

CO-2: Corrosion and its control



K L University

(Deemed to be University estd. u/s. 3 of the UGC Act, 1956)

(NAAC Accredited "A" Grade University)

KONERU LAKSHMAIAH EDUCATION FOUNDATION



Department of Chemistry
Koneru Lakshmaiah Education Foundation (**KLEF**)

Syllabus

CO1

Electro
chemistry:

Electroche
mical cells

Batteries

CO2

Corrosion &
Control:

Corrosion
Theories

Factors
affecting

CO3

WATER
Technology:

Hardness

Boiler
troubles

CO4

Molecules &
Materials:

Polymers-

Plastics

Overview Syllabus

1



Topic 2



- 👉 Examine the mechanism of **Corrosion**.
- 👉 Outline various ways of formation of anodes and cathodes causing corrosion.
- 👉 Predict appropriate corrosion control techniques in the given environment.

Corrosion and its Control

Introduction

**Causes of
corrosion**

**Theories of
corrosion**

**Corrosion
reactions**

**Factors
effecting the
corrosion**

**Types of
corrosion**

**Corrosion
control
methods**



Introduction



Destruction of a metal by chemical or electrochemical reaction with its environment.



Physical or mechanical decomposing of a metal is not called corrosion but is called erosion.



Corrosion and erosion together cause metal to be destroyed more quickly.



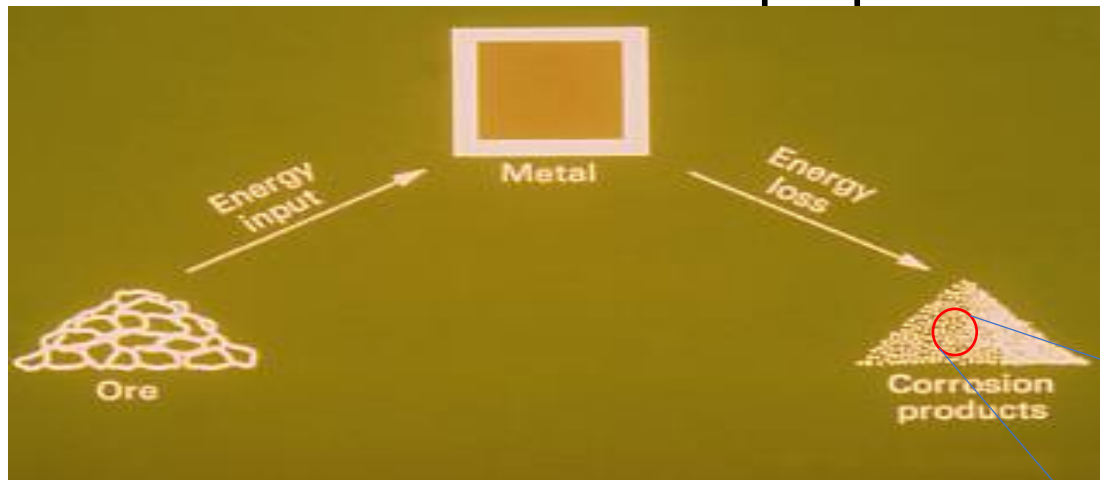
Corrosion is an unintentional reaction between a material and its environment.



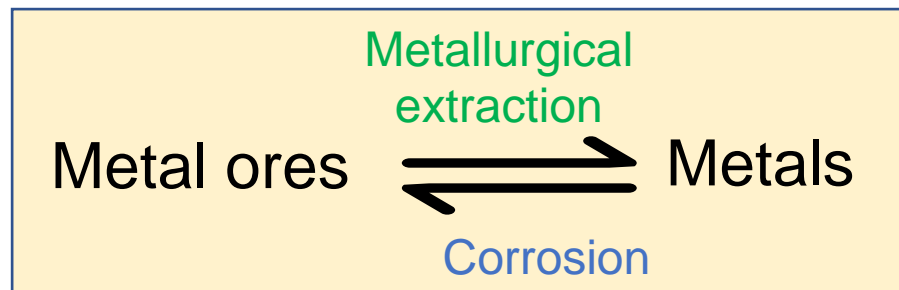
It is very important to consider corrosion when the structure or equipment is meant to last many years.

Introduction

Corrosion refers to the destructive and unintentional degradation of metallic material, through an unwanted chemical or electrochemical attack by its environment, which disfigures metallic properties.



It is a spontaneous process



Corrosion is driven by the low energy of metals

Introduction



Rusting of iron due to formation of oxide layer
($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)



Statue of Liberty ca. 1886 (left), today (right)

examples



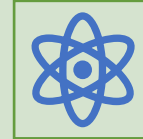
Tarnishing of silver;
Silver sulphide that form sulfur compounds in air.

Formation of green layer
opper due to formation of the
copper carbonate

Why Do Metals Corrode?



“**Ore**” is the chemically combined state of a metal



High amount of energy is required to extract/reduce the metal from ore.



The extracted metal is thermodynamically unstable due to its high energy.



Metal undergoes corrosion when it reacts with its environment.



Corroded metal is thermodynamically stable.

Corrosive effects or disadvantages

Corrosion destroys valuable metallic properties such as conductivity, malleability, and ductility.

It causes contamination of potable water.

Reduced life span of metallic parts of machines.

As a result of corrosion, enormous amounts of metal are wasted as compounds.

As metals lose their useful properties, machinery fails.

Worldwide, 2 to 2.5 billion dollars are lost to corrosion every year.



Why corrosion control?




Economic Aspects: It can be referred to cost of corrosion under Direct Loss & Indirect loss.

Health Aspects: Surgical instruments, implants, pacemakers, etc, are all prone to corrosion.

Cultural Aspects: Antiques & monuments may get extinct due to corrosion.

Safety Aspects: Machine parts in factories & home appliances can cause harm if corroded.



Methods of corrosion control

Surface
Coatings

Cathodic
Protection

Modifying the
environment

Use of pure
metal

Using metal
alloys

Use of Inhibitors

Proper
designing

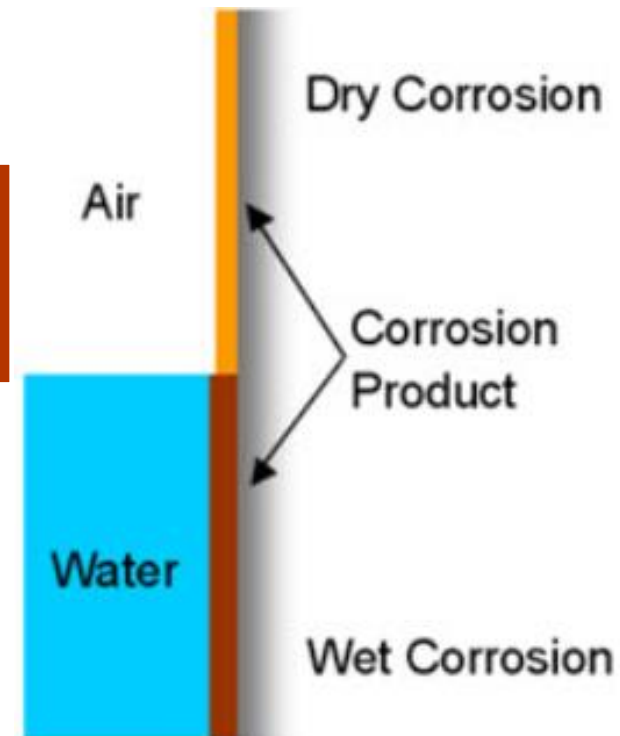
Types of Corrosion

Depends on the environment to which the metals are exposed



Dry Corrosion or Chemical Corrosion

Wet Corrosion or Electrochemical Corrosion



Dry Corrosion or Chemical Corrosion

If a metal is exposed to dry environment, the metal gets corroded

- Direct attack of O_2
- Corrosive gases like SO_2 , Cl_2
- Chemical action on metals through chemical reactions

Ex: A tarnished surface of a metal.

Metals (Al, Zn & Fe) have a natural tendency to form a thin film of their oxides.

Dry corrosion may be due to

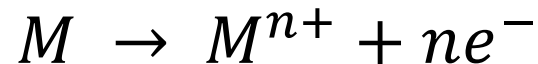
- Oxidation corrosion
- Corrosion by gases

Dry Corrosion or Chemical Corrosion

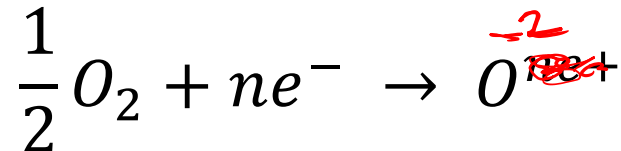
(i) Oxidation corrosion

→ When temperatures are extreme (low or high), dry oxygen attacks metals, causing them to corrode due to **oxidation**.

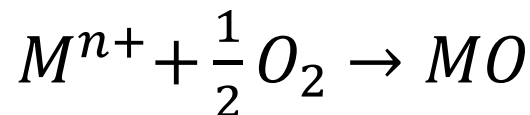
→ Metal gets oxidized to metal ions.



→ Reduce oxygen to form oxide ion.

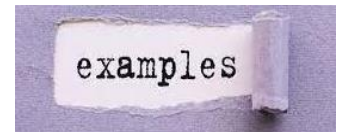
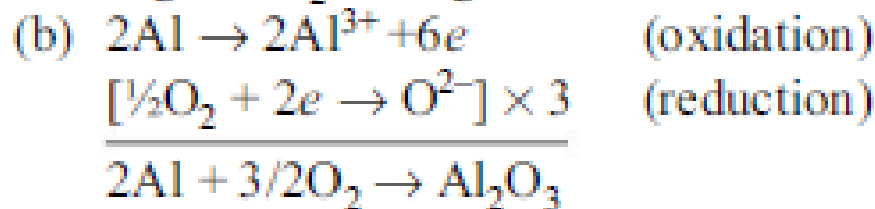
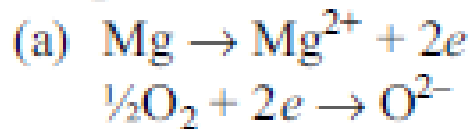


→ Metal ion and oxide ion combine to form metal oxide.

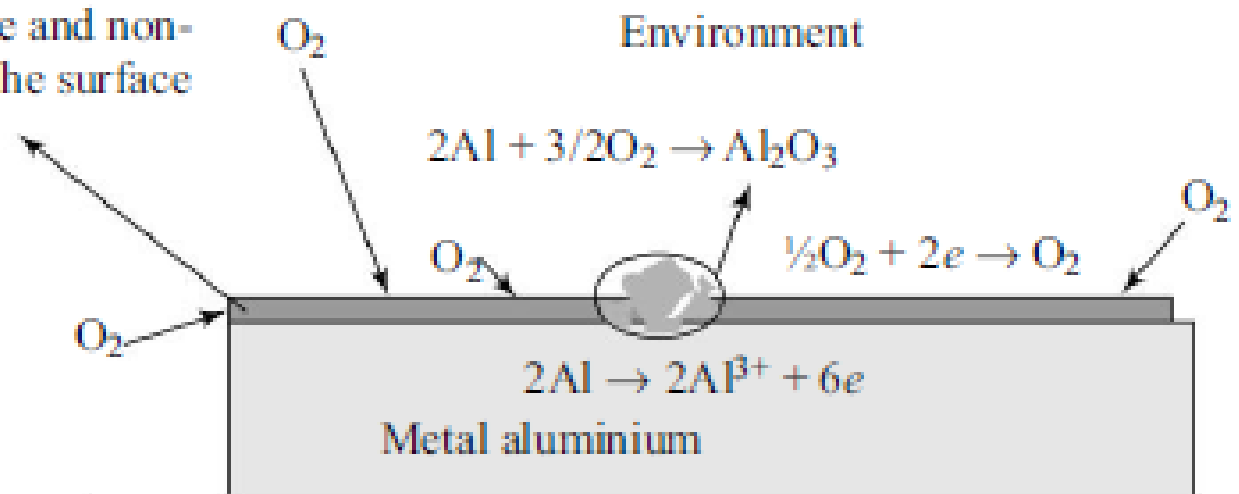


Dry Corrosion or Chemical Corrosion

(i) Oxidation corrosion

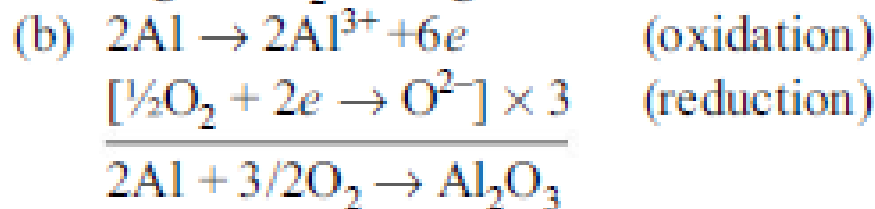
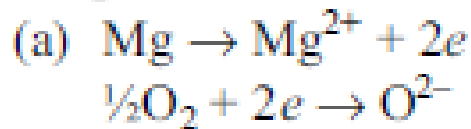


