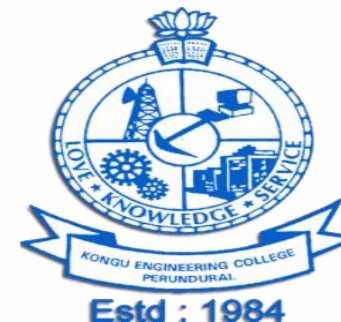




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DEPARTMENT OF CHEMISTRY  
WELCOMES YOU ALL



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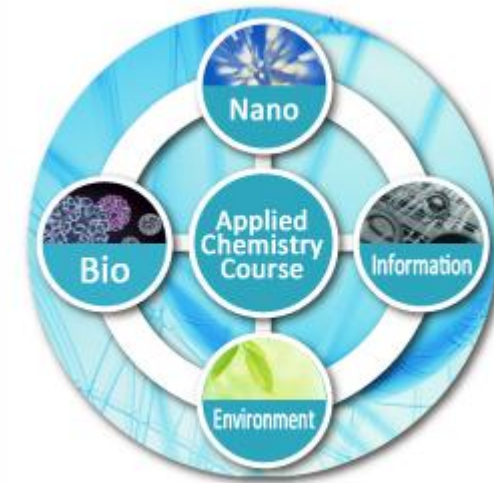


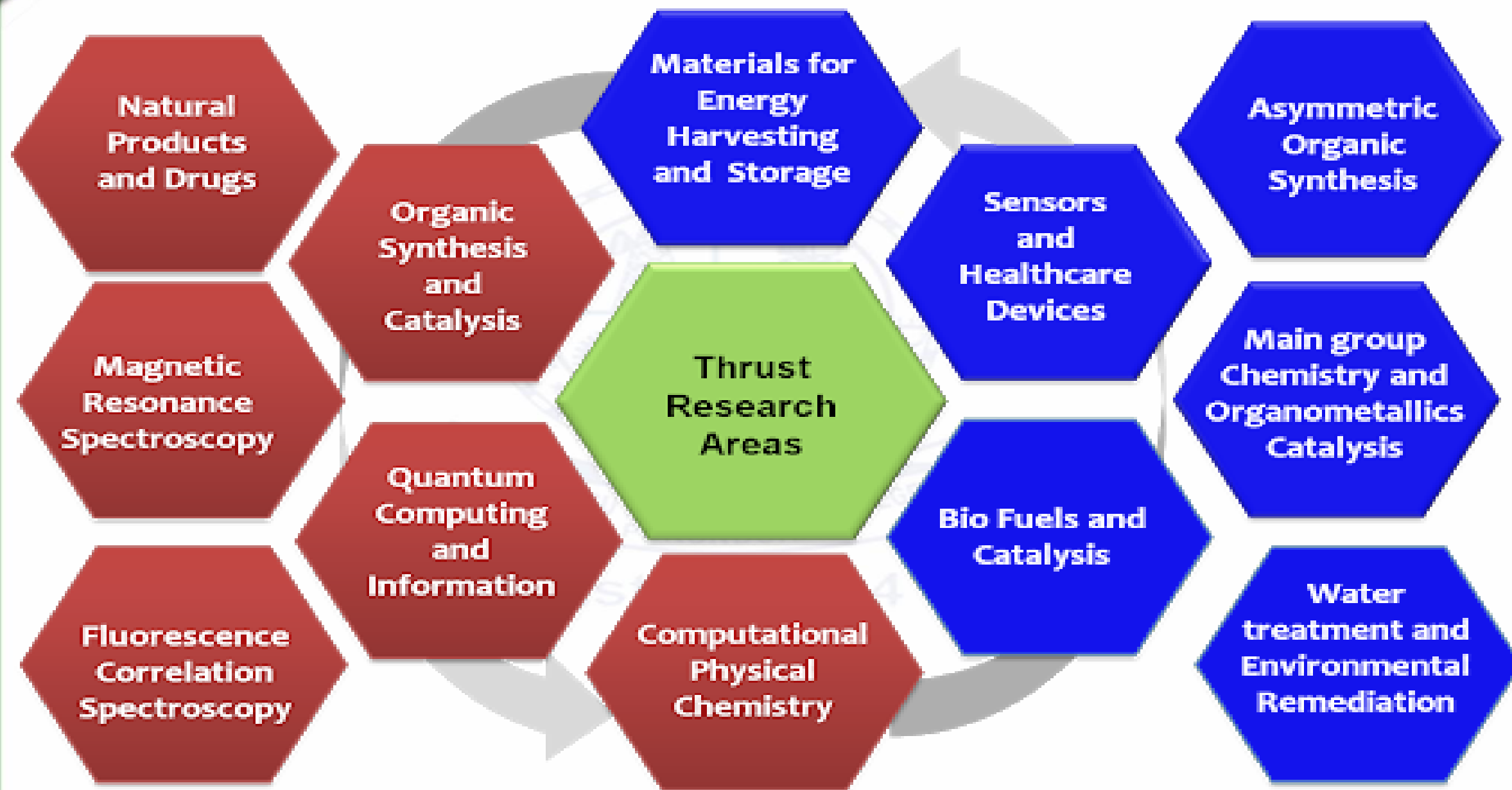
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Department of Chemistry  
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Perundurai, Erode - 638 060

# APPLIED CHEMISTRY

- The development of science and technology has been giving us a lot of benefits. The advanced technology has often required the basic research.
- **Applied Chemistry** is the scientific field for understanding basic chemical properties of materials and for producing new materials with well-controlled functions.
- Applied chemistry is increasingly important in solving environmental problems and contributing to the development of new materials, both of which are key issues in the 21<sup>st</sup> century.









Transform Yourself





Transform Yourself

## ***UNIT – II Corrosion and its control methods***



**Corrosion:** Introduction - chemical corrosion – Pilling-Bedworth rule - electrochemical corrosion and its types – galvanic corrosion – differential aeration corrosion with examples - galvanic series - factors influencing rate of corrosion – measurement of corrosion (wt. loss method only).

**Control methods** – sacrificial anodic protection method - corrosion inhibitors - protective coatings - pretreatment of metal surface – metallic coating: electroplating, electroless plating and hot dipping (tinning and galvanizing) methods – non-metallic coating: anodizing - organic coating: paints, constituents and functions - ceramic coatings.

WHAT ARE THOSE  
BROWN MARKS?

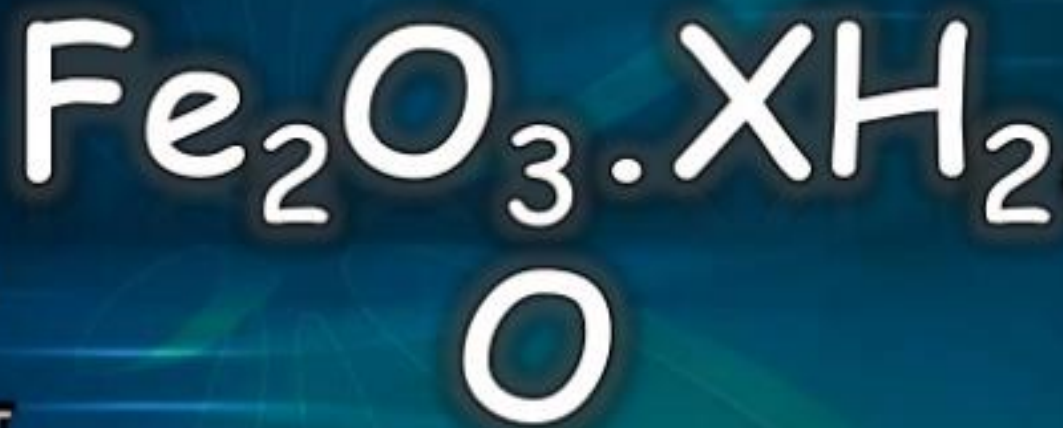
THE ORIGINAL  
RUST!





# CHEMICAL EQUATION OF CORROSION

Clip slide



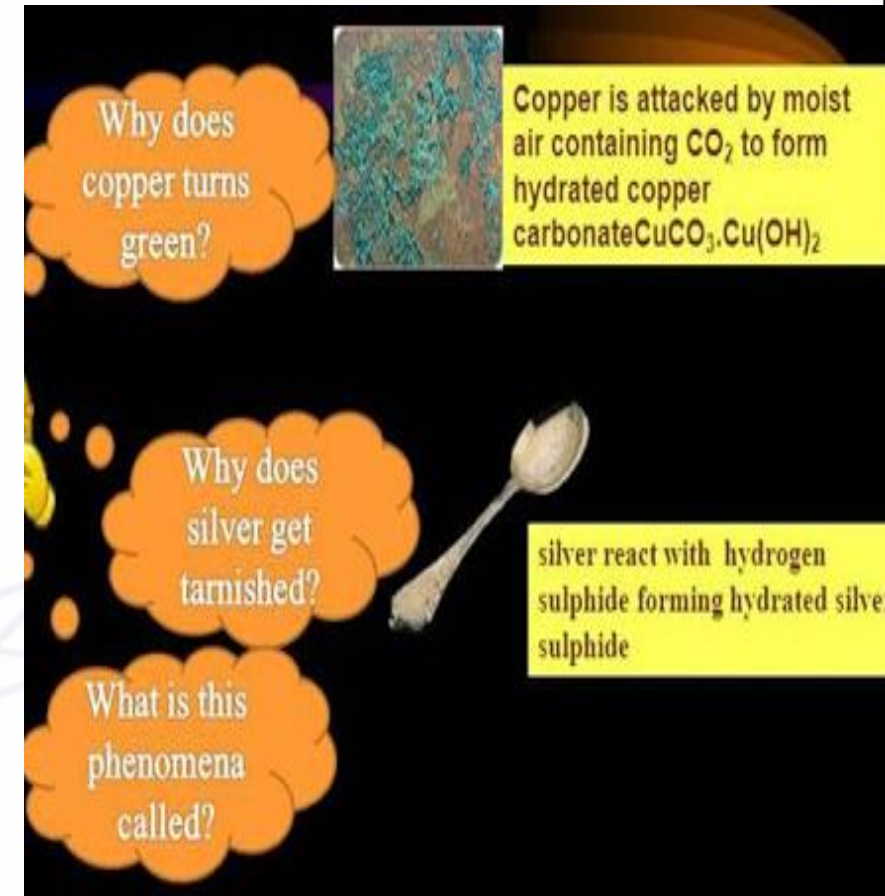
# Corrosion

- The serious consequences of the corrosion process have become a problem of worldwide significance.
- In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance and expensive overdesign.
- Humans have most likely been trying to understand and control corrosion for as long as they have been using metal objects. The most important periods of pre-recorded history are named for the metals that were used for tools and weapons (Iron Age, Bronze Age). With a few exceptions, metals are unstable in ordinary aqueous environments.



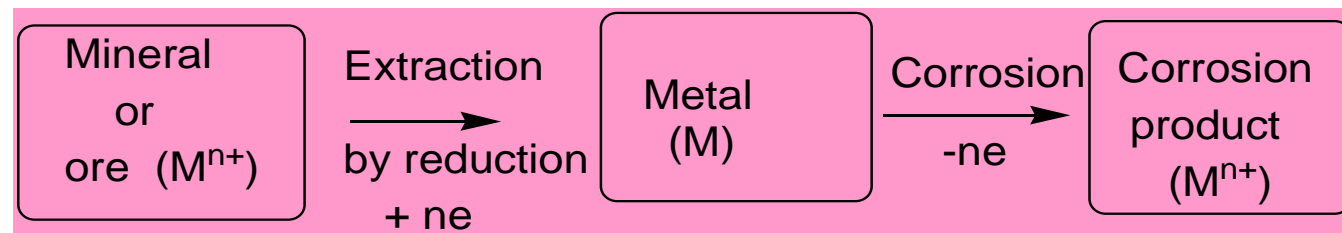


- **Corrosion** has been defined as a destructive chemical and electrochemical reaction of a metal with its environment (like  $O_2$ , moisture,  $CO_2$  etc.) which disfigures metallic products leading to reduction in their thickness and also causes loss of useful properties such as malleability, ductility, electrical conductivity and optical refractivity. Except few metals such as gold, platinum (called noble metal) are prone to corrosion.



