

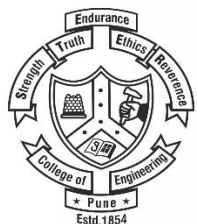


# Unit 1B

## Corrosion



Sr No and Name of the Unit	Topic Description
<b>Unit 1</b> <b>(A) Material Chemistry</b>  <b>(B) Corrosion and corrosion control</b>	Introduction to the basics of chemistry, Relevance of Chemistry to different Engineering specializations
	Classification & Properties of Materials: Metals and alloys, ceramics and glasses, refractories, Cement, polymers, composites
	Nanomaterials: definition, types, properties and applications
	<b>Electrochemistry of corrosion, Mechanism of dry corrosion</b>
	Mechanism of wet corrosion
	Factors affecting corrosion, Testing of corrosion: Weight-loss and weight-gain method, Microscopic exam
	Methods of corrosion prevention, Cathodic protection- Sacrificial anode
	Cathodic protection- Impressed current, Anodic protection
	Protective coatings- examples of Metallic coatings, Examples of non-metallic coatings- paints



# Introduction: Disasters

**22/04/1992- Guadalajara (Spain)**



.....it eventually caused the steel pipe to **corrode**, creating a hole in the pipeline....

**28/04/1998- Aloha Boeing 737 (Hawaii)**



..... which resulted in low bond durability, **corrosion**, and premature fatigue cracking.

**13/03/1984- Bhopal (India)**

.....such as the presence of iron from **corroding** non-stainless steel pipelines.....



# Introduction: Corrosion

The **unintentional** and **undesired destruction** of metal is called as its corrosion. It is the **gradual destruction** of materials by **chemical** and/or **electrochemical** reaction with their **environment**.

Or

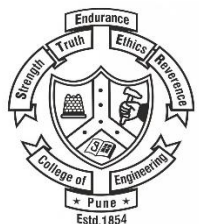
It is the process of **Deterioration** or **Degradation** of metals through an **unwanted** chemical or electrochemical attack by its **environment**.

➤ Compounds (Stable) → Separation → Metals (Unstable) =

Metallurgy

➤ Metal (Highly reactive, less stable) +  $O_2$  +  $H_2O$  = Corrosion

(Oxides, Sulfides, Nitrates)



# Introduction: Corrosion

Corrosion is gradual destruction of metal by chemical and/or electrochemical reaction with their environment

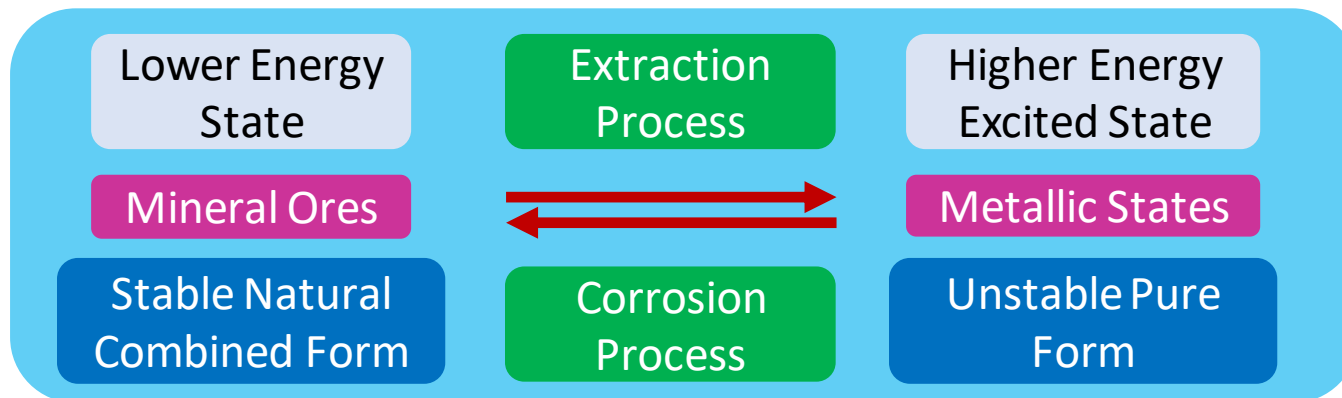
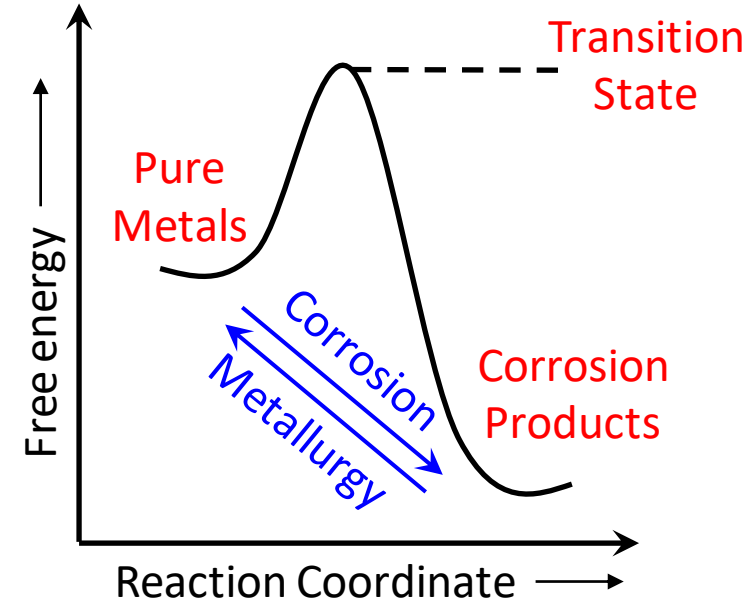
- **Metals**
- **Polymers**
- **Ceramics**
- **Corrosion Products**
  - Oxides
  - Sulphates
  - Nitrates
  - Sulphides





# Extraction of Metal

- Lowering of Gibb's Free energy
- Spontaneous Process
- $\Delta G$  is negative



# Extraction of Metals



<https://www.youtube.com/watch?v=9N6uXQ8KRYc>

# Effects of Corrosion

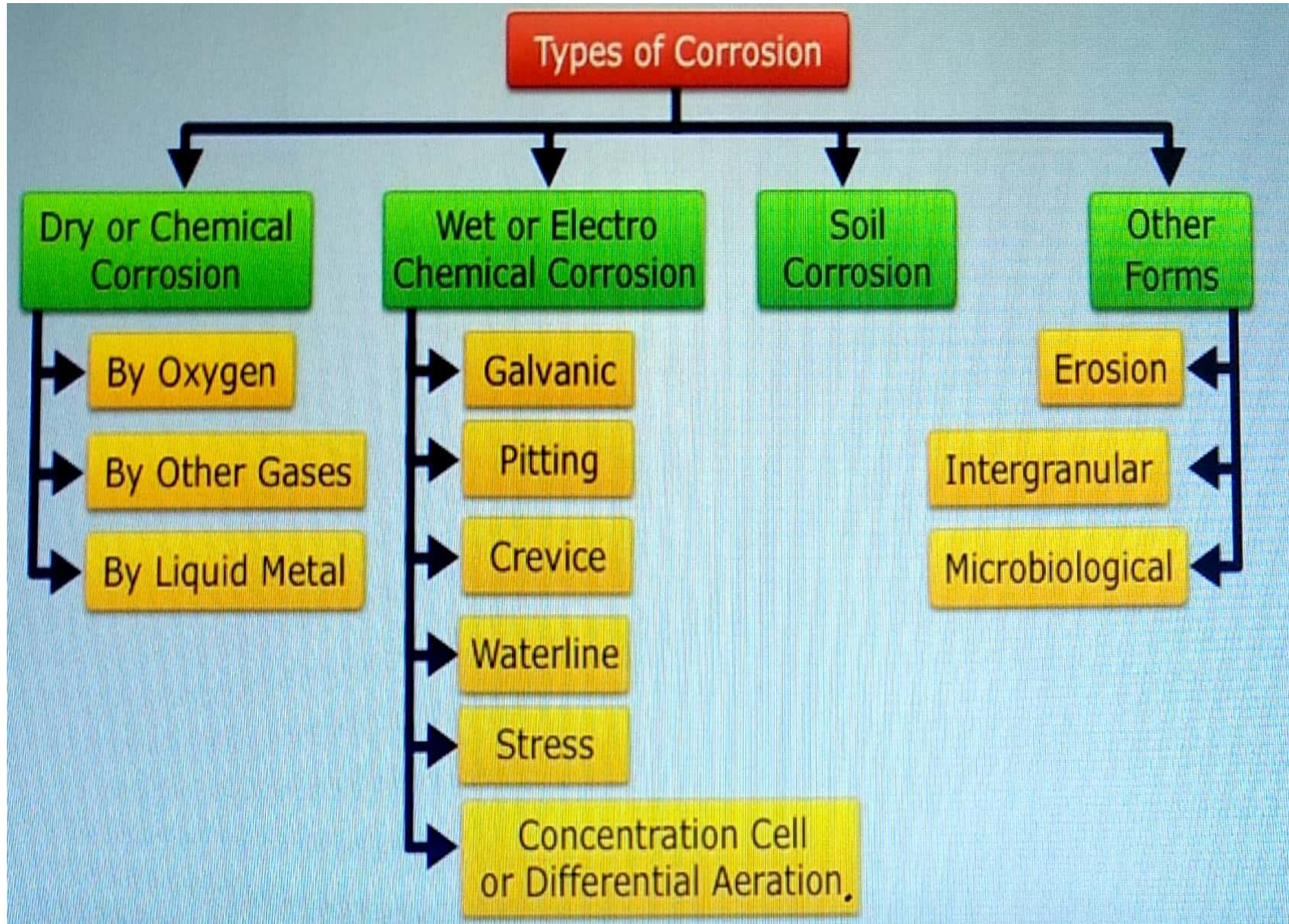
## Loss of useful properties due to corrosion

Weakening of metallic material due to loss of cross sectional area

Loss of properties such as Malleability & Ductility

Decaying of metal surfaces



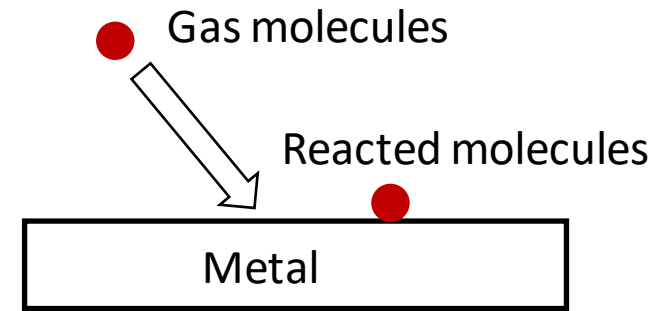


[https://www.youtube.com/watch?v=A\\_rI9rNVgR8](https://www.youtube.com/watch?v=A_rI9rNVgR8)

# Types of Corrosion

- **Direct chemical or Dry Corrosion or Atmospheric Corrosion**

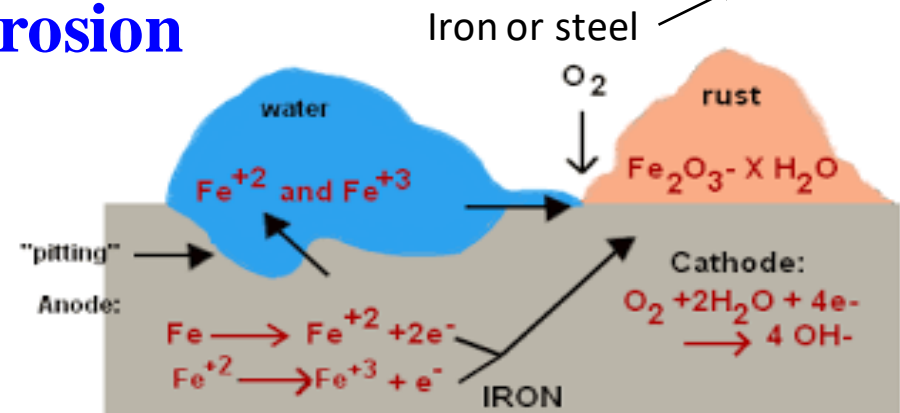
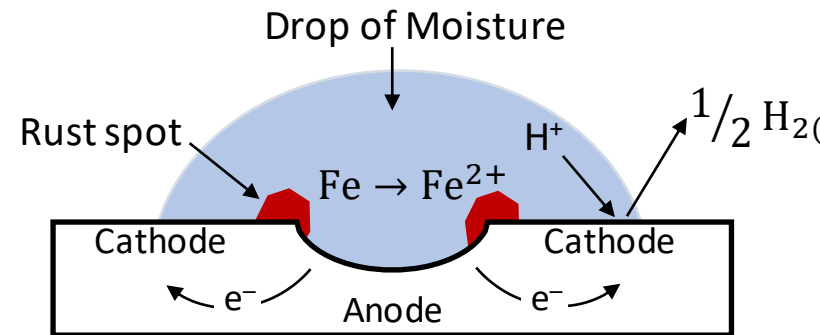
- Corrosion due to oxygen or oxidative corrosion
- Corrosion due to other gases
- Corrosion due to hydrogen



<https://www.youtube.com/watch?v=I3QLMI1AK9Y>

- **Electrochemical or Wet Corrosion or Immersion corrosion**

- Galvanic corrosion
- Concentration cell corrosion
- Crevice corrosion



# Types of Corrosion

- Dry or Direct chemical:

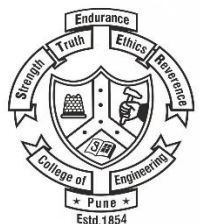
**Direct chemical reaction** of gases  $O_2$ , Halogens,  $H_2$ ,  $N_2$ ,  $H_2S$  etc. with metal surface in its immediate proximity

## Direct Chemical Corrosion

Oxidation Corrosion

Corrosion by other  
gases

Liquid metal Corrosion



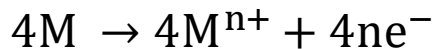
# Type of Corrosion

- Direct chemical or Dry corrosion

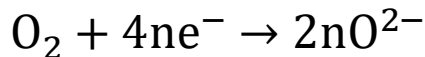
- Oxidative corrosion

- Carried out by direct action of Oxygen
- Alkali and alkaline metals react at Low Temperature
- Other metals react at high temperatures except Ag, Au, Pt

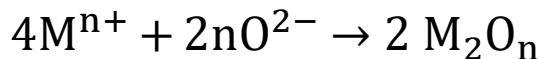
## Chemical Reactions:



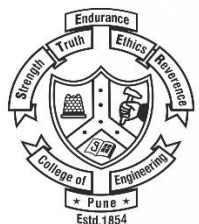
Oxidation



Reduction



Material Formation



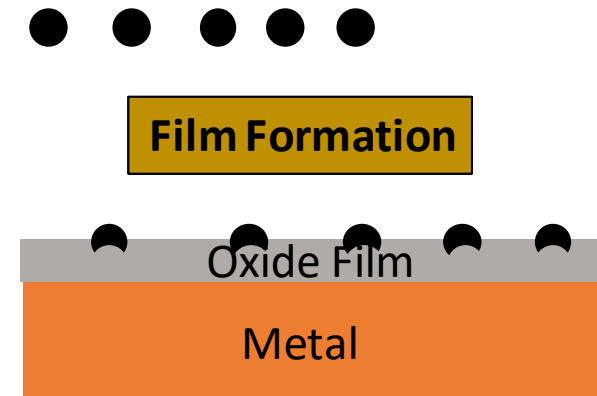


# Types of Corrosion

- Direct chemical or Dry corrosion

- Oxidative corrosion

1. **Adsorption:** Clean and uncorroded surface of a metal comes in contact with  $O_2$ . No chemical bond, Van der Waal's forces.
2. **Chemisorption:** Transfer of electrons from metal to  $O_2$ . Formation of Ionic/Covalent bonds
3. **Film formation:** Formation of a thin film of corrosion product on metal surface





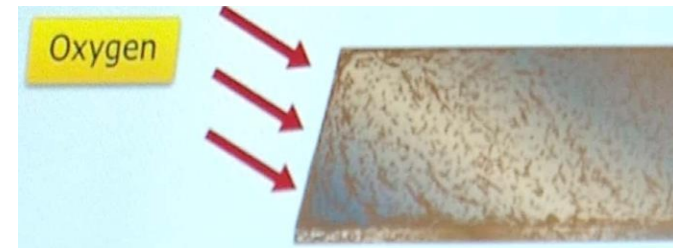
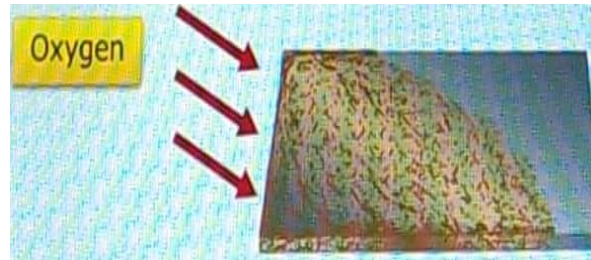
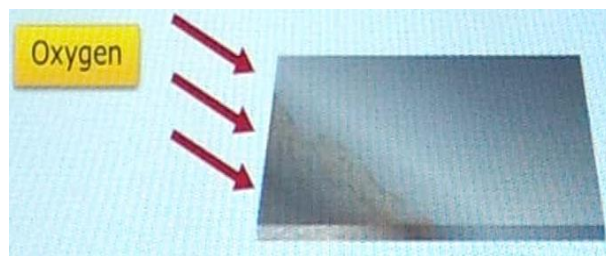
# Types of Corrosion

- Direct chemical or Dry corrosion

- Oxidative corrosion

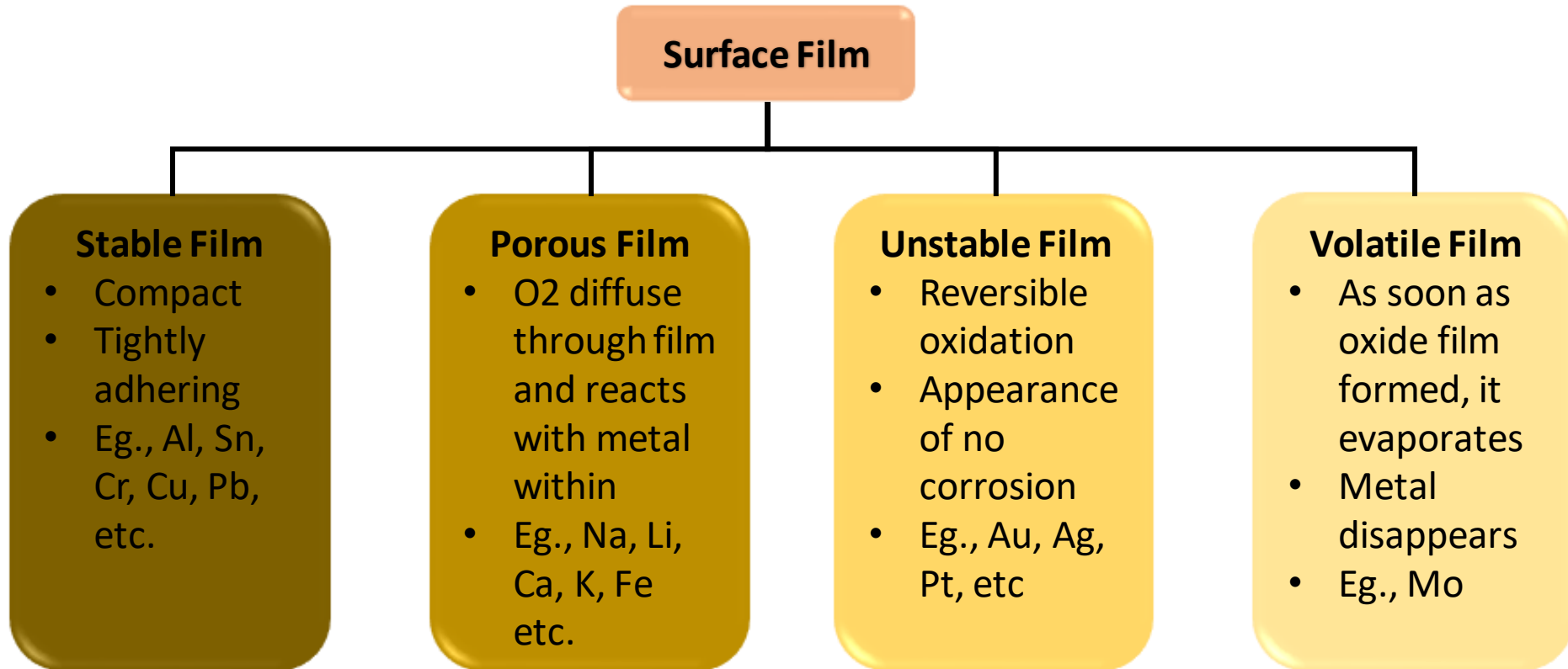
Rate of film formation depends:

- Temperature
- Presence of moisture
- on the affinity between gas and metal
- Nature of oxide film on the surface of metal



# Type of Corrosion

- Direct chemical or Dry corrosion
  - Oxidative corrosion



# Type of corrosion

- Direct chemical or Dry corrosion

## ➤ Oxidative corrosion

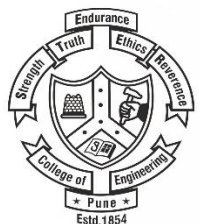
$$\text{Pilling – Bedworth Ratio} = \frac{\text{Volume of oxide formed}}{\text{Volume of equivalent amount of metal consumed to form oxide}}$$

P.B. Ratio > 1      Non-porous and protective coating  
Eg., Cr, Al, Ni etc.

