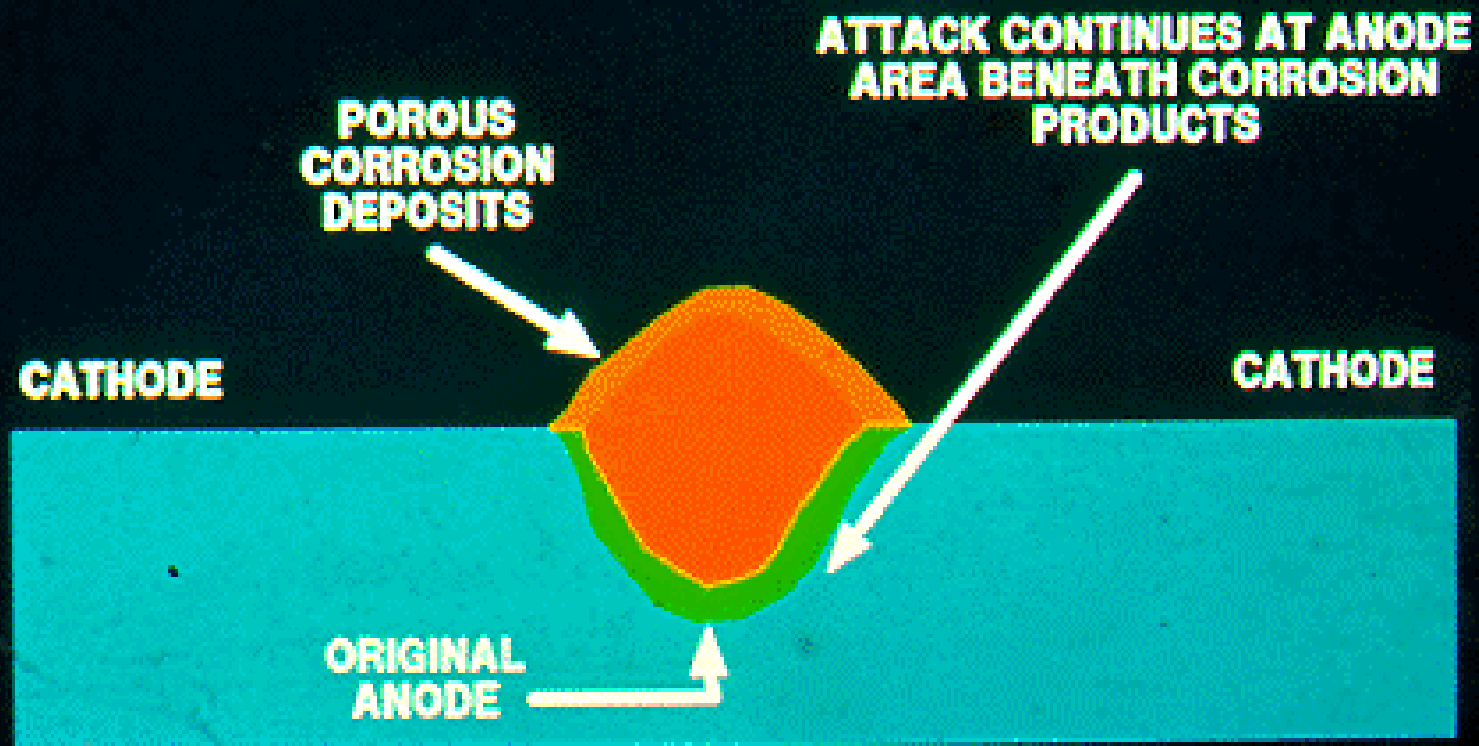
Pitting is usually due to the breakdown or cracking of the protective film on a metal at specific points

Pitting corrosion is characterized by small anodic area and large cathodic area, resulting in accelerated corrosion at the anodic area.

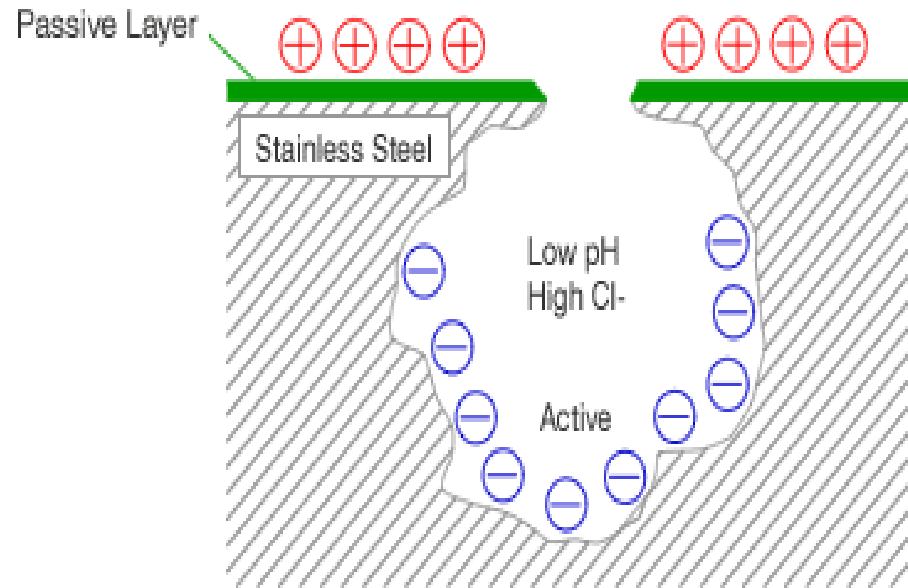
It is an autocatalytic process, with the initially formed pit produces conditions which are both stimulating and necessary for the continuing activity of the pit.

# Pitting Corrosion

## "PITTING" CORROSION BENEATH POROUS DEPOSITS

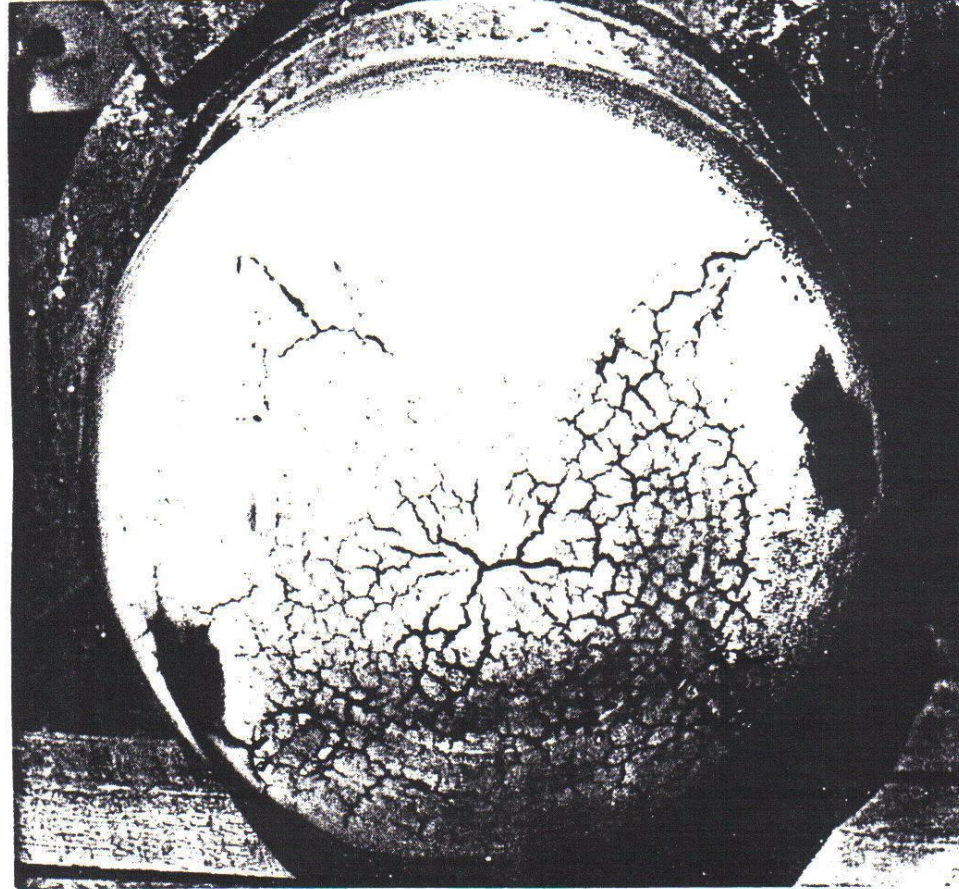


# Pitting Corrosion



Pitting is dangerous because it is a localized and intense form of corrosion and failure occurs with extreme suddenness.

# Stress Corrosion



Stress corrosion of stainless steel type 304, autoclave.  
(Mallinckrodt Chemical Works)



# Stress Corrosion

- Also known as stress cracking
- Cracking of metal caused by the **combined effect of a tensile stress and a specific corrosive environment** on the metal. Here, the corrosive agents are highly specific and selective.
- The metal atoms under stress possesses higher energy levels than the one with free from stress.
- The stressed part of the metal becomes more active than the stress free part.
- Hence: Anode - stressed part & Cathode - stress free part.

*Stressed part undergoes corrosion*

- Examples:

Season cracking of brass

Caustic embrittlement of steel

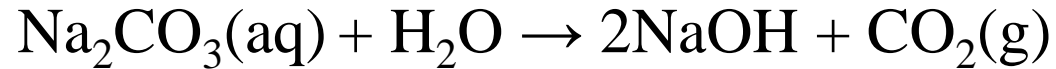


# Stress Corrosion



# Caustic Embrittlement

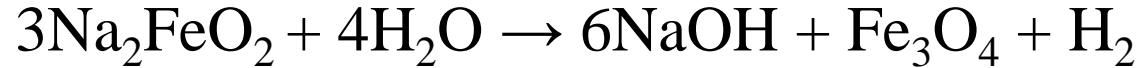
- This is a dangerous and occurring in mild steel, exposed to alkaline solutions at high temp. and stresses.
- Water fed into boilers may contain free alkali (Lime soda process).