Stable protective and non-porous film on the surface of Aluminium

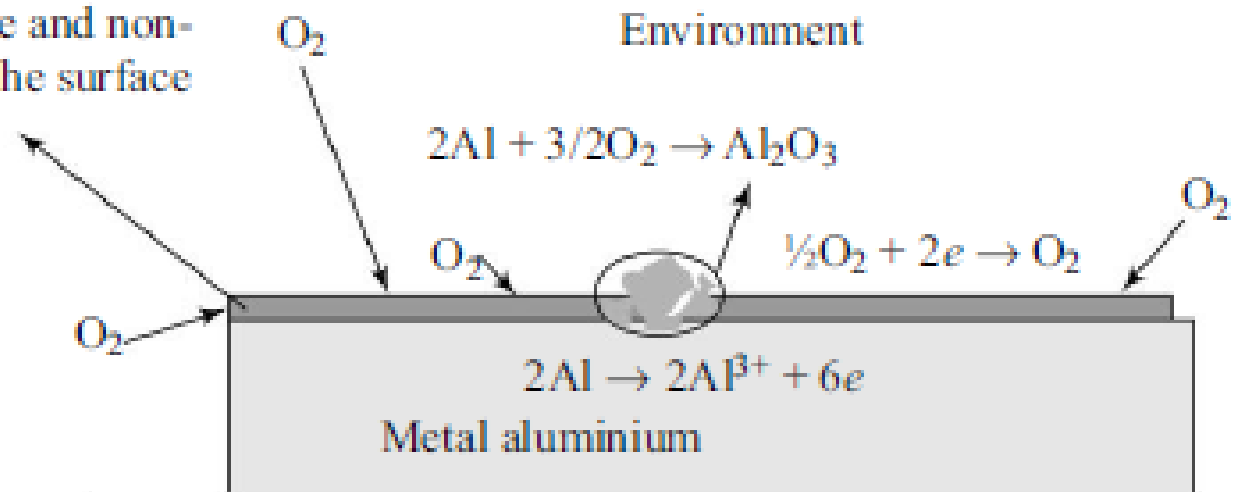


Dry Corrosion or Chemical Corrosion

(i) Oxidation corrosion



Stable protective and non-porous film on the surface of Aluminium



DIRECT CHEMICAL ATTACK THEORY (O R) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- **Protective and non porous oxide film:** Metals such as Al, Cr, Cu & W develop nonporous, stable oxide film on the surface. This film prevents further corrosion of the metal.

DIRECT CHEMICAL ATTACK THEORY (O R) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- Unstable oxide film: Au & pt develop unstable oxide film which instantaneously decomposes to form metal & oxygen.

DIRECT CHEMICAL ATTACK THEORY (OR) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- **Volatile oxide film:** Molybdenum develops an oxide which immediately vaporizes. As a result metal surface easily undergoes further corrosion.

DIRECT CHEMICAL ATTACK THEORY (O R) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- Porous and non protective film: Alkali and alkaline earth metals form porous oxide layer which further facilitates corrosion of the metal due to porous nature. Oxide layer cannot protect the metal from corrosion.

DIRECT CHEMICAL ATTACK THEORY (O R) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- Pilling Bedworth rule

$$\text{Pilling Bedworth rule} = \frac{\text{Vol. of metal oxide layer}}{\text{Vol of metal consumed}}$$

- If the ratio is <1 , the metal oxide layer is porous and non protective. Ex:-Oxide layer on alkaline metals

DIRECT CHEMICAL ATTACK THEORY (O R) MECHANISM OF DRY CORROSION

Oxidation Corrosion (Reaction with Oxygen)

- Pilling Bedworth rule

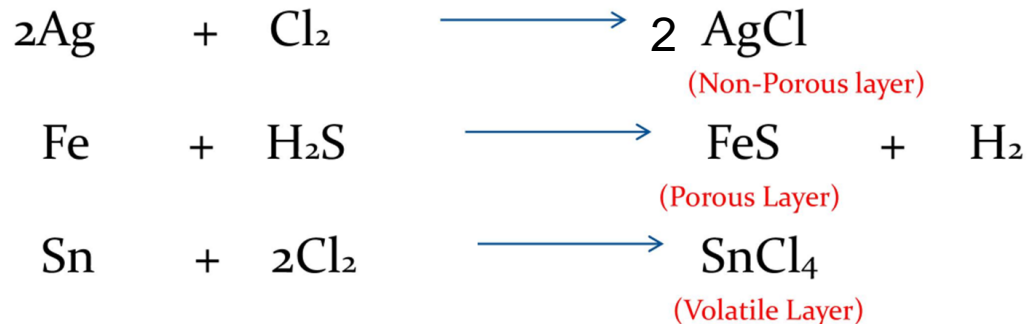
$$\text{Pilling Bedworth rule} = \frac{\text{Vol. of metal oxide layer}}{\text{Vol of metal consumed}}$$

- If the ratio is ≥ 1 , the metal oxide layer is non porous protective layer.
- It stops further corrosion of metal.
- Ex:-Oxide layer on Al, Cr, Cu, W.

Dry Corrosion or Chemical Corrosion

(ii) Corrosion by gases

- Few gases, such as SO_2 , Cl_2 , F_2 , attack metal by dry atmosphere.
- Degree of corrosion depends on the formation of thin film layer which maybe protective and non-protective.



- I. Dry Cl_2 reacts with Ag and forms AgCl as a thin protective and nonporous layer.
- II. When Tin is exposed to corrosion, the entire metal gets destroyed over time.

Wet Corrosion or Electrochemical Corrosion

- ✎ Corrosion of metal takes place in an aqueous corrosive environment.
- ✎ Corrosion occurs by the involving the transfer of electrons during oxidation and reduction.

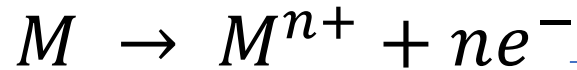
Corrosion of this type can be observed when

- a) a metal is in contact with an acid solution
- b) dissimilar metals are dipped partially.

- A lower potential in the metal is known as anodic.
- A higher potential in the metal is known as cathodic.
- Separate/current flows anodic and cathodic areas within the metal cause corrosion.

Electrochemical theory of wet corrosion

At the anodic area of the metal :



(Oxidation)

Dissolves in the medium

Forms an insoluble oxide film

At the cathodic area of the metal:



(Reduction)

Cathodic reactions can take place in a variety of ways depending on the nature of the corrosive environment:

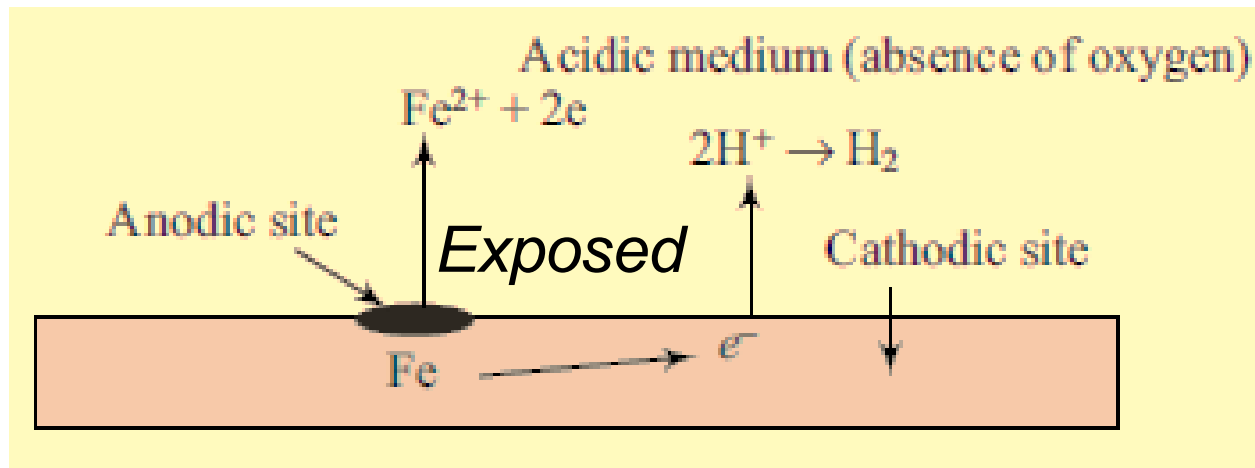
(a) Liberation of H₂

(b) Absorption of oxygen

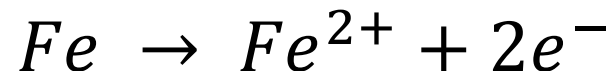
Electrochemical theory of wet corrosion

Evolution of Hydrogen type:

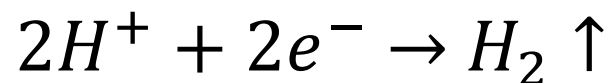
In acidic medium and in the absence of oxygen, H^+ ions are reduced to H_2 gas.