## Mechanism or Causes of corrosion

- Metals are electropositive in nature. Except few metals like gold, platinum (noble metal) other metals are found in nature as their compounds (such as oxides, hydroxides, carbonates, chlorides, sulphides, phosphates, silicates etc.) which are called their ore.
- Metals are thus obtained by extraction from their ores by reduction process.
- In nature, when metals exist as their compounds (or ore) they are stable and they are in the low energy states.
- However, during extraction of metals from their ores, free metals are become less stable and are in the higher energy state than in the ionic state.
- So, metals have a tendency to back to the ionic state and hence metal atoms are prone to get attacked by environment .
- This is the main reason for corrosion of metals.



# EFFECTS OF CORROSION

- *Reduces Strength*
- *Life time is reduced*
- *Metallic properties are lost*
- *Wastage of metal*





# Types Of Corrosion

## ➤ Dry or Chemical Corrosion

- ✓ It involves direct chemical attack of atmospheric gases like  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , halogen, moisture and inorganic acid vapours on metal. Ex. Turnishing of silver ware in  $\text{H}_2\text{S}$  laden air.

This can be classified as

- a. Corrosion by oxygen**
- b. Corrosion by other gases**
- c. Liquid –Metal corrosion**



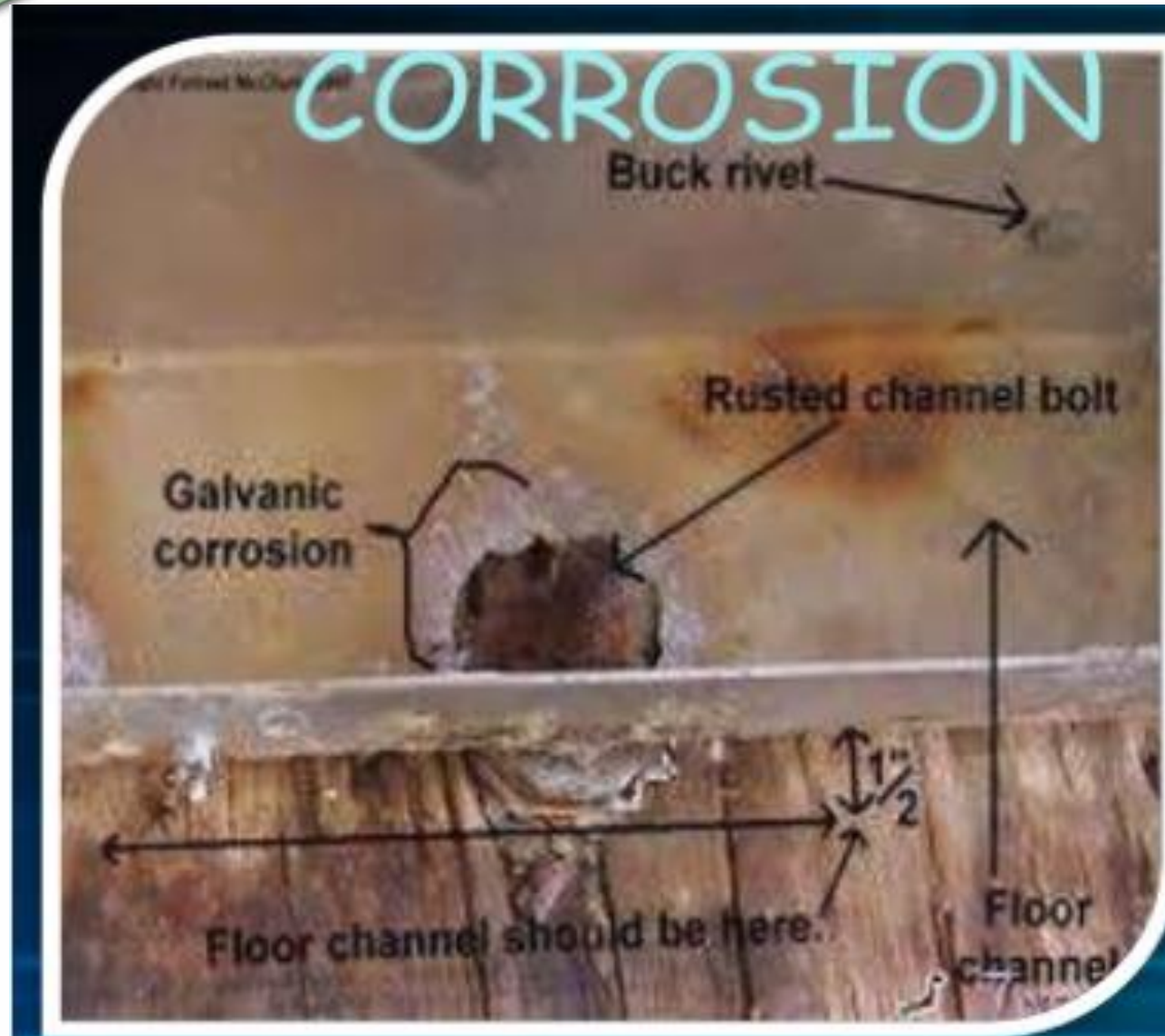
## ➤ Wet or Electrochemical Corrosion

- ✓ It occurs due to setting up of a large number of tiny galvanic cells in metals in presence of an impurity as well as in presence of moisture. Generally impurity (more active metal) act as anode and original metal act as cathode. so anode is the area where corrosion occurs. Ex: Rusting of iron in moist atmosphere.

This can be classified as

- a. Galvanic corrosion**
- b. Concentration Cell Corrosion or Differential aeration corrosion**





- **CHEMICAL REACTIONS.**

- **ELECTRONS REMOVED FROM ONE REACTANT TRAVEL THROUGH AN EXTERNAL CIRCUIT.**

- **MATERIAL TENDS TO DISAPPEAR.**

# Types of dry corrosion

## I. Oxidation corrosion

- Due to direct chemical reaction of atm.  $O_2$  with metal surface forming metal oxide
- Absence of moisture
- Increases with increase in temperature.

### Mechanism

- on exposure to atm., metal gets oxidized to form metal ions



- Electrons lost by metal are taken up by oxygen to form oxide ions



Metal Oxide



# Types of metal oxide film

I. Stable film

II. Unstable film

III. Volatile film

IV. Porous film

## I. Stable film

- ✓ Fine grained structure
- ✓ Formation of Oxide films are impervious in nature(non porous nature)
- ✓ Stop further oxygen attack
- ✓ Stable film acts as a protective coating. Eg: Al, Pb, Cu, Sn

## II. Unstable film

- ✓ Film produced on the surface of noble metals.(porous)
- ✓ Which decompose reversibly to the metal and the oxide which is liberated in the form of oxygen.
- ✓ Here corrosion is a continuous process. Eg: Ag, Au, Pt.

## III. Volatile film

- ✓ The oxide layers formed in some cases is volatile.
- ✓ Oxide film volatilizes as soon as it is formed.
- ✓ The fresh metal surface is kept exposed all the time for further attack.
- ✓ Thus it act as a nonprotective coating. **Eg:**  $\text{MoO}_3$  (Molybdenum oxide film)

#### IV. Porous film

- ✓ The oxide layers formed in some cases have pores or cracks.
- ✓ The atmospheric oxygen can easily move into the metal surface through pores of the layer.
- ✓ So corrosion is a continuous process. Eg: Alkali metals & alkaline earth metals.

#### Pilling – Bed Worth Rule

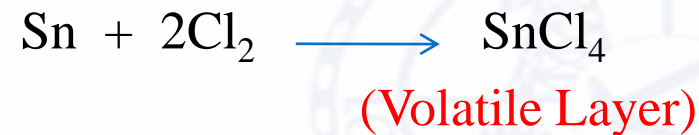
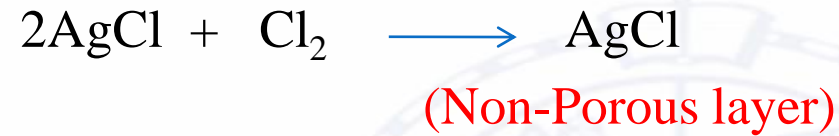
$$\text{Specific Volume Ratio} = \frac{\text{Volume of oxide formed}}{\text{Volume of metal}}$$

- A protective and Non-Porous metal oxide layer has volume equal to or greater than the volume of metal from which it is formed. Ex: Oxides of Al, Sn, Pb, Cu, etc.
- A Non-Protective and Porous metal oxide layer has volume lesser than the volume of metal from which it is formed. Ex: Oxides of Li, Na, K, Mg, Ca, Sr, etc.

# Types of dry corrosion

## II. Corrosion by Other Gases

- Other gases such as  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$ ,  $\text{CO}_2$  &  $\text{NO}_x$ . In dry atmosphere these gases react with metal and form corrosion products.



## Hydrogen Embrittlement (or) Hydrogen Corrosion

At high temperature



- $\text{FeS}$  is a Porous Layer and corrosion is a continuous process.
- Atomic hydrogen penetrates and occupies the voids of the metal. Then develops pressure which leads to cracking of the metal.
- This is known as Hydrogen Embrittlement (or) Hydrogen Corrosion



## Decarburisation

- ✓ Atomic hydrogen is highly reactive and combine with Carbon present in metal forming CH<sub>4</sub> gas which leads to cracking of the metal surface.
- ✓ The process of decrease in carbon content in steel is known as decarburation of steel.



### III. Liquid Metal Corrosion

- Occurs due to the action of flowing liquid metal at high temp on solid metals or alloys.
- As a result of this corrosion, solid metal becomes weak because it involves either
  - ✓ Dissolution of a solid metal by a liquid metal (or)
  - ✓ Due to the penetration of the liquid metal into the solid metal
- Observed in Nuclear power plant. In nuclear reaction where Na metal used as a coolant leads to corrosion of Cd. Liquid metal mercury dissolves most metals by forming amalgam.

# Wet or Electrochemical or Immersed Corrosion

## Occurs

- When a metal is contact with moist air or any liquid medium
- When two diff. metals are partially immersed in a soln.
- Chemically non- uniform surfaces of metals behave like electrochemical cells in the presence of water containing dissolved  $O_2$  &  $CO_2$
- Always occurs at anodic areas

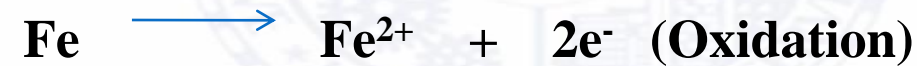
## Mechanism

- Involves oxidation- reduction process formation of large number of galvanic cells, that is the development of anodic and cathodic regions on the same metal. The electrons released at the anode are absorbed at cathode.
- Corrosion (oxidation) takes place at the anodic region.
- depending on the nature of corroding environment, electrons released at anode are consumed at the cathodic area by two ways:
  - ✓ **Evolution of  $H_2$**
  - ✓ **Absorption of  $O_2$**

## Hydrogen evolution Mechanism

- This type of corrosion takes place when base metals are in contact with acidic solutions or the solutions are completely free from dissolved oxygen.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen gas.

**Anode :**



**Cathode :**



**Over all Rxn :**





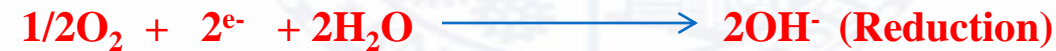
# Oxygen Absorption Mechanism

- Base metal are in contact with neutral, aqueous or slightly alkaline solution with some amount of dissolved oxygen.

**Anode :**



**Cathode :**



**Over all rxn:**



# Difference Between Dry and Wet Corrosion

## Dry Corrosion

- ✓ Occurs in the absence of moisture
- ✓ Involves direct attack of chemicals on the metal surface
- ✓ Slow process
- ✓ Corrosion products are produced at the site of corrosion
- ✓ Process of corrosion is uniform
- ✓ Eg: Tarnishing of Silver

## Wet Corrosion

- Occurs in the presence of conducting medium
- Involves formation of electrochemical cells
- Rapid process
- Corrosion occurs at anode but product is deposited at cathode
- Depends on the size of the anodic part of the metal
- Eg: Rusting of Iron

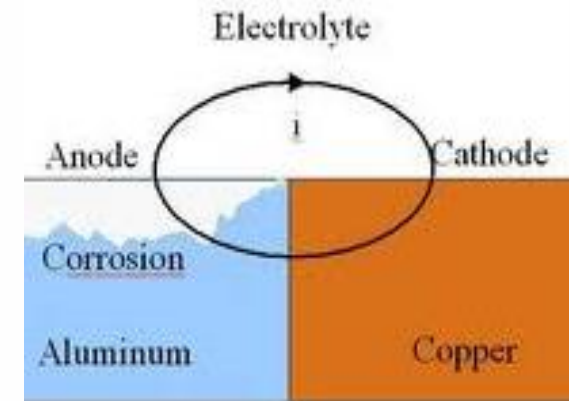
# Types of Electrochemical Corrosion

- Galvanic (Bimetallic) Cell Corrosion.
- Concentration cell corrosion (or) Differential aeration corrosion.