P. B. Ratio < 1      Porous and non-protective coating  
Eg., Alkali, alkaline earth metals

$$R_{PB} = \frac{V_{\text{Oxide}}}{V_{\text{Metal}}} = \frac{M_{\text{Oxide}} \cdot \rho_{\text{Metal}}}{n \cdot M_{\text{Metal}} \cdot \rho_{\text{Oxide}}}$$

- $R_{PB}$  - Pilling-Bedworth Ratio
- $M_{\text{oxide}}$  - Molecular wt. of oxide
- $M_{\text{metal}}$  - Molecular wt. of metal
- $n$  – no. of metal atoms taking part per one molecule of oxide
- $\rho_{\text{metal}}$  – density of metal
- $\rho_{\text{oxide}}$  – density of oxide



# Types of Corrosion

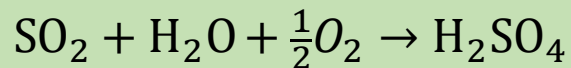
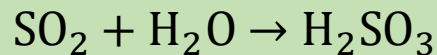
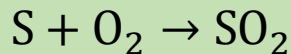
- Direct chemical or Dry corrosion

- Corrosion due to other gases

- Depends mainly on the chemical affinity between metal and gas

- CO
- SO<sub>2</sub>
- NO
- NO<sub>2</sub>
- N<sub>2</sub>O
- Cl<sub>2</sub>
- H<sub>2</sub>S
- F<sub>2</sub> etc.

Burning of Fossil Fuels



**Protective Film**



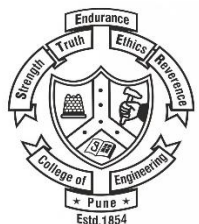
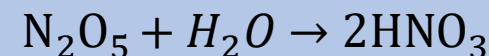
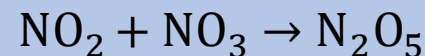
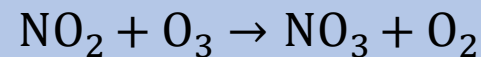
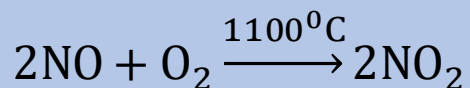
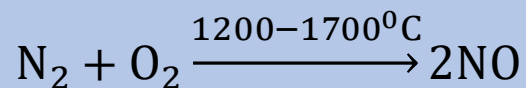
**Volatile film**

In petroleum industry at High Temp.



**Porous Film**

From combustion process



# Types of Corrosion

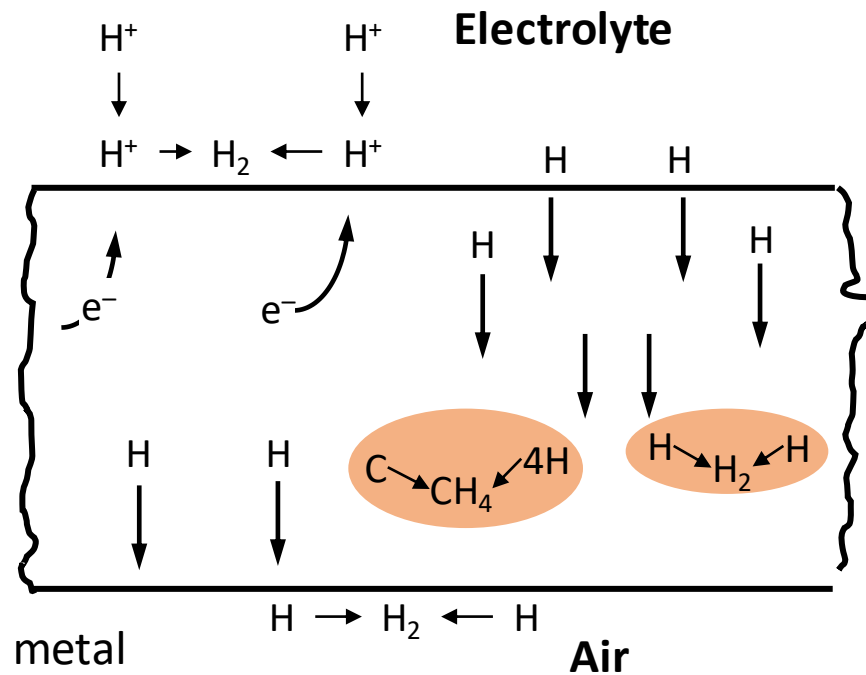
- Direct chemical or Dry corrosion

- Hydrogen Embrittlement

Metal's loss of ductility and reduction of load bearing capability due to the absorption of **hydrogen** atoms or molecules by the metal



H atom can diffuse into metal and react with C, N, S etc.



This leads to formation of bubbles and cracks in metal

<https://www.youtube.com/watch?v=Aa8WOKGjm4s>



# Types of Corrosion [https://www.youtube.com/watch?v=tXnMNFk\\_r4w](https://www.youtube.com/watch?v=tXnMNFk_r4w)

- **Electrochemical or Wet corrosion**

Presence of electrolyte like aqueous solution of salt, acid or alkali  
Formation of an “electrochemical cell”

## Electrochemical Cell

### ☐ Anode

Metal that corrodes. Metal undergoes oxidation

### ☐ Cathode

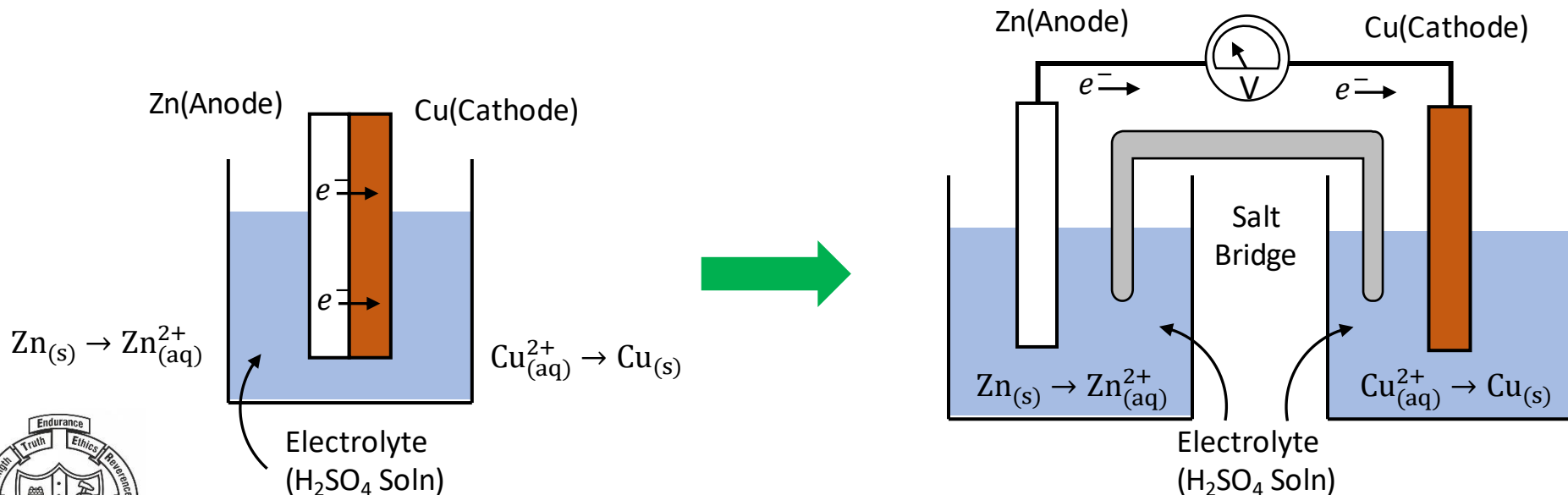
Any material where reduction occurs. May or may not affect the material

### ☐ Electrolyte

Liquid/Gas for migration of ions between cathode and anode

### ☐ Connection

Electrical connection to conduct electrons



# Types of Corrosion

## • Electrochemical Cell

- J. F. Daniell invented electrochemical (Galvanic) cell for supply of electrical energy.
- Devices in which chemical energy is converted to electrical energy by Oxidation-Reduction (Redox) reactions

## • Cell

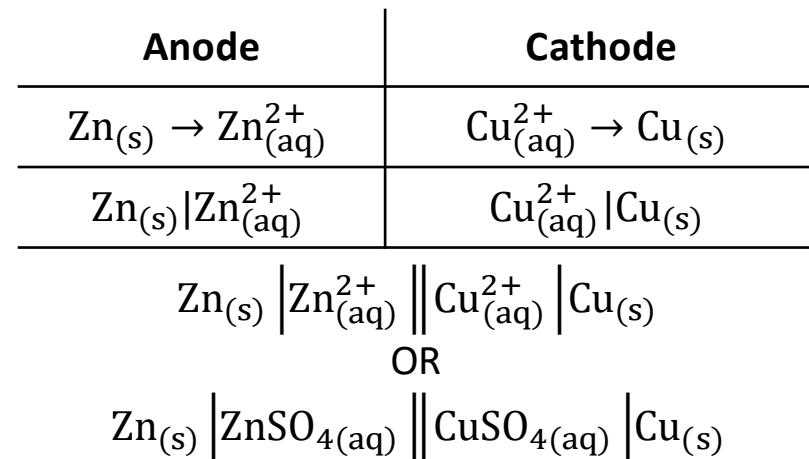
- Assembly of two Half cells

## • Electrode or Half Cell

- Metal dipped in its own solution
- Oxidation → Anode
- Reduction → Cathode

## • Types

- Galvanic Cell
- Concentration Cell

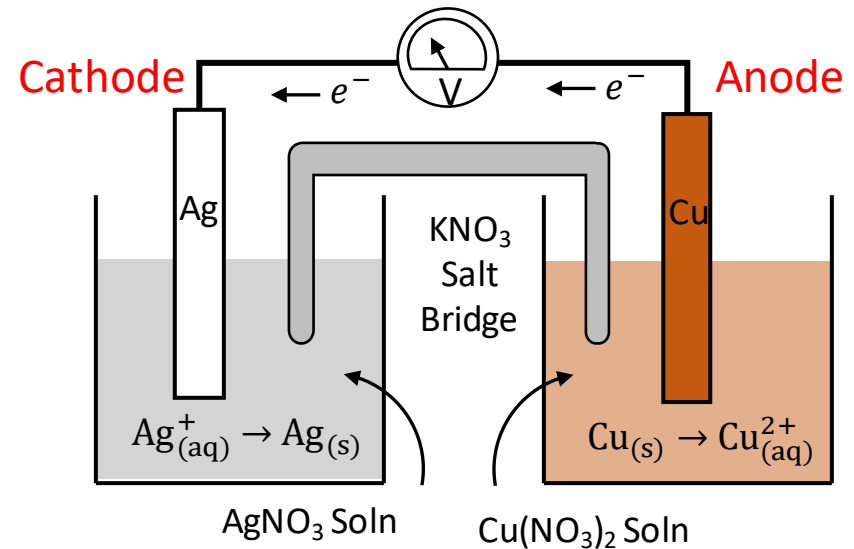
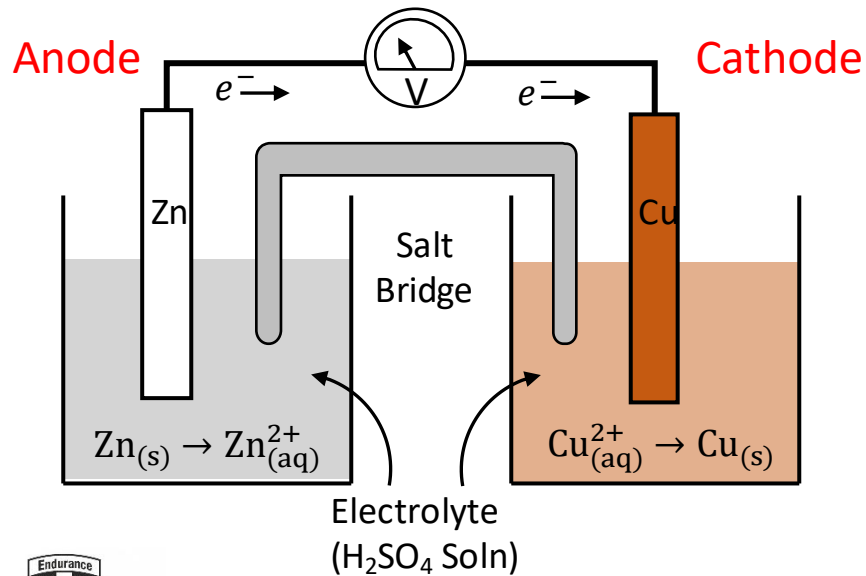


# Types of corrosion

## Galvanic Cell

- Electrodes made up of two **dissimilar metals** dipped in their own solution

**Daniell Cell**

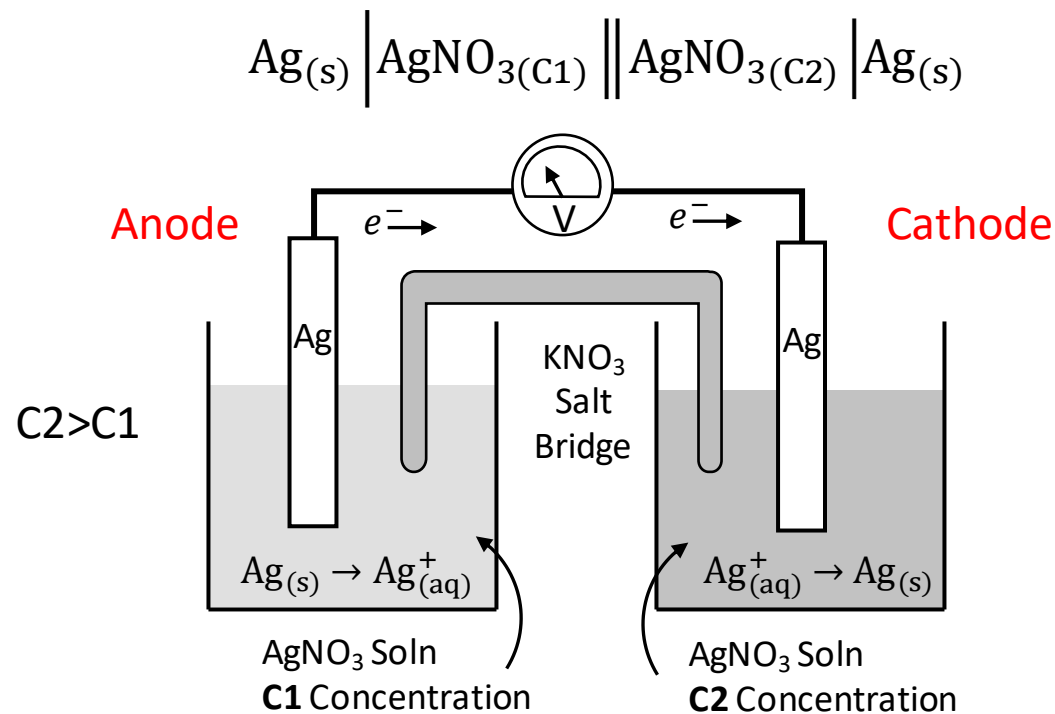


<https://www.youtube.com/watch?v=HIGITf-rhCE>

# Types of corrosion



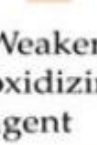
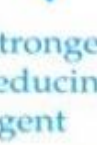
## □ Concentration Cell

- Electrodes made up of **same metal** dipped in its own solutions of **different concentrations**



# Electrochemical Series

$$\Delta G = -nFE$$

<div>Stronger oxidizing agent</div> 	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	2.87	<div>Weaker reducing agent</div> 
	$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78	
	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51	
	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33	
	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	1.09	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70	
	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	0.54	
	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	0.40	
	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0	
	$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13	
	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.26	
<div>Weaker oxidizing agent</div> 	$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40	<div>Stronger reducing agent</div> 
	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.45	
	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76	
	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83	
	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66	
	$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37	
	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71	
	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04	




# Galvanic Series

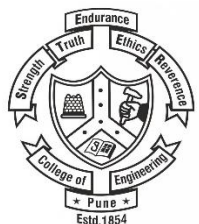
<https://www.youtube.com/watch?v=TKMgUCq3npg>

Most susceptible  
to corrosive attack  
(less noble)

Least susceptible  
to corrosive attack  
(More noble)

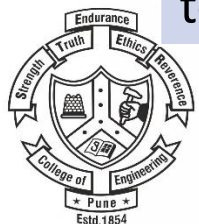


Magnesium and its alloys  
Zinc and its alloys  
Aluminium and its alloys  
Cadmium  
Mild Steel  
Cast iron  
Stainless steel 13% Cr, type 410 (active)  
Lead-tin solder, 50/50  
Stainless steel, 18/18 type 304 (active)  
Stainless steel, 18/18/3 Mo, type 316 (active)  
Lead  
Tin  
Brasses  
Aluminium Bronzes  
Copper  
Copper-nickel alloys  
Monel  
Titanium and its alloys  
Stainless steel, 18/18 type 304 (passive)  
Stainless steel, 18/18/3 Mo, type 316 (passive)  
Silver  
Gold  
Platinum

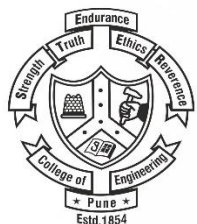


# Difference of Electrochemical and Galvanic Series

Electrochemical Series	Galvanic Series
ES is the list of chemical elements which shows their order of standard electrode potentials	GS is an arrangement of metals and semimetals according to their nobility
ES stems from the standard electrode potential relative to the standard hydrogen electrode potential	GS stems from the galvanic corrosion of metals and alloys
Position of metal is fixed in ES	Position of metal can vary in GS
Alloys are not included	Alloys are included
Predicts the relative displacement tendencies	Predicts the relative corrosion tendencies

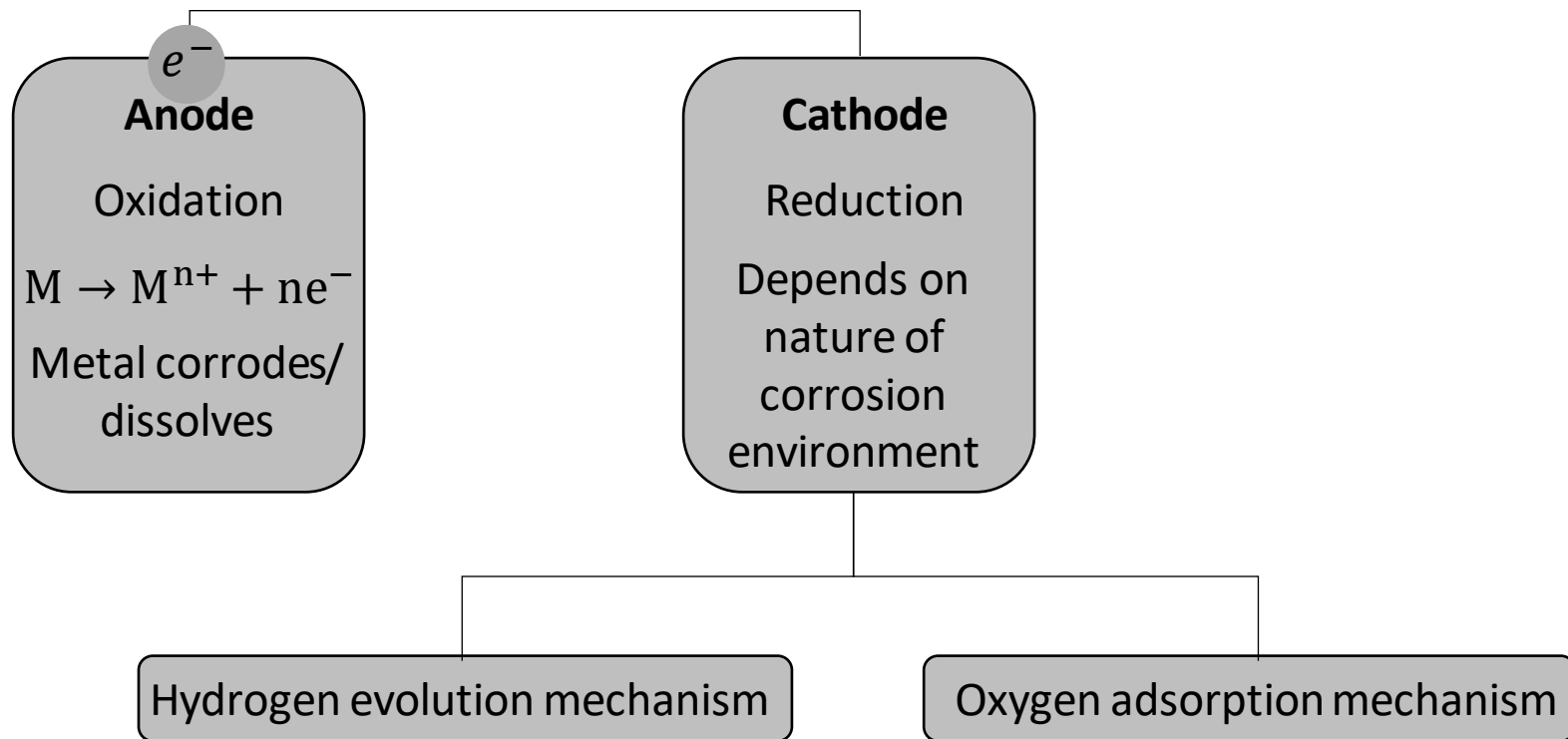


Sr No and Name of the Unit	Topic Description
<b>Unit 1</b> <b>(A) Material Chemistry</b>  <b>(B) Corrosion and corrosion control</b>	Introduction to the basics of chemistry, Relevance of Chemistry to different Engineering specializations
	Classification & Properties of Materials: Metals and alloys, ceramics and glasses, refractories, Cement, polymers, composites
	Nanomaterials: definition, types, properties and applications
	Electrochemistry of corrosion, Mechanism of dry corrosion
	<b>Mechanism of wet corrosion</b>
	Factors affecting corrosion, Testing of corrosion: Weight-loss and weight-gain method, Microscopic exam
	Methods of corrosion prevention, Cathodic protection- Sacrificial anode
	Cathodic protection- Impressed current, Anodic protection
	Protective coatings- examples of Metallic coatings, Examples of non-metallic coatings- paints