- Local stresses exist in metal sheets of boiler under rivets.
- Minute cracks develop on the metal sheets when the stress is relieved.
- This very dilute alkaline water flows into the minute hair-cracks and crevices by capillary action
- Inside the crack, the water evaporates and caustic soda conc. builds up
- This conc. alkali dissolves iron as sodium ferroate in crevices/cracks, where the metal is stressed and the conc. of alkali is much higher than that in the body of the liquid.

# Caustic Embrittlement

- The sodium ferroate decomposes, a short distance away from its point of formation



- NaOH is regenerated and magnetite is precipitated thereby enhancing further dissolution of iron
- When iron changes to these oxides, metallic properties like malleability and ductility are lost.
- It becomes brittle. The brittleness is caused by caustic alkali.
- NaOH concentration cell forms between the stressed and unstressed part of the metal

Iron		Conc. NaOH;	Dilute NaOH		Iron
		(stressed)	(unstressed)		
		ANODIC	CATHODIC		

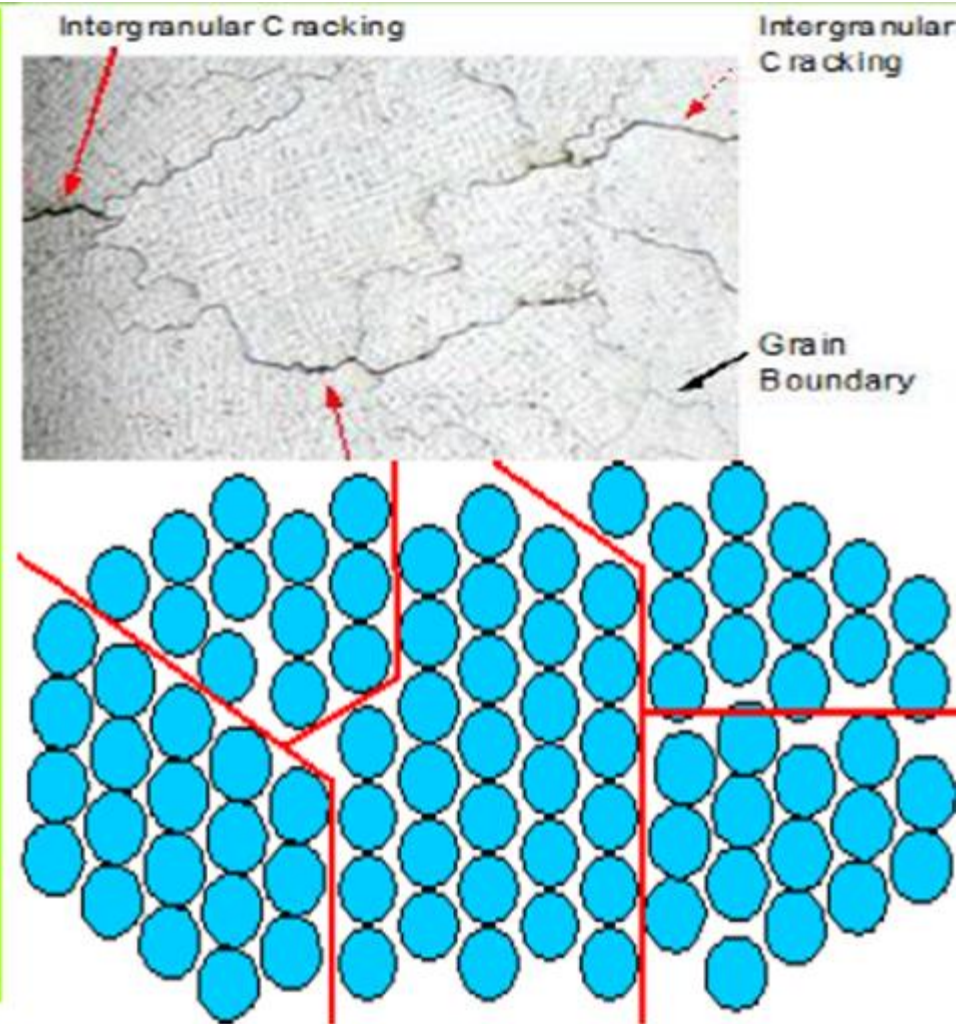
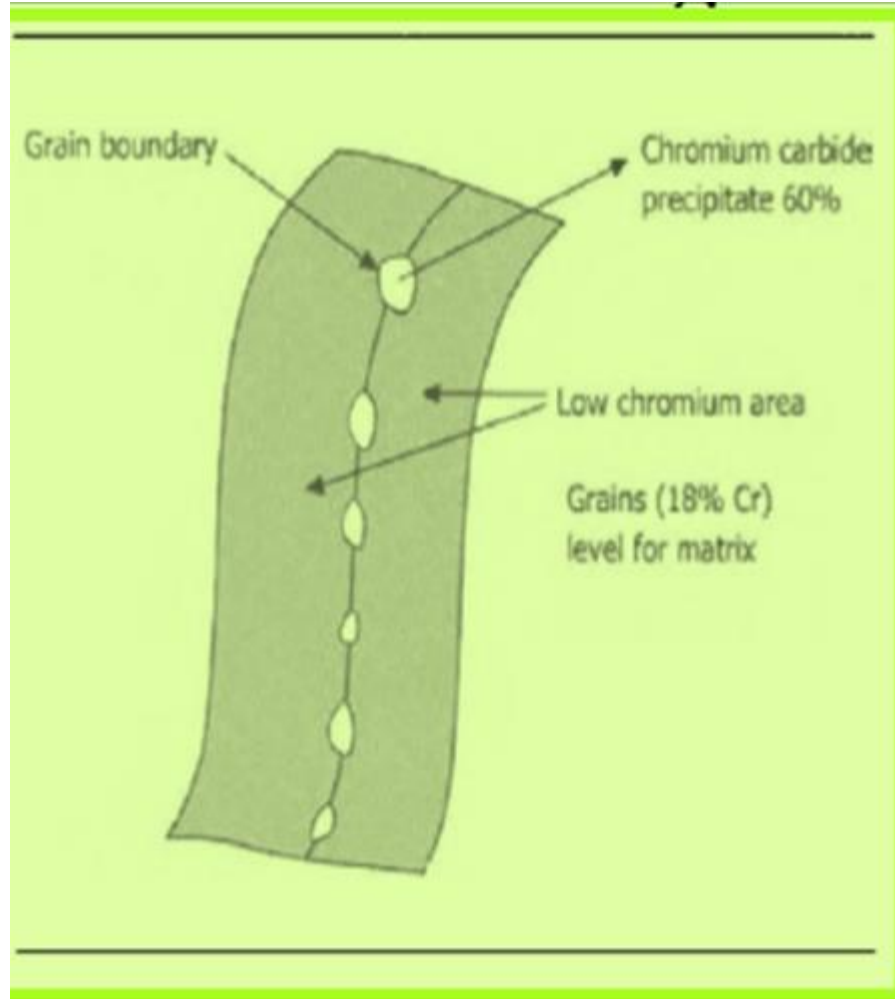
# Caustic Embrittlement

## *Prevention:*

- $\text{Na}_2\text{SO}_4$ , tannin or lignin is added to water.
- Boiler can be constructed by welding the sheets to avoid local stresses.
- Caustic embrittlement is avoided by using demineralized water



# Inter-granular Corrosion



# Factors affecting the Corrosion

## **Primary Factors (Factors related to the corroding metals):**

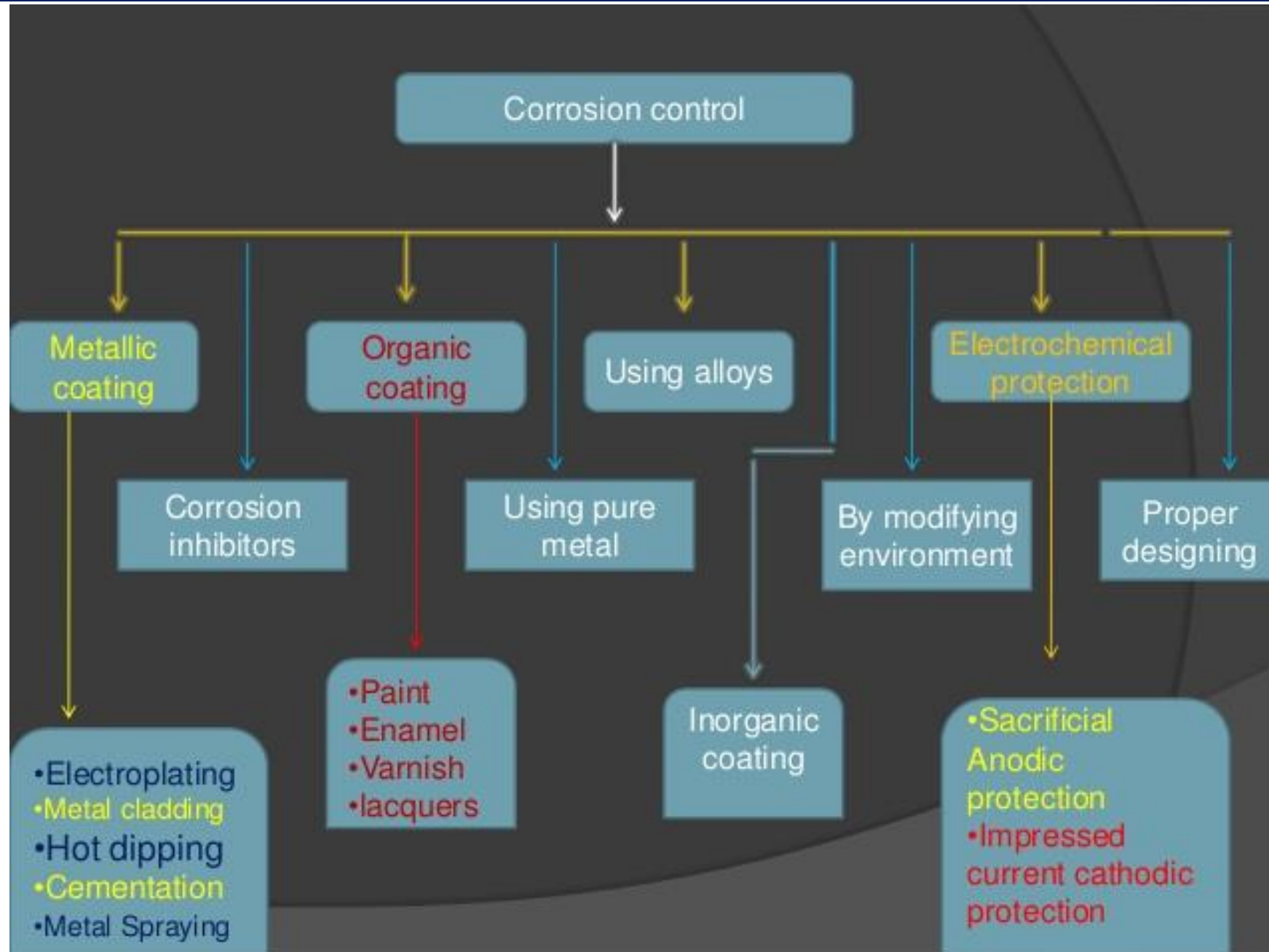
- Nature of metal and relative electrode potentials of metals
- Relative cathodic and anodic area
- Hydrogen over voltage
- Nature of the corrosion product