## Galvanic (Bimetallic) Cell Corrosion:

Galvanic Corrosion occurs at

- Electrochemically dissimilar metals must be present.
- These metals must be in electrical contact.
- The metals must be exposed to an electrolyte.



The metals higher in electrochemical series act as the anode and dissolve into the solution and the metal lower in the electrochemical series acts as the cathode.

### Cathodic reaction

1. Electrolyte in the acidic medium- Evolution of Hydrogen Gas
2. Electrolyte in the Neutral (or) Alkaline medium – Absorption of oxygen



## Examples:

1. Fe & Cu

Fe-Anode, Cu- cathode

2. Zn & Fe - Zn-Anode, Fe- cathode

3. Buried iron pipeline connected to copper plumbing.

4. Steel pipe connected to Copper plumbing

5. Lead-Tin solder around copper wires.

# Measures to prevent Galvanic Corrosion

- ✓ When joining two dissimilar metals together, galvanic corrosion can be prevented by **insulating the two materials** from each other. Ex: when bolting flanges of dissimilar metals together, **plastic washers can be used to separate the two metals.**
- ✓ Do not couple metals that are **far apart** in the galvanic series.
- ✓ Avoid **small anode—large cathode** combinations.
- ✓ Any coating being applied should be applied to the cathodic member and not to the anodic member. This is to prevent an unfavorable anode/cathode ratio.
- ✓ **Anodic parts may be made thicker to provide a longer life.**
- ✓ A **sacrificial metal** may be installed that would be anodic to both metals.

# Concentration Cell Corrosion or Differential Aeration Corrosion

- Occurs due to **diff. in potential between differently aerated areas.**
- Part of metal exposed to air is **more oxygenated part & acts as cathode**
- Part of metal immersed in electrolyte is **poorly oxygenated & acts as anode**

## Types of Differential Aeration Corrosion

- ✓ **Pitting Corrosion**
- ✓ **Pipeline Corrosion**
- ✓ **Crevice Corrosion**
- ✓ **Corrosion on wire fence**

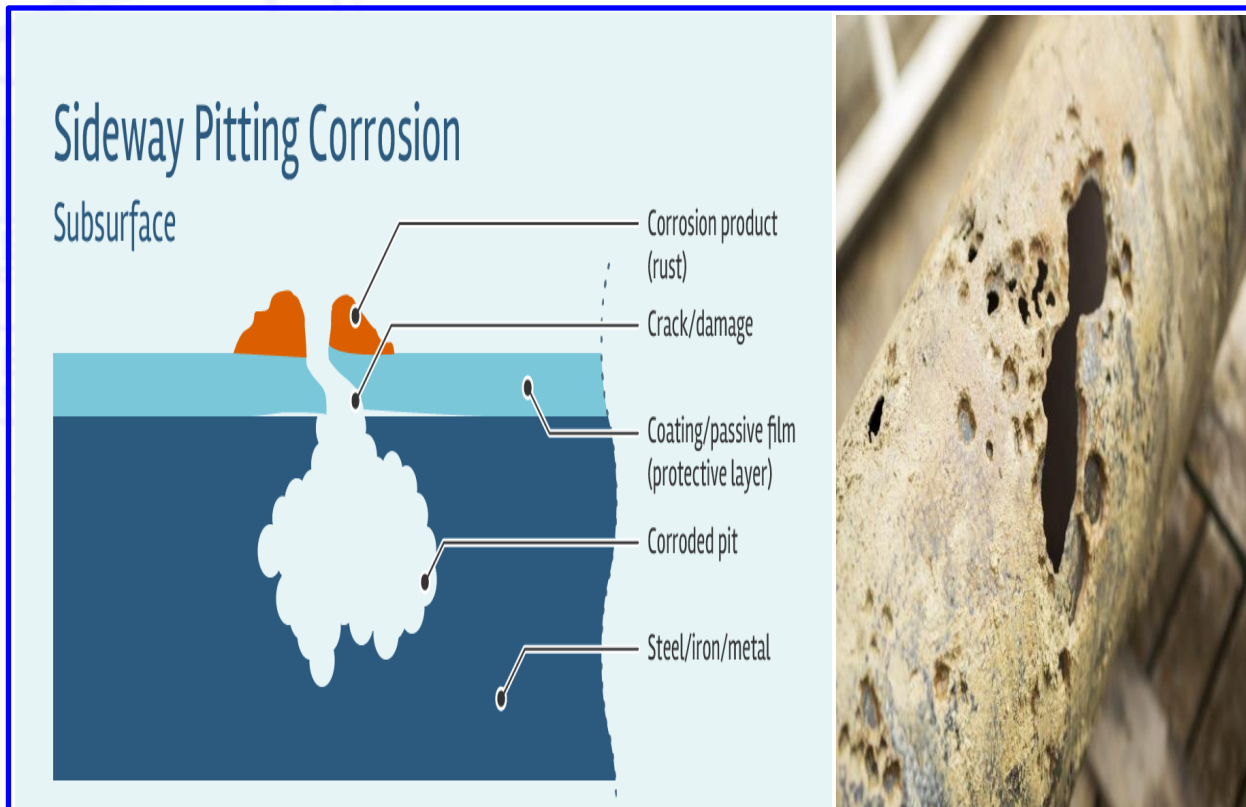


# Pitting Corrosion

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits.

## Preventive measures:

1. Preparing the surfaces with mirror finish.
2. Removing all contaminants.
3. Designing and fabricating to avoid trapped and pooled liquids.



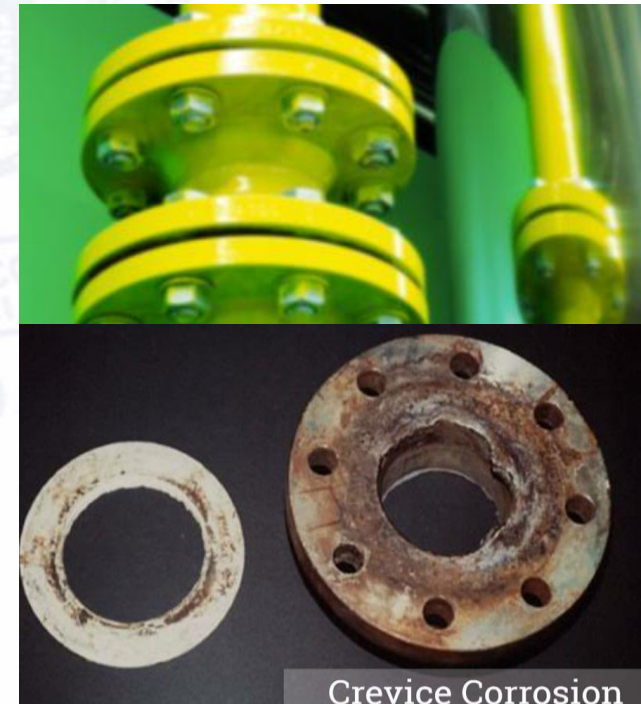
## Pipeline corrosion

Pipeline corrosion is the oxidation and electrochemical breakdown of the structure of a pipe used to convey any substance. Pipeline corrosion occurs on both the inside and outside of any pipe and related structures, exposed to corrosive elements. Many different types of corrosion can develop in pipelines.



## Crevice Corrosion

Crevice Corrosion refers to the localized attack on a metal surface at, or immediately adjacent to, the gap or crevice between two joining surfaces. The gap or crevice can be formed between two metals or a metal and non-metallic material.





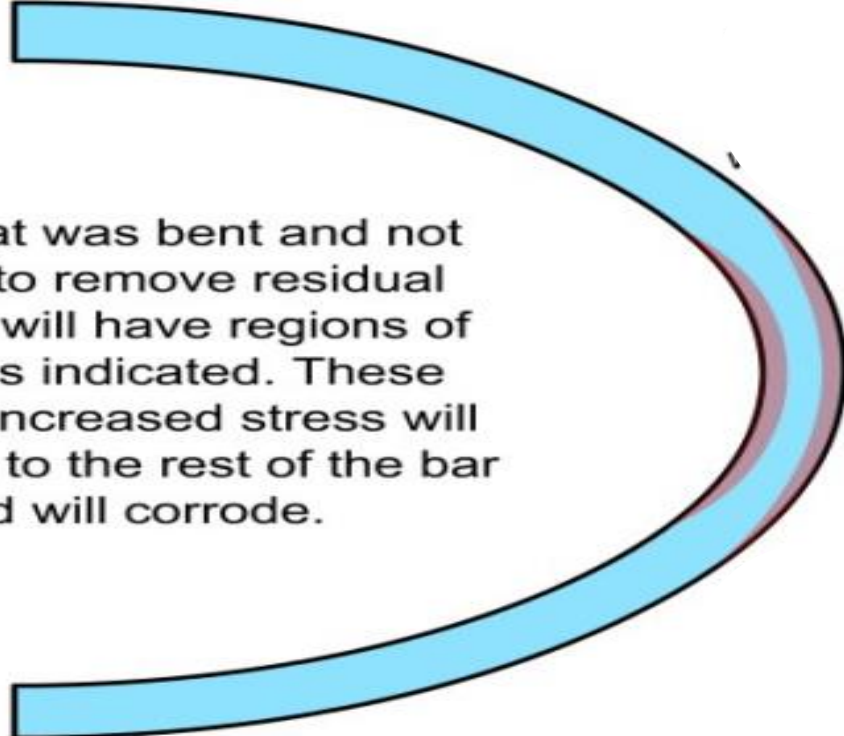
## Corrosion on wire fence

The areas where the wires cross are less aerated than the other parts of the fence. The corrosion takes place at the wire crossings because the less aerated part act as anode.



## Stress corrosion

Stress corrosion is another form of corrosion that is important to many fields including civil structures. Stress-corrosion occurs when a material exists in a relatively inert environment but corrodes due to an applied stress. The stress may be externally applied or residual.



A bar that was bent and not treated to remove residual stresses will have regions of stress as indicated. These areas of increased stress will be anodic to the rest of the bar and will corrode.



- The internal stress of metal arises when the metal is subjected to mechanical operations such as pressing, hammering, bending, welding or reverting.
- The metal atoms under stress are always at higher energy levels as compared to stress free atoms.
- The stressed part of the metal becomes more reactive than the stress free part.
- So that stressed part act as anode, and stress-free part acting as cathode.
- Stressed part undergoes corrosion on specific environment and initiating the crack.

Examples:

Seasonal cracking

- It occurs due to the following actions.
- Susceptible agent like copper and its alloys
- Attacking agent like ammonia
- Tensile stress
- Eg : cracks were developed on the surface of the brass cartridges in the monsoon season

## Corrosive environment (Caustic embrittlement of steel boilers)

- Mild steel boilers undergo corrosion at the stressed portion when the operating pressure are between 10atm and 20atm.
- Fine cracks may develop at the stressed portion of the boiler.
- Boiler water containing alkaline impurities pass into these cracks by capillary actions.
- This water evaporates and leaves behind caustic soda in the cracks, whose concentration thus increases.

➤

Iron (under stress)	Conc NaOH (in the cracks)	Dil NaOH (in boiling water)	Iron (main body)
------------------------	------------------------------	--------------------------------	---------------------

Iron under stress acts as the anode and gets corroded resulting in boiler failure. The boiler water contains  $\text{Na}_2\text{CO}_3$ , which is hydrolyzed at high temperature to give NaOH.