In the anodic area: Oxidation

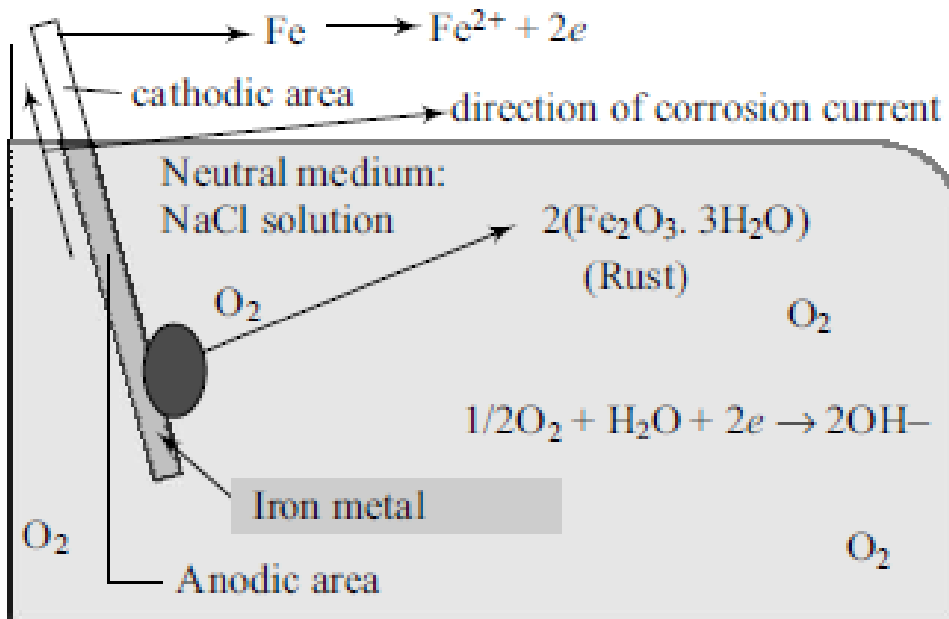


In the cathodic area: Reduction



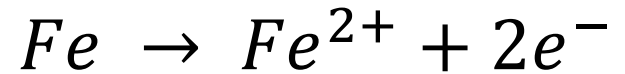
Electrochemical theory of wet corrosion

b) Absorption of Oxygen

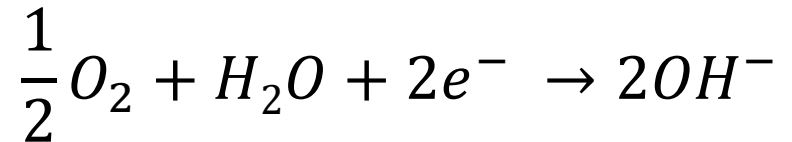


*Iron rusting in oxygen-rich
neutral medium*

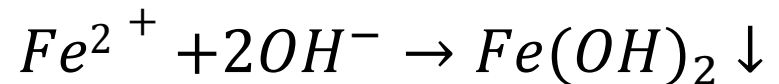
In the anodic area: Oxidation



In the cathodic area: Reduction

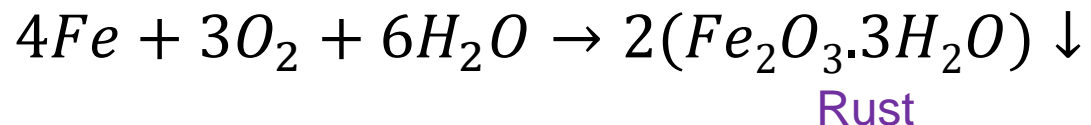


*If the solution is neutral and aerated,
hydroxyl ions are formed as follows.*

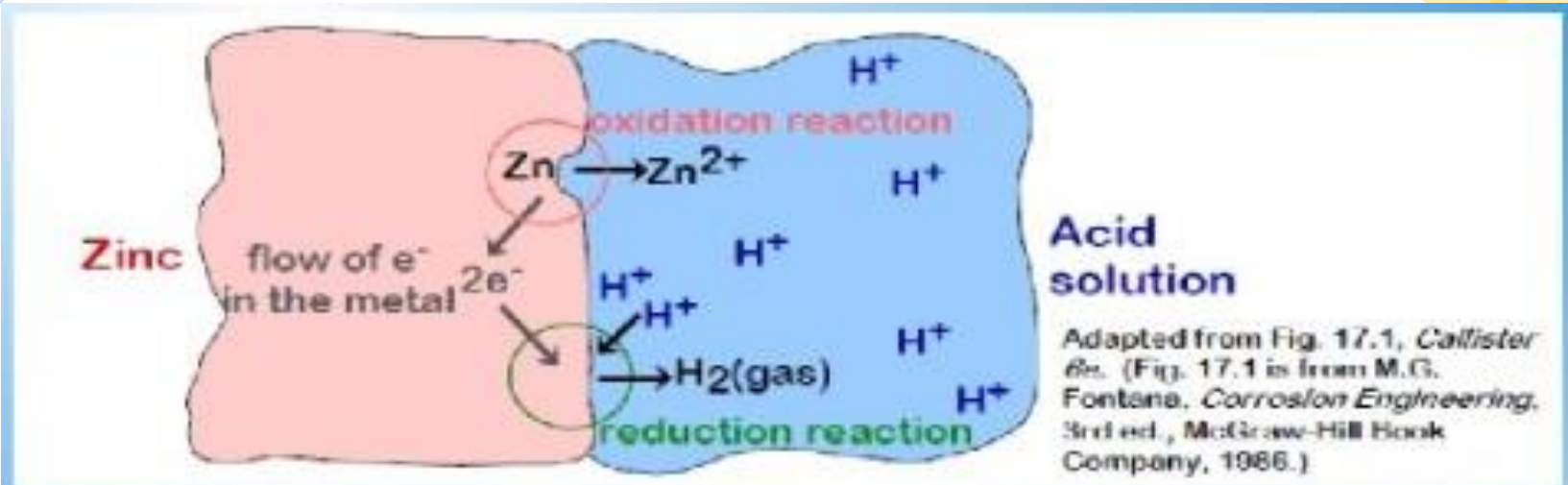


*Hydroxyl ions react with metal ions and
forms corrosion product.*

Net corrosion reaction:



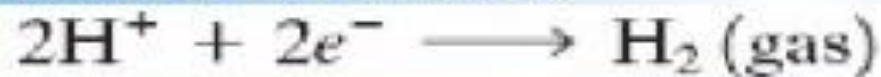
Ex. 1: Zinc metal immersed in an acid solution contain H^+



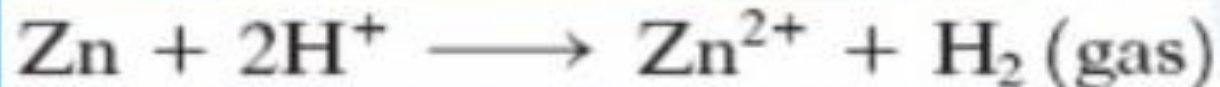
➤ zinc will experience oxidation or corrosion according to,



➤ H^+ ions are reduced according to,



➤ The total electrochemical reaction



Differences between dry and wet corrosion

Dry corrosion

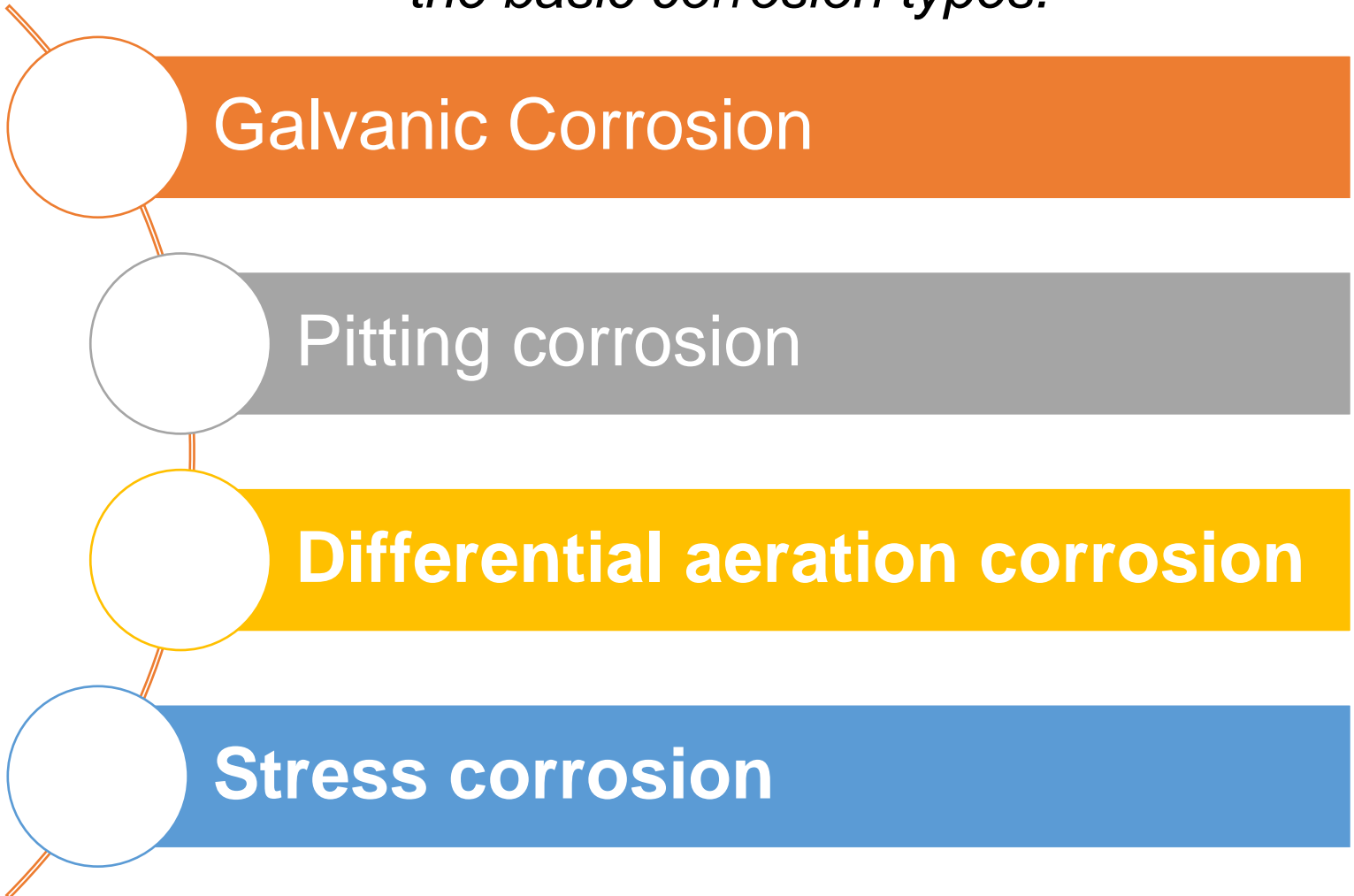
- It occurs in the absence of moisture.
- It involves direct attack of chemicals.
- It is slow process.
- Products are produced at site of corrosion.
- Process of corrosion is uniform.

Wet corrosion

- It occurs in presence of conducting medium.
- It involves formation of electrochemical cells.
- It is a rapid process.
- Corrosion occurs at anode, but rust is deposited at cathode.
- It depends on the size of the anodic part of metal.

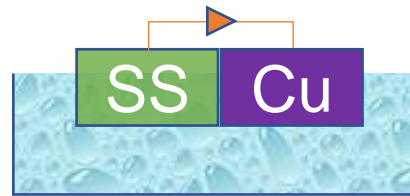
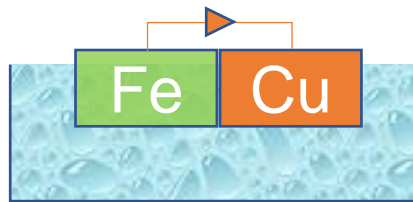
Different Forms of Wet Corrosion

Corrosion problems are often caused by one of the basic corrosion types.

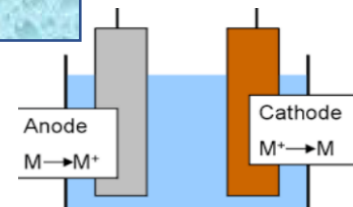


Galvanic or bimetallic corrosion

- It is an electrochemical process in which one metal corrodes before another metal is in contact with through an electrolyte.
- When two dissimilar metals are electrically connected, immersed, and exposed to a neutral environment in the presence of O_2 .
- Metals with lower reduction potential spontaneously oxidize and corrosion.
- Anode attack rates accelerate with time.