## **Secondary Factors (Factors related to the environment)**

- Concentration and nature of electrolyte
- pH of the medium
- Temperature
- Polarization



# Corrosion Control Techniques





# Corrosion Control Techniques

Various methods we discuss in this course for corrosion prevention are

- Selection of materials & design improvement
- Change of the metal
- Change of environment
- Use of coatings for separating metal from environment

# Corrosion Control by selection materials

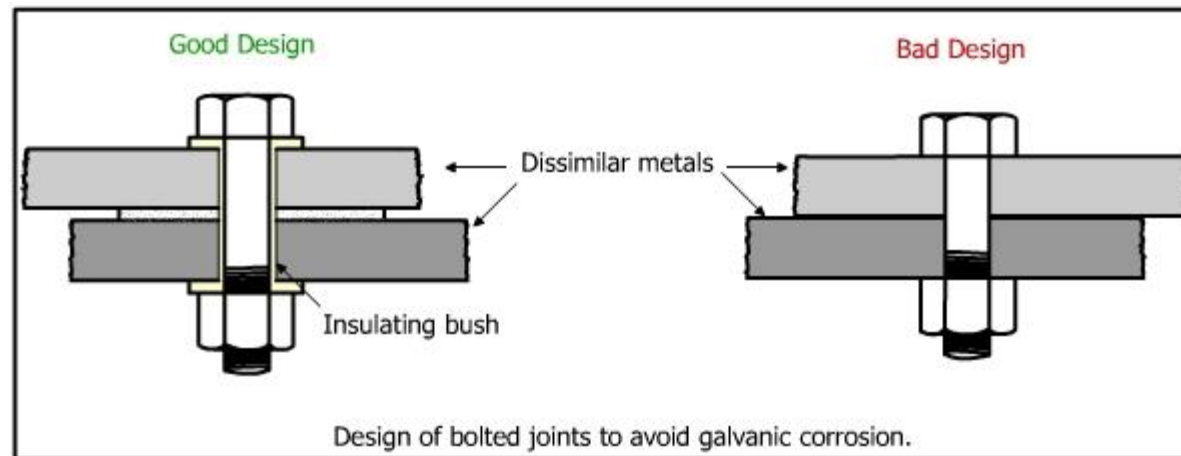
- Noble and pure metals show greater resistance to corrosion  
Impurities in metal causes heterogeneity, which decreases corrosion-resistance of the metal
- Suitable alloying of metals  
Corrosion-resistance of most of the metals is best increased by alloying them with suitable elements, but the alloy should be completely homogeneous  
e.g., Cr is the best alloying metal for iron or steel

# Corrosion Control by proper designing

The design of the material should be such that **corrosion, even if it occurs, is uniform** and does not result in an intense and localized corrosion

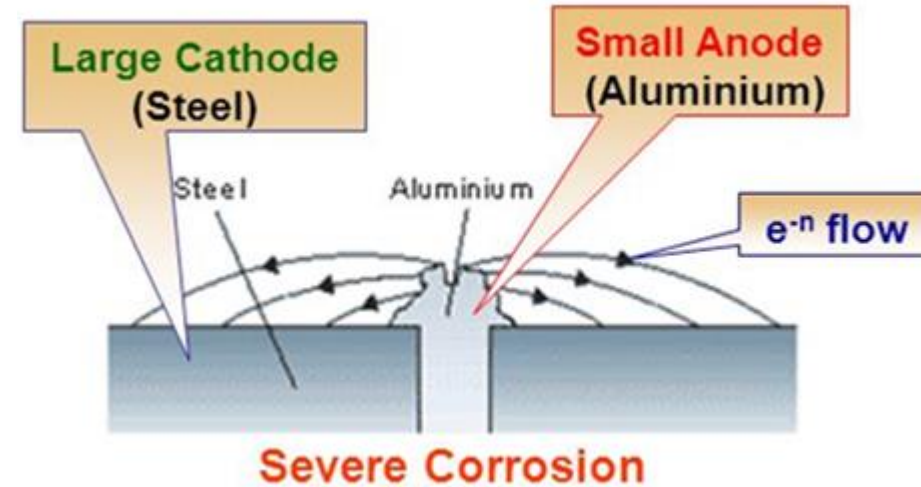
*Some important design principles are:*

- **Avoid the contact of two dissimilar metals** having large difference in their electrode potentials
- Whenever the direct joining of dissimilar metals, is unavoidable, an insulating fitting may be applied in between them to avoid direct metal-metal electrical contact



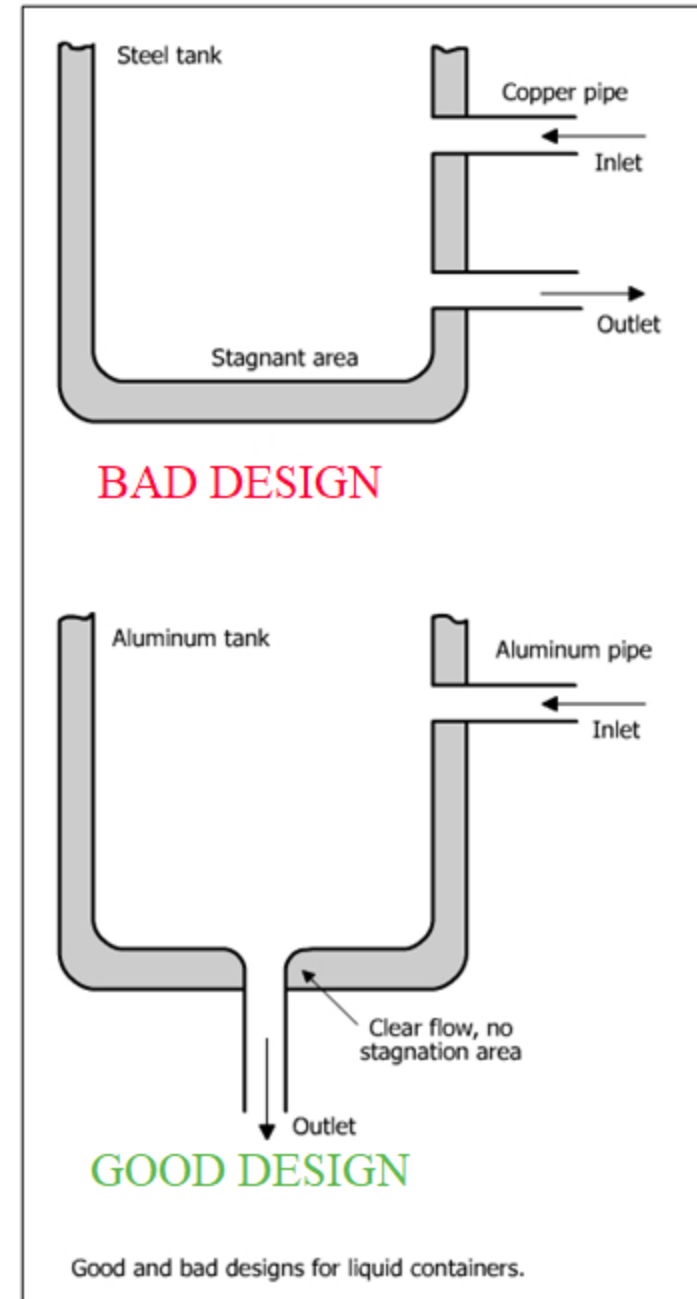
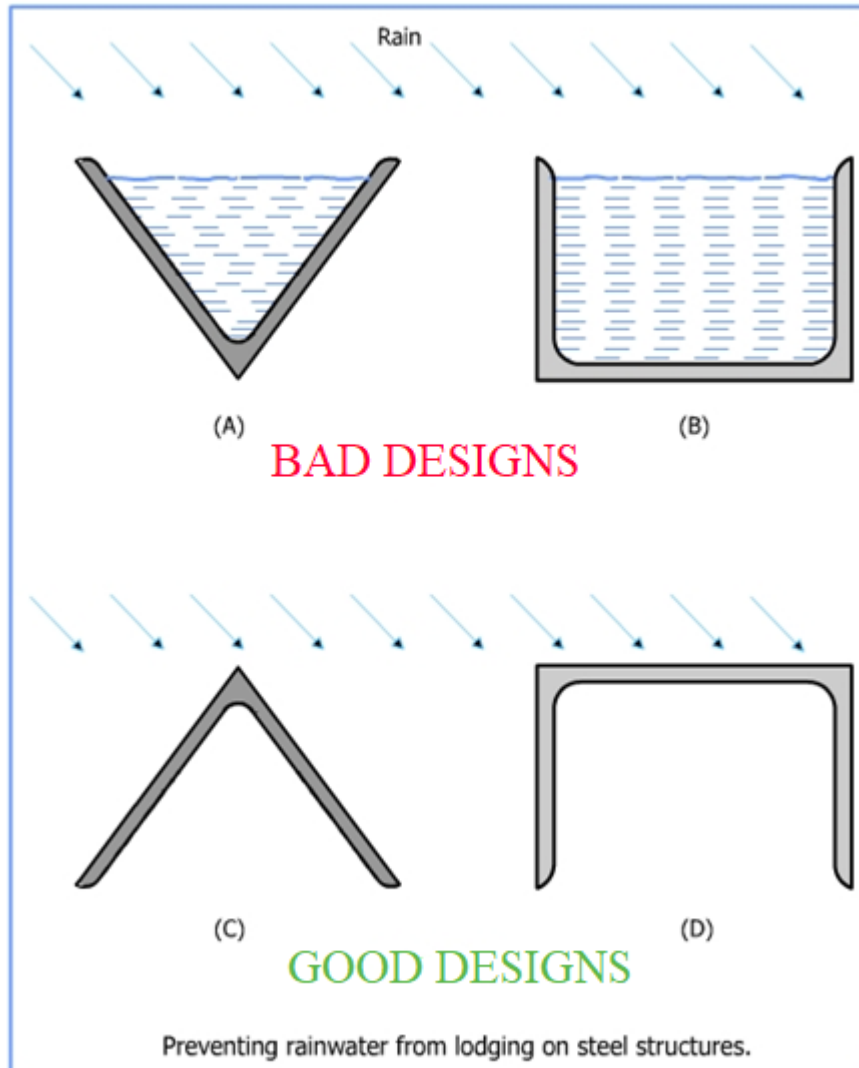
# Corrosion Control by proper designing