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \xrightarrow{\Delta} 2\text{NaOH} + \text{CO}_2$$

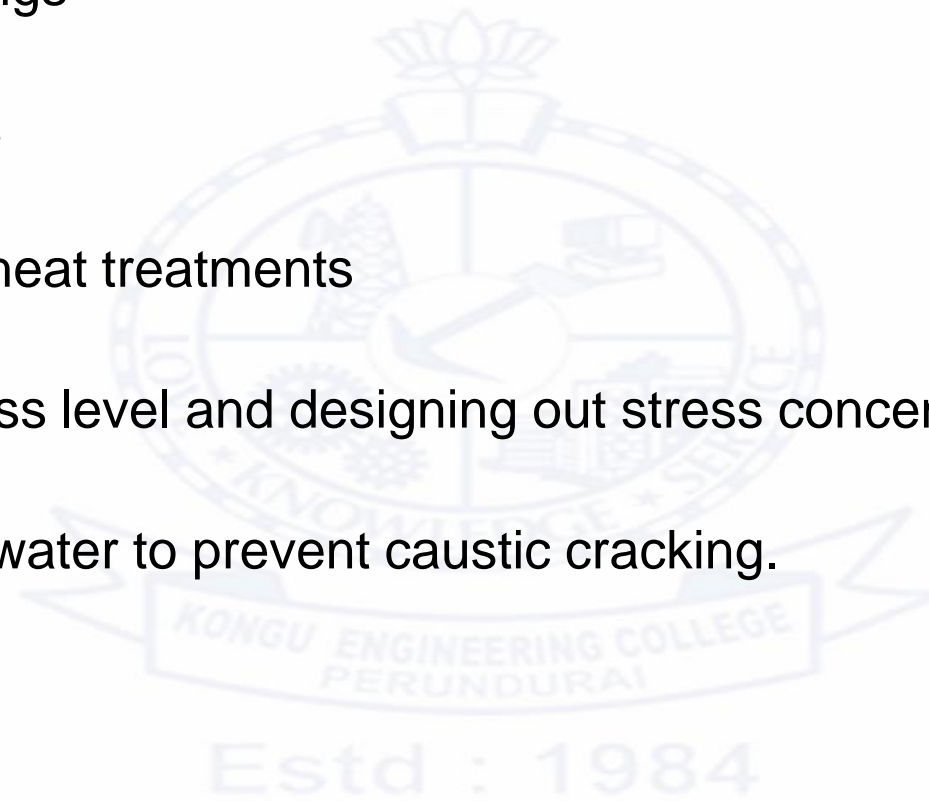
The NaOH formed flows into hair-thin cracks and crevices. There it reacts with iron and forms  $\text{Na}_2\text{FeO}_2$  (sodium ferroate) which decomposes to give  $\text{Fe}_3\text{O}_4$  and NaOH.

$$2\text{NaOH} + \text{Fe} \rightarrow \text{Na}_2\text{FeO}_2 + \text{H}_2$$
$$3\text{Na}_2\text{FeO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 + 6\text{NaOH}$$

NaOH thus formed, further reacts with iron to cause corrosion. This is called caustic embrittlement.

### Preventive measures:

- Applying protective coatings
- Using corrosion inhibitors
- Performing stress- relief heat treatments
- Reducing the overall stress level and designing out stress concentrations
- Adding  $\text{Na}_2\text{SO}_4$  to boiler water to prevent caustic cracking.





# Intergranular Corrosion

- Intergranular corrosion is sometimes also called "intercrystalline corrosion" or "interdendritic corrosion".
- In the presence of tensile stress, cracking may occur along grain boundaries and this type of corrosion is frequently called intergranular stress corrosion cracking (IGSCC) or simply "intergranular corrosion cracking".
- This is a form of corrosive attack that progresses preferentially along interdendritic paths of metal or alloy (i.e grain boundaries).
- Positive identification of this type of corrosion usually requires microstructure examination under a microscopy although sometimes it is visually recognizable as in the case of weld decay.



### **Example:**

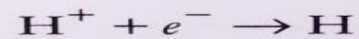
- For stainless steel(18% Cr, 8% Ni) containing more than 1% C is heated to high temperature at 650°C and cooled.
- A rapid reaction occurs between carbon and chromium to form chromium carbide at the path of grain boundaries and results in the formation of galvanic cells.

### **Prevention of Intergranular Corrosion**

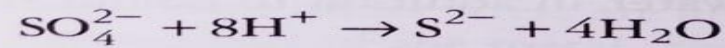
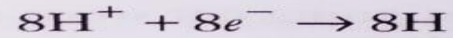
- Intergranular corrosion can be prevented through: Use low carbon (e.g. 304L, 316L) grade of stainless steels
- Use stabilized grades alloyed with titanium (for example type 321) or niobium (for example type 347). Titanium and niobium are strong carbide- formers. They react with the carbon to form the corresponding carbides thereby preventing chromium depletion.
- Use post-weld heat treatment.
- Applying protective coatings

# Microbiological Corrosion

- This corrosion involves degradation of materials by bacteria, moulds and fungi or their byproducts. Some types of bacteria consumes oxygen and cause differential aeration types of system, which results in corrosion.
- Occurs mainly less oxygenated area.
- This corroding material can be either a metal (such as steel or Al alloys) or a nonmetal (such as concrete or glass).
- **Examples:**
- Sulphur reducing bacteria such as Desulphovibrio which flourish in oxygen free conditions assist the corrosion of iron apparently by consuming hydrogen produced in the cathodic reaction, that enhancing the rate of cathodic reaction.



The bacteria make use of  $\text{H}^+$  to reduce sulphate  $\text{SO}_4^{2-}$  concentration. The overall corrosion cell reaction is as follows:



The corrosion product FeS is formed as a result of the above reactions.

## Preventive Measures of Microbial Corrosion

There are many approaches that can be used to prevent or to minimize MIC.

- Material change or modification ( Selecting resistant materials)
  - Environmental or process parameter modification ( Frequent cleaning)
  - Use of organic coatings
  - Controlling chemistry of surrounding media and removal of nutrients.
  - Cathodic protection
  - Use of biocides
- forms of Metallic Corrosion 55



# Galvanic Series

- The series prepared by studying the corrosion of metals and alloys in a given environment like sea water
- The oxidation potential of different metals and alloys are determined at 25°C and tabulated in the descending order. Metals occupying higher positions in the series undergo corrosion in a vigorous manner.

## Need for Galvanic series

- Electrochemical series does not account for the corrosion of all metals and alloys.

### Ex: Zn/Al couple

- ✓ Zn (below Al in the EMF series) is corroded
- ✓ While Al acts as cathode and protected.

Anodic

Anodic or Active End
Magnesium
Zinc
Aluminum Alloys
Cadmium
Cast Irons
Steel
Aluminum Bronze
Red Brass, Yellow Brass, Naval Brass
Copper
Lead-Tin Solder (50/50)
Admiralty Brass
Manganese Bronze
Silicon Bronze
400 Series Stainless Steels**
90-10 Copper-Nickel
Lead
70-30 Copper-Nickel
17-4 PH Stainless Steel †
Silver
Monel
300 Series Stainless Steels ** †
Titanium and Titanium Alloys †
Inconel 625 †
Hastelloy C-276 †
Platinum †
Graphite
Cathodic or Noble End

Cathodic

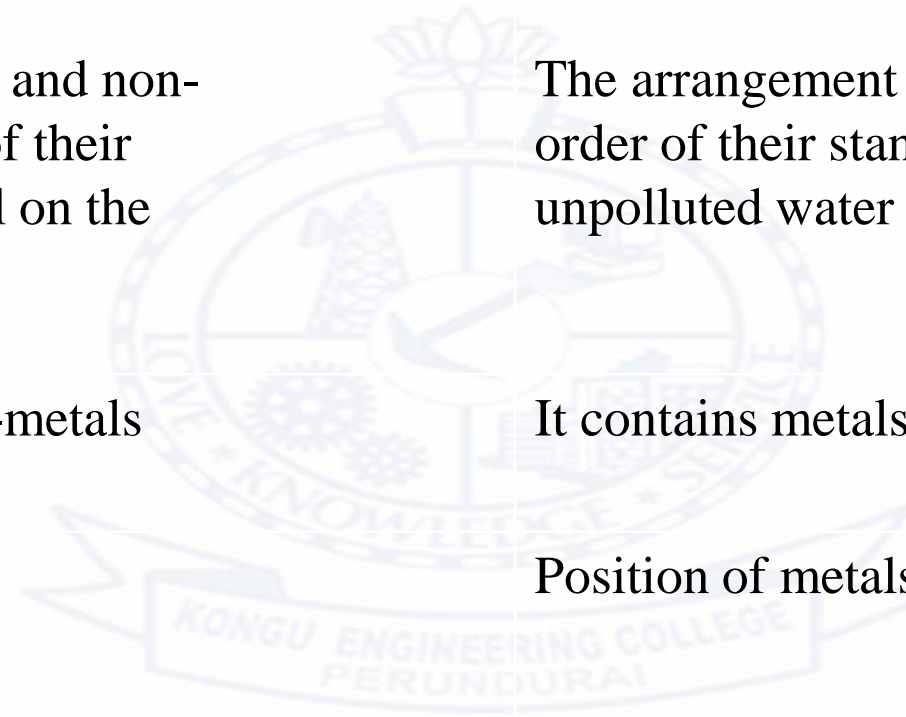
# Difference between Electrochemical and Galvanic series

## Electrochemical Series

- ✓ The arrangement of metals and non-metals in increasing order of their standard reduction potential on the hydrogen scale
- ✓ It contains metals and non-metals
- ✓ Position of metals is fixed
- ✓ It gives no information regarding the position of alloys
- ✓ It predicts the relative displacement tendencies

## Galvanic Series

- The arrangement of metals and alloys in decreasing order of their standard oxidation potential in an unpolluted water
- It contains metals and alloys
- Position of metals is not fixed
- It includes alloys and gives the information of corrosion behaviour
- It predicts the relative corrosion tendencies



# Factors influencing rate of corrosion

The nature and extent of corrosion depend on the metal and environment.

## I. Nature of Metal

### a. Nature of the metal (Position of metal in galvanic series)

- Metal higher up in the galvanic series high reactivity becomes anodic and undergoes corrosion

### b. Relative areas of anode and cathode

- large cathodic area and small anodic area leads severe corrosion

### c. Electrode potential difference

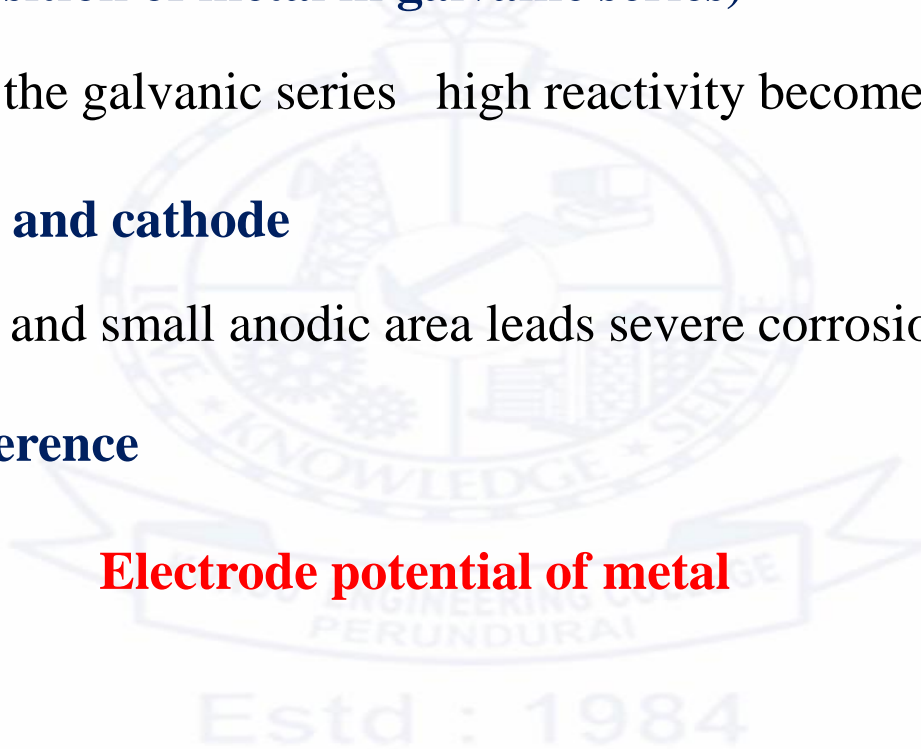
**Corrosion rate  $\propto$  Electrode potential of metal**

### d. Nature of surface film

- **Specific Volume Ratio =  $\frac{\text{Volume of oxide formed}}{\text{Volume of metal}}$**

If SVR > 1; film is nonporous and protects metal from corrosion

if SVR < 1; film is porous and increases the corrosion rate



### e. Surface state of the metal

Impurity creates heterogeneity and leads galvanic corrosion

### f. Hydrogen overvoltage

The metal low hydrogen overvoltage more susceptible for corrosion results in faster the cathodic reaction to increase the corrosion.