# Mechanism of Wet Corrosion

- Corrosion by electrochemical mechanism
- Electronic current flows from anodic to cathodic areas



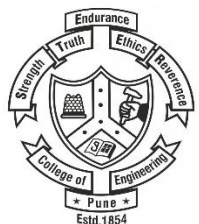
# Mechanism of Wet Corrosion

- Hydrogen evolution mechanism

- Occurs when metals are exposed to acidic environment
- Displacement of Hydrogen by Metals

- $M \rightleftharpoons M^{2+} + 2e^-$  At anode
- $\text{Acid} \rightleftharpoons H^+ + [\text{Conjugate Base}]^-$
- $2H^+ + 2e^- \rightarrow H_2 \uparrow$  At Cathode

- All metals above hydrogen in electrochemical series will dissolve in acidic medium with evolution of hydrogen gas
- Corrosion is of uniform type



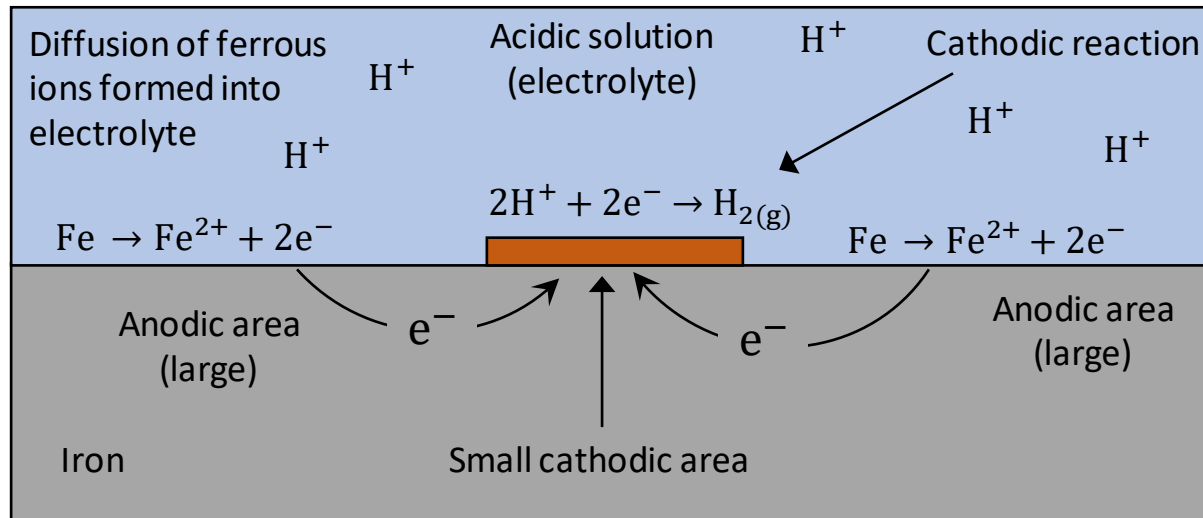


# Mechanism of Wet Corrosion

- Hydrogen evolution mechanism

E.g.: Industrial waste of acidic nature or small copper scrap is stored in steel tank

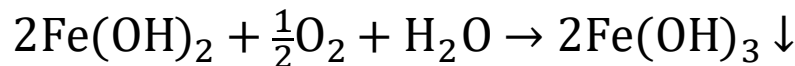
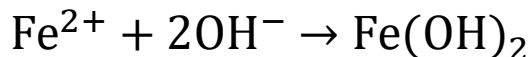
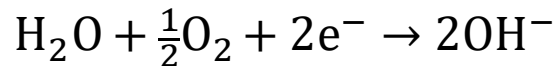
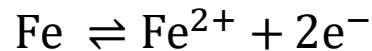
- Industrial waste or copper scrap become Cathodic (small area)
- Steel become anodic (large area) in acidic medium
  - $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$
  - $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$



# Mechanism of Wet Corrosion

- Oxygen Absorption mechanism

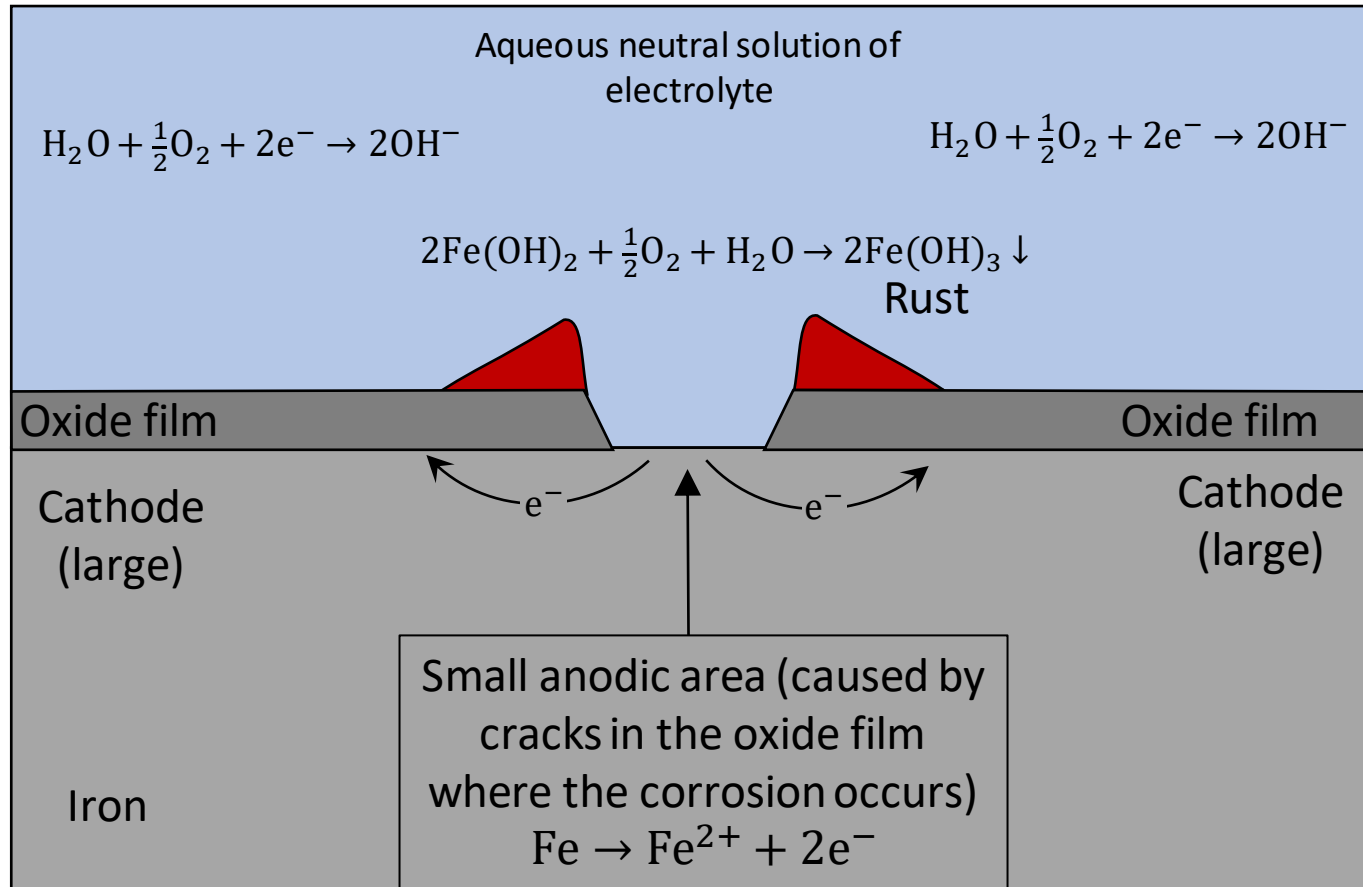
- Occurs when metals are exposed to natural or slightly **alkaline** environment containing oxygen
- **Oxygen adsorption** takes place at **cathode**
- Cathode is larger while anode is small area
- Localized corrosion only on the area exposed



**Rust**

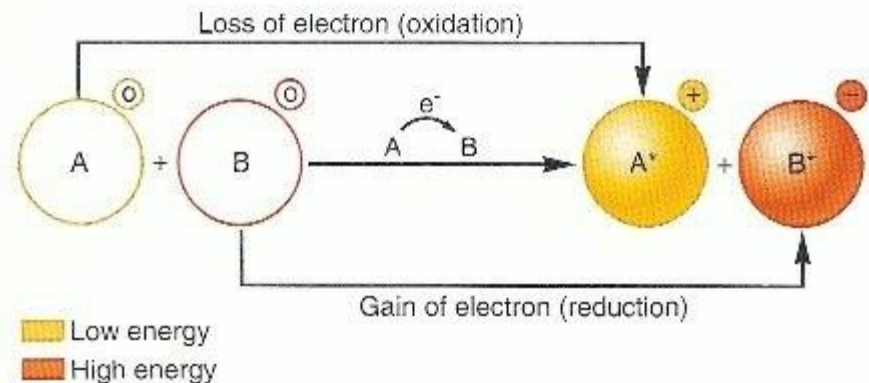
# Mechanism of Wet Corrosion

- Oxygen Absorption mechanism



# Wet or Electrochemical Corrosion

- Corrosion of metal by aqueous conducting medium
- With formation of anodic and cathodic areas
- Aqueous medium may be
  - Water
  - Aqueous medium
  - Sea water
  - Dew
  - Fog
  - High humidity



# Wet or Electrochemical Corrosion or Immersion corrosion

- **Anodic area:**

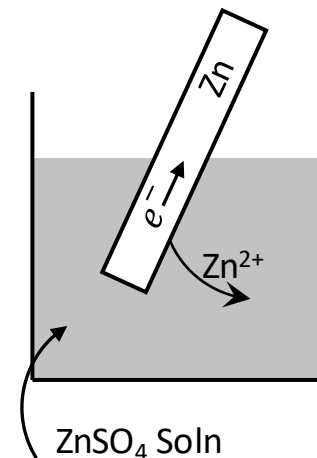
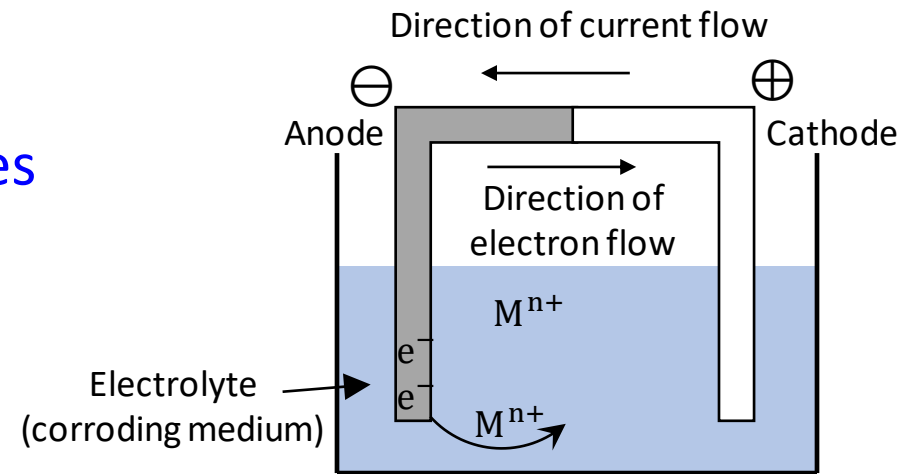
- dissolves, corrodes or oxidizes
- Metallic ions or cations
- Electrons are set free

- **Cathodic area:**

- Reduction takes place
- Anions are formed

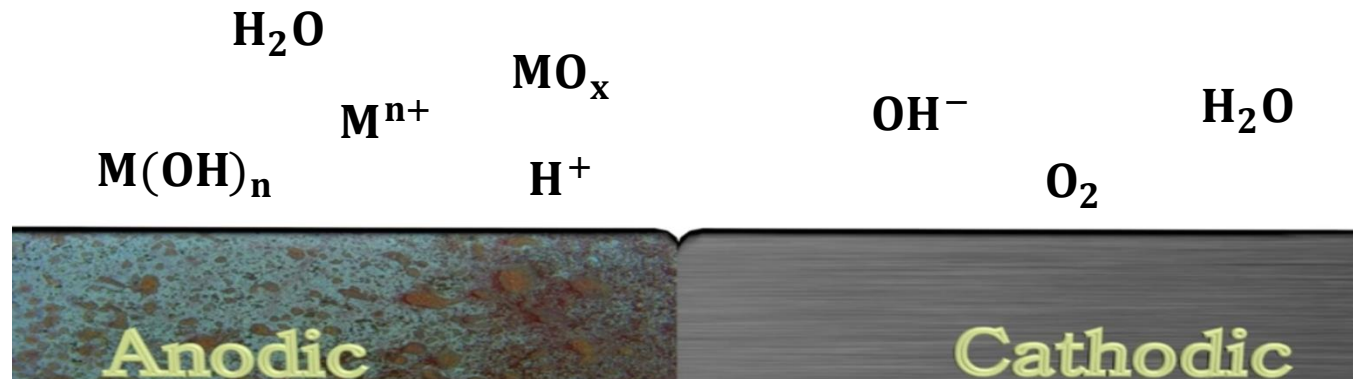
- **Rate of electrochemical corrosion depends on-**

1. Solubility of corrosion products
2. Location of corrosion products



# Galvanic Corrosion

- Corrosion of a metal by attack of aqueous conducting medium, **with formation of galvanic cell**
- Eg. Zn-Cu in direct contact
- Steel screws corrode in contact with brass in marine environment
- **Galvanic cell is formed when,**
  - Two dissimilar metals in contact
  - Stressed and unstressed parts on the same metal
  - Impurities in metal

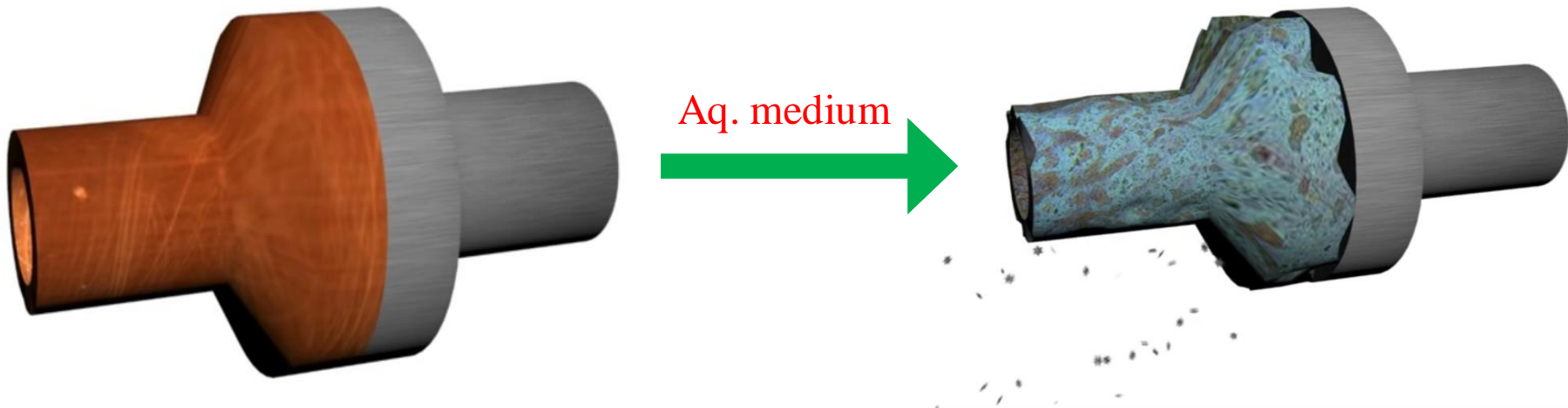




# Galvanic Corrosion

## ➤ Two Dissimilar Materials

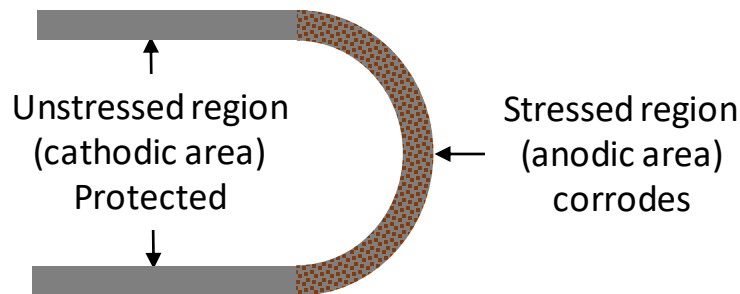
- Metals in contact along with aqueous conducting medium creates galvanic cell
- Metals or alloy higher placed in galvanic series acts as **anode** and get corroded.
- Other metal acts as **cathode** and does not get corroded



# Galvanic Corrosion

## ➤ Stressed and Unstressed Parts on the same metals

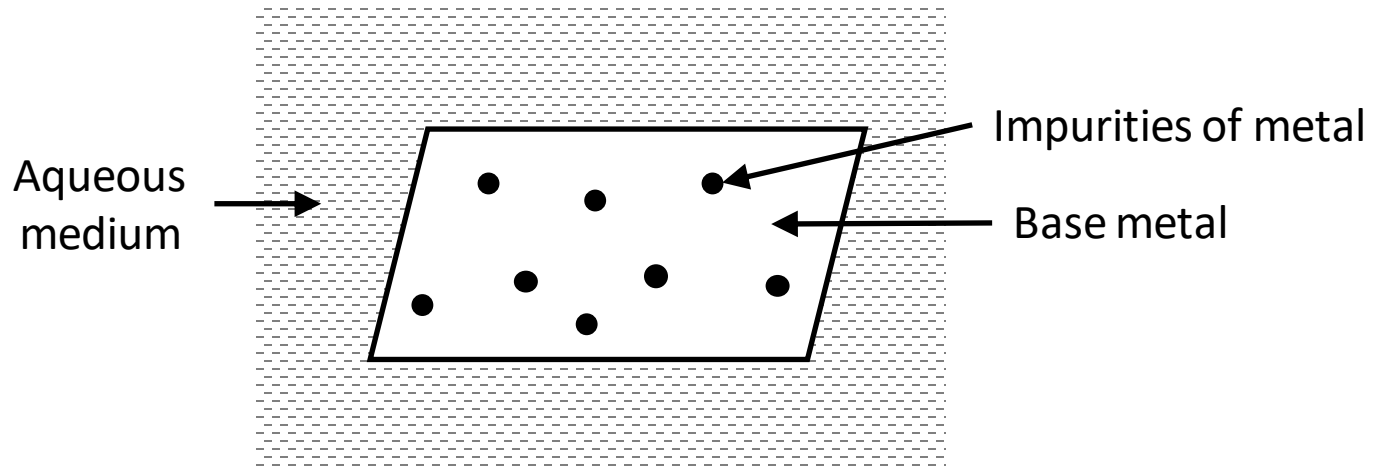
- Working on metal disturbs grain structure of metal
- Worked part is stressed (acts as **anode**)
- Unworked part is unstressed (acts as **cathode**)
- In aqueous conducting medium it acts as galvanic cell



# Galvanic Corrosion

## ➤ Impurities in metals

- Impure metal or improperly made alloy in aqueous medium
- Large number of tiny galvanic cells are formed on surface
- If impurity acts as anode, the small pits formation on surface