If the contact between two dissimilar metals is unavoidable, two metals are chosen in such a way that the anodic metal should be as large as possible and cathodic metal should be as small as possible



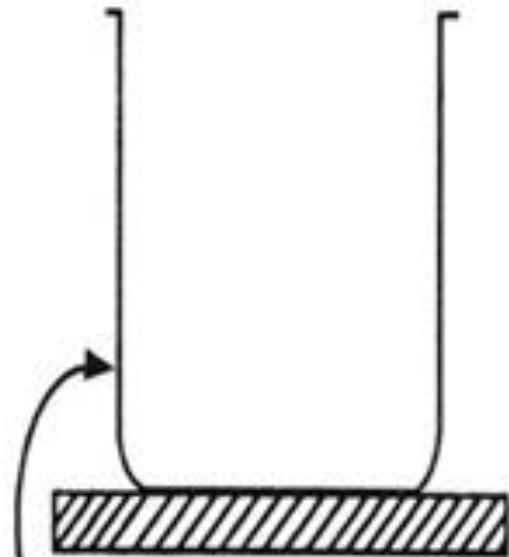
# Corrosion Control by proper designing

- Avoid residual moisture

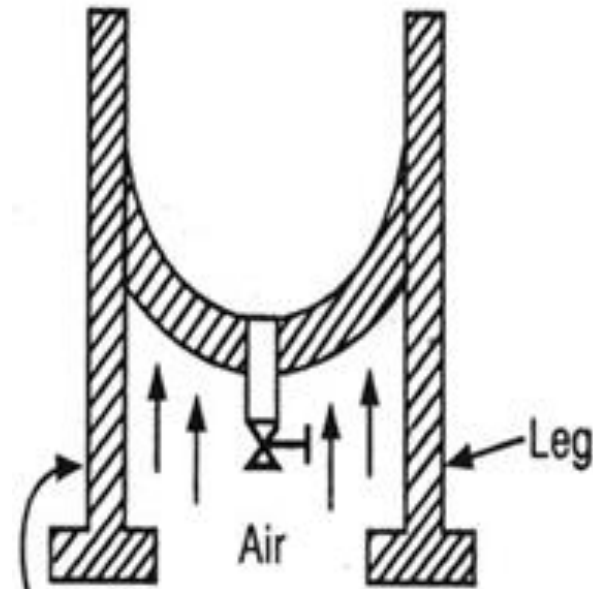


# Corrosion Control by proper designing

- Metallic equipment should be supported on legs to permit air circulation and to avoid the formation of damp areas under the equipment



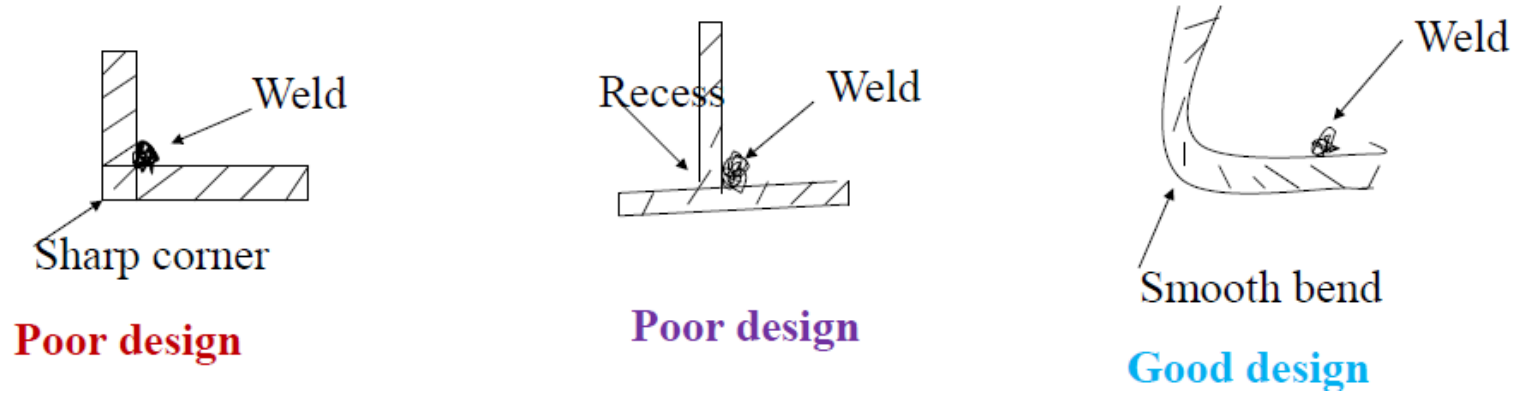
Poor design, because it prevents free circulation of air



Best design, because it allows free circulation of air and proper drainage and easy washing

# Corrosion Control by proper designing

- Avoid sharp corners



- The anodic metal should not be painted or coated because any break in coating would lead to rapid localized corrosion
- Residual stress in fabricated articles should be avoided
- Avoid crevices

# Corrosion Control by cathodic protection

The principle involved in this method is to force the metal to be protected to behave like a cathode, there by corrosion does not occur.

Two different methods:

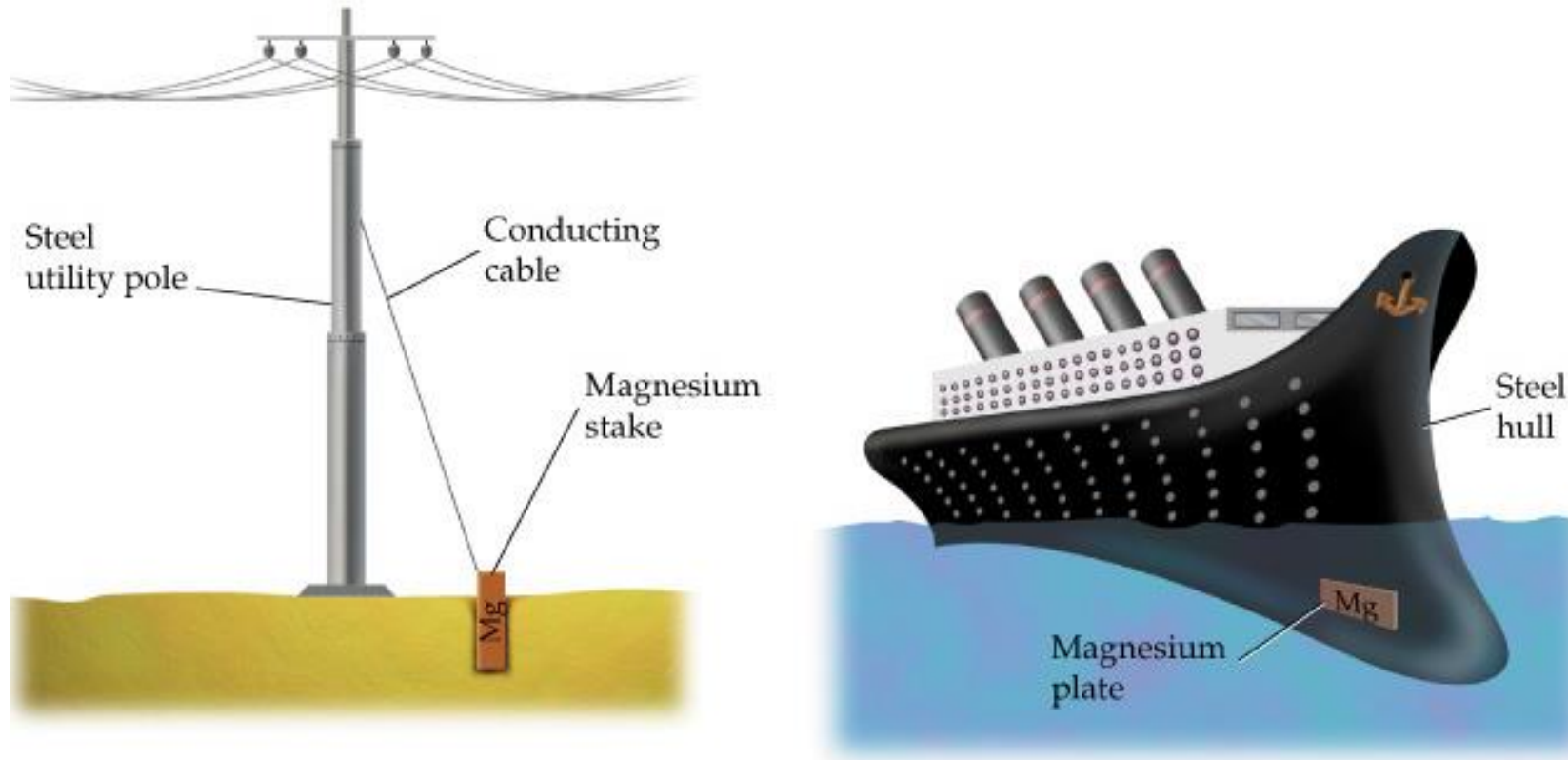
- Sacrificial anodic method
- Impressed current method