## II. Nature of Environment

### a. Temperature

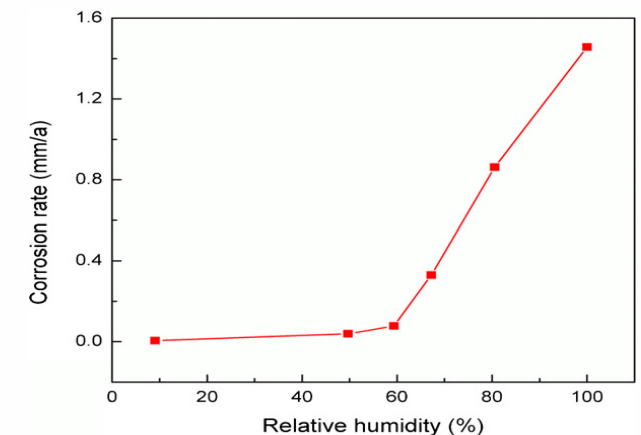
Corrosion rate increases with temperature. Increase in temperature increases the conductance of the medium, reduces passivity of the metal, and thereby increase the rate of corrosion.

### b. Humidity

**Humidity**-concentration of water vapour in the atmosphere.

Corrosion rate increases with humidity

**Critical humidity**-sudden increase in the corrosion rate at a particular point





### **c. Corrosive gases**

presence of gases like  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  etc., enhances the corrosion rate

### **d. Suspended Solids**

presence of suspended solids in environment enhances the corrosion rate

### **e. pH**

Lower the pH of metal environment higher is the corrosion rate. Acidic environment increases corrosion rate than alkaline environment

### **f. Conductance of the medium**

The presence of conducting species in the atmosphere increase the corrosion rate. This rate is more in a wet atmosphere (more conducting) than in dry atmosphere.

### **g. Polarization of electrodes**

Departure of electrode potentials from their equilibrium values. Polarization at the electrodes is due to concentration changes in the electrode region.

Polarization occurs in cathode- Cathode polarization- Reduces the rate of corrosion

Polarization occurs in Anode- Anode polarization- Increase the rate of corrosion

### 3.5.1 Nature of the Metal

#### *(a) Position of Metal in the Galvanic Series*

The extent of corrosion depends upon the position of the metal in the galvanic series. When two metals are in electrical contact, **the metal higher up in the galvanic series** becomes **anodic** and suffers corrosion. Further, the rate and severity of corrosion depend upon the difference in their positions in the galvanic series. The greater the difference, the faster the corrosion of anodic metal.

#### *(b) Relative Areas of Anode and Cathode*

Corrosion will be severe if the anodic area is small and the cathodic area is large. Larger cathodic area of the cathode will create a demand for more electrons, which can be met by the smaller area of the anode, only by undergoing more corrosion.

#### *(c) Overpotential*

Corrosion rate is **inversely proportional** to the overvoltage of a metal in the corrosive environment. For example, when Zn metal is placed in 1 N  $\text{H}_2\text{SO}_4$ , it undergoes corrosion with evolution of  $\text{H}_2$  gas. Initially,



the rate of corrosion is quite slow, because of high overvoltage of 0.7 V. But after the addition of a few drops of  $\text{CuSO}_4$ , the corrosion of zinc is accelerated due to decrease in  $\text{H}_2$  overvoltage to 0.33 V. Thus reductions in overvoltage of the corroding metal/alloy accelerate the corrosion rate.

#### **(d) Nature of the Surface Film**

The rate of corrosion is influenced by the nature of the metal oxide film formed on the metal surface. According to **Pilling–Bedworth rule**,

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide film formed}}{\text{Volume of metal ion consumed}}$$

- **Specific volume ratio > 1**; the oxide film formed will be nonporous and it protects the metal from further corrosion.

**Example:** Oxides of Al, Sn, Pb, Cu, etc.

- **Specific volume ratio < 1**; the oxide film formed is porous, through which oxygen can easily diffuse and is therefore nonprotective in nature.

**Example:** Oxides of Li, Na, K, Mg, Ca, Sr, etc.

### (e) Purity of the Metal

Impurity present in a pure metal creates heterogeneity and leads to galvanic corrosion. If the percentage of purity increases, the corrosion rate decreases.

For example, iron impurity present in Zn metal forms an electrochemical cell and undergoes corrosion.

<i>Metal</i>	<i>% of purity</i>	<i>Corrosion Rate</i>
Zinc	99.999	1
	99.99	2650
	99.95	5000

### (f) Stress

The metal part under stress can become the anode and undergo corrosion. This type of corrosion is called stress corrosion.

## 3.5.2 Nature of the Environment

**(a) Temperature** The rate of chemical reactions and diffusion of ions increases with temperature. Hence, corrosion increases with temperature. A passive metal may become active at higher temperature.

**(b) Humidity** Concentration of water vapour present in the atmosphere is known as humidity. If the humidity increases, the corrosion rate also

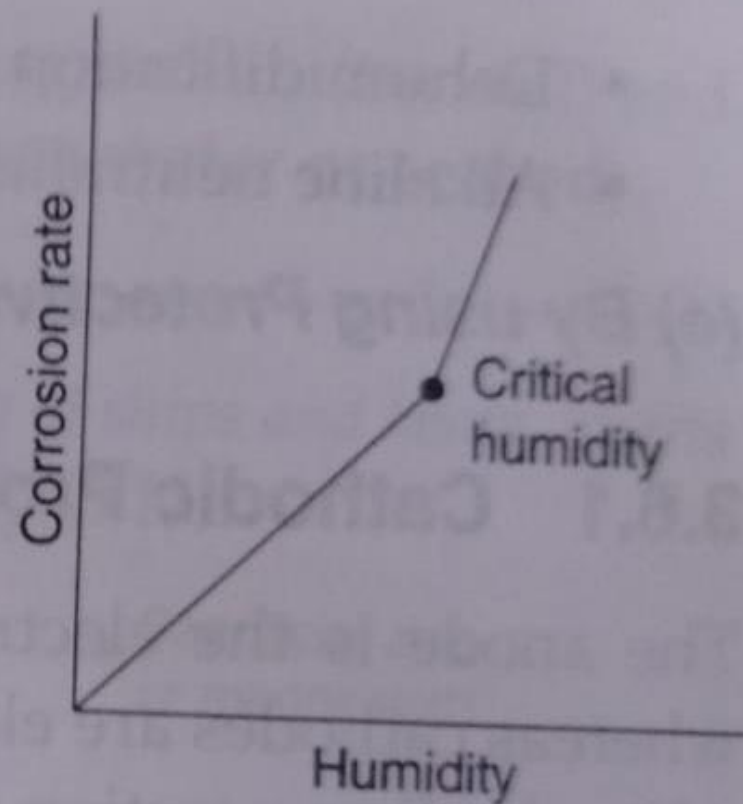


increases. But at a particular point, a sudden increase in the corrosion rate is observed, called **critical humidity**.

**(c) Presence of Corrosive gases** Corrosive gases like  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , fumes of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , acetic acid, etc., enhance the corrosion rate.

**(d) Presence of suspended solids** Suspended particles like chemically active, chemically inactive and chemically neutral dust particles enhance the corrosion rate.

**(e) pH** The corrosion rate is maximum when the environment is more acidic ( $\text{pH} = 5$ ) and minimum when the environment is more alkaline ( $\text{pH} = 11$ ). In general, an acidic medium is more corrosive than alkaline or neutral medium.



**Fig. 3.10** Critical humidity

# Measurement of Corrosion Rate by Weight Loss Method

## Measurement of Corrosion Rate by Weight Loss Method

Corrosion is a natural process by which materials (usually metals) gradually degraded by the chemical and/or electrochemical reactions with their environment, which generally result in the loss of their useful properties (such as strength). Corrosion processes are complex in nature and studies thereof have become an interdisciplinary research field, combining fundamental sciences and engineering. Indeed, corrosion monitoring and measurements are much essential to reduce cost for the repairing and replacing the corroded parts/ devices. The notable corrosion monitoring techniques and corrosion measurement techniques are listed below.

Estd : 1984

## **Corrosion Monitoring Techniques**

- Electrochemical Methods (EC)
- Electrical Resistance Monitoring (ER)
- Linear Polarization Resistance Monitoring (LPR)
- Hydrogen Monitoring
- Weight Loss Coupons
- Non-Destructive Testing Techniques (NDT) and
- Analytical Techniques

## **Corrosion Measurement Techniques**

- Polarization curves
- Linear Polarization Resistance
- Open Circuit Potential Decay
- AC Impedance Measurement
- Electrochemical Noise Measurement
- Weight Loss Measurement

## Weight Loss Method:

It is the simplest form of corrosion measurement method. It is also known as immersion method. In this method, a sample specimen is exposed to a corrosive environment (Conc.H<sub>2</sub>SO<sub>4</sub> Medium) for a specific period of time (Roughly 7 Days) and subsequently removed from the medium and then a detailed examination is carried out.

The corrosion rate is estimated by using the equation (1).

$$\text{Corrosion Rate (CR)} = \frac{K \times \Delta W}{A \times t \times \rho} \longrightarrow (1)$$

Where, Corrosion Rate is expressed in mm / year

‘ΔW’ is the weight loss of the sample specimen in gram,

‘A’ is the area of the specimen in cm<sup>2</sup>

‘t’ is the exposure time of the specimen in the corrosive environment in hours

‘ρ’ is the density of the specimen in g/m<sup>3</sup> and

‘K’ is the constant, i.e.,  $K = 8.76 \times 10^4$ .



### **Requirements:**

1. Mild steel / Stainless steel/ Carbon steel specimen of specified dimensions
2. Glass hook
3. Corrosive Environment (Conc. $\text{H}_2\text{SO}_4$ )
4. Screw Gauge
5. Vernier Caliper
6. Emery Sheet
7. Balance
8. Hot air Oven
9. Desiccator

**Procedure:**

- Take the specimen of mild steel / stainless steel / carbon steel of specified dimensions.
- Initially, surface smoothness and cleaning is done by emery sheet.
- After cleaning the surface, take the initial weight ( $W_1$ ) in gram using balance.
- Then, measure length (l) and breadth (b) of specimen using Vernier Caliper.
- Thickness of the specimen is measured by Screw Gauge.
- Take a glass hook, hold the specimen and immerse in corrosive environment (Conc. $H_2SO_4$ ) to specified period of time (Roughly 7 Days).
- After the specified period of time, the specimen was carefully removed.
- It was then cleaned with inhibited acid (15 % HCl) to remove corrosion products on the surface of the specimen. Then it was further rinsed with running water.
- Next, specimen was placed in a hot air oven at 100-105°C for 15 minutes for drying.

- After drying, the specimen was placed in the desiccator to cool and then it was weighed again.
- The final weight was noted ( $W_2$ ). The difference between initial and final weight was calculated. i.e.,  $\Delta W = W_1 - W_2$
- After substituting the values of  $K$ ,  $\Delta W$ , Area of specimen( $A$ ), time ( $t$ ) in hours and density ( $\rho$ ) of specimen in the equation (1), we can get the corrosion rate for the test specimen.

**Corrosion rate is expressed in the following units**

1. Miles Penetration year (MPY)
2. Millimeters Per Year (MM/Y)

$$1\text{MPY} = 0.0254 \text{ MM/Y}$$

#### **Advantages of Weight Loss Method**

1. The sample exposures are simple and usually low cost.
2. This method is applicable to all environments like gases, liquids and solids
3. Visual inspection and corrosion deposits can be observed and analysed in this method.
4. By this method localized corrosion can be identified and measured.
5. In this method, inhibitor performance can be easily assessed etc.

## Limitations of Weight Loss Method

1. In this method, long exposure periods may be required to obtain meaningful and measurable weight loss.
2. This technique only determines the average rate of metal loss over the period of exposure.
3. This method can not be used to detect rapid changes in the corrosion behaviour during the process.
4. The reuse of a used sample specimen for corrosion monitoring is generally not recommended.
5. This method can be quite labor intensive.
6. The weight loss method may be misleading in situations where the corrosion rate varies significantly over time because of unrealized process factors etc.



# Corrosion Control methods

Corrosion can be controlled in two methods

## By modifying the metal

- Use of pure metal
- Using metal alloys
- Proper designing
- Anodic Protection  
made passivating metal structures  
into more anodic
- Cathodic Protection  
made the metal structure to behave like  
cathode

## By modifying the environment

- Use of Inhibitors
  1. Anodic inhibitors
  2. Cathodic inhibitors
  3. Vapour-phase inhibitors (VPI)
- Surface Coatings
  1. Inorganic coating
  2. Organic Coating
  3. Ceramic Coating

## Corrosion control by modifying the metal

### 1. Selection of the metal

- Selection of right type of metal is the main factor for corrosion control.
  - ✓ Eg: Noble metals that are immune to corrosion are used for producing ornaments and surgical instruments.

### 2. Using pure metal:

- Presence of impurities in a metal cause heterogeneity and decreases the corrosion-resistance of the metal.
  - ✓ Eg: Presence of just 0.02% of iron in aluminium decreases its corrosion resistance.