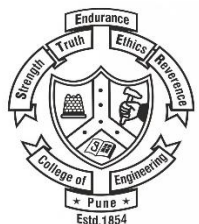


# Concentration Cell Corrosion

OR

## Differential aeration cell corrosion

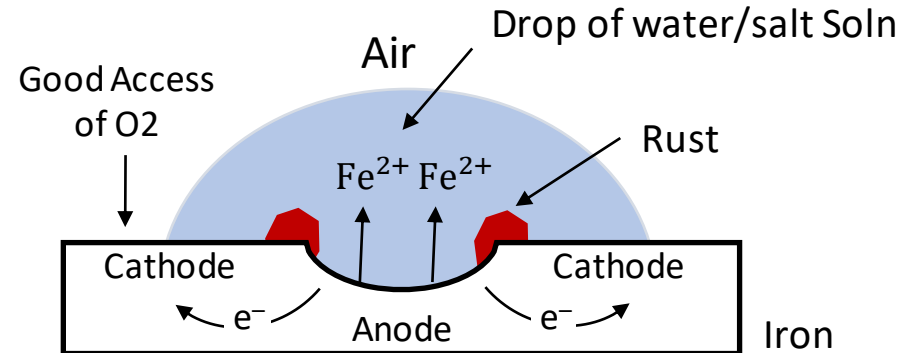
- Metal in contact with **higher concentration** or **more oxygen**
  - It acts as cathode
  - Do not gets corroded
- Metal in **lesser contact with oxygen** or **lower electrolyte**
  - Acts as anode
  - Gets corroded
- Formation of concentration cell only when aqueous conducting medium in contact of metal



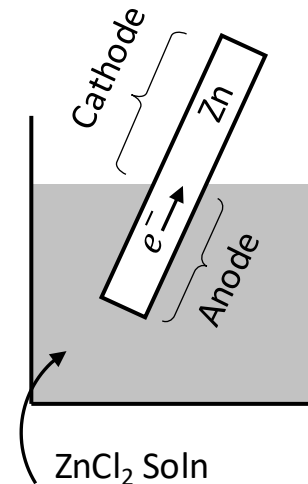
# Concentration Cell Corrosion

## Differential aeration

- One part of metal exposed to different air conc. builds potential diff.
- Low  $O_2 \rightarrow$  Anodic (Oxidation)
- High  $O_2 \rightarrow$  Cathodic (Reduction)



- $Zn \rightarrow Zn^{2+} + 2e^-$
- $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow OH^-$

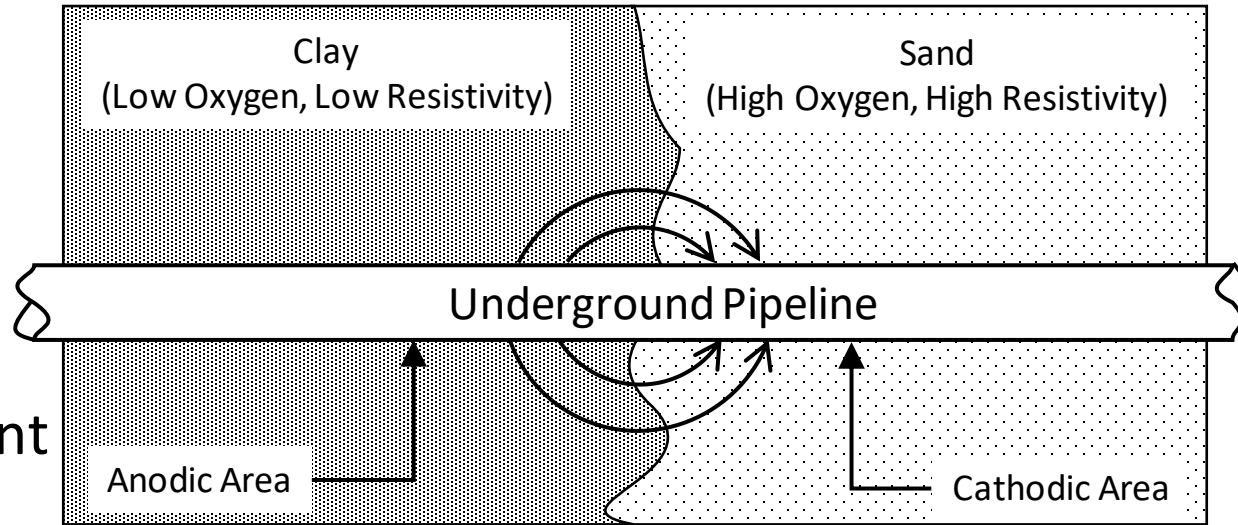


# Miscellaneous corrosion

## Soil Corrosion

### Factors affecting soil corrosion

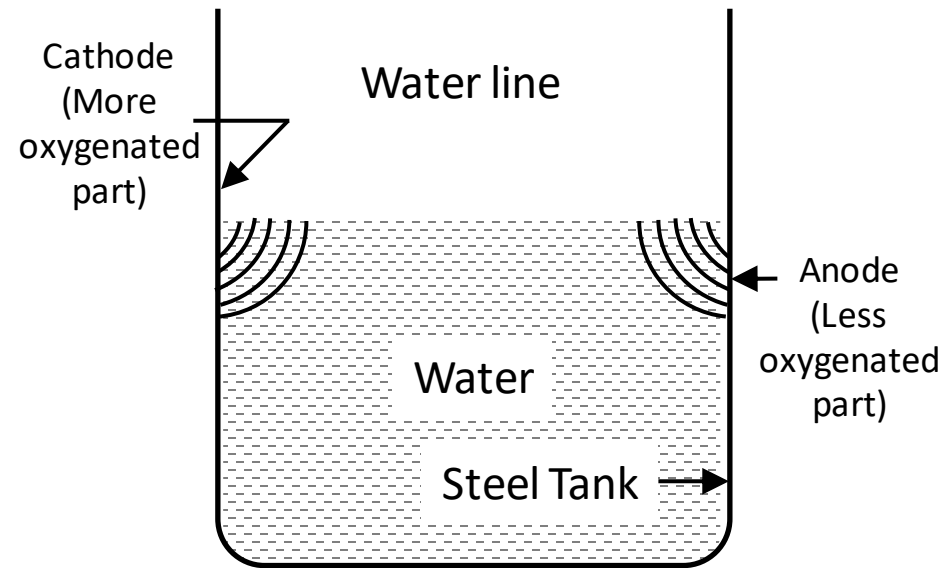
1. Aeration
2. Water retention
3. Dissolved Salt Content
4. Soil Resistivity
5. Soil Acidity
6. Presence of Ionic Species





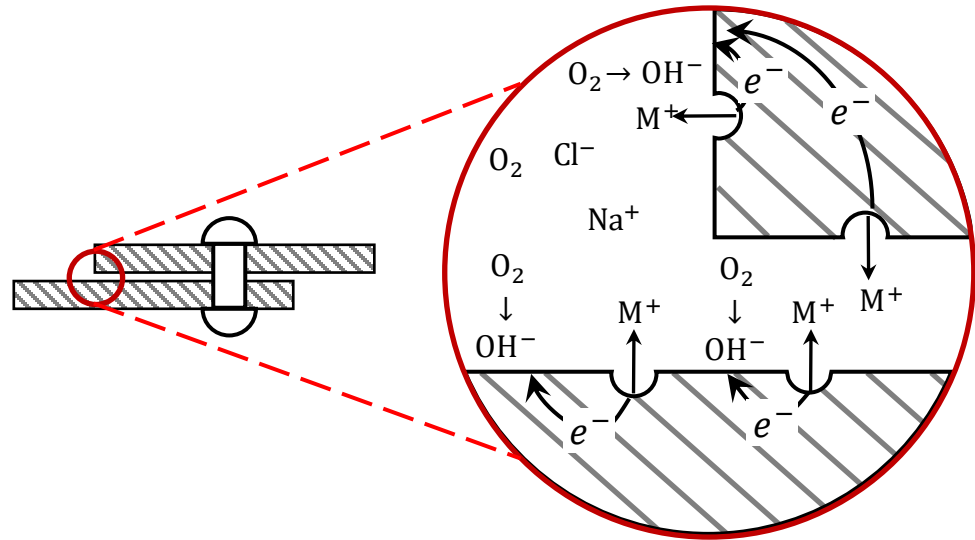
# Miscellaneous Corrosion

## Waterline Corrosion



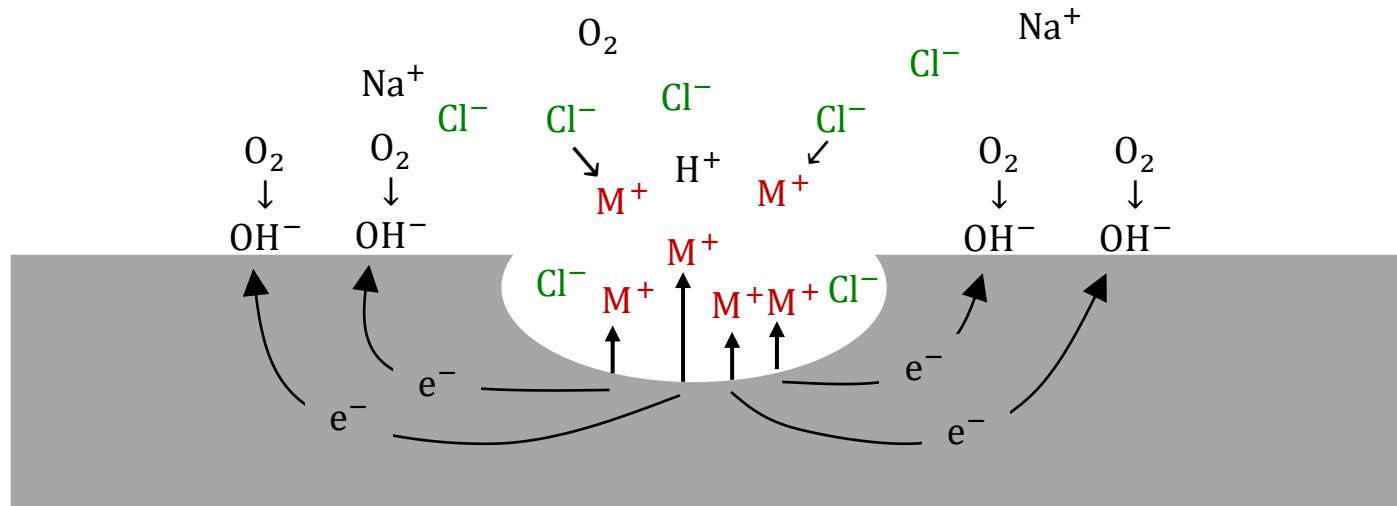
# Crevice Corrosion

- When two pieces of metals are not fitted properly, resulting into small gap between them
- Metallic surface in gap is poorly oxygenated and gets corroded



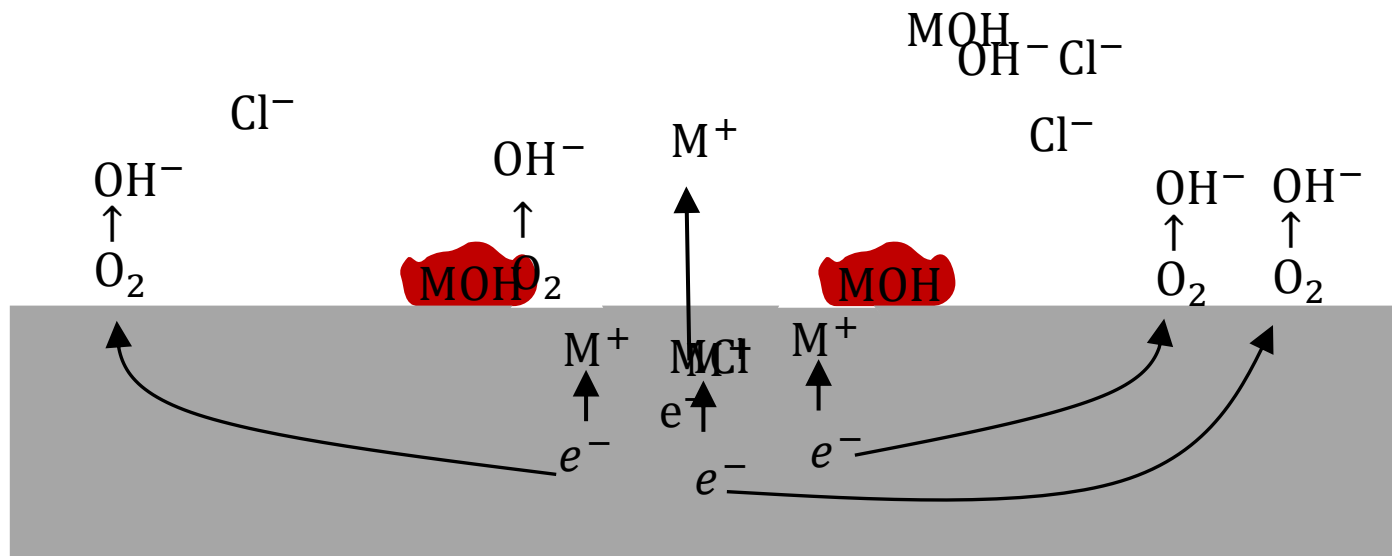
# Pitting Corrosion

- Corrosion is extremely localized
- Cavities or holes in metal
- Pitting may penetrate deep into metal
- Very destructive and can ruin metal
- Pits usually grow in the direction of gravity
- Corrosion pit is a type of autocatalytic process



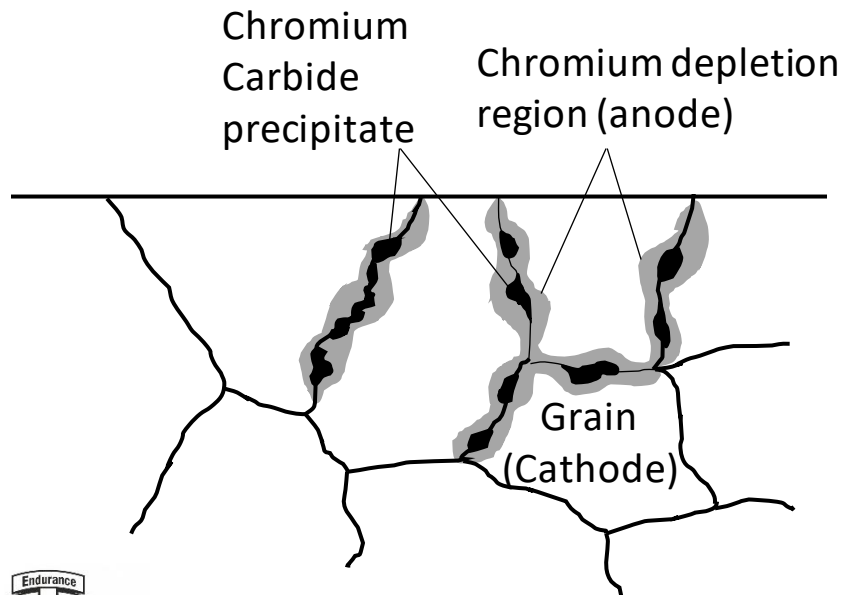
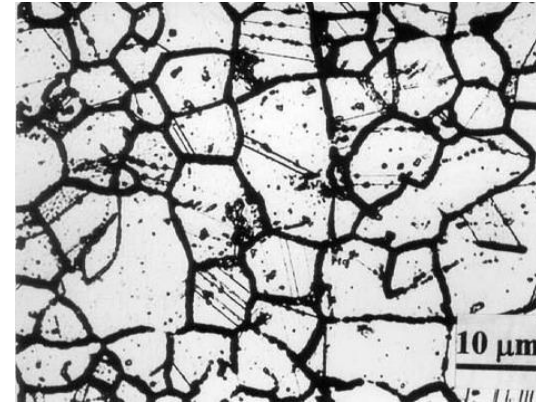
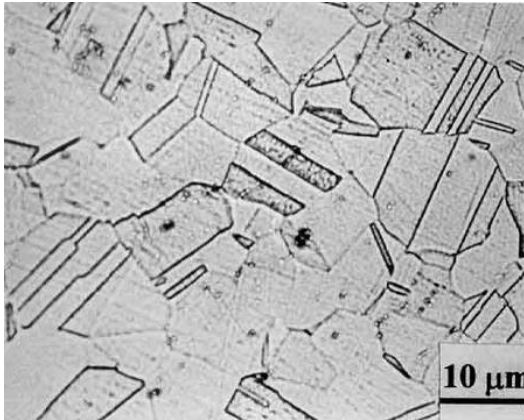
# Pitting Corrosion

1. Dissolution of Metal
2. Reduction of  $O_2$  to  $OH^-$
3. Formation of corrosion product near the “pit”
4. Further dissolution of Metal leading to charge concentration in the “pit”
5. Reduction of  $O_2$  away from pit its access cut by accumulation of corrosion product
6. Transport of  $Cl^-$  to the pit and formation of Metal chloride (soluble)
7.  $MCl$  moves out and reacts with  $OH^-$  to form corrosion product



# Intergranular Corrosion

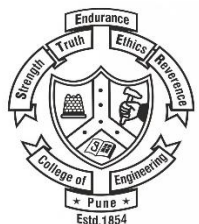
- Only in alloy



- Due to improper cooling certain compounds precipitate at the grain boundaries
- Precipitated compounds act as cathode
- Grain boundaries act as anode

# Passivity or Passivation

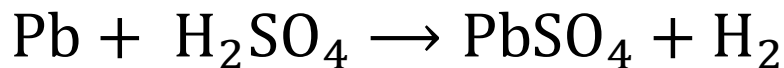
- Phenomenon in which metal exhibits outstanding higher corrosion resistance than its position in electrochemical or galvanic series
- It is due to formation of highly protective but very thin film
- Ti, Al, Cr and stainless steel containing Cr are passive in oxidising environment
- They become chemically active in reducing environment
- In absence of oxygen passive metal becomes chemically active and corrodes
- Passivation applies to certain environmental conditions which can maintain protective oxide film.
- Passivation is not static state but dynamic



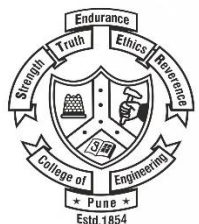


# Pseudopassivity

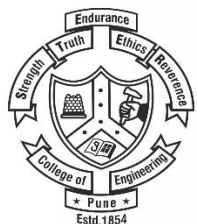
- Physical isolation of metal from corroded environment
- Deposition of thick protective reaction product films on metal
- E.g.: Lead sulphate film on lead in sulphuric acid



- Anodic polarisation can be used for achieving Pseudopassivity in metal
- E.g.: Al, Fe when treated with concentrated nitric acid produce protective oxide film
- However, in dilute nitric acid rapid corrosion occurs because dilute nitric acid stimulates Cathodic reaction



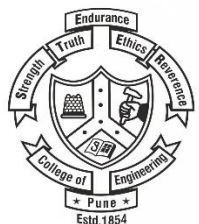
Sr No and Name of the Unit	Topic Description
<b>Unit 1</b> <b>(A) Material Chemistry</b>  <b>(B) Corrosion and corrosion control</b>	Introduction to the basics of chemistry, Relevance of Chemistry to different Engineering specializations
	Classification & Properties of Materials: Metals and alloys, ceramics and glasses, refractories, Cement, polymers, composites
	Nanomaterials: definition, types, properties and applications
	Electrochemistry of corrosion, Mechanism of dry corrosion
	Mechanism of wet corrosion
	<b>Factors affecting corrosion, Testing of corrosion: Weight-loss and weight-gain method, Microscopic exam</b>
	Methods of corrosion prevention, Cathodic protection- Sacrificial anode
	Cathodic protection- Impressed current, Anodic protection
	Protective coatings- examples of Metallic coatings, Examples of non-metallic coatings- paints



# Factors affecting corrosion rate

1. Nature of metal

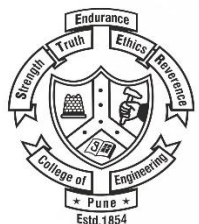
2. Nature of environment



# Factors affecting corrosion rate

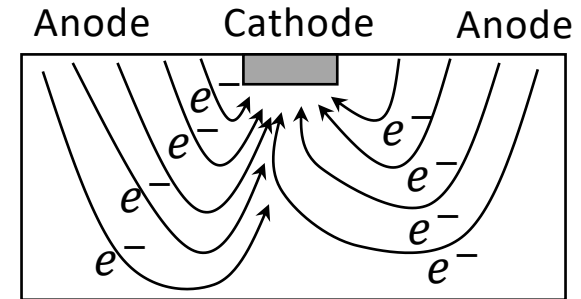
## Nature of metal

- **Position of metal in Galvanic Series**
  - According to Nernst, all metals pass into solution in the form of ions
  - But they do not corrode at same rate under similar environmental conditions
  - If metals are more apart in galvanic series then corrosion will be faster of anodic metal and more current is generated during corrosion



# Factors affecting corrosion rate

## Nature of metal



- Relative area of cathode and anode
  - If cathodic and anodic areas are equal then corrosion is not accelerated
  - If cathodic area is larger than anodic area then corrosion at anode is much larger
  - Better design is by use of two metals is one in which anodic area is larger than cathodic area

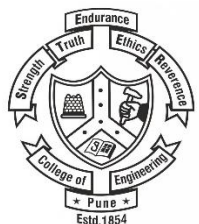
# Factors affecting corrosion rate

## Nature of metal

- Purity of metals

- Due to impurities, tiny galvanic cells are formed when there is conducting medium