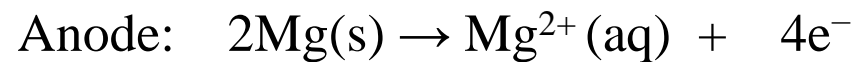
# Corrosion Control by sacrificial anodic method

- Zn and Mg are more reactive metals than Fe and hence they become anodic part in contact with Fe
- Effective only when proper quantities of sacrificial anodes are used
- Number and spacing of anodes depend upon the system to be protected
- Examples:  
Ship's steel hulls, offshore drilling platforms, oil and gas pipelines under sea, containers used to store water and other liquids are protected by this method

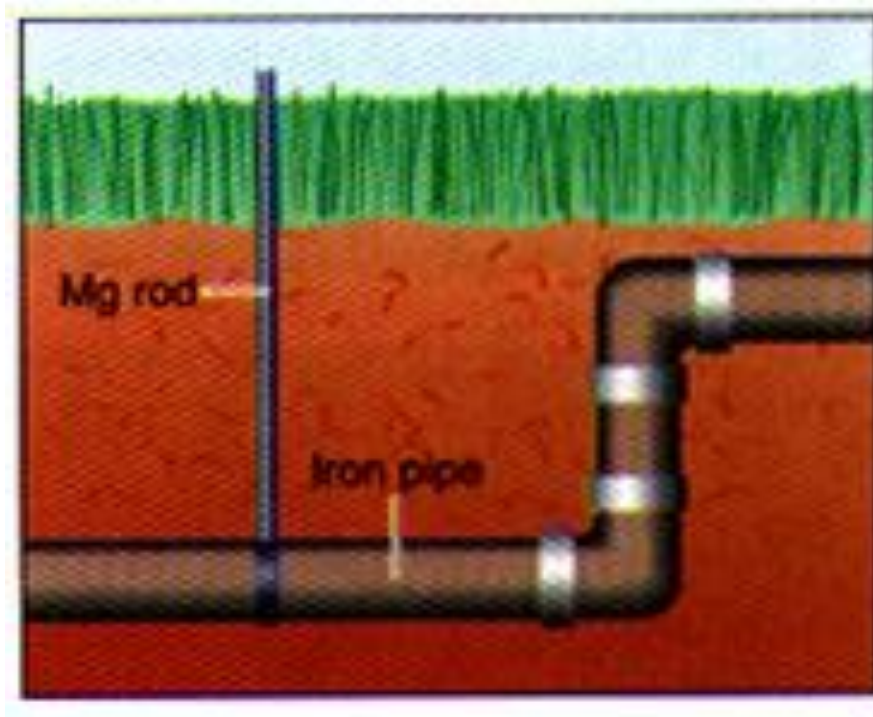
# Corrosion Control by sacrificial anodic method



The magnesium sacrifices itself to prevent corrosion of the iron (steel)



# Corrosion Control by sacrificial anodic method



- Anodic part: More reactive metal
- Cathodic part: Structure to be protected

*The anode is sacrificed to protect the structure.*

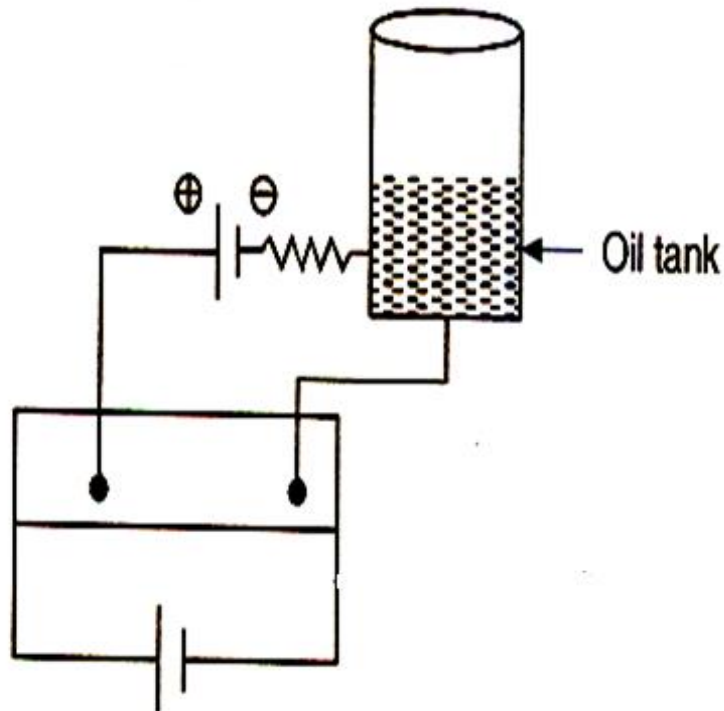
## Advantages:

- No external power supply is required
- Can be used in remote and difficult to reach areas
- Low installation cost
- Minimum maintenance cost.



# Corrosion Control by impressed current method

- The metallic structure is made cathode with the use of impressed current by connecting it to the negative terminal of the external power source
- The anode may be made up of steel, graphite and platinum group metals
- The inert anode is surrounded by back fill consisting of coke breeze, gypsum to improve electrical contact



## Advantages:

- Applicable to large objects
- Uncoated parts can be protected

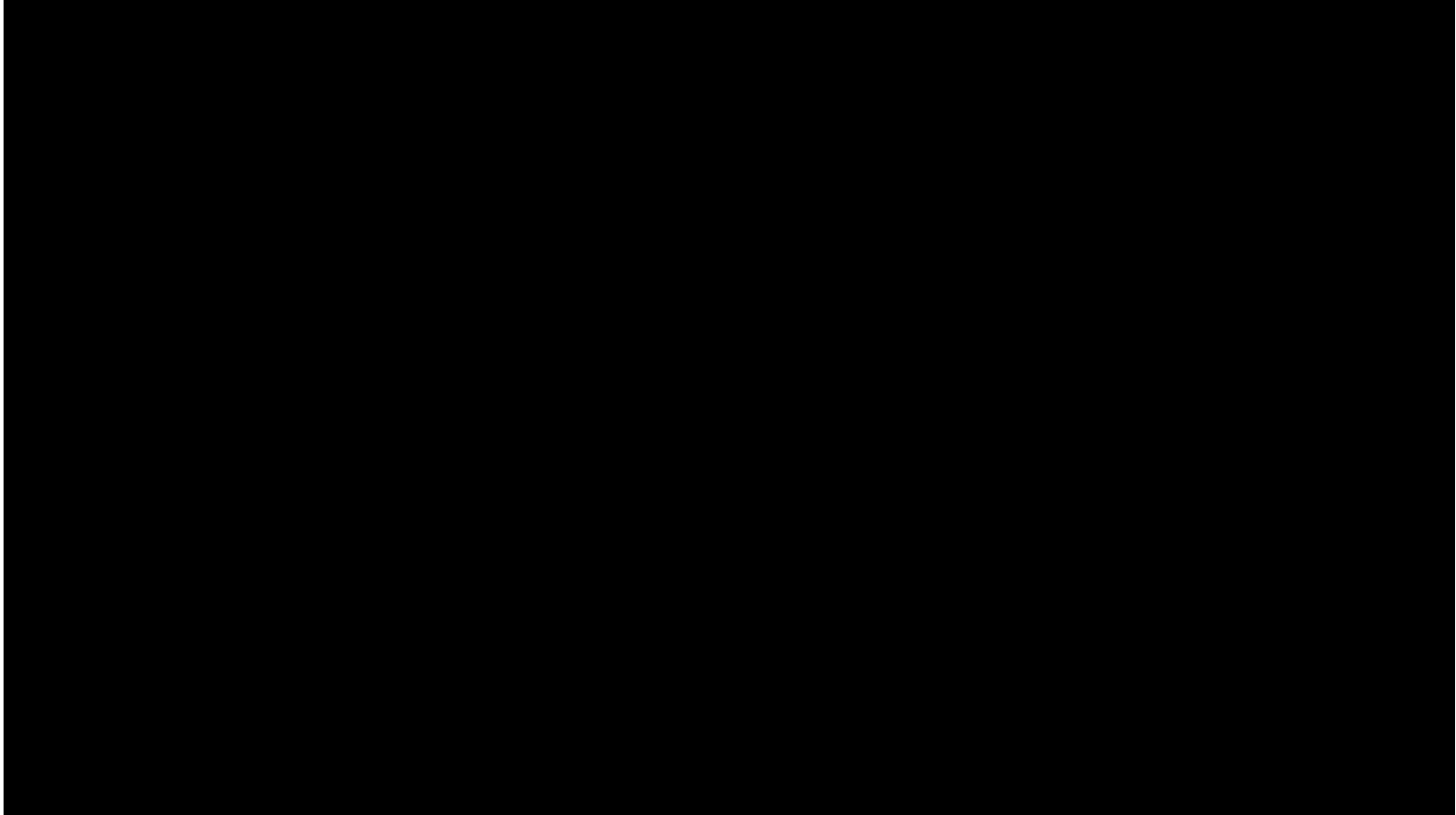
## Limitations:

- Larger installation cost
- Higher maintenance cost

# Corrosion Control by anodic protection method

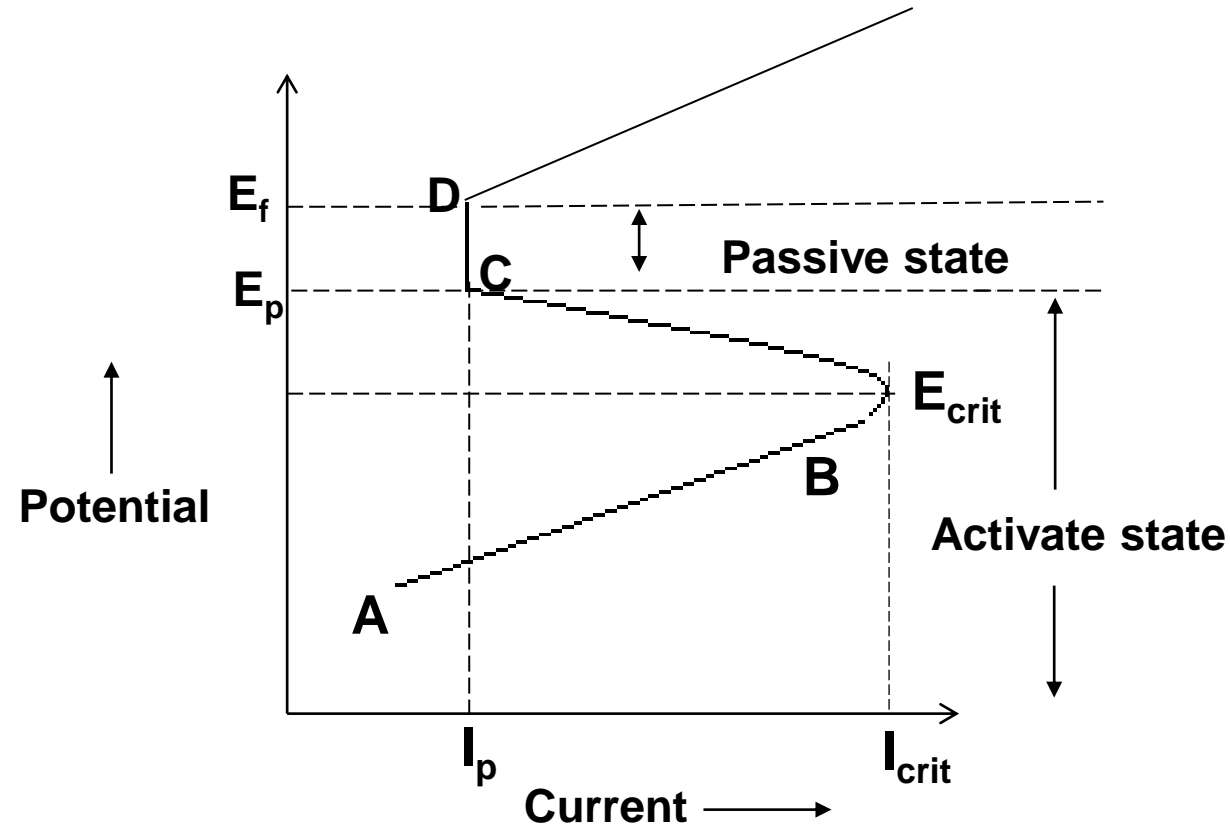
- Some of the metals like Ti and ferrous alloys (stainless steel) can not afford cathodic protection
- The principle of anodic protection is

*the growth of protective oxide surface film by the application of anodic current on the metal / alloy appliance in a suitable oxidising environment*



# Corrosion Control by anodic protection method

- When a passivating metal is immersed in an electrolyte with increasing oxidizing power behaves as shown in the following graph.

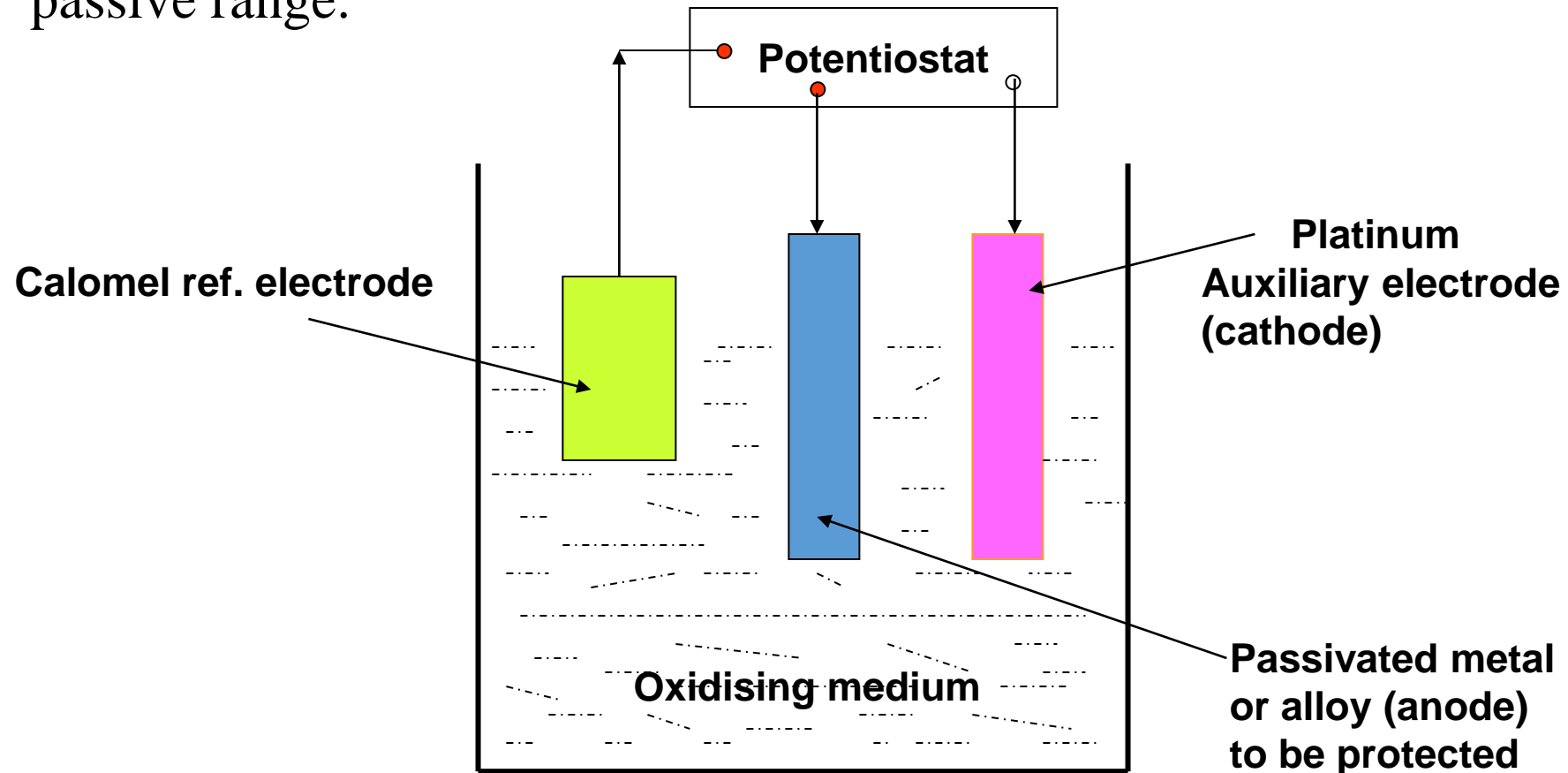




# Corrosion Control by anodic protection method

The anodic protection to a structure is applied by using a device called potentiostat.

In operation, the potentiostat maintains a constant potential between the tank and the reference electrode, corresponding to the passive range.



# Corrosion Control by anodic protection method

- **Advantages:**

Its applicability even in extremely corrosive environment.

Low current demand

- **Limitations:**

It is restricted to the metals that show active-passive behavior.

Its initial installation cost is high.

Cannot reduce the corrosion rate to zero unlike cathodic protection.

This needs continuous supply of electric current.