### 3. Using metal alloys:

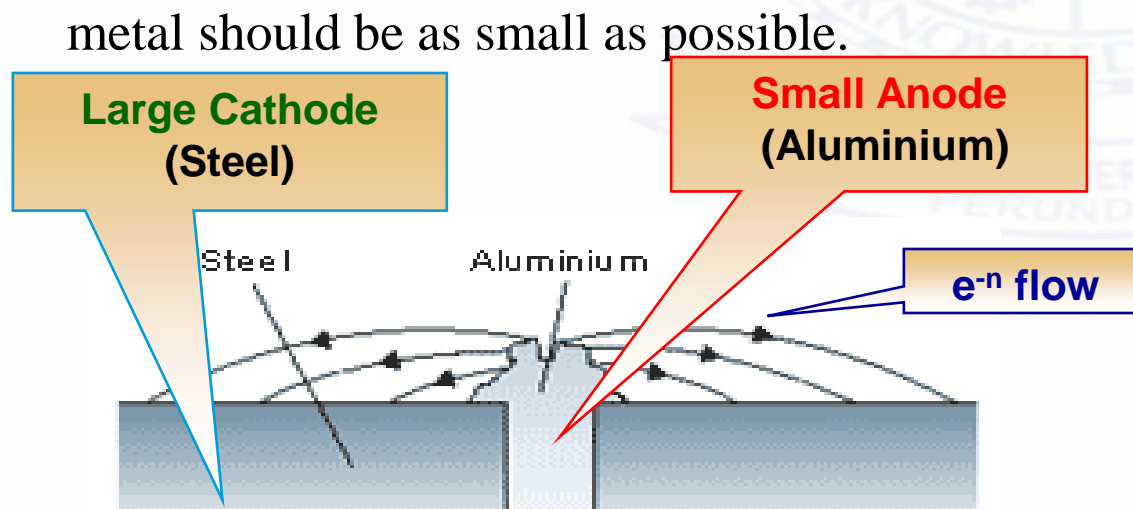
- Corrosion resistance can be improved by alloying the metal with suitable metal.
  - ✓ Eg: Presence of chromium in stainless steel produces a protective oxide film.

## Corrosion Control by modifying the design

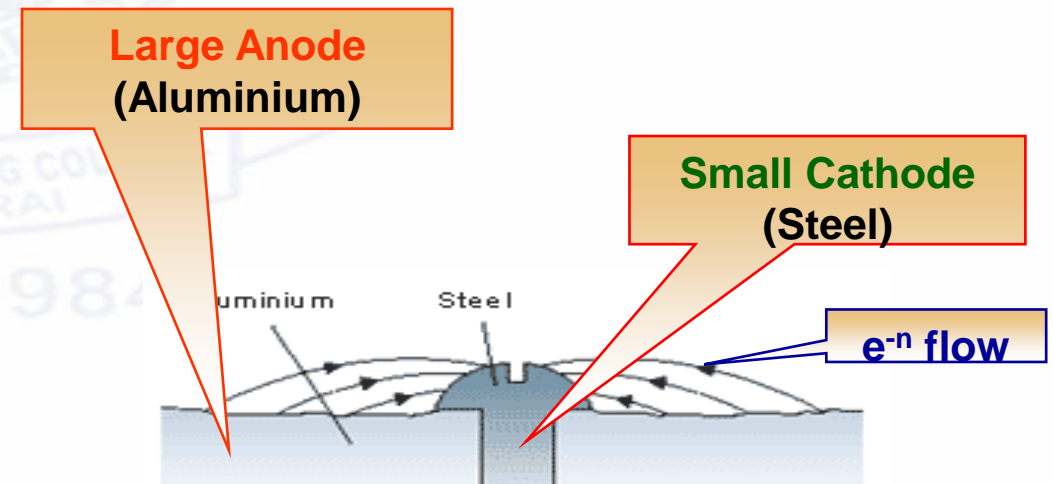
Metallic materials should be designed in such a way to resist corrosion

### Important Design Principles:

- The contact of two dissimilar metals in the presence of the corroding solution should always be avoided, otherwise the more active metal will act as anode and corrosion will be localized.
- 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.



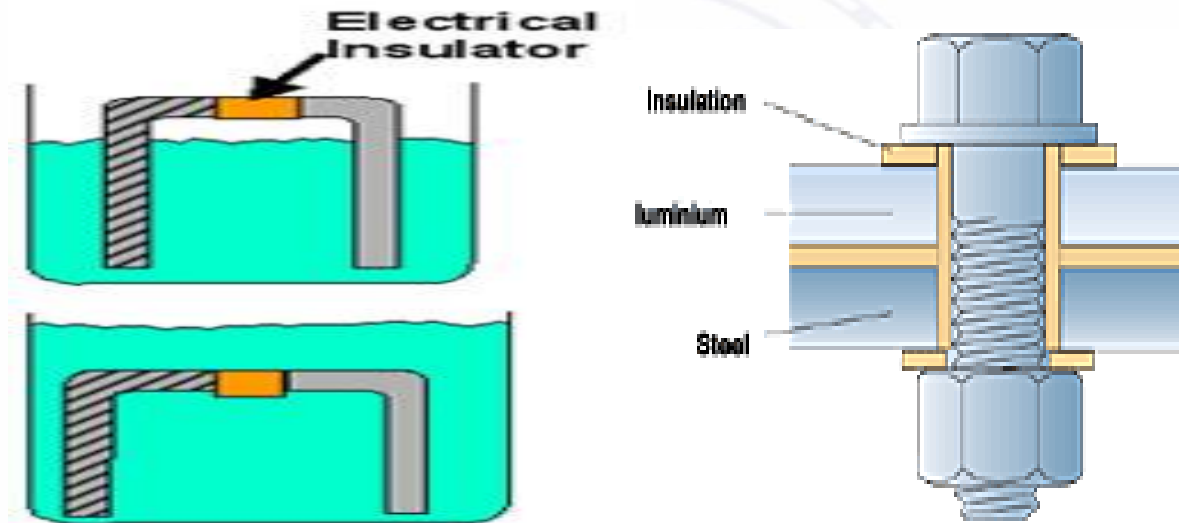
**Severe Corrosion**



**Negligible Corrosion**

## Important Design Principles:

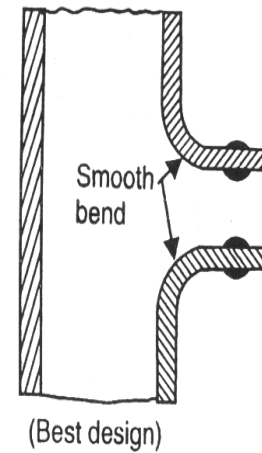
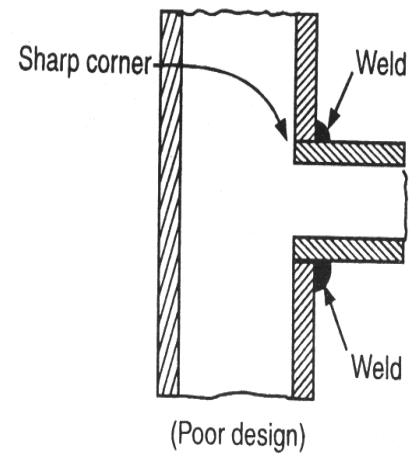
- The (contacting) two dissimilar metals should possess close positions in the galvanic series.
  - ✓ If direct contact is not possible to avoid, the metals can be insulated well before connecting to avoid the direct electric contact of metals.



- The design should provide easy cleaning and flushing of the corner and bends in the metallic equipment.
  - ✓ i.e. Sharp corners and recess should be avoided.

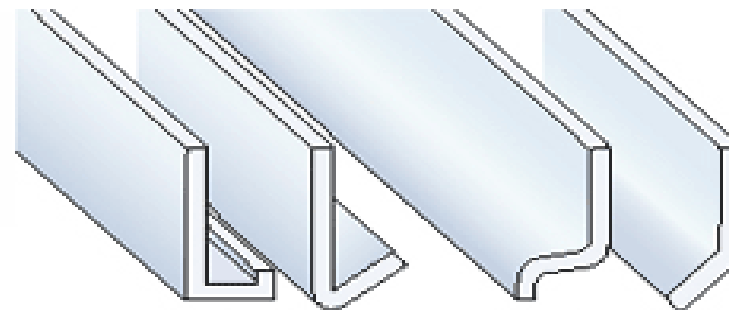
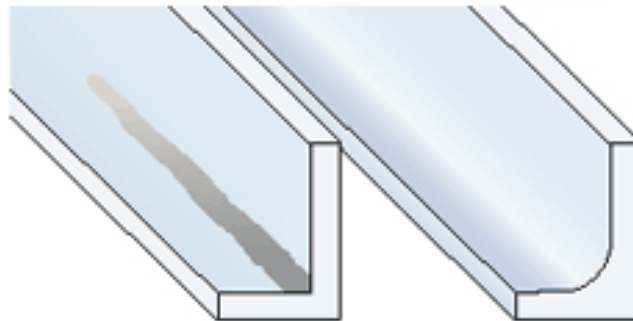


## Important Design Principles:



➤ Avoid angles and pockets in which water can collect.

➤ The risk of dirt build-up is reduced with radiused corners.



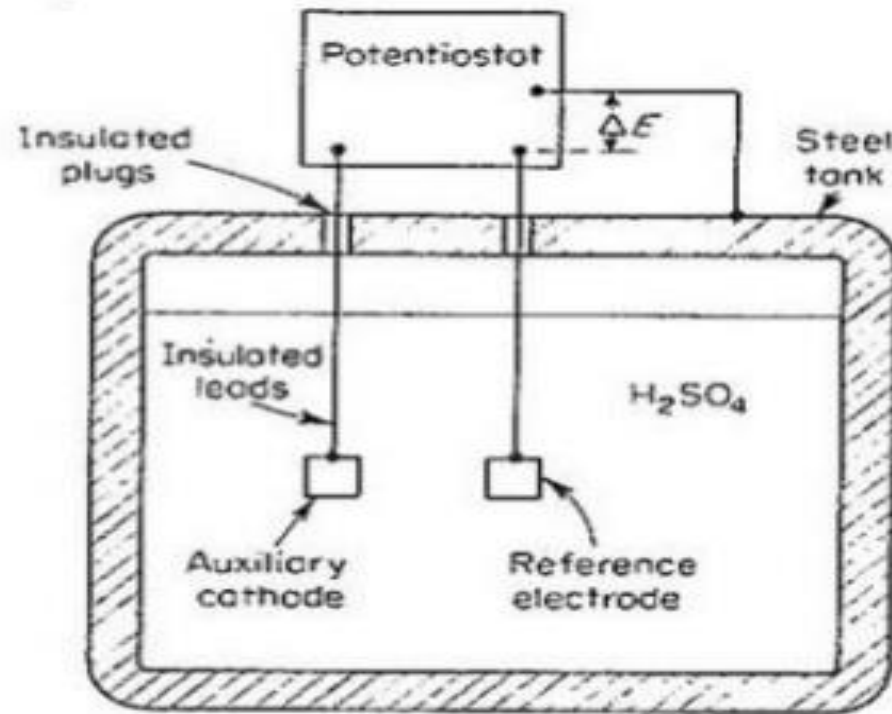
## Anodic Protection

**Formation of a passive protective film on the surface of metal by applying anodic current.**

**Prevention of corrosion by impressed anodic current method is called anodic protection.**

- Anodic protection(AP) is a technique to control the corrosion of a metal surface by making it as an anode of an electrochemical cell.
- Metals like Ti and alloys like steel, when made as anode exhibit passivity by forming their oxide layers
- If anodic current is applied carefully to metals like Ti, Ni, Fe, Cr and their alloys, they are passivated and the rate of metal dissolution is decreased.
- To anodically protect a structure, a device called potentiostat (electronic device) is used

- This method is used for carbon steel storage tanks containing extreme pH environments like  $\text{Conc. H}_2\text{SO}_4$  where the other method is not suitable.
- That requires small current.
- A drawback of the method is that it cannot be applied to metals that do not passivate.



Anodic Protection of a steel storage tank containing Sulfuric acid.

# Corrosion control by modifying the environment

## Corrosion Inhibitors:

- Substance which on addition in small quantities to the corrosive environment reduces the corrosion of metal is called inhibitors.