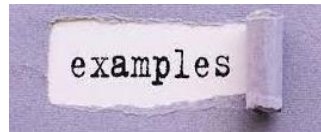
Bimetallic couples



Galvanic or bimetallic corrosion



Steel pipe connected to copper



Zinc coating on mild steel

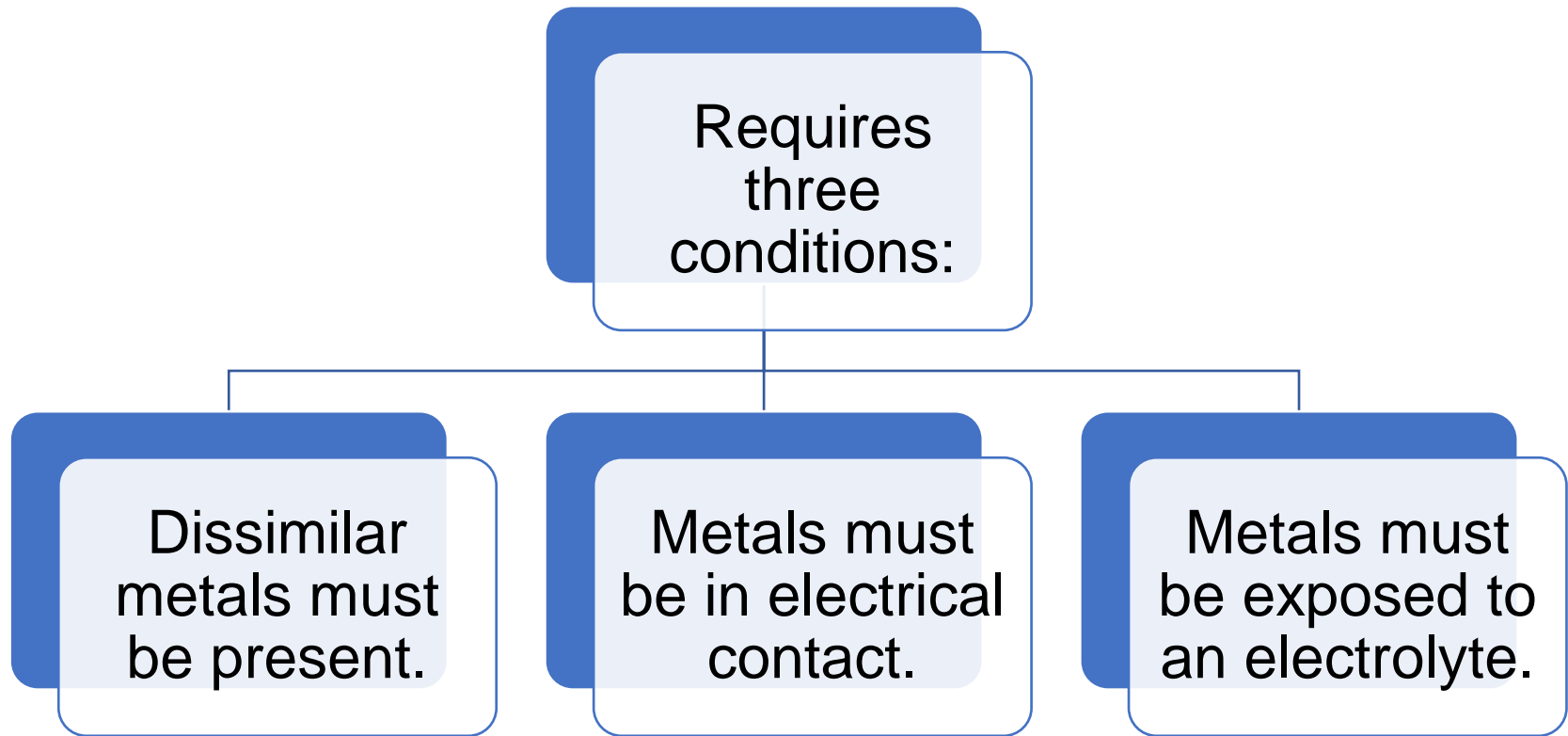


Tin coating on copper vessel



Steel propeller shaft in bronze bearing

Galvanic or bimetallic corrosion

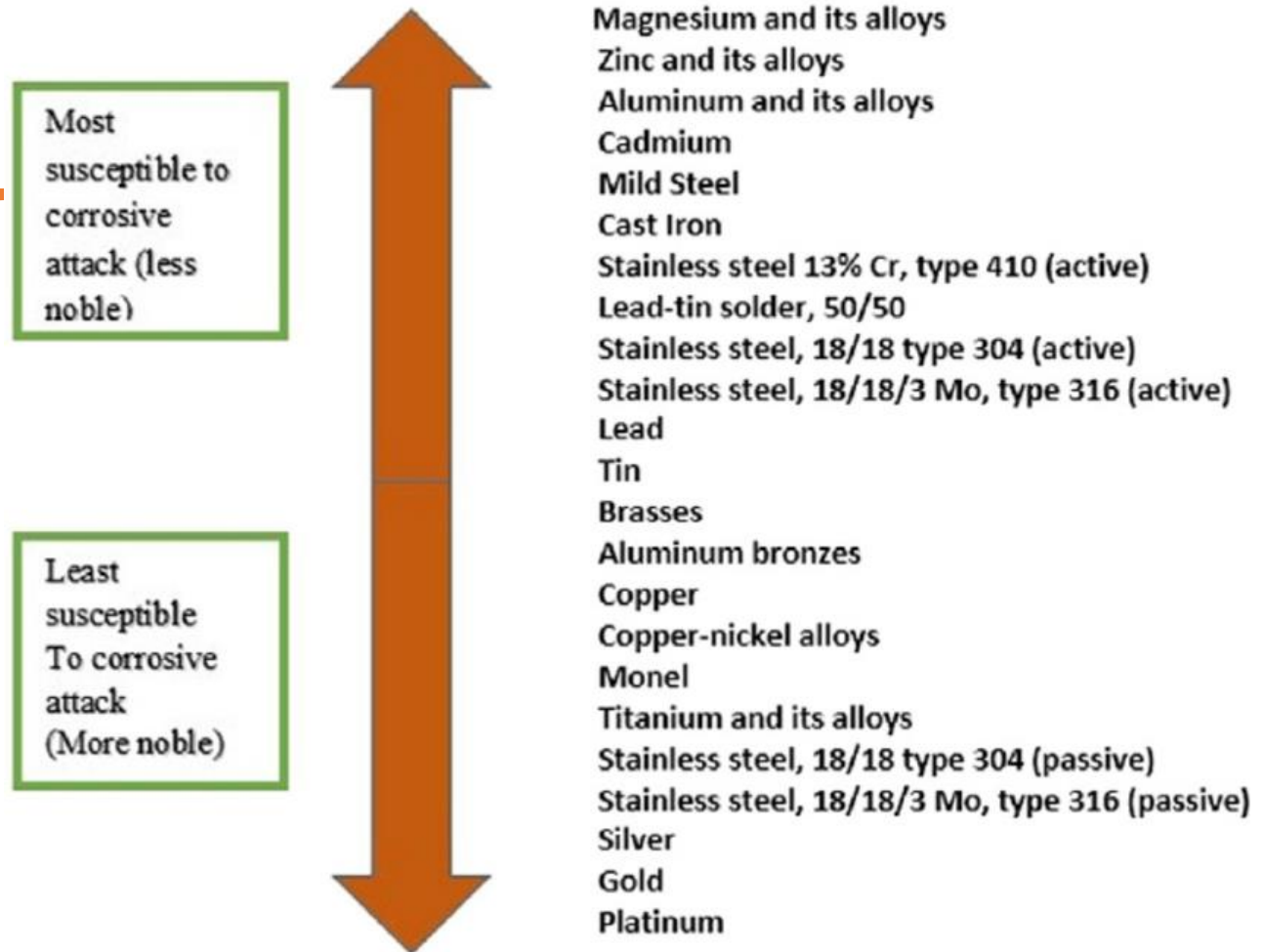


Galvanic or bimetallic corrosion

EMF series and galvanic series of materials can be used to estimate galvanic effects.

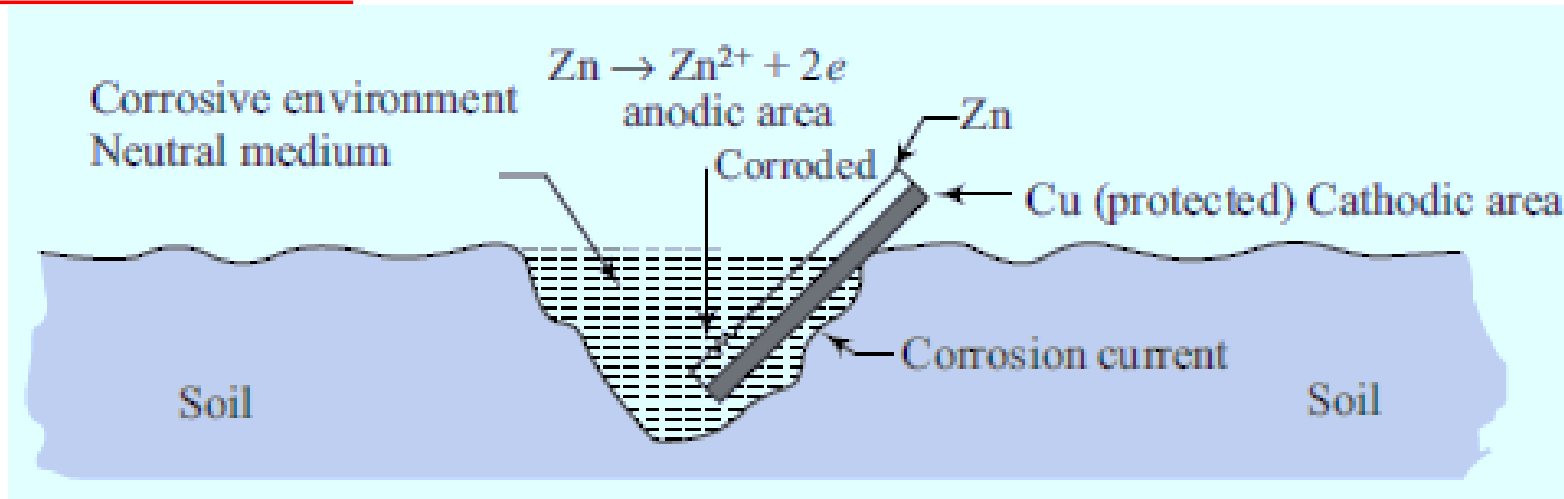
- A metal with a high standard oxidation potential acts as an anode, while a metal with a low reduction potential acts as a cathode.

Corrosion Susceptibility of metals

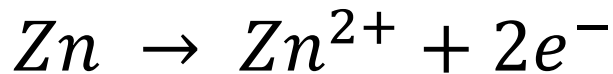


Galvanic or bimetallic corrosion

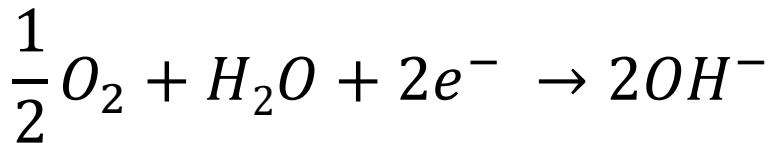
Mechanism



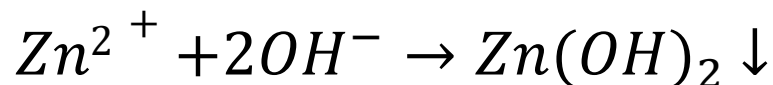
In the anodic area



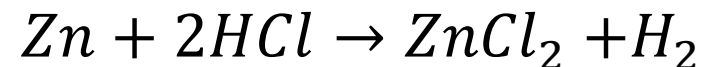
In the cathodic area



Overall



In an acid medium



Factors of Galvanic Corrosion

- Difference between the electrode potentials of the two metals.
 - A greater difference equals a stronger corrosion force.
- Contact resistance at the boundary between the two metals.
 - Corrosion is decreased due to high contact resistance.
- Electric resistance of electrolyte solution.
 - Solution dilution provides low corrosion rate.
- Anode-to-cathode areas ratio.
 - Low corrosion due to large area difference.
- Presence of passive film.
- Electrolyte solution properties
 - pH, oxygen content, temperature and flow rate.

Ways to prevent galvanic corrosion

- Materials with **similar corrosion** potentials should be selected.
- Electrical connection can be broken if the two metals are **insulated** from each other.
- The protective **coating** should be applied to both materials.
- The two materials should be **separated by inserting** a suitably sized spacer.
- A **sacrificial anode** should be installed, which is anodic to both the metals.
- A corrosion **inhibitor** can be added to the environment.

Pitting corrosion



Pitting of metal occurs when the protective layer breaks.

is an electrochemical oxidation-reduction (redox) process,



It is a non uniform corrosion resulting from a localized accelerated attack.



Leads to formation of cavities or holes in the material.



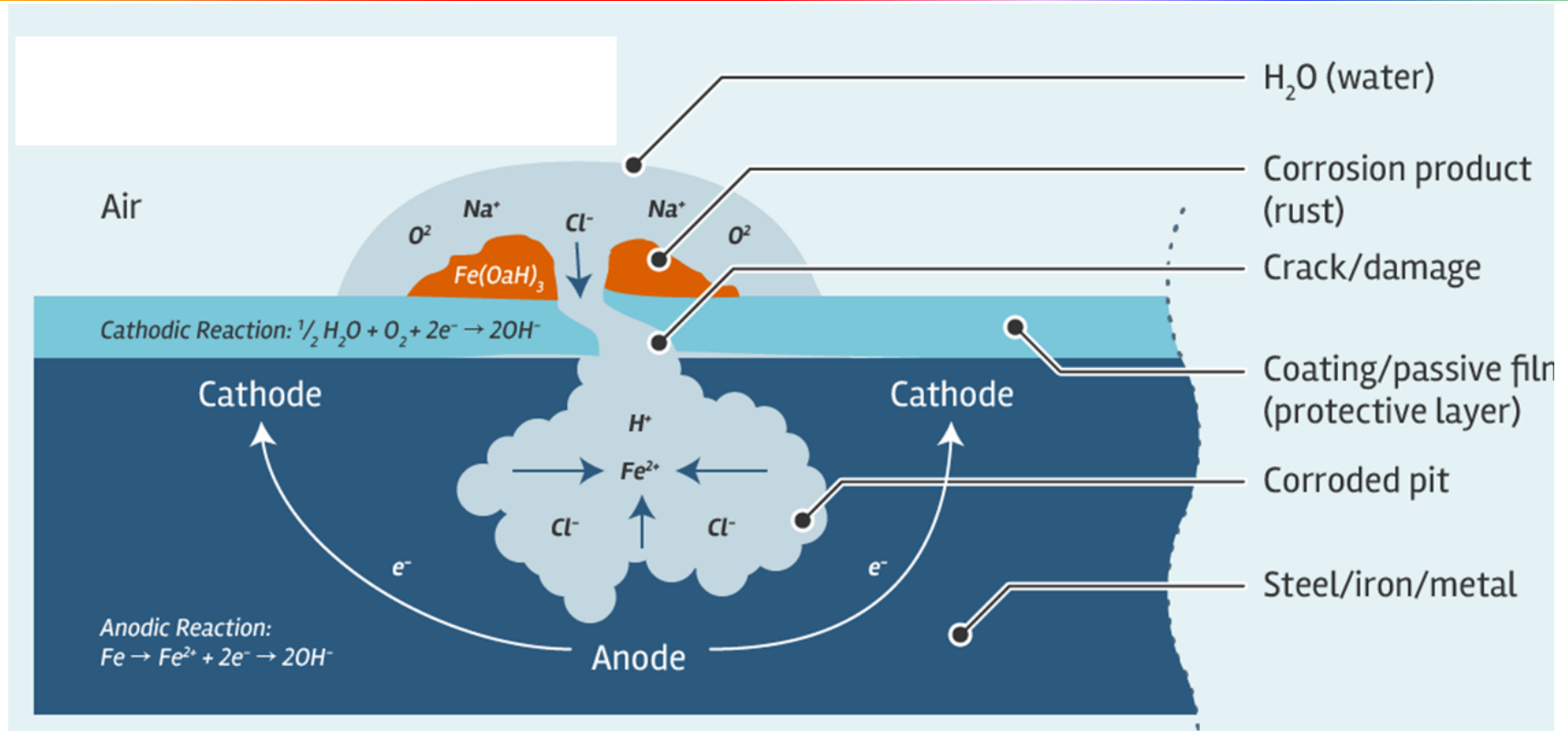
A pit or a hole forms at the anode when the anodic area and cathodic area are not equal.