# Corrosion Control by Inhibitors

- An inhibitor is a substance when added in small quantity to the electrolyte medium, inhibits the anodic or cathodic reactions

Types of inhibitors:

- Anodic Inhibitors
- Cathodic Inhibitors

# Corrosion Control by Anodic Inhibitors

- Substances used to stop anodic reaction.
- They form insoluble compounds with the metal ions formed at the anodic part .
- These insoluble compounds form a protective film on the anodic surface.
- This film isolates the anode from the electrolyte medium and stops its corrosion.
- The anions such as chromate, tungstate, molybdate, phosphate etc., are used to arrest anodic process.
- Effective only when they are added above their critical concentrations.
- If the added inhibitor is insufficient, it cannot plug all the anodic sites and leads to severe pitting corrosion

# Corrosion Control by Cathodic Inhibitors

- Substances used to retard cathodic reaction.
- They form a protective film on cathodic surface and isolate it from the electrolyte medium thereby preventing corrosion.
- Two major reactions taking place on cathodic surface depending on the nature of corrosive environment and are

Hydrogen evolution type

Oxygen absorption type

# Corrosion Control by Cathodic Inhibitors

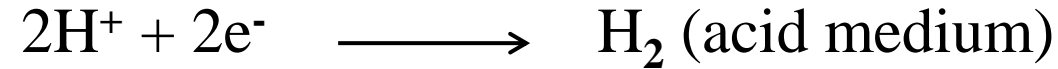
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Hydrogen evolution type

Oxygen absorption type

# Corrosion Control by Cathodic Inhibitors

## Hydrogen evolution:



This reaction can be prevented either by

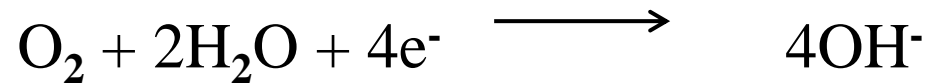
- (i) Retarding the diffusion of  $\text{H}^+$  to the cathode.
- (ii) Increasing hydrogen over voltage

- Addition of certain organic compounds, containing N or S, retards the diffusion of  $\text{H}^+$ .
- Such substances when added to corroding environment, are adsorbed on the cathodic sites forming a protective film that suppresses cathodic reaction.  
e.g., Urea, thiourea, mercaptans and other heterocyclic compounds.
- Substances added deposit as adherent metallic film on the cathode areas and thereby prevents the evolution of  $\text{H}_2$ .
- Oxides of Arsenic, antimony or salts like sodium meta arsenite are used since hydrogen overvoltage for these metals is quite high

# Corrosion Control by Cathodic Inhibitors

## Oxygen absorption type:

(in neutral or slightly alkaline medium)



- This reaction can be easily stifled either by removing the oxygen from the corrosive media or by decreasing the diffusion rate of oxygen to cathode.
- Reducing agents such as  $\text{N}_2\text{H}_4$ ,  $\text{Na}_2\text{SO}_3$  etc., remove oxygen from the corroding environment by combining with it.



- Decreasing the diffusion rate of oxygen is achieved by adding salts such as  $\text{ZnSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{NiSO}_4$  etc., to the aqueous environment.
- They undergo hydrolysis and form a deposit of their insoluble hydroxide on the cathodic sites.





# Corrosion Control by Cathodic Inhibitors

- The protective film being impermeable to oxygen prevents its further diffusion to cathodic sites.
- The action of an inhibitor depends on the nature of the metal to be protected as well as corrosive environment
- It is therefore necessary to choose an appropriate inhibitor for a particular system

# Corrosion Control by Surface coatings

- A protective coating on the surface of metals and alloys isolates them from corrosive environment, thereby preventing the corrosion
- Types:
  - Metallic coatings
  - Inorganic coatings
  - Organic coatings

# Corrosion Control by Metal coatings

Coating of a metal on a substrate metal requiring protection against corrosion is metallic coating

- **Types:**

*Anodic metal coating*: Coating the substrate metal with a more anodic metal

Eg: Galvanizing

*Cathodic metal coating*: Coating the substrate metal with a more cathodic metal

Eg: Tinning

# Galvanizing process

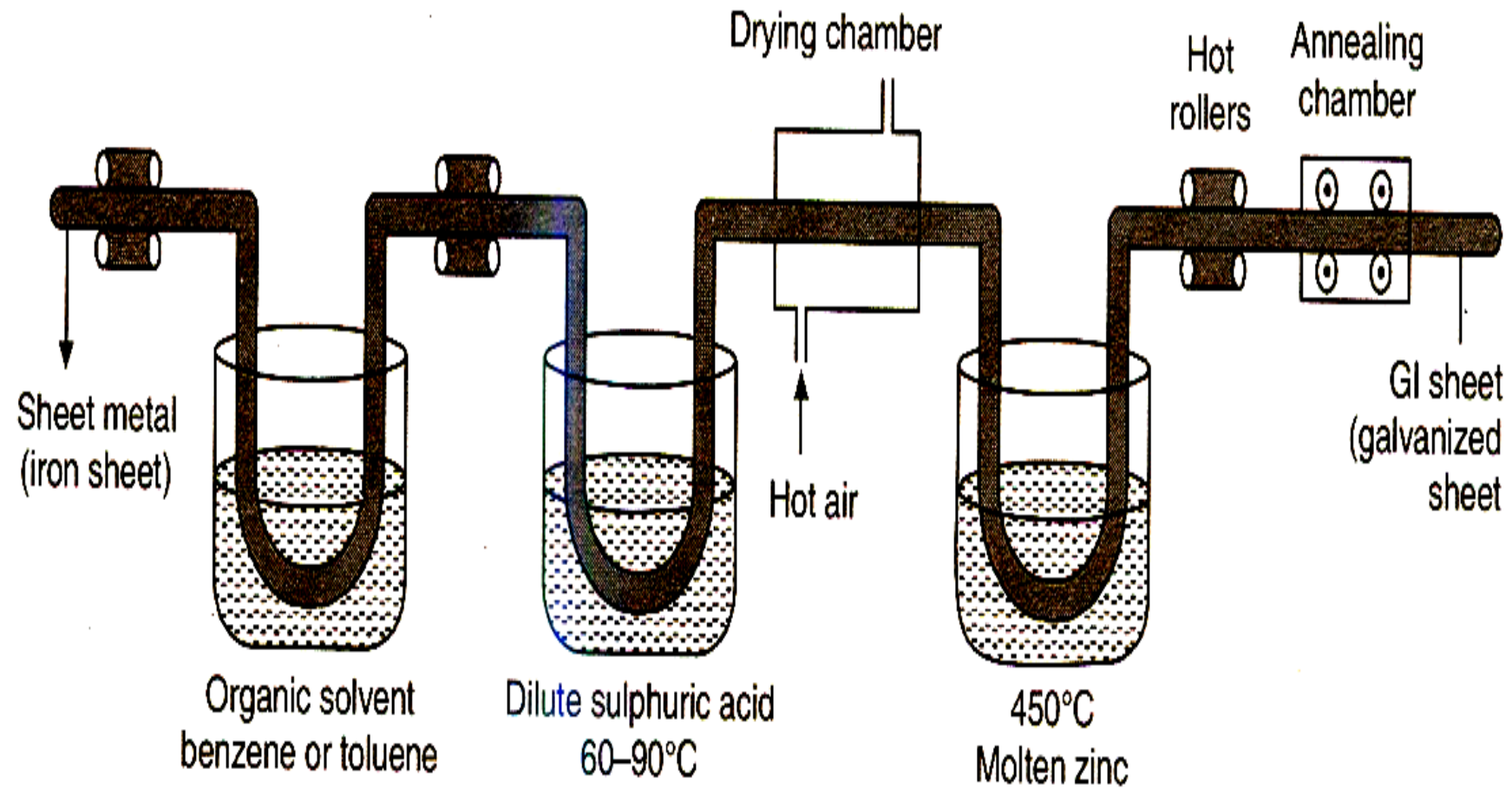
- Giving a Zn metal coating on iron and mild steel is known as galvanizing
- When the coating breaks or cracks zinc acts as anode and the substrate iron and mild steel acts as cathode
- Zinc becomes sacrificial anode and provides protection to iron and mild steel.

roofing sheets, fencing wire, buckets, pipes, wires are usually galvanized

## Process:

- Done by hot dipping process
- Objects are degreased, pickled and cleaned
- They are dipped in molten zinc bath (425 – 430 °C)
- $\text{NH}_4\text{Cl}$  flux is spread over the bath to prevent its oxidation
- Excess liquid Zn is squeezed out and the objects with Zn coating are cooled