Zn purity %	Relative corrosion rate
99.999	1
99.99	2650
99.95	5000



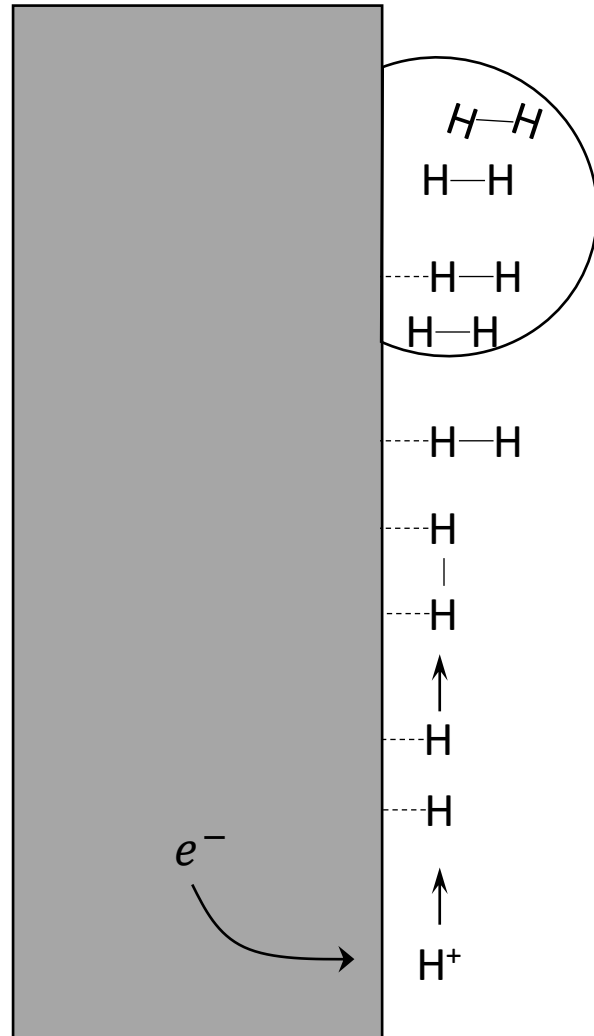
# Factors affecting corrosion rate

## Nature of metal

- Nature of protective films
  - If oxide film is protective, nonporous, strongly adhered then metal is resistant to corrosion
  - But if the film is porous, loosely adhered then corrosion of metal take place



# Factors affecting corrosion rate



## Nature of metal

- **Hydrogen overvoltage or overpotential**
  - Metal having higher position in EMF series than hydrogen, the corrosion of metal in acidic medium liberates hydrogen gas
  - Tiny bubbles of hydrogen gas adhere to the metal surface and the acidic solution is not in well contact of metal
  - Such metal develops corrosion resistance to some extent or metal behaves as if it is in lesser place than its actual position in EMF series
  - To restore position extra voltage is necessary. This extra voltage is known as overvoltage
  - Zn, Pb, Cr, Ni

# Factors affecting corrosion rate

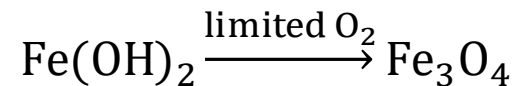
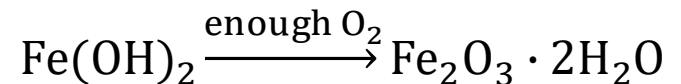
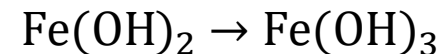
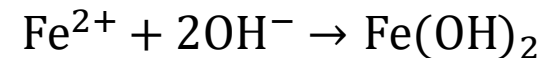
## Nature of environment

- Temperature

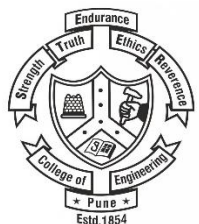
Temperature increases, Corrosion Increases

- Presence of moisture

- Atmospheric corrosion of few metals is slow in dry air
- Moisture provides solvent for  $O_2$  and other gases
- Moisture provides electrolyte for setting corrosion cell
- Moisture may also react with metals and metal oxides



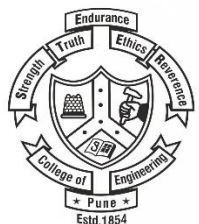
Magnetite  
(Adhering)



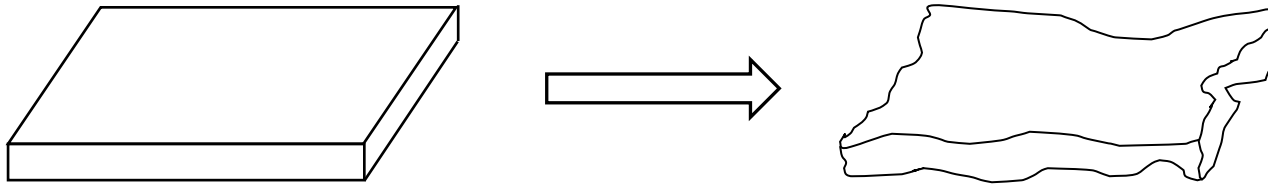
# Factors affecting corrosion rate

## Nature of environment

- Conductance of medium
  - Conductance Increases Corrosion
  - Stray current
- Nature of electrolyte
  - Nature of electrolyte changes Electrode potential  
Eg. Crevice corrosion more when  $[Cl^-]$  more
- Effect of pH
  - Acidic environment more corrosive than Alkaline
  - Many metals are resistant alkalis



# Testing of Corrosion



## How to measure corrosion ??

Length

Breadth

Thickness

Volume

Mass/Weight

Not sensitive  
enough

- Weigh Before/After (fraction of mg in few mg)
- Weight loss has to be scaled to the size of the specimen
- Corrosion is a surface phenomenon, Weight loss is related to surface area

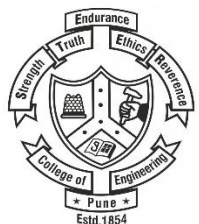
# Testing of Corrosion

**Example:** A metal coupon having a total surface area of  $10 \text{ cm}^2$  loses  $1 \text{ mg}$  when exposed to a particular environment for a month

What is the total corrosion suffered by the metal coupon?

What is the rate of corrosion units of per month and per day? Which unit is more appropriate for measuring corrosion?

If  $\rho$  is the density of the metal calculate the rate of corrosion in terms of  $\rho$  in the units,  $\mu\text{m}/\text{day}$  and  $\mu\text{m}/\text{year}$ ?



# Testing of Corrosion

**Example:** A metal coupon having a total surface area of  $10 \text{ cm}^2$  loses  $1 \text{ mg}$  when exposed to a particular environment for a month

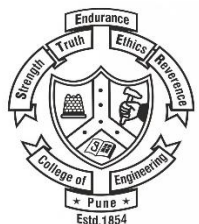
What is the total corrosion suffered by the metal coupon?

$$\text{total corrosion} = \frac{\Delta W}{A} \frac{\text{mg}}{\text{cm}^2} = \frac{1}{10} \frac{\text{mg}}{\text{cm}^2}$$

(Weight loss is related to Surface Area as corrosion is a surface phenomena)

What is the rate of corrosion units of per month and per day? Which unit is more appropriate for measuring corrosion?

$$\begin{aligned} \text{rate of corrosion} &= \frac{1}{10} \frac{\text{mg}}{\text{cm}^2 \text{ month}} = \frac{1}{10} \frac{\text{mg}}{\text{cm}^2 (30 \text{ or } 31 \text{ days?})} && \text{(Per day is a better unit)} \\ &= \frac{1}{10} \frac{\text{mg}}{(0.1 \text{ dm})^2 \text{ month}} = \frac{100}{10} \frac{\text{mg}}{\text{dm}^2 \text{ month}} && \text{("mdm" and "mdd")} \end{aligned}$$



# Testing of Corrosion

If  $\rho$  is the density of the metal calculate the rate of corrosion in terms of  $\rho$  in the units,  $\mu\text{m}/\text{day}$  and  $\mu\text{m}/\text{year}$ ?

$$\begin{aligned}\text{rate of corrosion} &= \frac{\Delta W}{A\rho} = \frac{1}{10 \text{ cm}^2 \text{ month}} \frac{\text{mg}}{\rho \text{ gm}} \frac{1 \text{ cm}^3}{\text{gm}} = \frac{1}{10^4 \text{ month}} \frac{\text{cm}}{\text{gm}} = \frac{1}{10^4 \text{ month}} \frac{10^4 \mu\text{m}}{\text{gm}} \\ &= 1 \frac{\mu\text{m}}{\text{month}}\end{aligned}$$

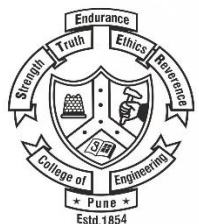
This gives us “penetration” or “depth” of corrosion

$$\text{Rate of corrosion} = \frac{\Delta W}{At}$$

OR

$$\text{Rate of corrosion} = \frac{\Delta W}{A\rho t}$$

Corrosion penetration rate





# Testing of Corrosion

## Weight loss method

$$\text{Rate of corrosion} = \frac{K\Delta W}{A\rho t}$$

cm day<sup>-1</sup>  
cm year<sup>-1</sup>  
μm day<sup>-1</sup>  
m day<sup>-1</sup>

K = conversion factor

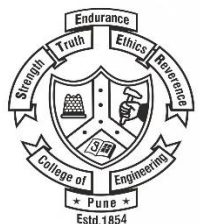
ΔW= grams

Density(ρ)=gm/cm<sup>3</sup>

Time(t)= hour

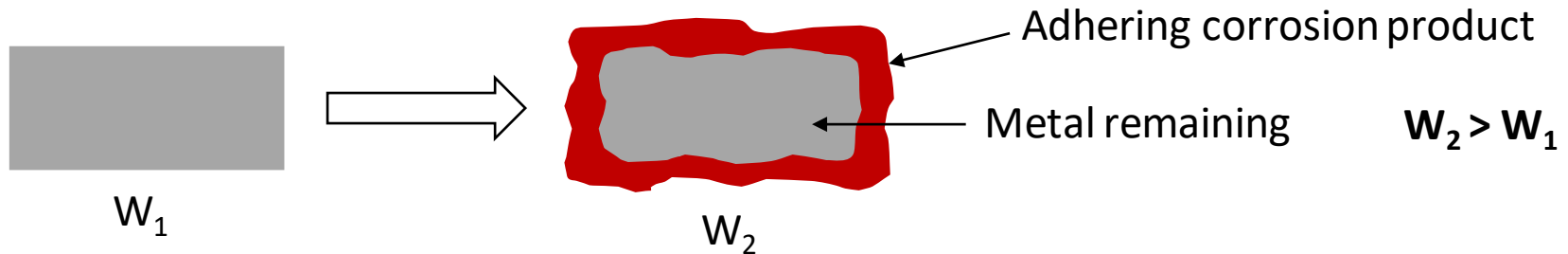
Desired Corrosion rate unit	Area Unit (A)	K-factor
mils/year (mpy)	in <sup>2</sup>	5.34 x 10 <sup>5</sup>
mils/year (mpy)	cm <sup>2</sup>	3.45 x 10 <sup>6</sup>
millimeters/year (mmpy)	cm <sup>2</sup>	8.75 x 10 <sup>4</sup>

mil = 10<sup>-3</sup> inches

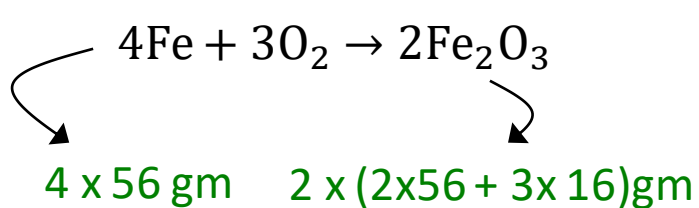


# Testing of Corrosion

**Weight gain method:** What if material gains weight due to corrosion?

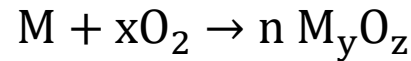


Scaled (eg., oxidized) specimens often experience weight gain after corrosion



If we know exact composition (eg., type of oxide) and weight gain we can calculate metal in oxide and thus metal corroded

# Testing of Corrosion



Weight of Oxide formed =  $W_2 - W_1$

moles of Oxide formed =  $(W_2 - W_1)/M_{\text{oxide}}$

1 mole of oxide is formed by  $1/n$  moles of Metal. Therefore,

$$\text{Moles of metal corroded} = \frac{1}{n} \frac{(W_2 - W_1)}{M_{\text{oxide}}}$$

$$\text{Weight of metal corroded} = M_{\text{metal}} \frac{(W_2 - W_1)}{n \cdot M_{\text{oxide}}}$$

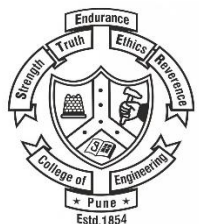
$$\text{Rate of corrosion} = \frac{M_{\text{metal}}(W_2 - W_1)}{n \cdot M_{\text{oxide}} \cdot A \cdot t \cdot \rho_{\text{metal}}}$$

Mol. Wt. of metal =  $M_{\text{metal}}$

Mol. Wt. of Oxide =  $M_{\text{oxide}}$

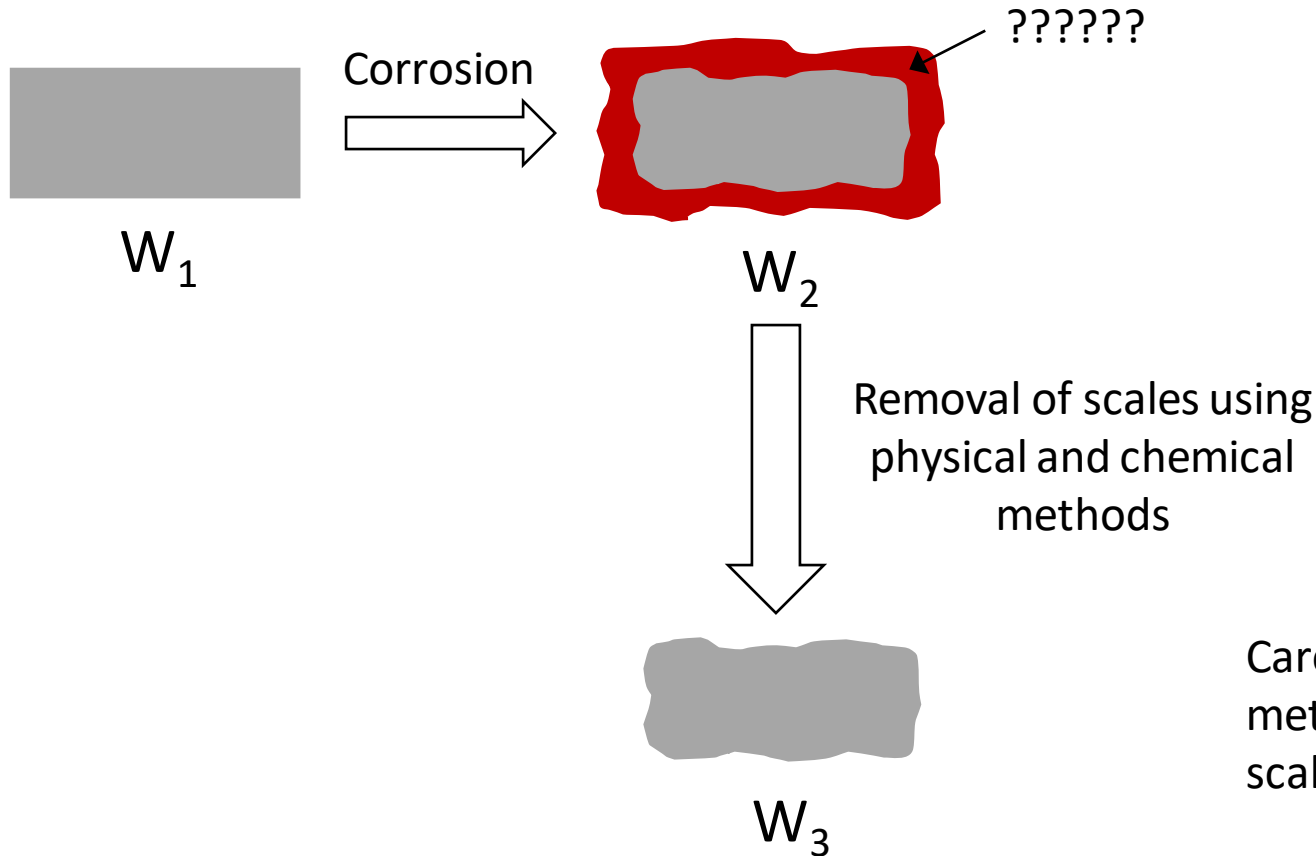
Initial weight of specimen =  $W_1$

Final weight of specimen =  $W_2$



# Testing of Corrosion

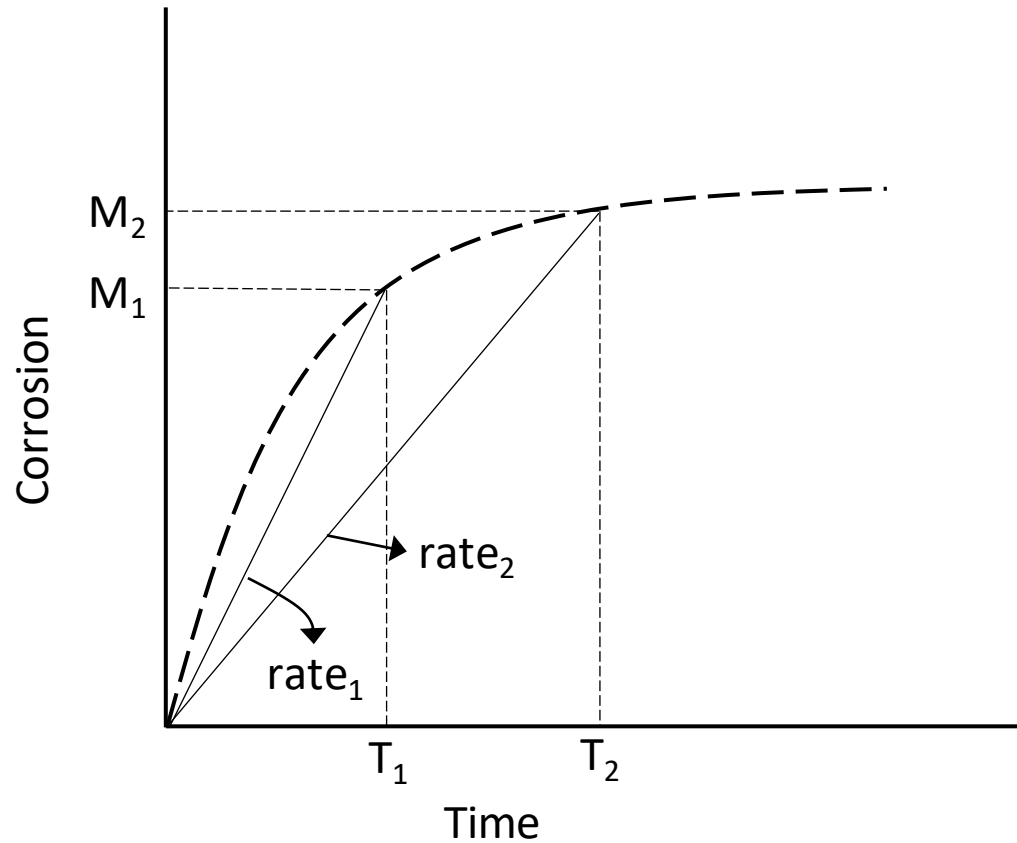
What if we do not know the exact nature of Oxide??