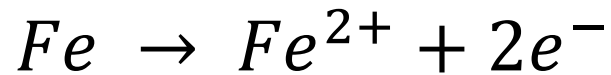
Causes of pitting corrosion

- ☞ Damage/cracking of protective film over the metal.
- ☞ Materials having poor surface finish.
- ☞ Presence of impurities on metal surfaces (sand & dust).
- ☞ Stagnant water conditions favor pitting (low velocity)
- ☞ Chemical attack
(Chloride damages the protective oxide layer).

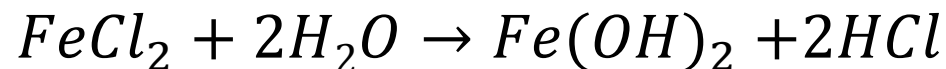
Mechanism of pitting corrosion



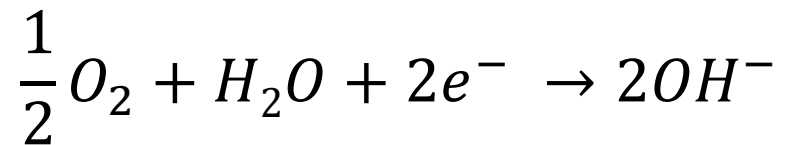
In the anodic area: Oxidation



Overall,



In the cathodic area: Reduction



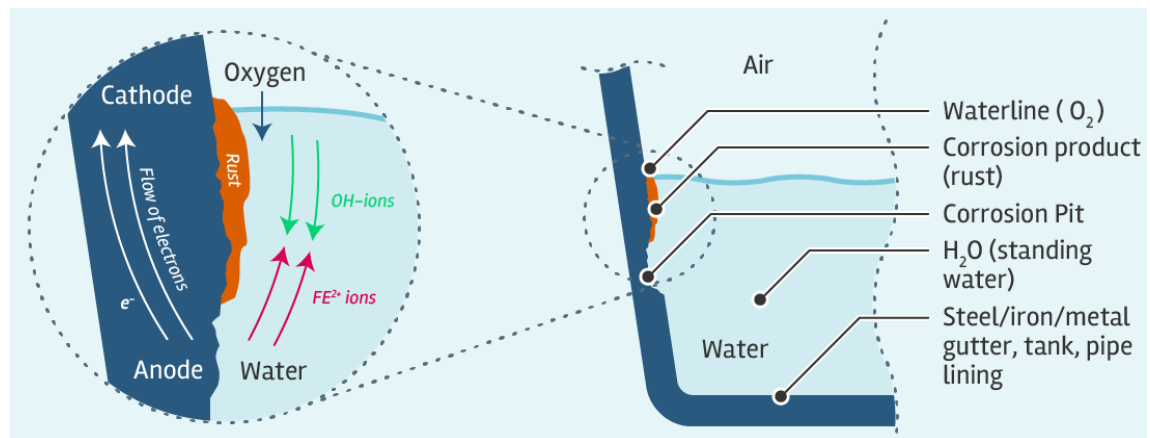
Ways to prevent pitting corrosion

- Selection of appropriate **material**;
- Controlling oxygen level
- Providing stirring of the electrolyte;
- Control of the electrolyte composition (PH, chloride ions);
- Corrosion inhibitors;
- Anodic & Cathodic protection;
- Corrosion protection coatings.

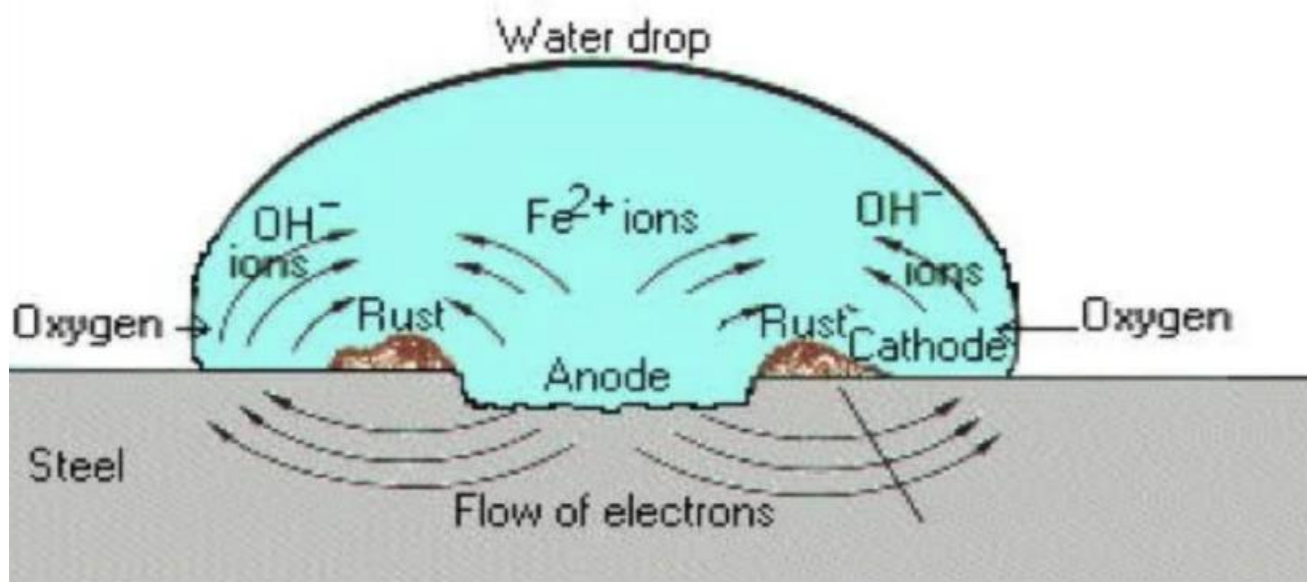


Differential aeration corrosion

- It takes place when there is an uneven supply of oxygen to areas of the same metal component.
- It is caused by varying electrolyte concentrations or aeration levels.
- When a poorly oxygenated area is adjacent to an area with a good supply of oxygen, an anodic/cathodic reaction occurs.
- Oxygen-less metal parts act as anodes, while oxygen-rich metal parts act as cathodes.



Mechanism of differential aeration corrosion



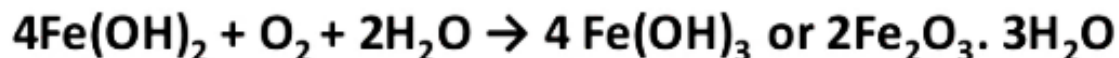
In case of Iron metal

Reaction at anode:- $\text{Fe(s)} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)

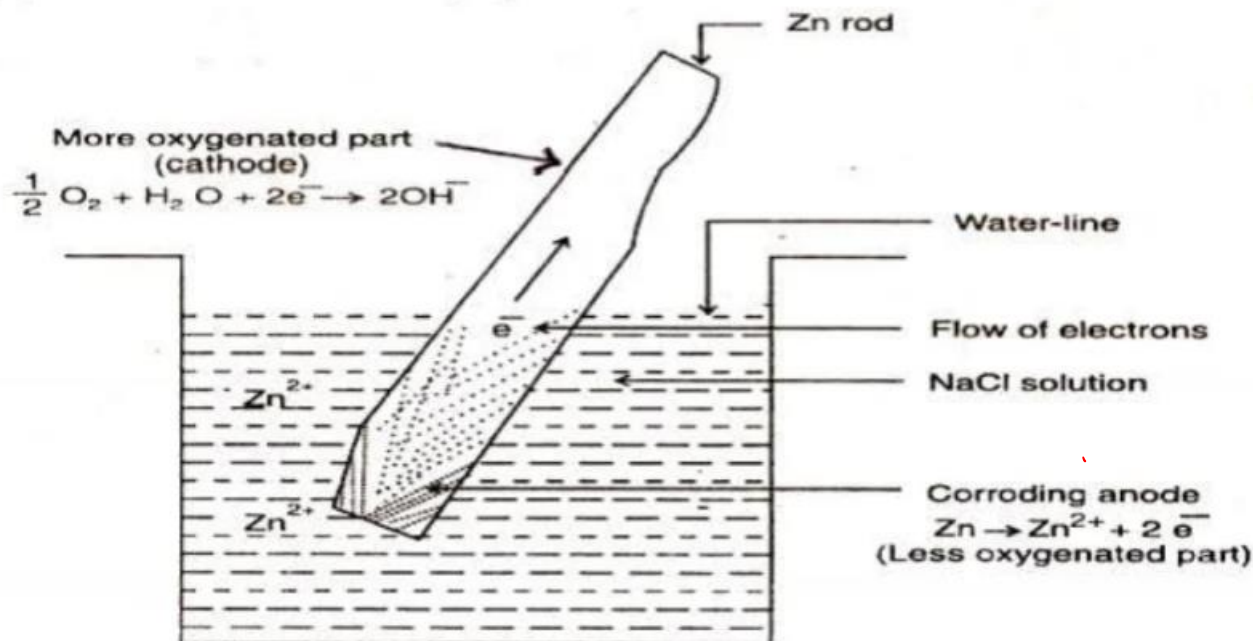
Reaction at cathode:- $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall Reaction:- $\text{Fe} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2$ Or $2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2$

In the presence of excess Oxygen:-



Mechanism of differential aeration corrosion



Similarly in case of Zn metal

Reaction at anode:- $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (Oxidation)

Reaction at cathode:- $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall Reaction:- $\text{Zn} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2$ Or $2\text{Zn} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Zn(OH)}_2$

Ways to prevent differential aeration corrosion

- Using metallic coating, electroless plating or chemical conversion methods.
- Maintaining the materials own protective film.
- Controlling the chemistry of fluids and using inhibitors.

Stress corrosion

- ➡ Stress-corrosion occurs when a relatively inert material is subjected to a **significant amount of stress**.
- ➡ Stress can either be externally **applied or residually present**.
- ➡ Metal develops **internal stress** during manufacturing processes like fabrication, heat treatment, and rolling.
- ➡ Areas under **stress act as anodes**, having high energy levels & electrode potentials.
- ➡ Areas that are **stress-free act as cathodes** and have low electrode potentials & energy levels.



Stress corrosion

👉 **For examples:**

1) Caustic embrittlement:

- It is a corrosion problem caused by an excess of NaOH in boilers.
- A great deal of stress is placed on the riveted areas, bends, and joints inside the boiler.
- As a result, they corrode.



2) Underground Steel pipeline:

Under high internal pressure, steel pipelines used to transmit oil and gas fail due to stress corrosion cracking.



Passivity

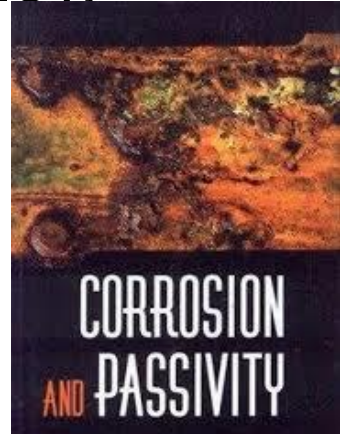
There is a phenomenon known as passivity or passivation when a metal or alloy exhibits a much higher corrosion resistance than would be expected based on its chemical composition.