# Galvanizing process



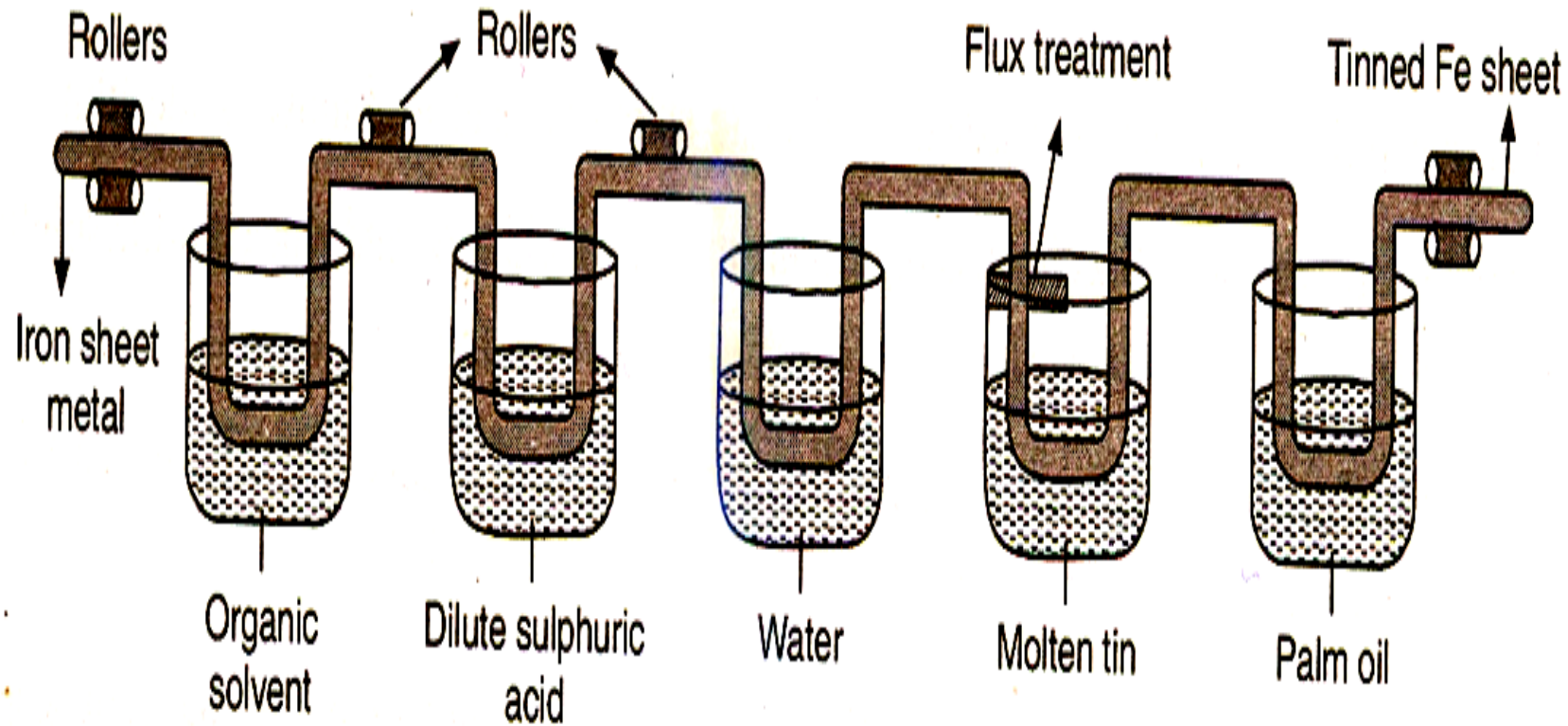
# Tinning process

- Giving a coating of tin on iron and mild steel is called tinning
- Tinning protects the article until the coating covers the surface completely, by isolating it from the environment
- When the coating cracks or breaks intense or pitting corrosion of the articles at the exposed region occurs
- This is because tin is cathodic with iron and small anodic regions are in contact with large cathodic area.

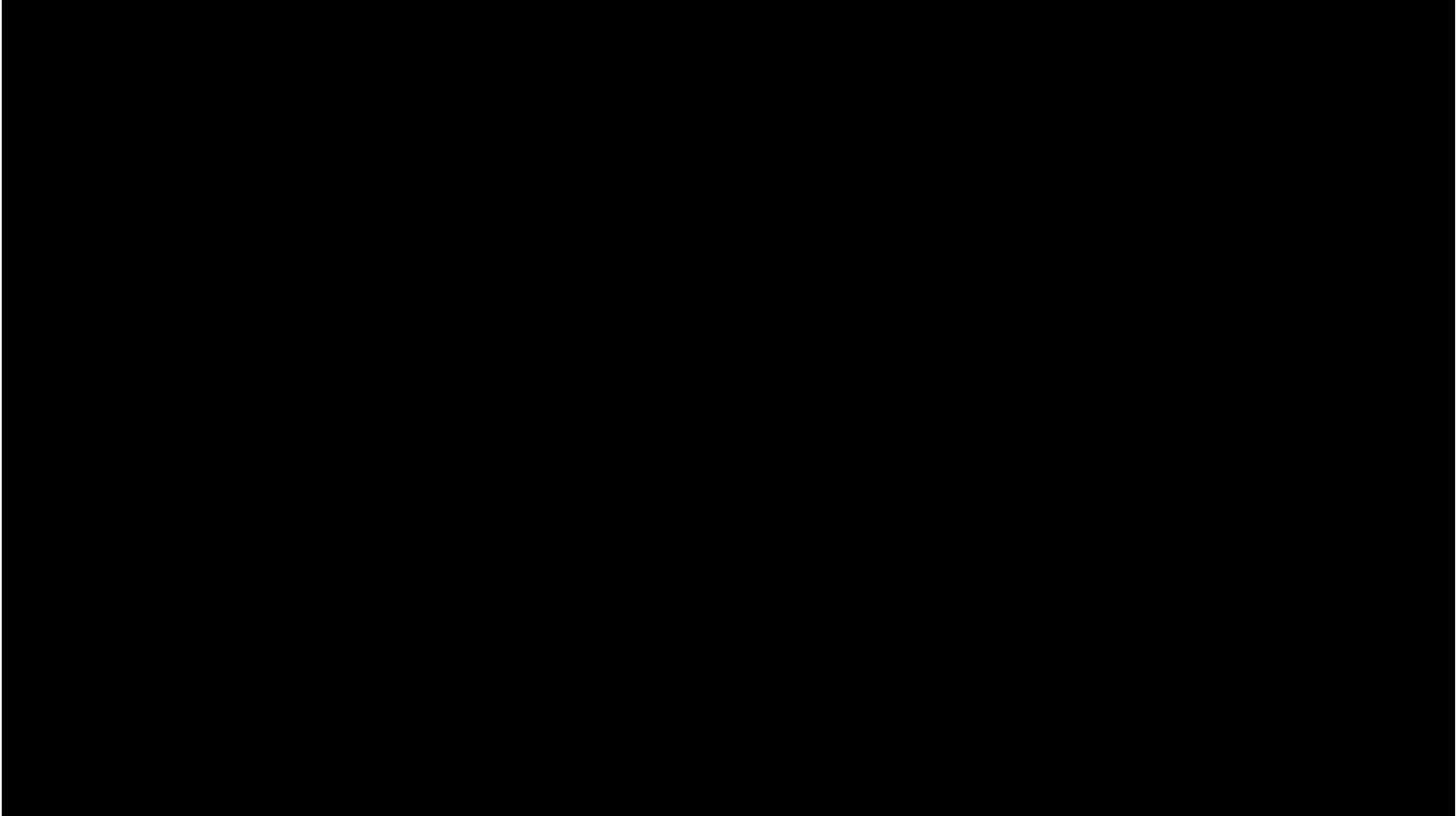
## Process:

- Tinning is done by hot dipping
- Steel sheet is degreased , pickled and cleaned. It is dipped in molten tin (250 °C)
- It is covered with  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  flux to protect liquid tin from oxidation by air
- Excess tin is then squeezed out from it by passing through rollers kept in palm oil

# Tinning process



- As tin salts are nontoxic, Therefore tinned iron and mild steel sheets are used to prepare tins, cans and containers for storing food materials
- Galvanized sheets cannot be used to prepare tins or cans for storing food materials, because zinc salts are toxic





# Comparison of Galvanizing & Tinning processes

Galvanizing	Tinning
A process of coating Zn over iron / steel to prevent it from rusting (anode metal coating)	A process of coating Sn over iron to prevent it from corrosion (cathode metal coating)
Hot rollers used to wipe excess coat are not immersed in oil	Hot rollers are immersed in oil
Galvanized containers cannot be used to store acidic foodstuffs because zinc reacts with food acids forming highly toxic zinc compounds.	Tin coated containers can be used to store foodstuffs because tin is nontoxic and does not react to cause any food poisoning
Zinc protects the underlying iron by sacrificial action	Tin protects the base metal iron due to its noble nature.
Zinc continues to protect iron by sacrificial action in the event of puncture/break in coating	Tin protects the iron until the coating is perfect and any break causes rapid corrosion of iron

# Corrosion Control by Organic coatings

- Organic coatings are inert barriers (like paints, varnishes, lacquers, and enamels) applied on a metallic surface for both corrosion protection and decoration.
- These involve a relatively thin barrier between the substrate material and the environment.
- These coatings should not be used where the environment would rapidly attack the substrate material.
- The protective value of such a coating depends on
  - (i) its chemical inertness to the corrosive environment,
  - (ii) its good surface adhesion,
  - (iii) its impermeability to water, salts and gases and its proper application method

# Corrosion Control by Inorganic coatings (Chemical conversion coatings)

## PHOSPHATE COATINGS:

- These are produced by the chemical reaction of base metal with an aqueous solution of phosphoric acid and phosphates of Fe, Zn, Mn along with Cu salts as accelerators.
- Coatings are usually applied to Fe, steel, and Zn by either immersion or spraying or brushing.
- This type of coating is usually grey, and they may not offer complete resistance to atmospheric corrosion and are mainly used as an adherent base/primer coat for paint, lacquers, etc.
- Such coatings may impair the welding strength. The chemical reaction between the phosphating solution and the base metal results in the formation of a surface film, consisting of crystalline Zn-Fe or Mn-Fe phosphates.

THANK YOU

The decomposition potential in an electroplating process is

1. The maximum potential that is required to start the plating process
- 2. The minimum potential that is required for a continuous plating process**
3. The potential required to decompose the metal at anode
4. The potential required to deposit the metal at the cathode

Which polarization can be eliminated by raising the temperature of electroplating bath?

1. Activation
- 2. Concentration**
3. Kinetic
4. Gaseous

Which of the following factors will not affect the nature of electrodeposit in electroplating?

1. Current density and pH
2. Organic additives and throwing power
3. Metal salt and electrolyte concentration
- 4. Reducing reagent and its concentration**

[https://forms.office.com/Pages/ResponsePage.aspx?id=Qr2-Kf\\_xPUyWiAZ-NGDcH9ujTOYR80RPgu9FEcr24HNUNkVISzIWk0Q0c3VlhZOUVPTFdINkxPWC4u](https://forms.office.com/Pages/ResponsePage.aspx?id=Qr2-Kf_xPUyWiAZ-NGDcH9ujTOYR80RPgu9FEcr24HNUNkVISzIWk0Q0c3VlhZOUVPTFdINkxPWC4u)