Care should be taken that metal underneath the scales is not affected

$$\Delta W = W_3 - W_1$$

# Testing of Corrosion



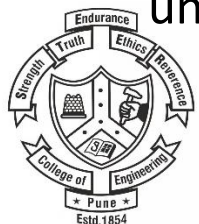
# Testing of Corrosion

## Advantages of weight loss/gain method

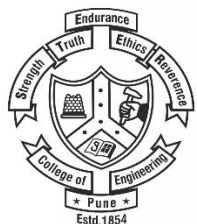
- Sample exposures are simple and usually of low cost
- Applicable for all environments like gas, liquid and solids
- Visual inspection and corrosion can be identified and measured
- Localized corrosion can be identified and measured
- Inhibitor performance can be easily assessed

## Disadvantages of weight loss/gain method

- Long exposure periods may be required in some cases
- Determines only average rate of corrosion
- Cannot detect rapid changes in the corrosivity
- Reuse of used sample is not recommended
- Processes for determining weight loss can be labour intensive in some cases
- Can be misleading in cases where rate of corrosion varies with time due to unrealized process factors



Sr No and Name of the Unit	Topic Description
<b>Unit 1</b> <b>(A) Material Chemistry</b>  <b>(B) Corrosion and corrosion control</b>	Introduction to the basics of chemistry, Relevance of Chemistry to different Engineering specializations
	Classification & Properties of Materials: Metals and alloys, ceramics and glasses, refractories, Cement, polymers, composites
	Nanomaterials: definition, types, properties and applications
	Electrochemistry of corrosion, Mechanism of dry corrosion
	Mechanism of wet corrosion
	Factors affecting corrosion, Testing of corrosion: Weight-loss and weight-gain method, Microscopic exam
	Methods of corrosion prevention, Cathodic protection- Sacrificial anode
	Cathodic protection- Impressed current, Anodic protection
	Protective coatings- examples of Metallic coatings, Examples of non-metallic coatings- paints





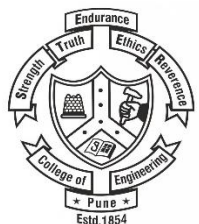
# Methods to Control Corrosion

## Choose the material carefully

- Use of corrosion resistant material (plastic, stainless alloys, fiberglass)
- Usage of Pure metals
- If pure metal cannot be used use a alloys with least impurities
- Avoid contact of dissimilar metals
- If contact of dissimilar metals cannot be avoided use metals close to each other in Galvanic series

## Making environment less corrosive

- Utilizing homogeneous **high resistivity backfill** or inhibitors
- **Deaeration** to remove gases like  $O_2$ ,  $CO_2$  etc.
- **Dehumidification**
- **Alkaline neutralization** by adding bases like  $NH_3$ ,  $NaOH$  etc.
- **Deactivation** by adding chemicals to  $O_2$  or other gases



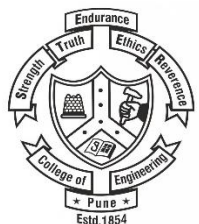
# Methods to Control Corrosion

## Protecting the material

- Utilize coatings and linings that electrically insulate the structure from the electrolyte (paints, plastic films, etc)
- Use of Cathodic and Anodic Protection

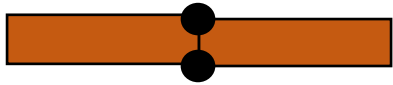
## Proper Design

- Joints should be welded with same metal/alloy
- Avoid use of rivets and bolts to avoid formation of crevice
- Design should minimize moisture retention (avoid sharp corners & prefer design which can be completely drained)
- Prefer design which allow free circulation of air



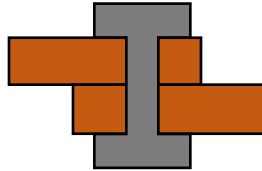
# Methods to Control Corrosion

A



Best Design

B



Poor Design

C

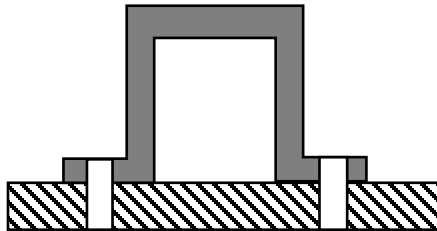


Good Design

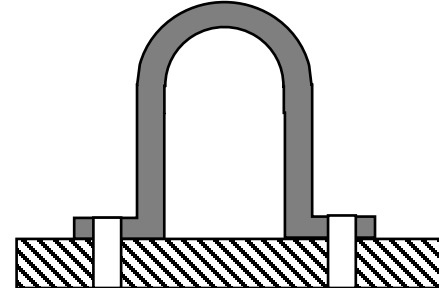
D



Best Design

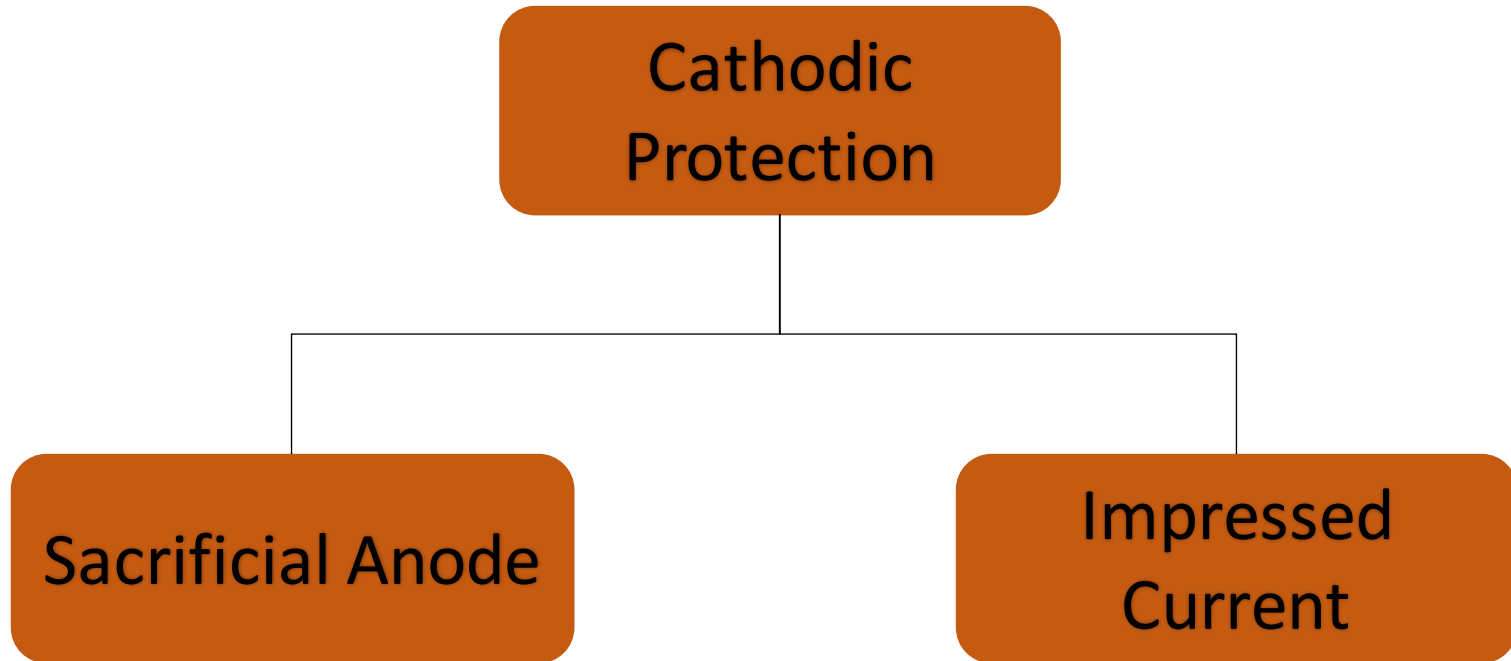


Poor Design



Good Design

# Corrosion control



# Corrosion Control

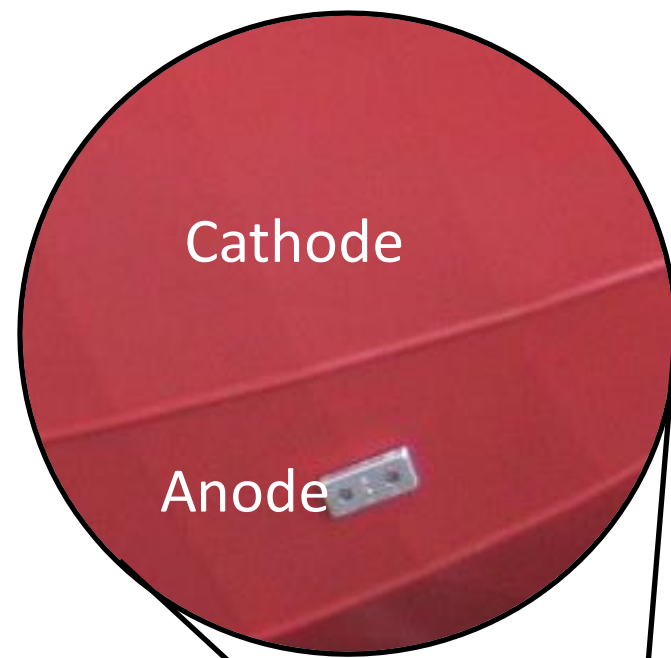
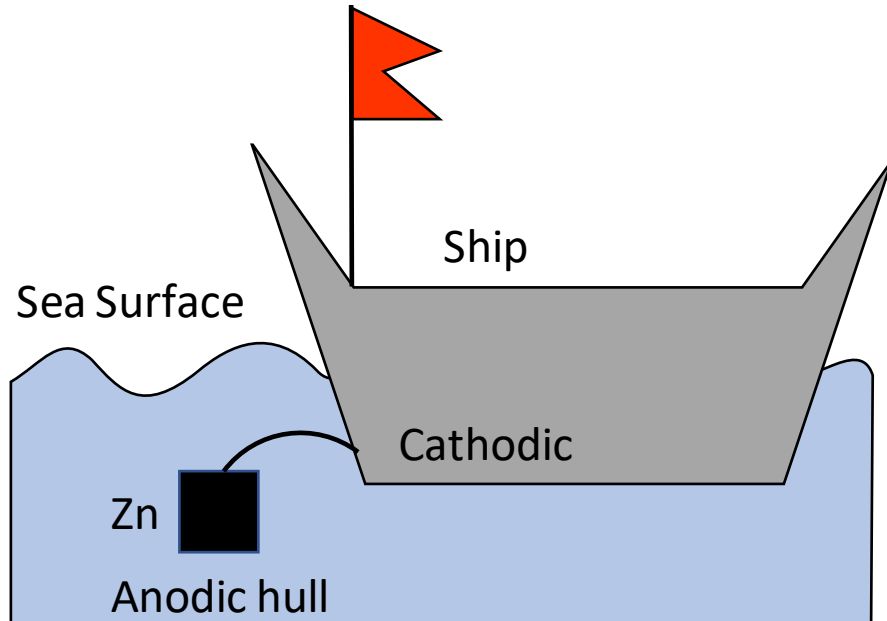
## Cathodic Protection (Sacrificial Anode)

- Science of cathodic protection was born in 1824 when Sir Humphry Davy represented his work at Royal Society of London
- Topic of his representation was rapid decay of copper sheeting on ships of war due to sea water
- He controlled such corrosion using iron anode
- Thus cathodic protection is applicable for,
  - Marine and underground structures
  - Water storage tanks
  - Gas pipelines
  - Oil platforms supports
  - Other facilities exposed to corrosive environment



# Corrosion Control

## Cathodic Protection (Sacrificial Anode)



[https://www.youtube.com/watch?v=jQoE\\_9x37mQ](https://www.youtube.com/watch?v=jQoE_9x37mQ)



# Corrosion Control

## Cathodic Protection (Sacrificial Anode)

Protection of a metal from corrosion under water by making it act as an cathode



Saline water

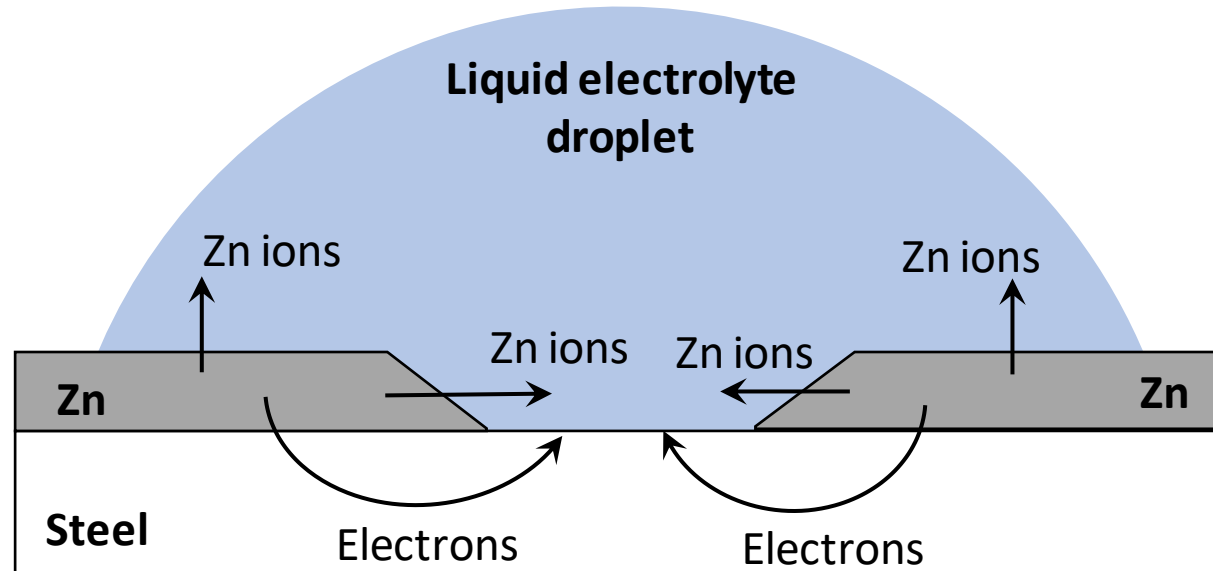




# Corrosion Control

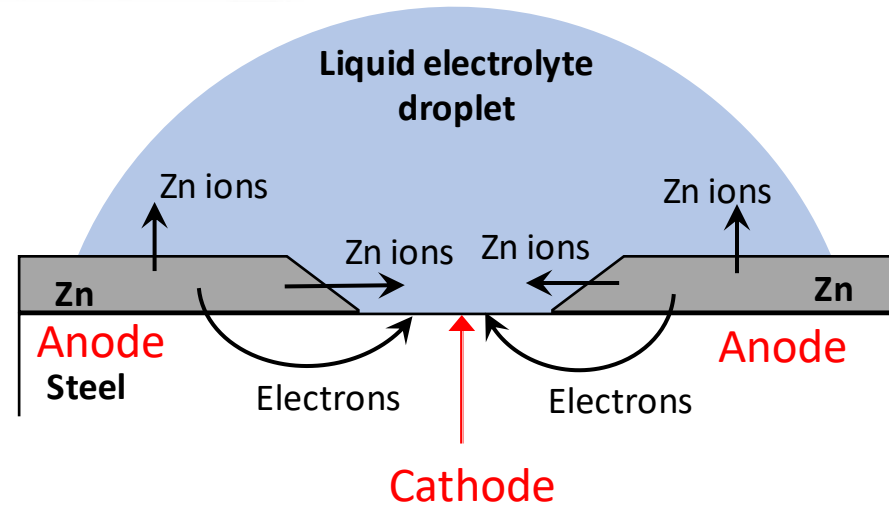
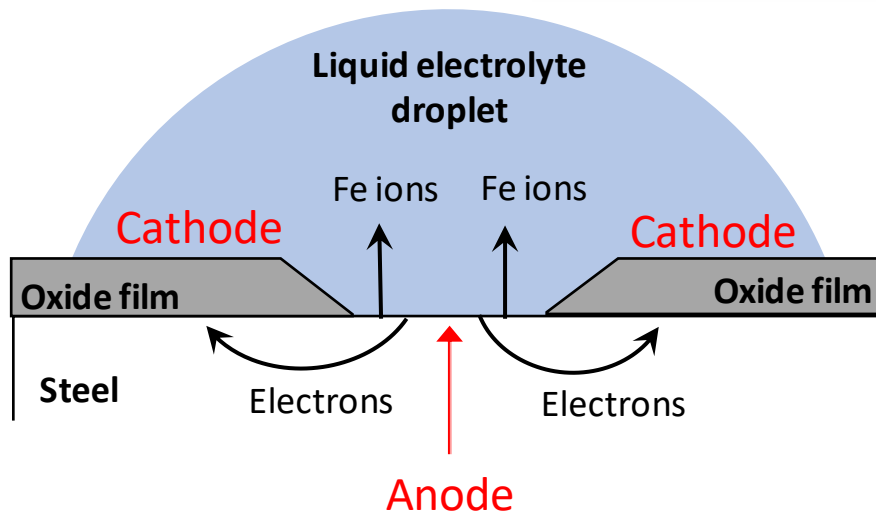
## Cathodic Protection (Sacrificial Anode)

- Can also be termed as **Galvanic Cathode Protection**
- When metals such as magnesium or zinc are placed in the environment in contact with a more noble metal such as steel, a current flows from the more active anode to the noble cathode (corrosion cell).



# Corrosion Control

## Cathodic Protection (Sacrificial Anode)

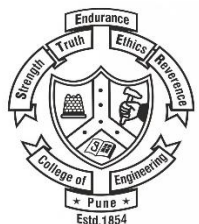


# Corrosion Control

## A) Sacrificial Anode Cathodic Protection (SACP)

### Conditions

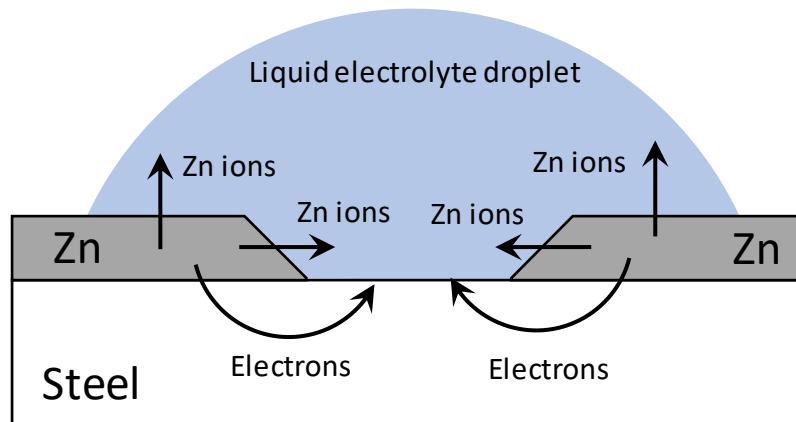
- Typically work best with electrically isolated structures.
- No external power source, limited driving potential (driving potential based on the galvanic series)
- Limited output makes it ineffective when trying to protect large uncoated surfaces.
- Require a low resistivity electrolyte to function well.



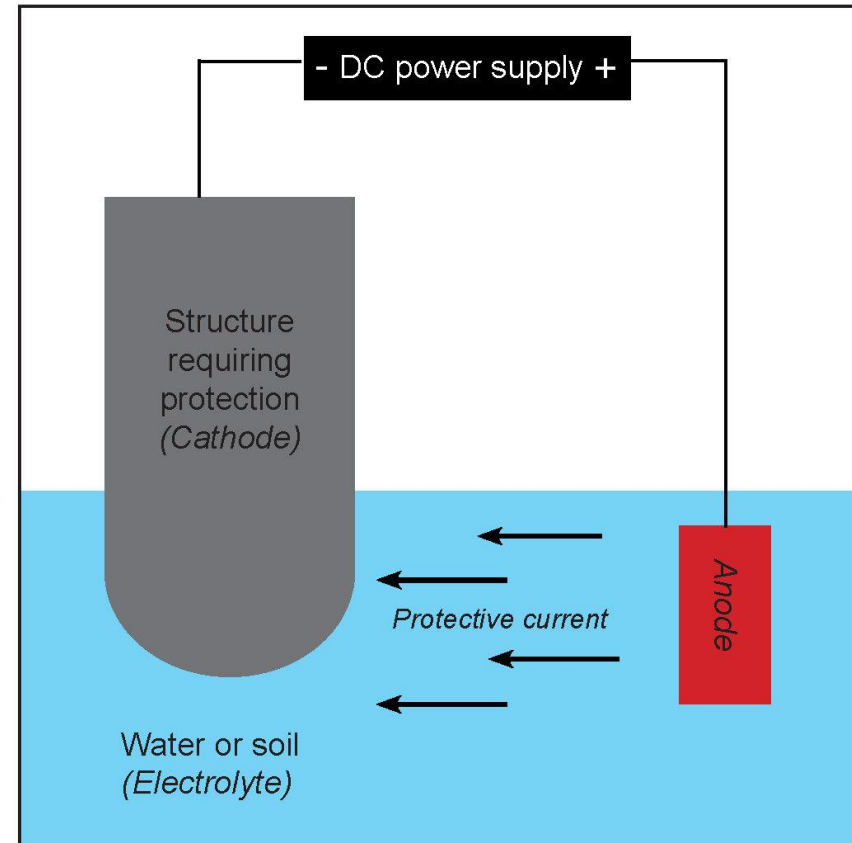
# Corrosion Control

## Cathodic Protection

Protection of the metal to be protected to a more easily corroded "sacrificial metal" to act as the anode.