Passivity is the result of the formation of a

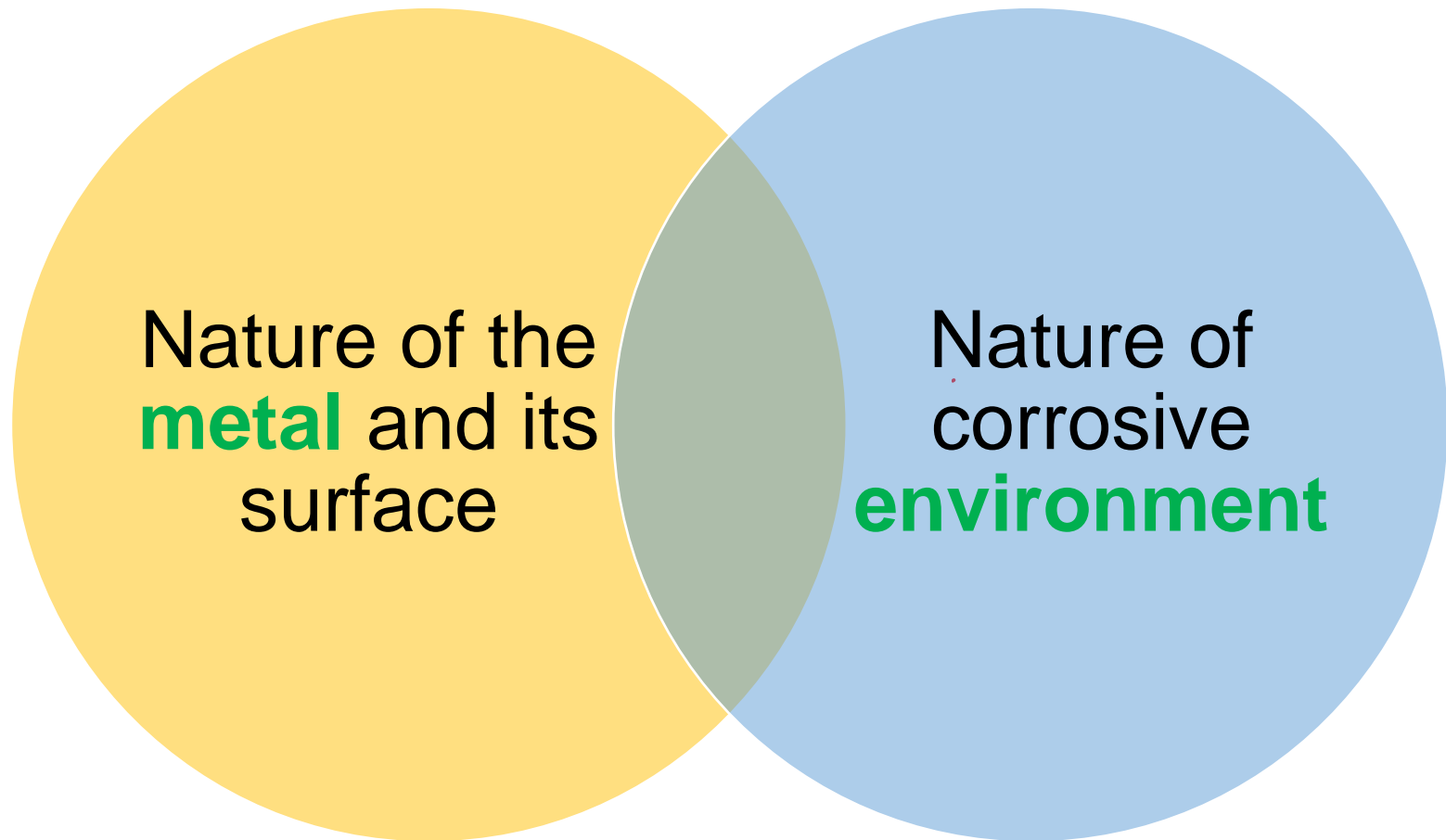
- Highly protective.
- Very thin (0.0004mm)
- Quite invisible film on the surface of metal or alloy.
- makes it more noble.

Passivity film is

- Insoluble.
- Non-porous
- Self healing nature
- Examples of passive metals and alloys are Ti, Al, Cr and wide variety of stainless-steel alloys, containing Cr.



Factors Influencing the rate of Corrosion



Factors Influencing the rate of Corrosion

1) *Nature of the **metal** and its surface*

1) Purity of the metal:

- Impure metals corrode easier than pure ones.
- As a result of impurities, tiny electrochemical cells form where anodic parts corrode.

2) Position of metal in galvanic series

- Metal at the top of the series act as **anode** that corrode easily.
- Metal at the bottom of the series acts as **cathode** that protected.

Factors Influencing the rate of Corrosion

1) *Nature of the **metal** and its surface*

3) Surface of the metal:

- Due to dirt accumulation, metals with rough surfaces are more likely to corrode.
- Polished surfaces do not corrode easily.

4) Physical state of the metal:

- ✓ A metal's physical state influences its corrosion rate.
- ✓ The smaller the grain size of a metal or alloy, the greater the corrosion rate

Factors Influencing Corrosion

2) *Nature of corrosive environment*

1) Temperature:

- Temperature accelerates almost all chemical reactions.
- As a result, corrosion rates also increase with temperature.

2) Humidity of air:

- ✓ As air humidity increases, corrosion increases.
- ✓ Since humidity acts as a solvent for oxygen, it is essential for the formation of corrosive cells

3) Nature of atmosphere:

- ✓ The corrosion rate increases if the air is polluted by smoke or gases (H_2S , SO_2) & electrolytes (NaCl & $(\text{NH}_4)_2\text{SO}_4$).

Factors Influencing Corrosion

2) *Nature of corrosive environment*

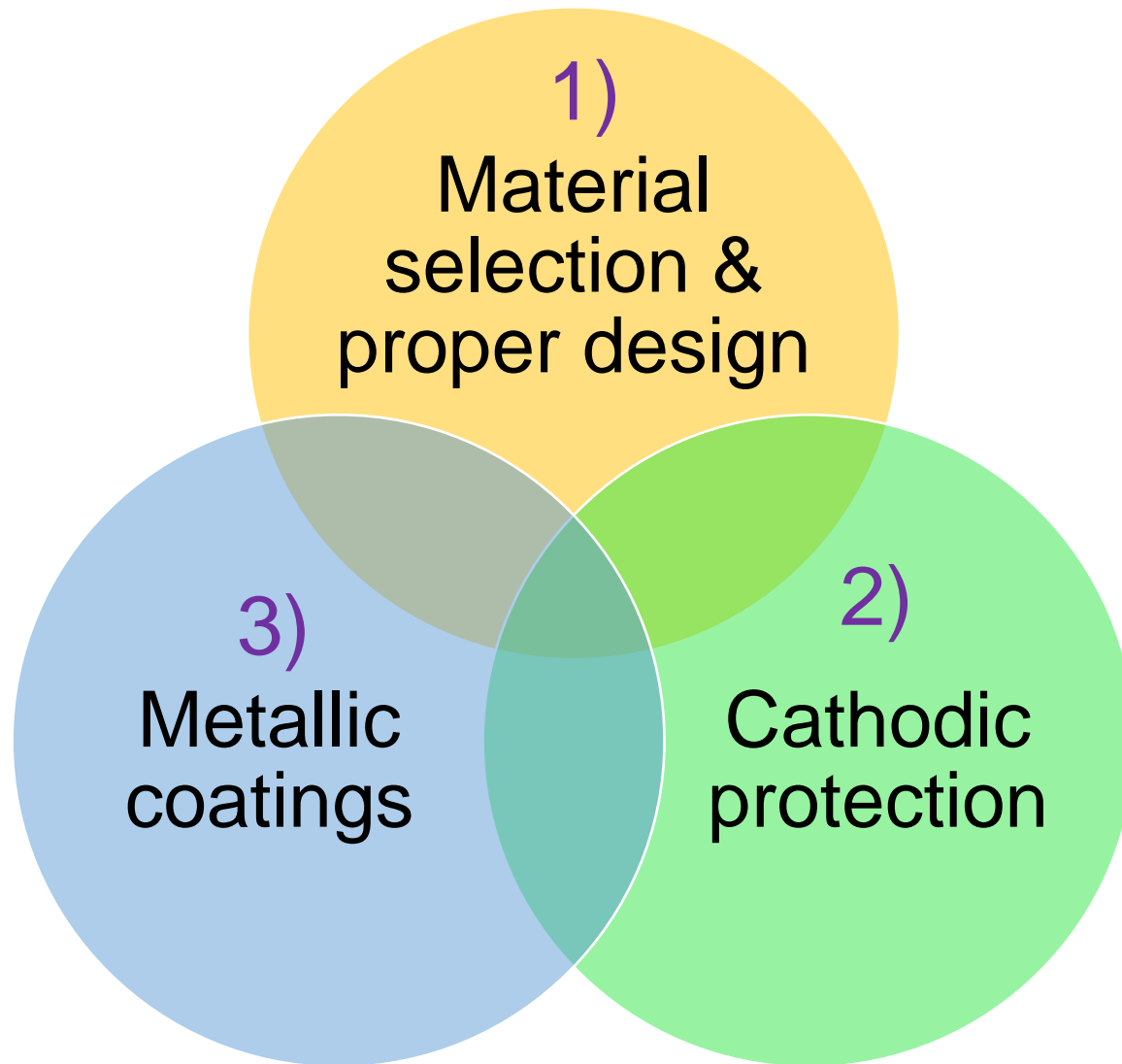
4) Effect of P^H :

- Generally, acidic media are more corrosive than alkaline or neutral media.
- In low P^H conditions, hydrogen ions are more prevalent, which accelerates corrosion.

5) Corrosive medium conductivity:

- ✓ Clay/mineralized soils have a higher conductance than dry sandy soils.
- ✓ Thus, metals submerged in clay/mineralized soil corrode faster.

Protection methods of corrosion



Protection methods of corrosion

1) Material selection & proper design

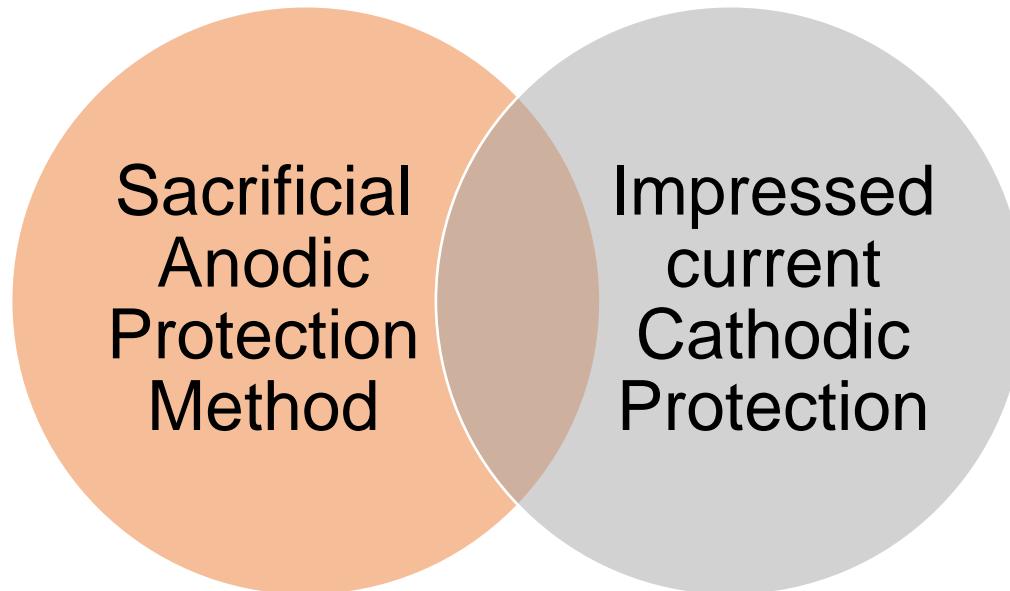
- Using pure metal
 - Corrosion is accelerated by metal impurities.
- Using metal alloys
 - A homogeneous alloy reduces corrosion rates.
- In a corroding environment, **avoid contacting** dissimilar metals.
- A dissimilar metal should have **more anodic surface** area than a cathodic surface.
- An **insulating material** is placed between two dissimilar metals.
- In the case of the same metal, a proper design should **avoid cracks** between adjacent parts.
- **Sharp corners** should be avoided to prevent stagnant areas & solid accumulation.