### Types of Inhibitors: 1. Anodic inhibitors

#### 2. Cathodic inhibitors

#### 3. Vapour-phase inhibitors (VPI)

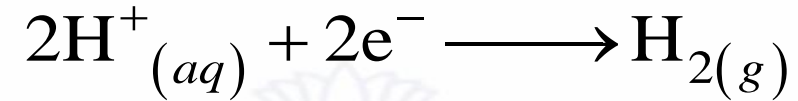
### 1. Anodic inhibitors:

- Chemicals like chromates, phosphates, tungstates, when added to corrosive environment produces sparingly soluble compounds by reacting with metal ions (produced because of corrosion).
- The sparingly soluble compounds get absorbed on the metal surface forms a protective film and thereby reduces corrosion rate.
- This type of corrosion control is not fully reliable because, certain areas of metal are not covered by the film and this leads to severe corrosion.



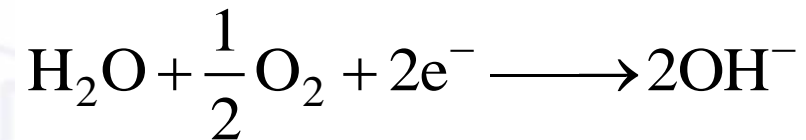
## 2. Cathodic inhibitors:

- In acidic solution, the main cathodic reaction is liberation of H<sub>2</sub>.



In an acidic solution, the corrosion can be controlled by slowing down the diffusion of H<sup>+</sup> ions through the cathode. This can be done by adding organic inhibitors like amines, pyridine, etc. They absorb over the cathodic metal surface and act as a protective layer.

- In a neutral solution, the cathodic reaction is,



The formation of ions is only due to the presence of oxygen. By eliminating the oxygen from the medium, the corrosion rate can be reduced. Oxygen can be removed by adding some reducing agents like Na<sub>2</sub>SO<sub>3</sub> or by deaeration.

### 3. Vapour-Phase Inhibitors(VPI)

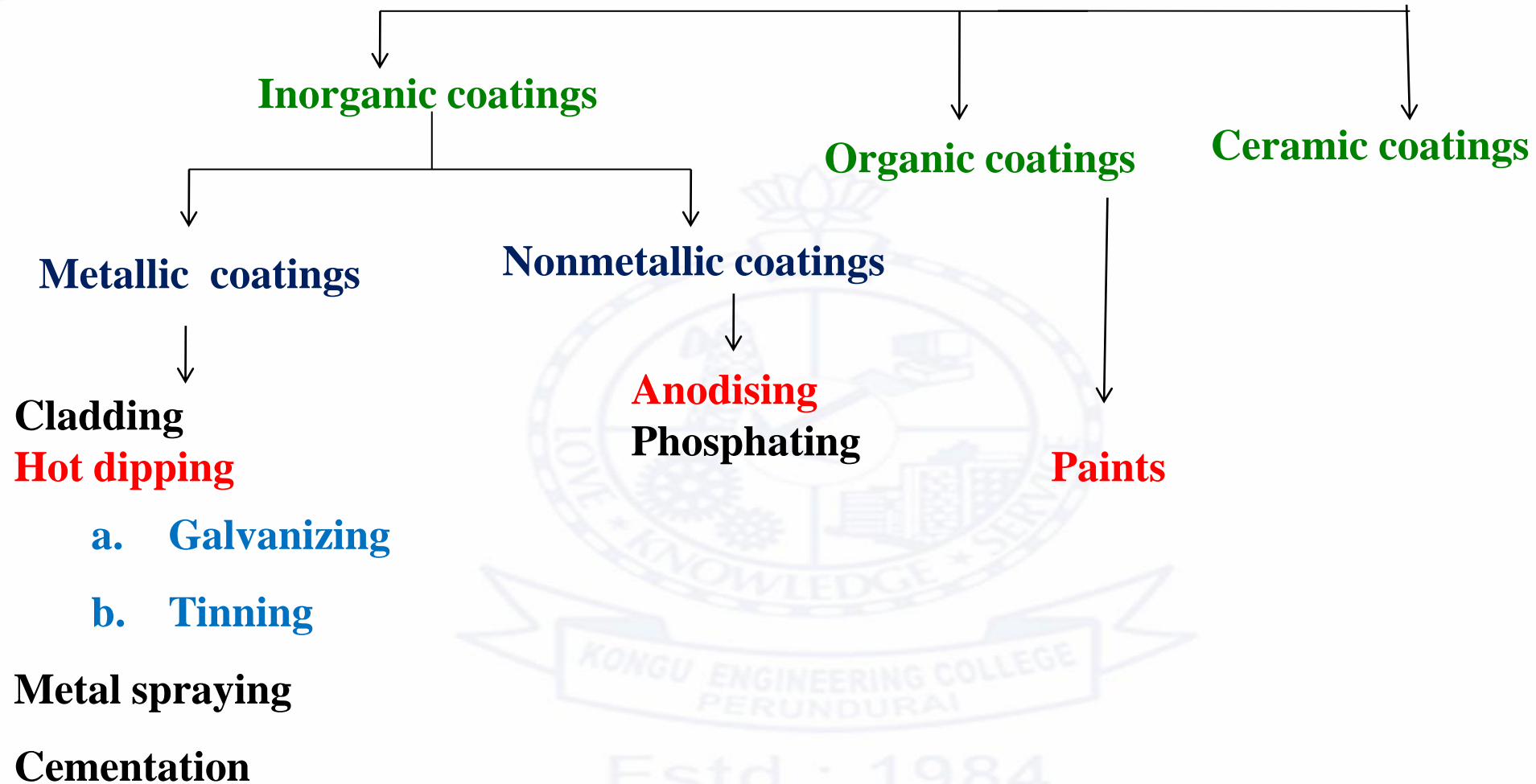
- This type of inhibitors are organic inhibitors, which readily vaporize and form a protective layer on the metal surface. VPI is used to avoid corrosion in closed spaces, storage containers, packing materials, etc.,

Ex. Phenyl thiourea

### Protective Coatings

- The common and oldest method of protection of a metal from its surroundings is by surface coatings
- Metallic surface can be protected from corrosion by covering it by organic or inorganic coating.
  - ✓ Used to protect the metals from corrosion
  - ✓ Used for decorative purpose
  - ✓ They also impart some special properties like hardness, electrical properties, thermal insulating properties

# Protective Coatings



## Requirements for protection

- Coating applied must be chemically inert to the environment
- Coatings must prevent the penetration of the environment

# Pre-treatment of metal surface

## I. Mechanical Method

## II. Chemical Method

- ✓ Solvent Cleaning
- ✓ Alkali Cleaning
- ✓ Acid Pickling

## III. Electrochemical Method

### I. Mechanical Cleaning :

Removes loose rust, oxide scales, dirt – by using bristle brush/sand paper/detergents like soap.

- **Sand Blasting:** sand of different grain size were blasted on the metal surface with pressure of 25 to 100 atm





### ➤ Flame Cleaning:

- ✓ Removes loosely adhering scales – heating the metal surface with hot flame followed by wire brush



## II. Chemical Cleaning :

### 1. Alkali Cleaning

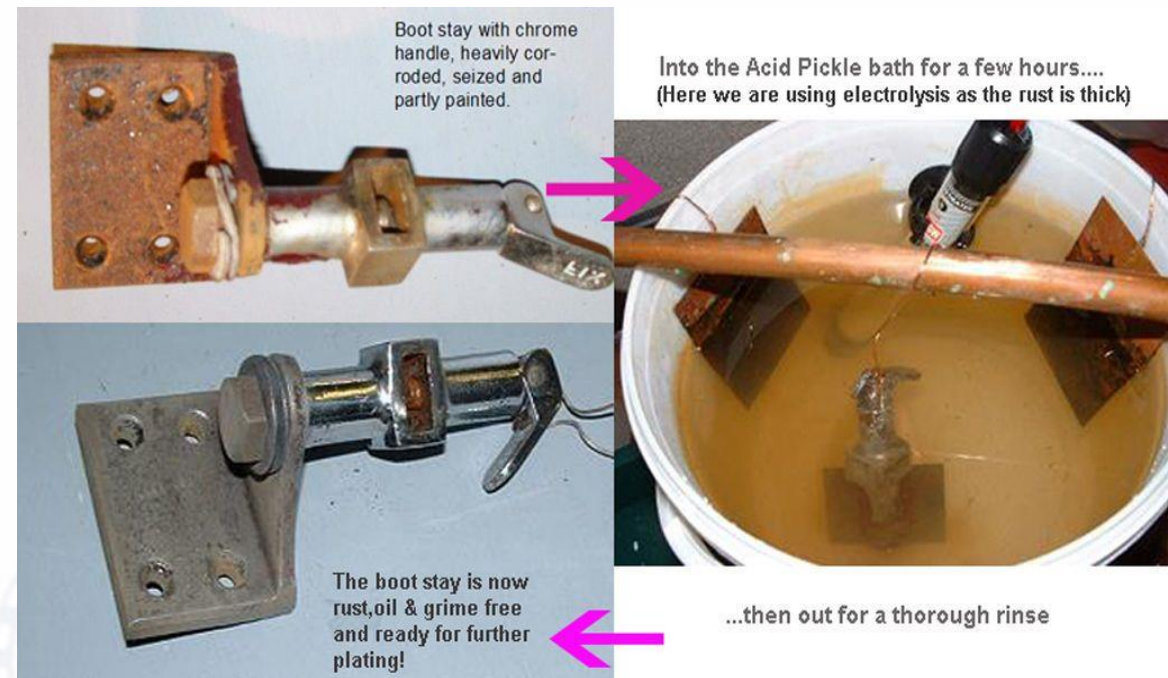
- ✓ Removes old paint – alkali cleansing agents like trisodium phosphate along with soaps and wetting agents



### 2. Acid Cleaning

- ✓ **Pickling and etching:** Removes scales which are adherent - metals except aluminium are immersed in acid pickling solution

## 2. Acid Cleaning



## 3. Solvent cleaning

- ✓ Removes oils, grease and fatty substances by the organic solvents like naphtha,  $\text{CCl}_4$ , toluene, acetone.
- Then the metal surface is cleaned with steam and hot water containing wetting reagents



# Protective Coatings

## I. Metallic Coatings

### Hot dipping:

- It is a process of producing a coating of low melting point metals such as Zn, Sn, pb ,Al, etc., over the surface of Fe, steel, copper which have high melting points
- The process involves immersion of a metal in a bath of its molten coating & covered by a molten layer.
- The flux cleans the base metal & prevent oxidation of metal coating with molten solution.
- Hot dipping is widely applied either by
  - ✓ **Galvanizing** (coating of Zn on Fe or steel)
  - ✓ **Tinning** (coating of Sn on Fe or steel)