Galvanic Cell Protection

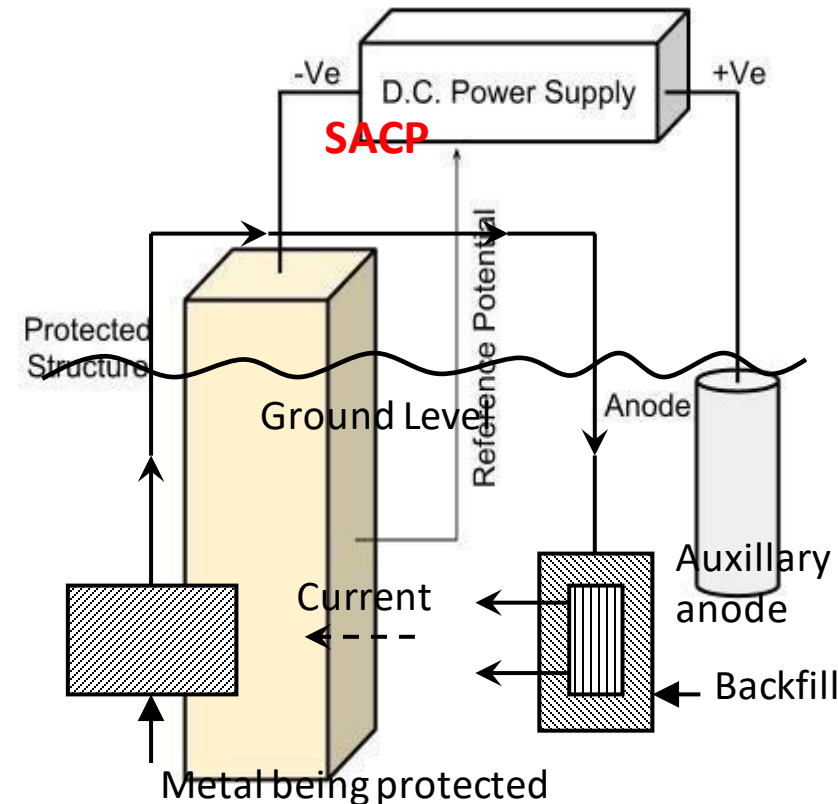
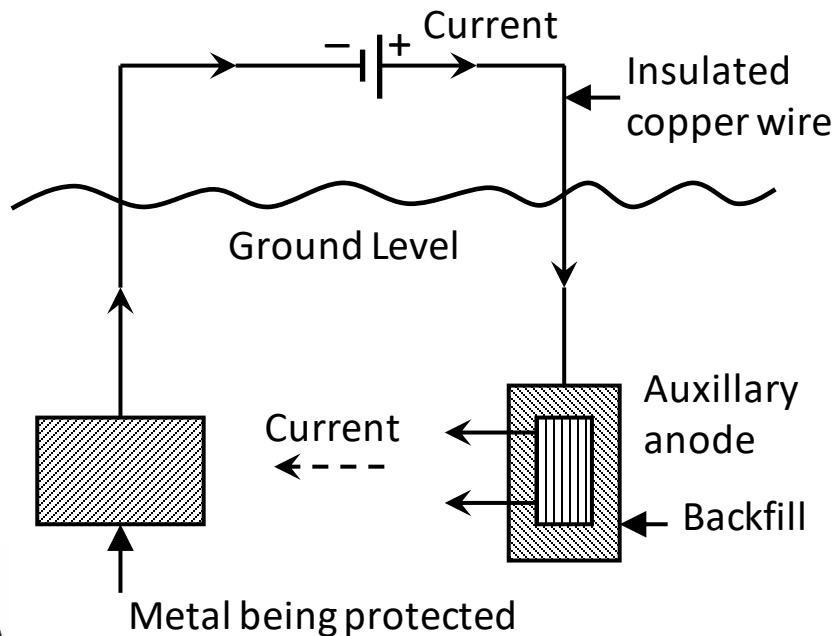


Impressed Current Protection

# Corrosion Control

## B) Impressed Current Cathodic Protection

- Utilize an external power source to develop a high potential difference between the surface to be protected and an anode.



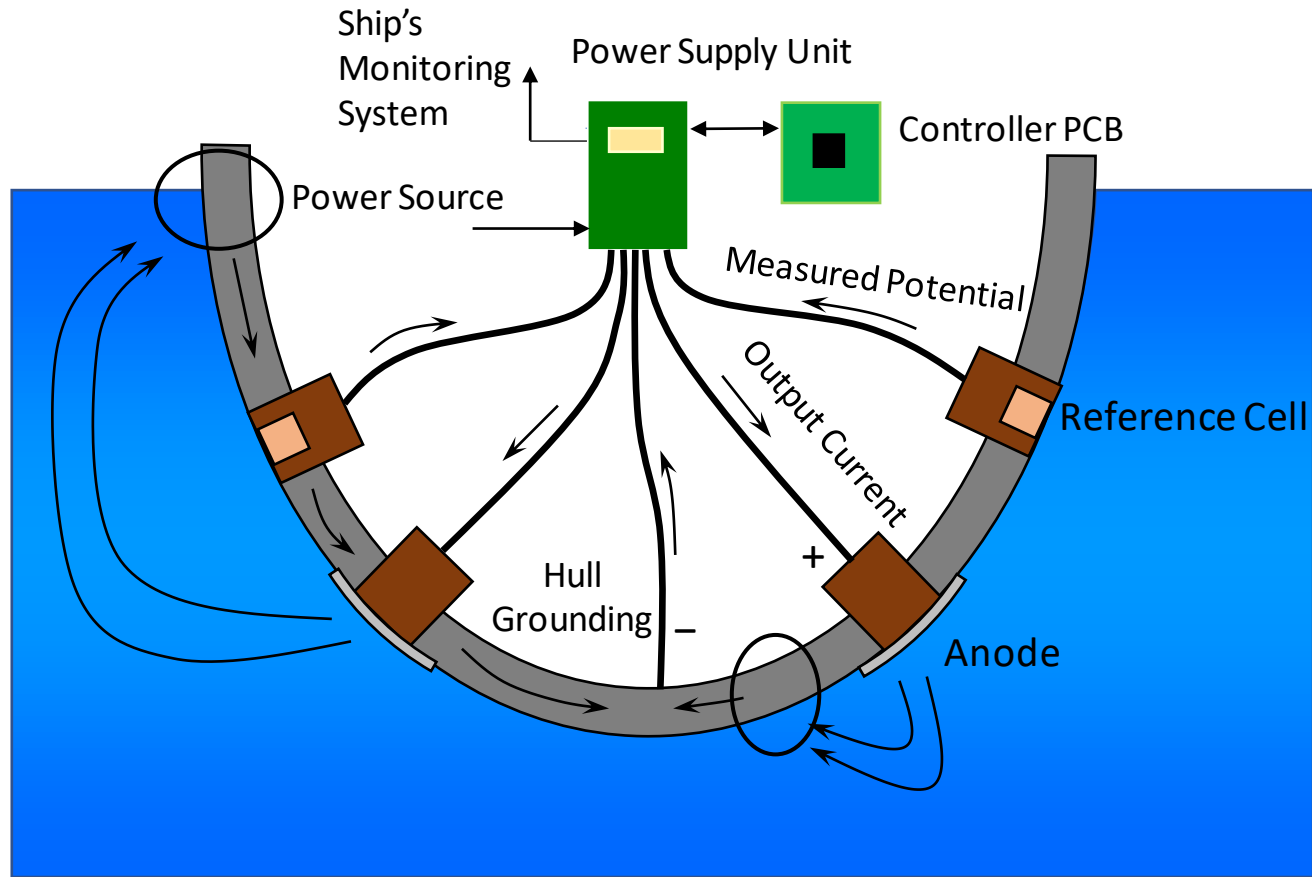
# Corrosion Control

## B) Impressed Current CP: Commercialization



# Corrosion Control

## B) Impressed Current Cathodic Protection





# Corrosion Control

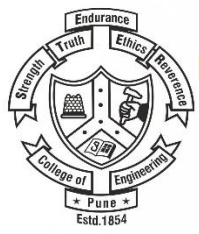
## Impressed Current CP: Pros & Cons

### Pros

- Unlimited driving potential.
- Capable of protecting large steel structures when designed properly.
- Requires less anodes than a galvanic system.
- Output can be controlled using a permanent reference electrode, desirable when the electrolyte resistivity is known to change.

### Cons

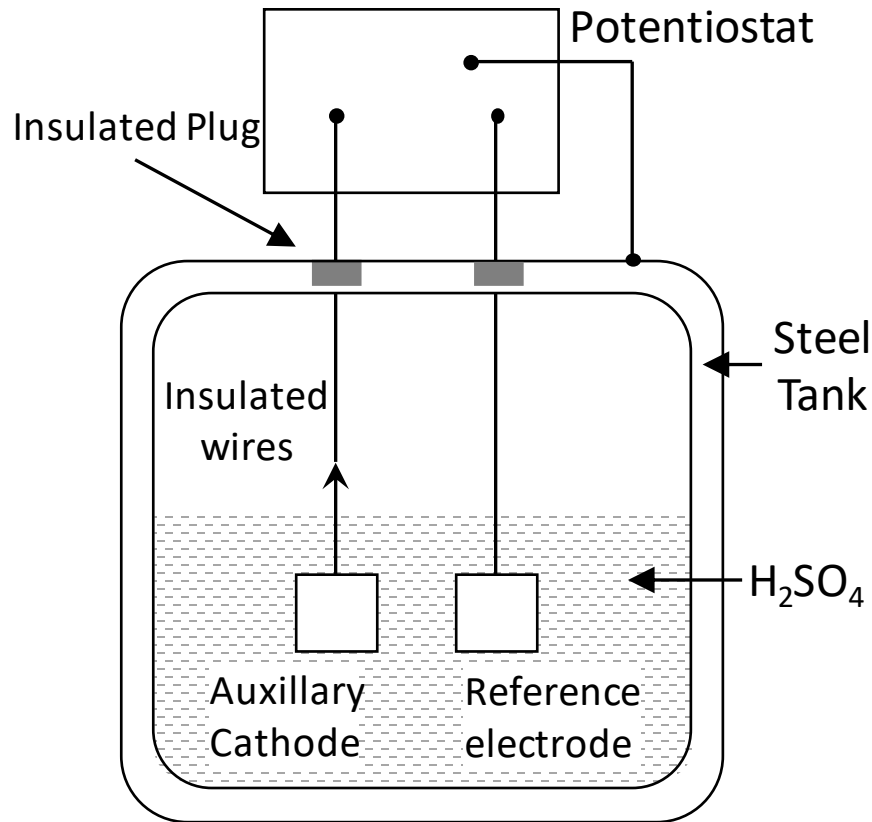
- Initial costs can be more expensive.
- Requires an external DC power source along with an AC supply.
- System requires routine maintenance and monitoring.
- Anode wires can be susceptible to damage.





# Corrosion Control

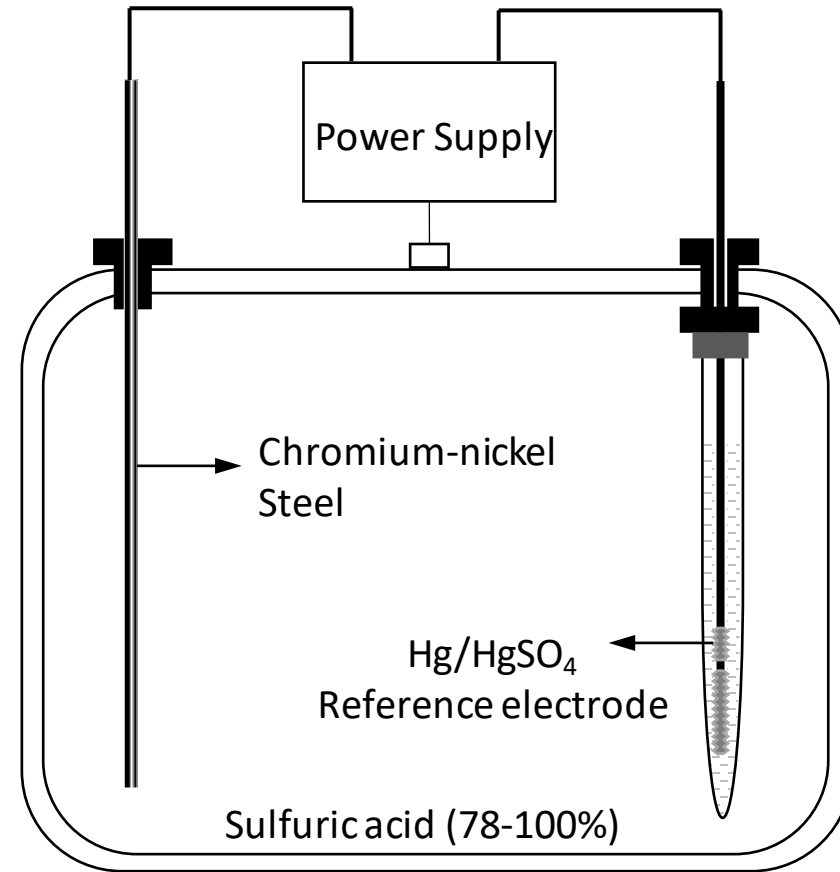
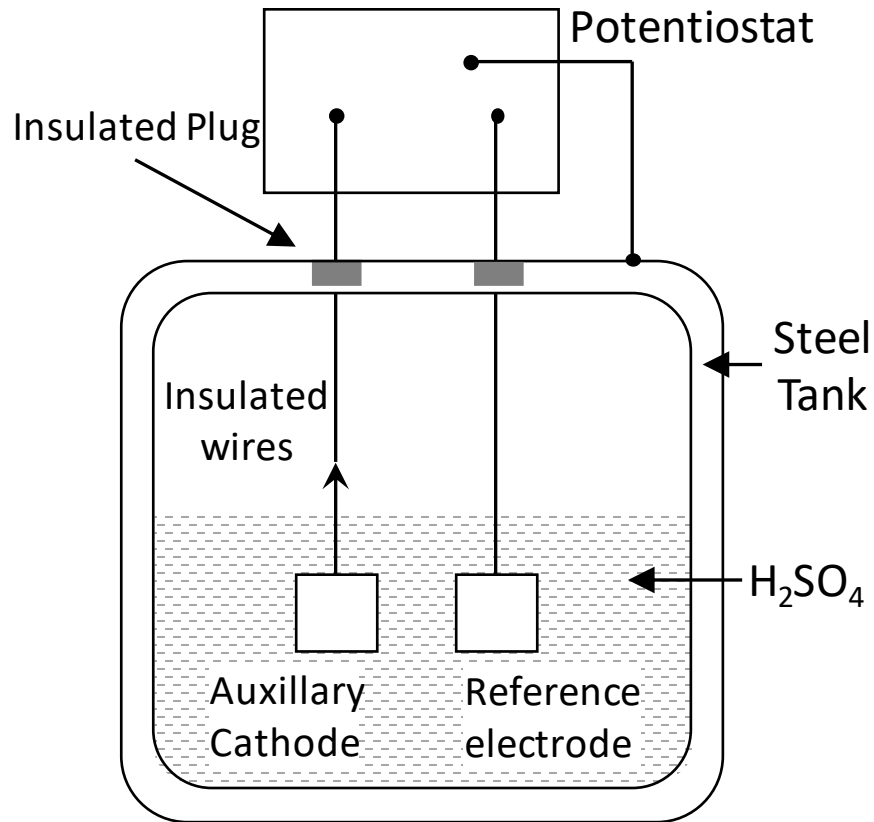
## Anodic Protection



- Corrosion control of metal by making it an anode by controlling the electrode potential in a zone where the metal is passive or more noble.
- The application of anodic current to the metal decreases the rate of H<sub>2</sub> evolution.
- Potentiostat is essential to protect the metal anodically.
  - Potentiostat is a device which maintains the metal at a constant potential.
  - Use of Potentiostat shifts the corrosion potential to passive potential which stops the corrosion.
- The potential range depend upon the metal and the environment.

# Corrosion Control

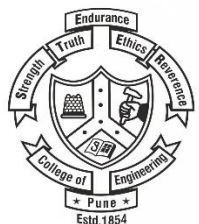
## Anodic Protection



# Corrosion Control

## Comparison between CP and AP

Factors	Cathodic protection	Anodic protection
Suitability	To all metals in general.	Only to those exhibiting active-passive behavior
Environment	Only for moderate corrosion environment.	Even aggressive chemical corrosives.
Cost benefit	Low investment, but higher operative costs..	Higher investment, but low operative costs.
Operation	Protective currents to be established through initial design and field trials	More precise electrochemical estimation of protection range possible.



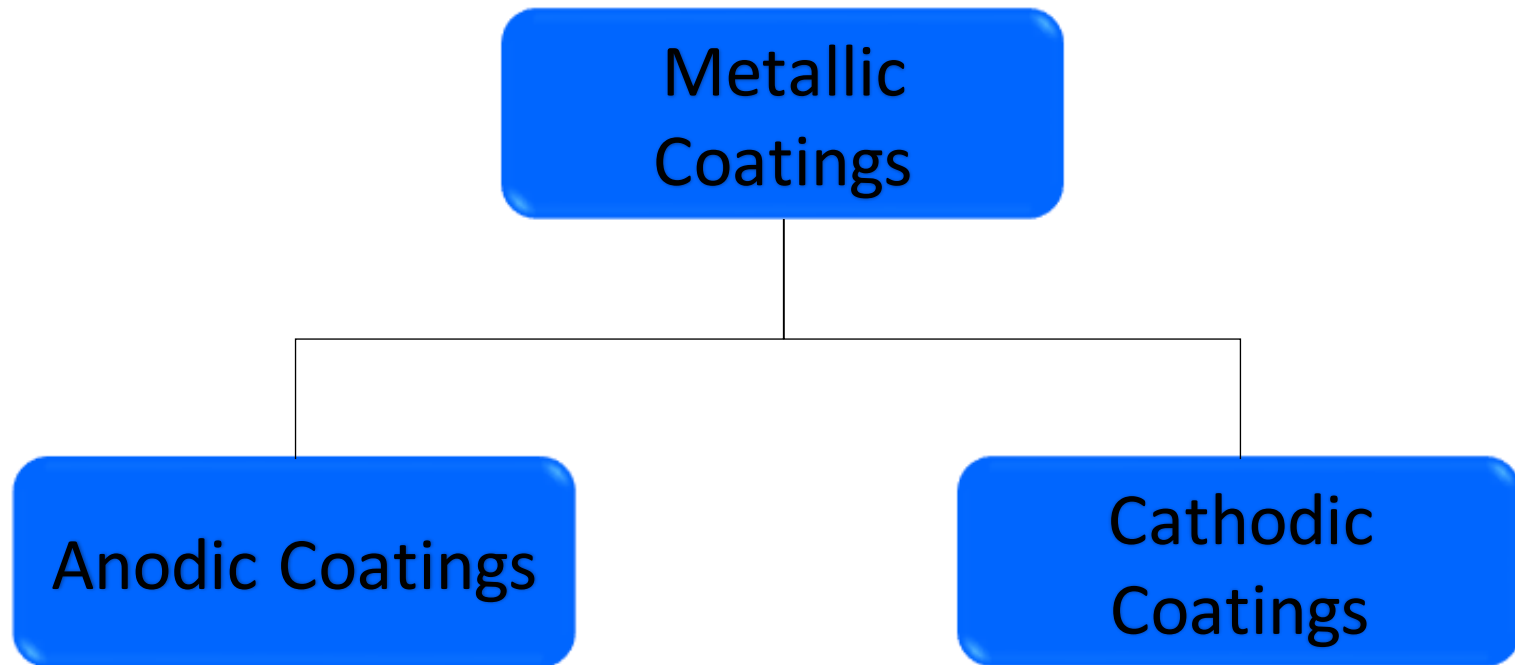
# Corrosion Control

## Metallic Coating

- Metallic coatings contain a metallic element or alloy.
- Metallic coatings can be applied by using a sprayer, electrochemically, chemically or mechanically.
- These coatings are applied on equipment requiring a shiny or glossy appearance and protection from sunlight, corrosion and oxidation.
- Zn, Sn, Ni, Cu, Cr, Al and Pb are commonly used in the metallic coatings



# Corrosion Control



# Corrosion control

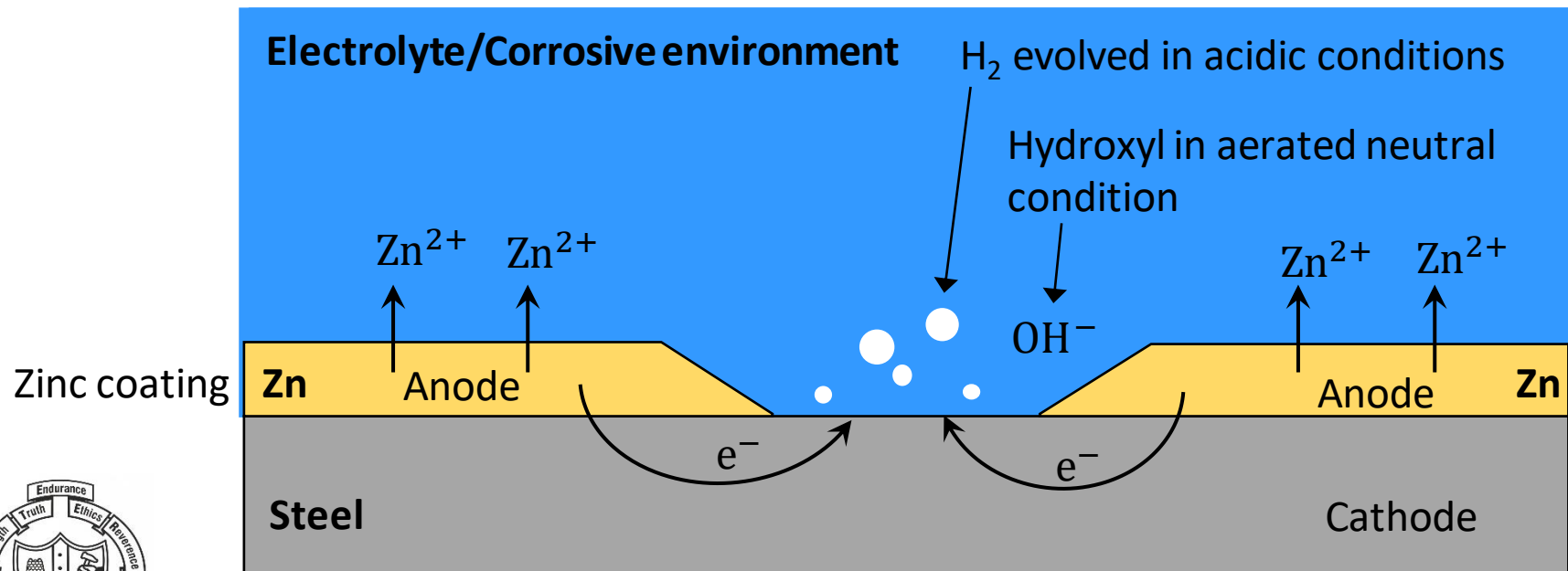
## Anodic Coating

- Coating of metals which are anodic to the base metal
- As long as coat layer is intact, corrosion of the metal is under control
- If discontinuous occur, a galvanic cell is formed
- Anodic coating protects the underlying base metal sacrificially
- e.g. Coating of Al, Cd, Mg or Zn (or sometimes their combination) on Steel