Protection methods of corrosion

2) Cathodic protection

In this method, the corroding metal is forced to behave like a cathode.

Cathodic protection has two types:



Protection methods of corrosion

1) Sacrificial Anodic Protection Method:

This method involves connecting a metallic structure to an anodic metal using a wire.

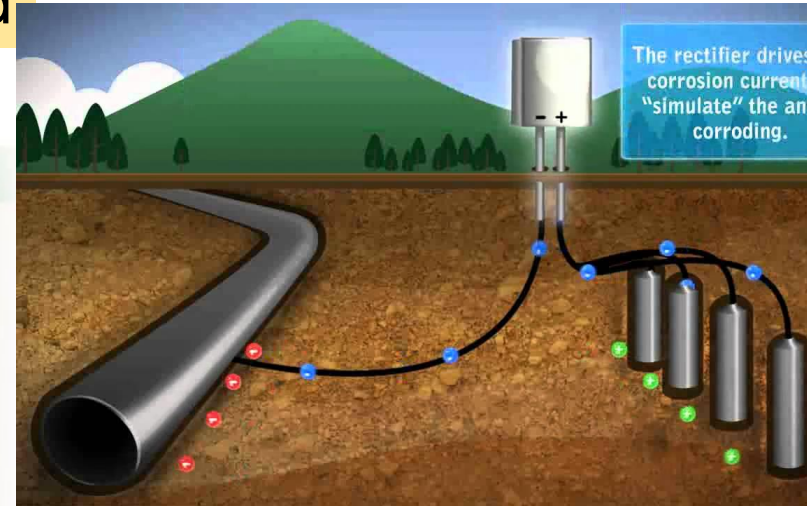
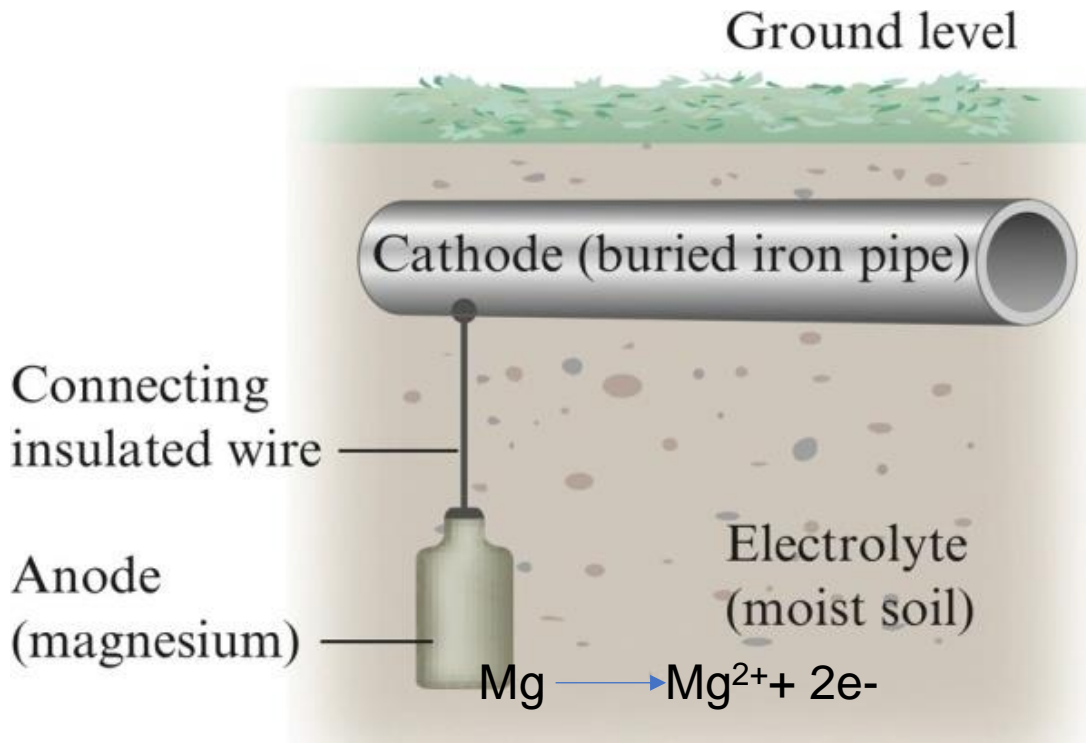
As a result, more anodic metal corrodes while more parent metal is protected during corrosion.

This metal is known as the sacrificial anode, which is periodically replaced with a fresh one.

Magnesium and zinc are commonly used as sacrificial anodes

Protection methods of corrosion

1) Sacrificial Anodic Protection Method



Applications:

Important applications of sacrificial anodic method include protection of buried lines, underground cables, marine structures etc.

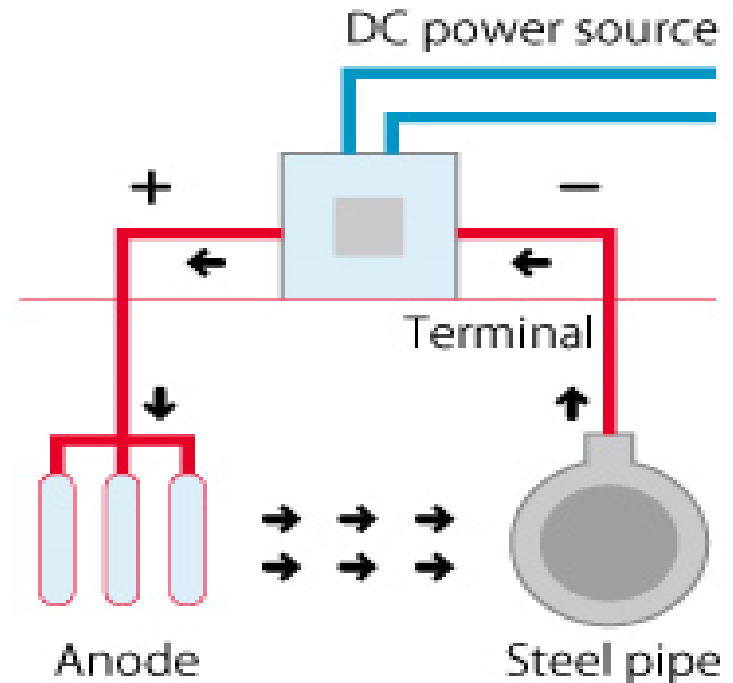
Protection methods of corrosion

2) Impressed Current Cathodic Protection

- Using this technique, the metallic object to be protected is made cathode by connecting it to the negative terminal of the DC source.
- Positive terminal is connected to an insoluble anode such as graphite, scrap iron, or platinum.

Applications:

- Submarines are protected against corrosion by connecting the negative terminal of DC generators to the surface.
- Water tanks, buried oil or water pipelines, transmission line towers are protected by this method.





**Then how to
coat a metal
on other
metal?**

Base Metal = On which coating occurs
Coat Metal= By which coating occurs

Protection methods of corrosion

2) Metallic coatings

Base metal is protected from corrosive environments by these coatings.

There are two types.

- **Anodic Coatings:** (Sacrificial Coating)
- **Cathodic Coatings:** (Noble Coating)

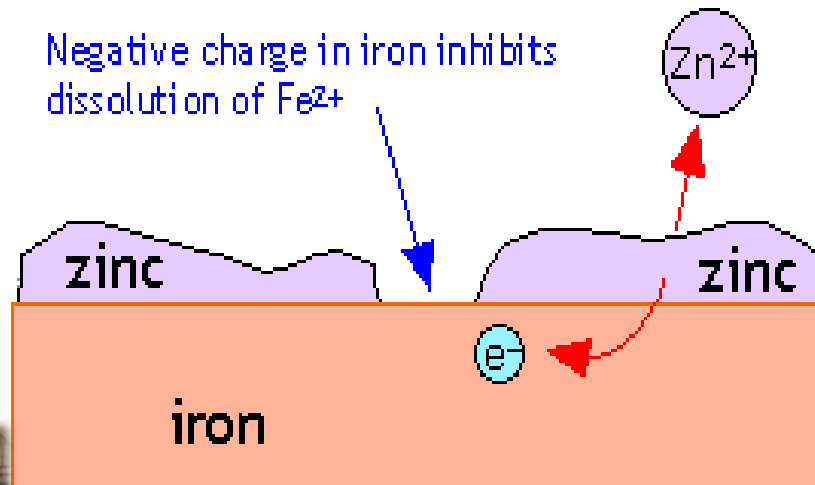


Protection methods of corrosion

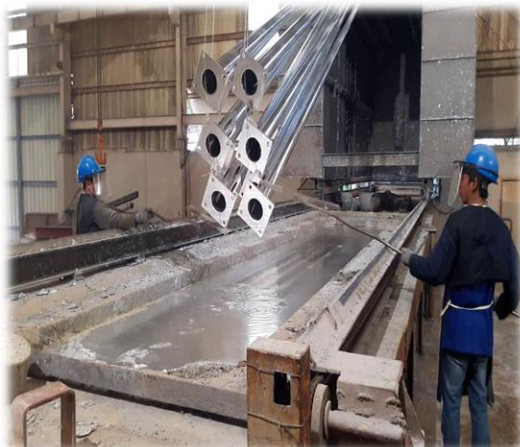
2) Metallic coatings: a) Anodic Coatings: (Sacrificial Coating):

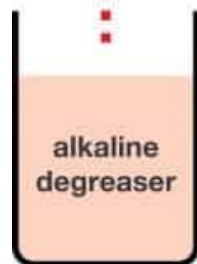
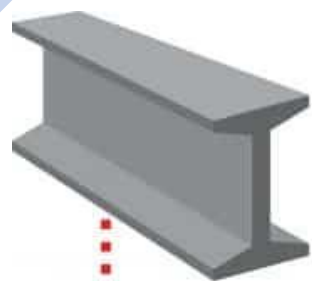
- Ex: Steel (Iron) is coated with Zinc.

Zinc serves as anode and Iron serves as cathode.

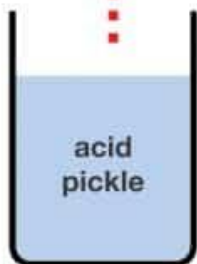
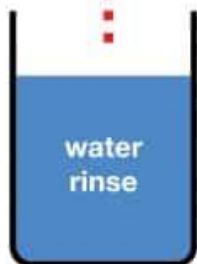


Sacrificial coating





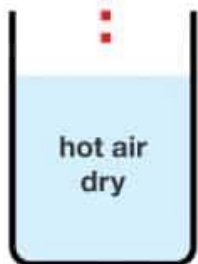
paint and oil removed



rust and mill scale removed



ZAC to activate steel surface



reduces splash and increases dip speed



galvanize at 450°C



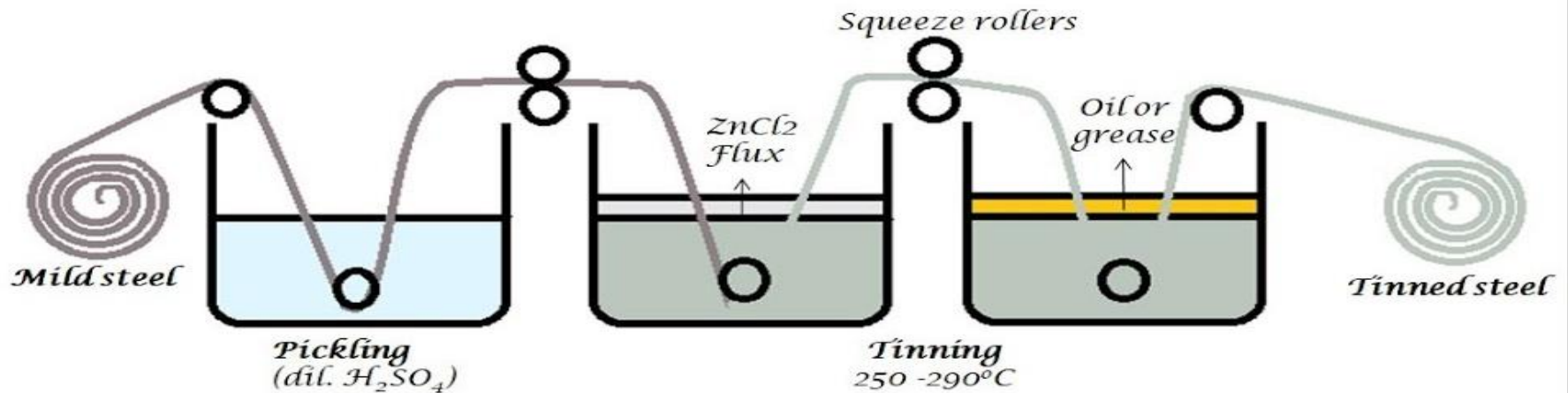
quench and passivate

Protection methods of corrosion

2) Metallic coatings: b) Cathodic Coatings: (Noble Coating):

- Ex: Steel (Iron) is coated with Tin

Steel serves as anode and Tin serves as cathode.