## Galvanization Process

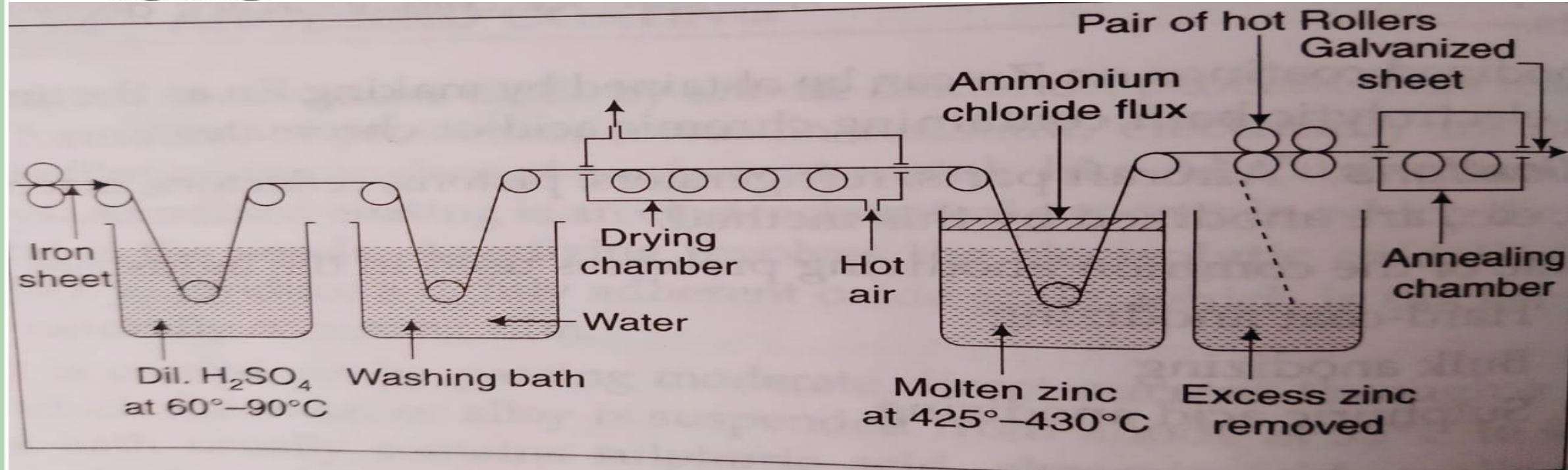
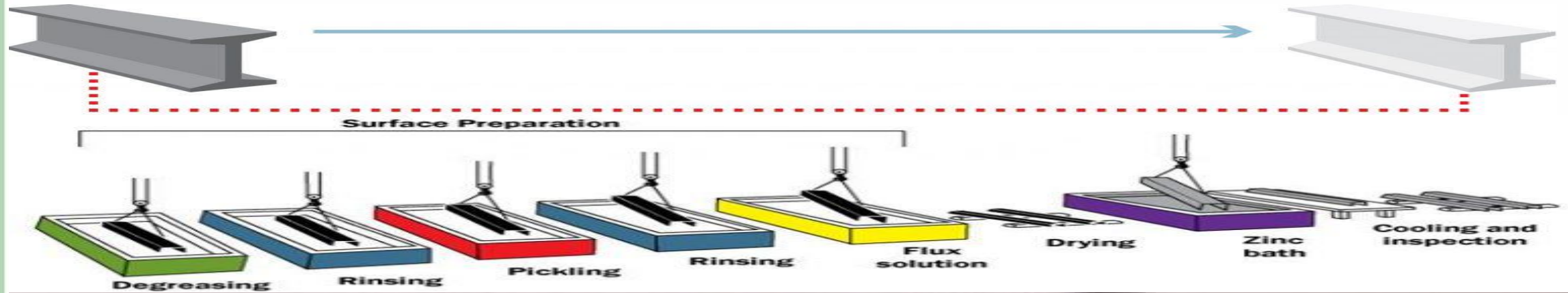
- It is the process in which iron or steel is protected from corrosion by coating with a thin layer of zinc.
- The base metal iron or steel is cleaned by acid pickling with dil.  $\text{H}_2\text{SO}_4$  for 15-20 min at a temperature of 60 - 90°C
- Sheet is then washed and dried
- It is dipped in a bath of molten zinc maintained at 425°C – 430°C
- The surface of the bath is covered with ammonium chloride flux to prevent oxide formation
- Sheet is taken out and excess zinc is removed by passing it between a pair of hot rollers
- Sheet is subjected to annealing process at 650°C and cooled slowly
- An alloy of zinc and iron are formed at the junction of the base metal and coating metal
- It is used to protect Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets and tubes.
- **Defects :** Galvanized utensils are not used for cooking because of solubility of Zn.



# Galvanization Process

Before Galvanizing

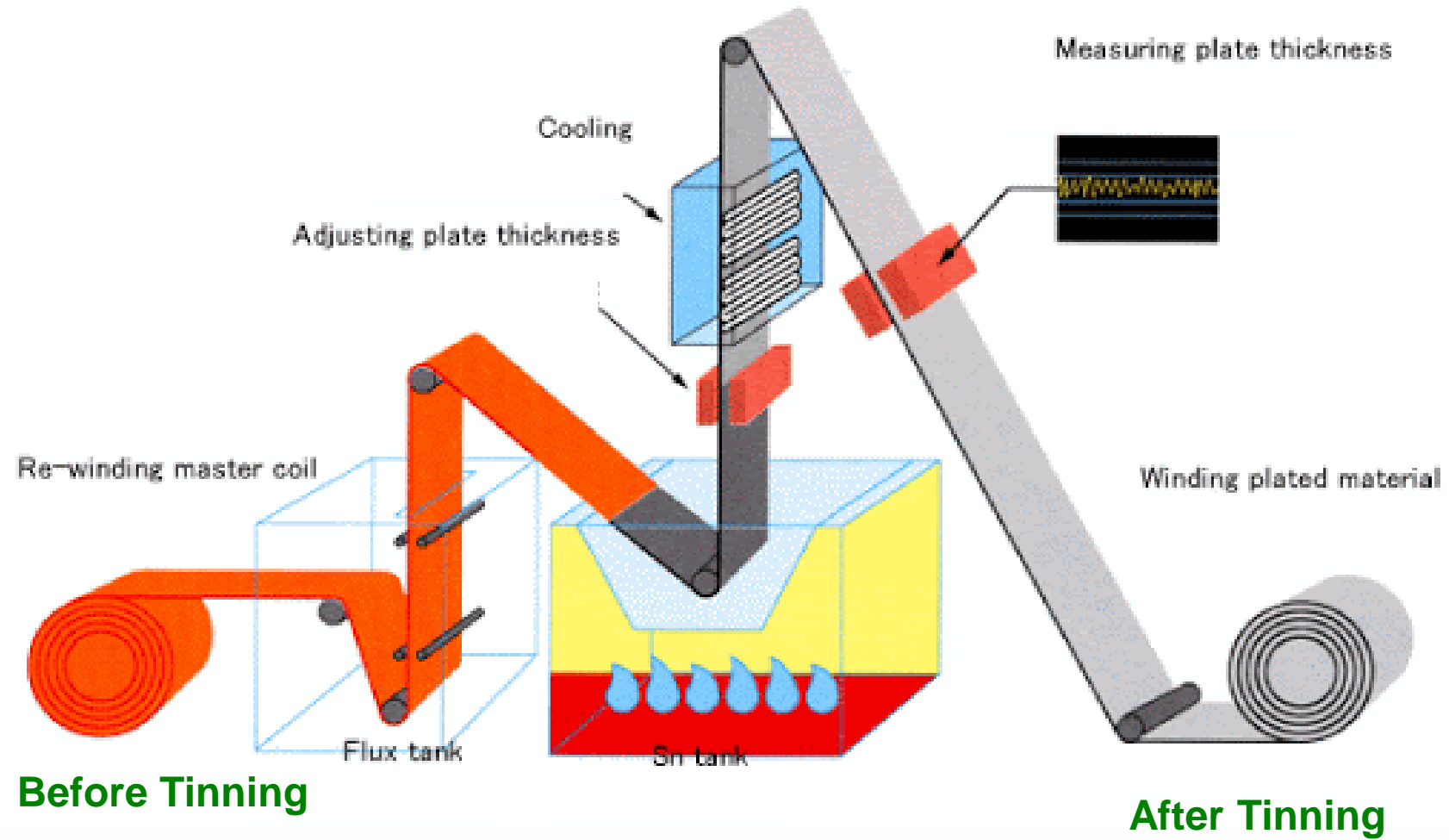
After Galvanizing



# Tinning Process

- Tinning is the process of coating of tin over the Iron sheet or steel articles
- A pre-treated cleaned iron sheet is passed through a bath of molten flux then passes through a tank of molten tin
- Finally through a layer of palm oil which protect hot tin coated surface against oxidation.
- Uses: It is widely used for coating of steel, copper, brass & bronze etc.
- It is used to store food stuff, ghee oils, kerosene, pickles and used for refrigerators equipment.

## Tinning Process



# Protective Coatings

## II. Nonmetallic Coatings - Anodising

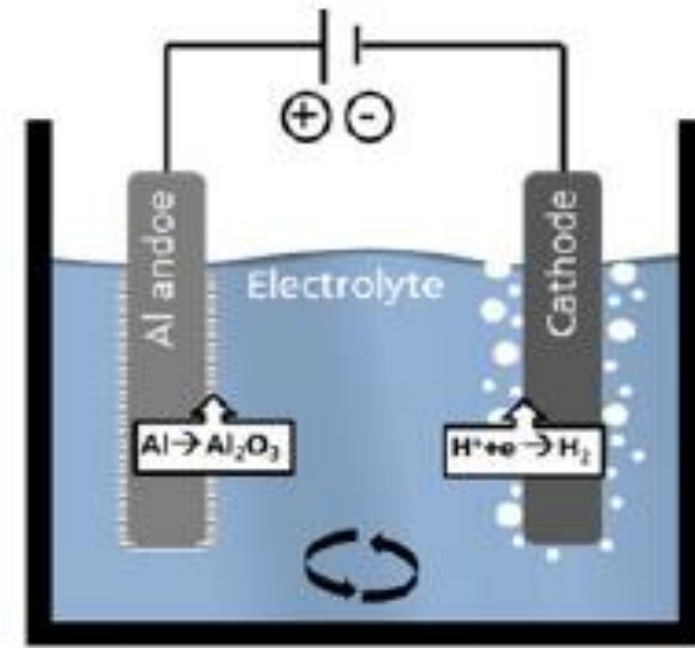
- It is an electrochemical process in which an oxide Layer is chemically built on the surface of the metal
- It is generally produced by anodic oxidation process on metals such as Al, Zn, Mg and their alloys.
- Process converts the metal surface into a decorative, durable, corrosion resistant and anodic oxide finish

### Aluminium Anodizing

- ✓ **Anode:** Al (base metal)
- ✓ **Cathode:** Inert material of good conductivity
- ✓ **Electrolyte:** Sulphuric acid, chromic acid(5-10%)
- ✓ **Temperature:** 35 - 40°C

On electrolysis ,  $O_2$  liberated at the anode combines with Al to form oxide film. Outer part of film is very porous and prone to corrosion. Hence it has to be sealed by treatment with hot water /steam.

- ✓ **Applications:** Aircraft parts, refrigerators, windows, tiffin carriers, soap box, etc.,





# Organic coatings - Paints

Paint is mechanical dispersion of one or more finely divided components in a medium (thinner + vehicle)

When paint is applied to a metal surface the thinner evaporates, while vehicle undergoes slow oxidation forms a film

## Characteristics of good paint

- ✓ Spread easily on metal surface
- ✓ High covering power
- ✓ Not crack on drying
- ✓ Should adhere well to the surface
- ✓ Colour of the paint should be stable
- ✓ Corrosion-water resistant
- ✓ Smooth appearance
- ✓ Dry quickly

## Pigment Volume Concentration

$$PVC = \frac{\text{Vol. of Pigment in paint}}{\text{Vol. of pigment in paint} + \text{Vol. of nonvolatile vehicle in paint}}$$

## Constituents of paints

Pigments	Antiskinning agent
Thinners	Plasticizers
Vehicle	Fillers
Drier	

Activate Windows  
Go to Settings to activate Windows

- The important constituents of paints are

### 1. Pigments

- It's a solid substance which imparts desired color to the paint
- protects from UV light
- provide strength and increase weather resistance of the film. Ex. Pb, ZnO - white colour

### 2. Thinner or Solvent

- It's a volatile portion and easily evaporates
- Used to dilute the paint and reduces the viscosity
- Dissolves all the components of paints. Ex. Kerosene, alcohol

### 3. Vehicle or drying oil

- it's a nonvolatile component and film forming material
- it imparts water repellency. Durability and toughness to the film. Ex. Castor oil, coconut oil

### 4. Driers

- Act as catalysts and increase the rate of drying process. Ex. Borates

### 5. Antiskinning agent

- Prevents skinning of the paint. Ex. Polyhydroxy phenol

### 6. Plasticizers

- Increase the elasticity of the film and minimize its cracking. Ex. Triphenyl phosphate

### 7. Fillers

- increase the volume of the paint and reduces the cost
- Fill the voids in the film and prevents shrinkage. Ex. China clay, asbestos



# Protective coatings - Ceramic coatings





## Protective coatings - Ceramic coatings

- A ceramic is an inorganic compound dissolved in liquid polymer that is applied to the exterior of a vehicle to protect it from external paint damage.
- Coatings, chemically bonds with the surface and creates a layer of protection
- Due to its chemically intrinsic properties, it does not break down in normal atmospheric conditions like rain or summer.
- Can provide high-performance oxide layers on metals and alloys to solve the problems of corrosion, wear, heat, insulation and friction
- Some ceramic coatings include thermal spray coating, plasma spray coating, sputter coating, dry-film lubricants and other wet chemical and electrochemical coatings
- Thickness of ceramic films can range from 50 nm to several micron meters
- Ex:  $\text{Si}_3\text{N}_4$  , silicon carbide, boron nitride, cerium oxide, etc

### **Advantages:**

Increase lifetime of parts, prevent corrosion, reduce heat on hightemperature components, reduce friction, stop thermal / acidic corrosion, improve appearance of surfaces

### **Disadvantages:**

Extremely brittle and hard to repair; de-bonding can occur during the expansion and shrinkage; corrosion easily forms at the cracks; heavier than organic coatings; its expensive, needs special equipment