# Corrosion Control

## Anodic Coating



# Corrosion Control

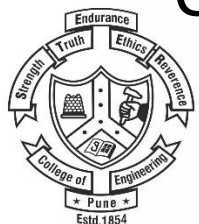
## Cathodic Coating

- Coating of metals which are cathodic (noble) to the base metal
- They protect the base metal as they have higher corrosion resistant than the base metal
- If the coatings are punctured, then more corrosion damage occurs, since galvanic cell will be set up
- This leads to formation of small anode and large cathode, resulting in severe corrosion

Eg., Coating of Sn on Fe

Sn is lower in electrochemical series than Fe

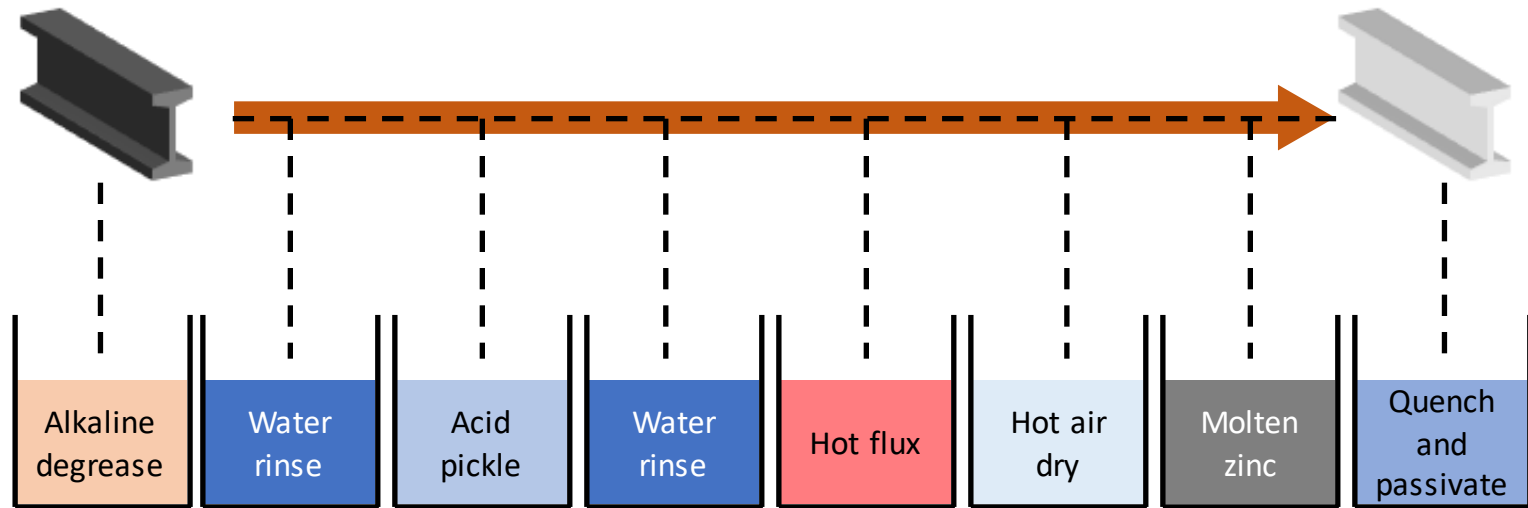
Other examples are Ni, Cu, Cr





# Corrosion Control

## Galvanizing



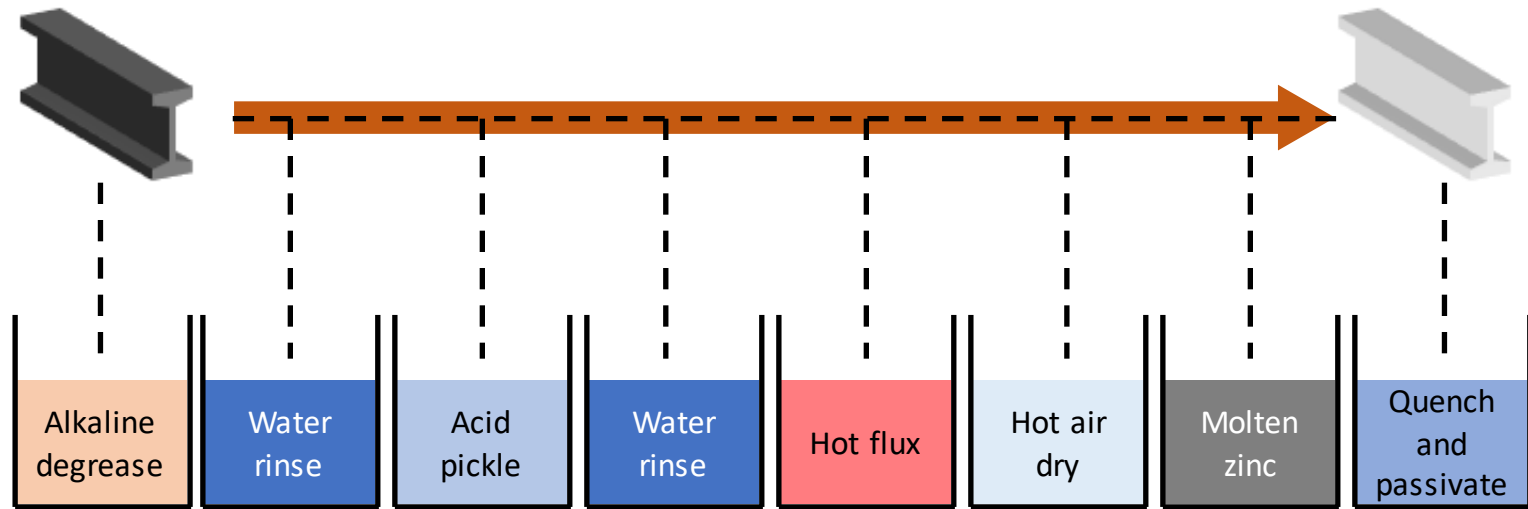
1. Cleans surface from organic impurities like grease, oil, dirt etc.
2. To clean surface from residual alkaline solution
3. To remove oxide layers or scales
4. To remove residual acid from surface

6. Dried thoroughly
7. Dipped in molten Zinc (Galvanizing)
8. Quenched. Dipped in Water. Outer surface hardens.

5.  $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$  Flux. To prevent oxidation of metal

# Corrosion Control

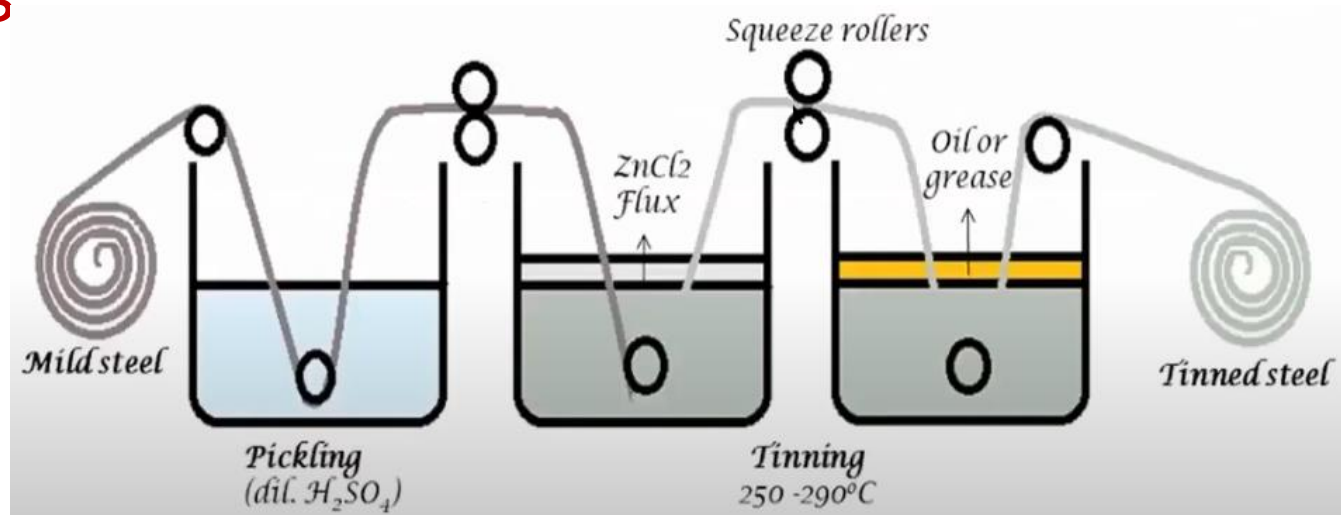
## Galvanizing



- Galvanizing is the process of immersing iron or steel in a bath of molten zinc to produce a corrosion resistant, multi-layered coating of zinc-iron alloy and zinc metal.
- While the steel is immersed in the zinc, a metallurgical reaction occurs between the iron in the steel and the molten zinc.
- This reaction is a diffusion process, so the coating forms perpendicular to all surfaces creating a uniform thickness throughout the part.

# Corrosion Control

## Tinning



Pickling: To remove scales, oxides

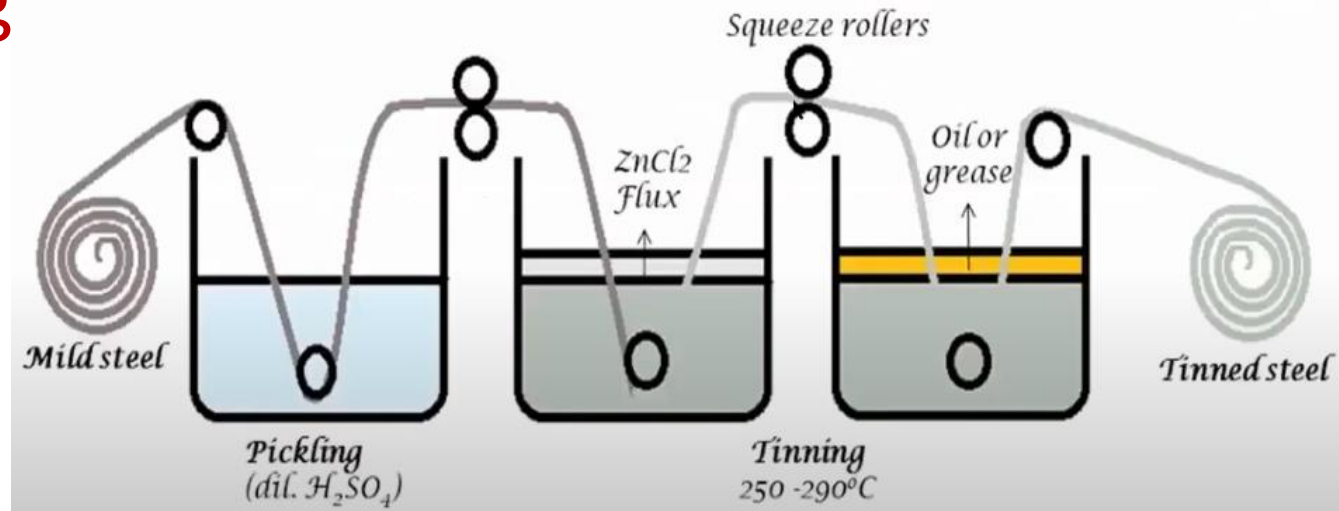
ZnCl<sub>2</sub> Flux: To dry the surface and prepare the surface for proper adhering with Tin

Squeeze rollers to even out the tin Layer and adjust thickness

Oil Grease: To prevent oxidation of Hot Tin coating on the surface

# Corrosion Control

## Tinning

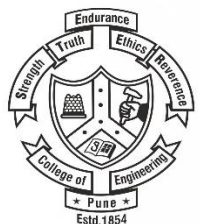


- **Tinning** is the process of thinly coating sheets of wrought iron or steel with tin, and the resulting product is known as tinplate.
- The term is also widely used for the different process of coating a metal with solder before soldering.
- Tin coating thickness on one or both sheet surfaces ranges from about 0.4 to 2.1  $\mu m$ .
- Solders of tin–lead, tin–antimony, tin–silver, and tin–zinc also form an important application.

# Corrosion Control

## Comparison between cathodic and anodic coating

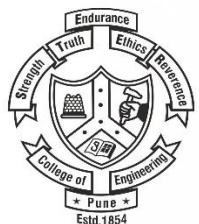
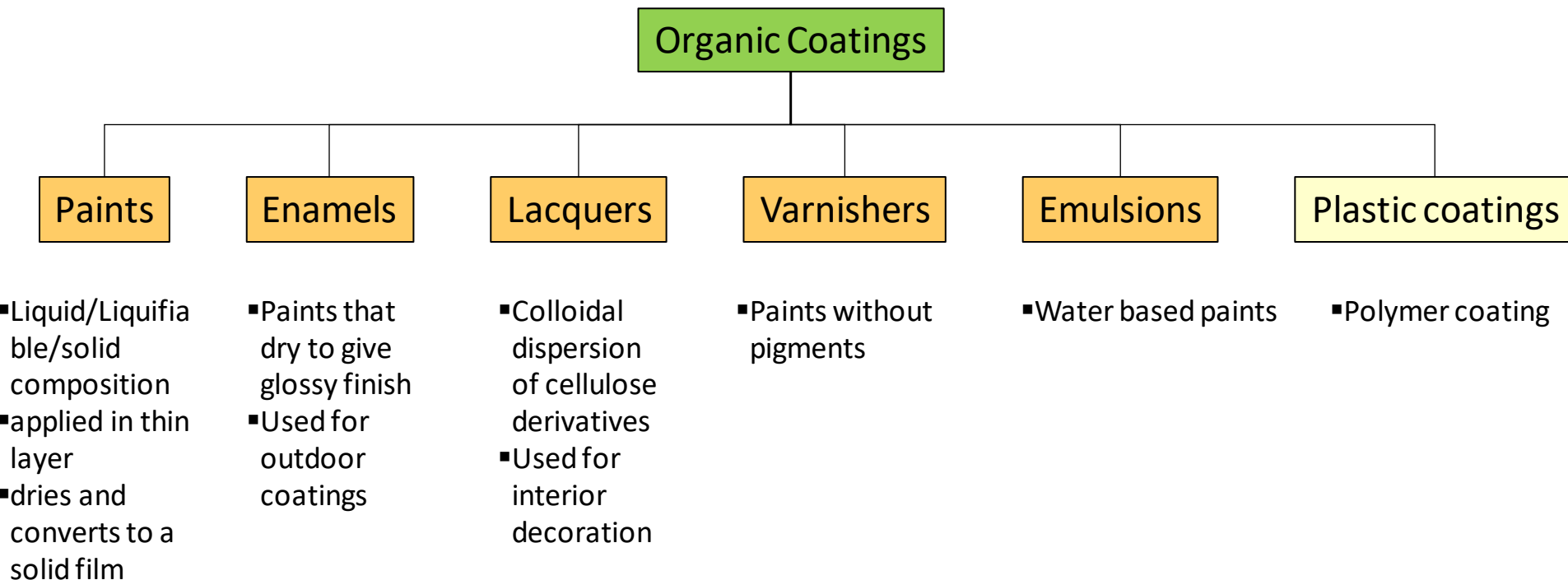
Cathodic coating	Anodic coating
If the <b>base metal</b> is coated with metal which is <b>cathodic</b> to it, it is called a cathodic coating.	If the <b>base metal</b> is coated with metal which is <b>anodic</b> to it, it is called an anodic coating.
This type of coating prevents the metal from corrosion.	It protects the base metal from corrosion.
When this coating loses its strength, it causes imbalanced cathode and anode and causes corrosion at a severe rate.	Failure of this coating causes the formation of galvanic cells.
The best example of such type of coating is coating <b>tin on iron</b> .	The well-known example of this type of coating is the <b>coating of zinc on iron</b> .



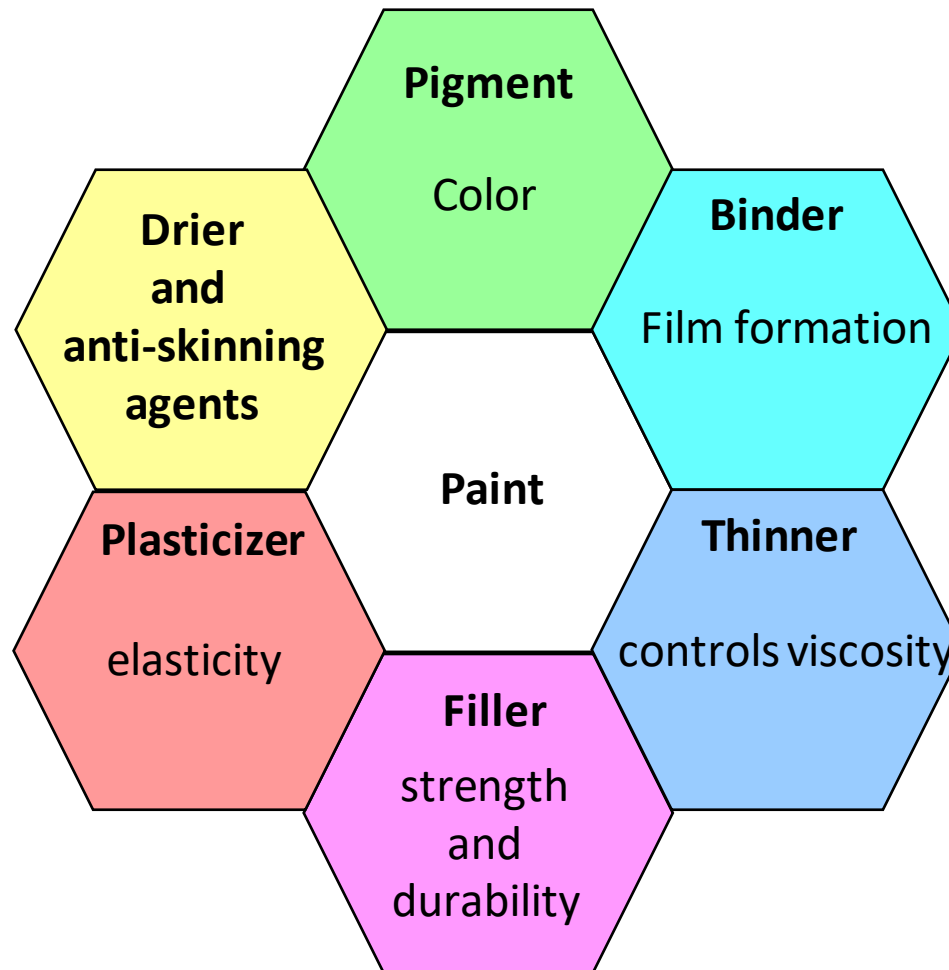
# Corrosion Control

## Organic Coatings

- Provides inert barrier on the surface from corrosive environment
- Also useful for decorative purpose



# Corrosion Control



# Corrosion Control

## Paints

### Pigment

- Imparts color
- Increases weather resistance
- UV resistance
- provides strength to paint

White: White lead  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

Blue: Prussian Blue  $\text{K}_2[\text{Fe}(\text{CN})_6]$

Black: Carbon Black

Green: Chromium Oxide  $\text{Cr}_2\text{O}_3$

### Thinners

- Volatile Solvent to adjust consistency
- increases penetration power of vehicle
- increase elasticity of paint film
- retains constituent solids into vehicle

Turpentine oil, benzene, xylol,  
naptha, kerosene, acetone etc.

### Binders/Vehicle/Drying Oil

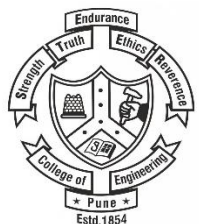
- Film forming component
- provides adhesion
- durability
- glossiness

Synthetic: acrylics, polyesters,  
polyurethanes, epoxy resins etc.

Natural: linseed oil, dehydrated  
castor oil, perilla oil tung oil etc.

### Filler or extender

- Improves durability by preventing film cracking and filling voids in the film
  - provides toughness
  - may also impart color
  - reduces cost
- $\text{BaSO}_4$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ , gypsum, silicates  
of Al, Mg etc.





# Corrosion Control

## Plasticizers

- Provide plasticity to the paint
- minimize cracking

tricrecyl phosphate, triphenyl phosphate, di butyl phthalate etc.

## Driers

- increases drying power of vehicle
- accelerates drying of the oil film by oxidation, polymerization and condensation

Borates, tungstates, resinsates, linoleates of Ni, Zn, Co, Mn

## Antiskinning agent

- Prevents skinning of paint
- polyhydric phenols