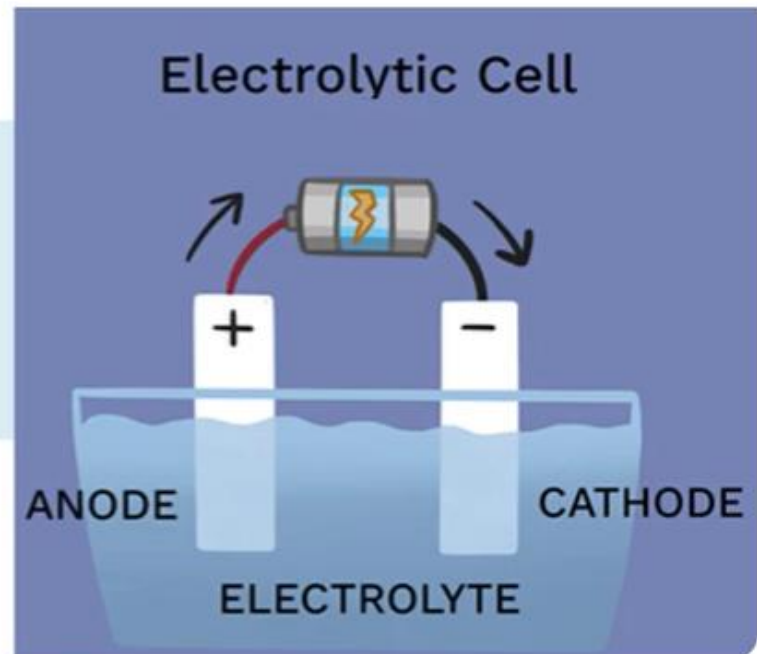
Electroplating

Electroplating:

Coating of coat metal on the surface of base metal by passing a direct current through an electrolytic solution is called electroplating.

At Anode: Oxidation takes place
(loosing of electrons)

At Cathode: Reduction take place
(gaining of electrons)

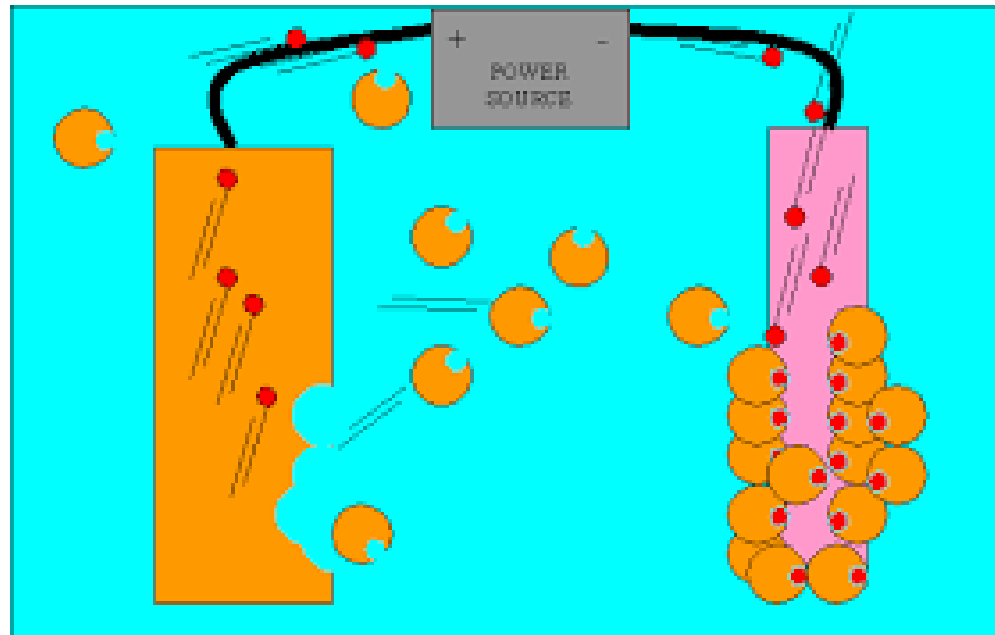


Electroplating

Electro plating is the process of deposition of a metal, nonmetal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.

The process of electroplating consists of two steps

- Surface preparation
- Electro deposition



Electroplating

1) *Surface preparation*

1) Mechanical Cleaning:

- The metal surface is cleaned mechanically with brushes, knives, cutters, chisels, then heated and washed.

2) Alkali cleaning:

- ✓ Alkaline solution of sodium hydroxide, sodium carbonate, etc., removes oils, greases and impurities.

3) Solvent Cleaning:

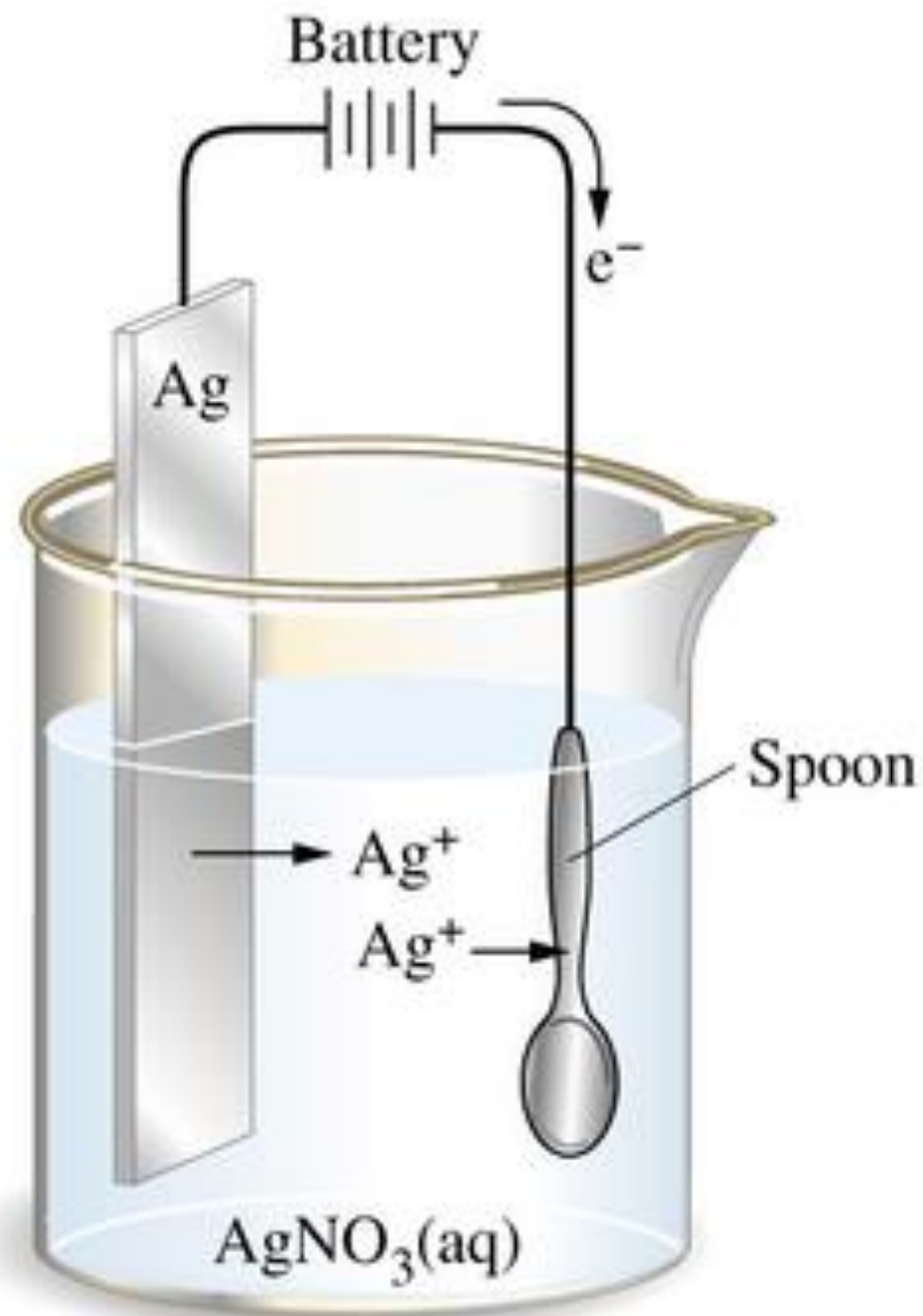
- ✓ Oils, Fatty substances and greases are removed by Solvents wash (CCl_4 , & acetone)
- ✓ metal surface is washed with hot water

Electroplating

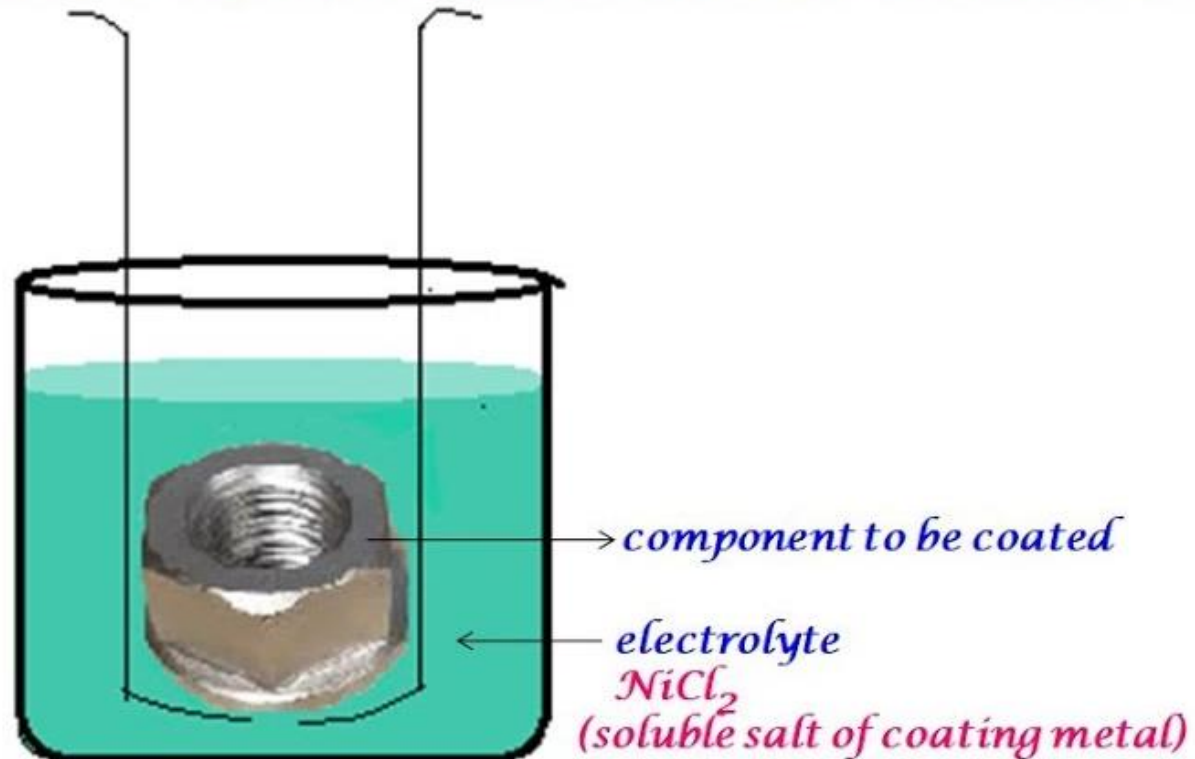
1) *Electro-deposition:*

Electroplating With Gold:

- Cathode: Article to be electroplated (Spoon)
- Anode: Block of gold metal
- Electrolyte: Aqueous solution of AuCl_3 or Potassium auro-cyanide $\text{K}[\text{Au}(\text{CN})_2]$
- Process: Gold metal act as anode undergo dissolution, get deposited on the cathode (spoon) by passing electricity.



ELECTROLESS PLATING OF NICKEL



metal ions (M^{n+}) + reducing agent \rightarrow metal (M) + oxidised product



**Thanks You
For Your Attention**

Do u have

**Any
QUESTION?**