

CO-2: Corrosion and its control



K L University

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(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.



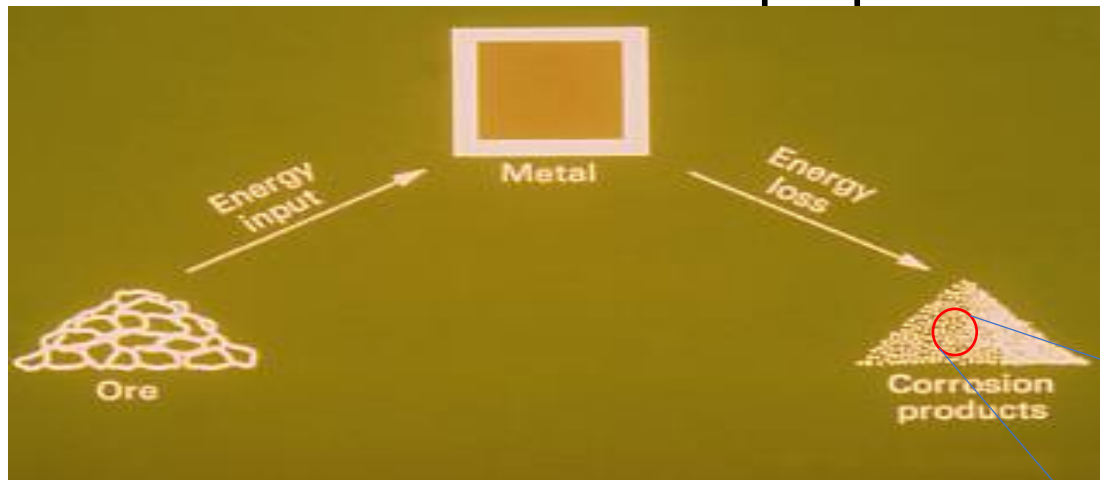
Corrosion is an unintentional reaction between a material and its environment.



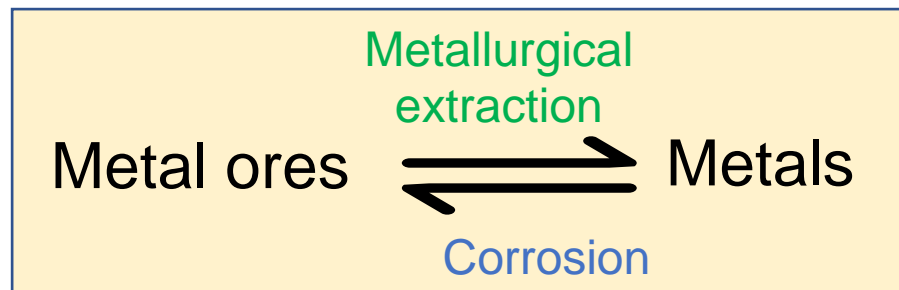
It is very important to consider corrosion when the structure or equipment is meant to last many years.

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



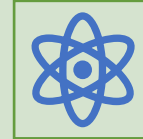
Tarnishing of silver;
Silver sulphide that form sulfur compounds in air.

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

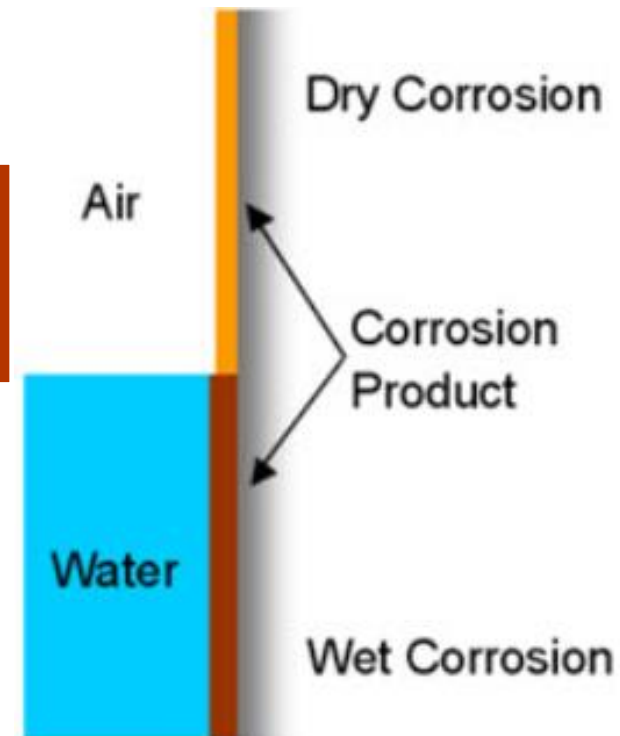
Depends on the environment to which the metals are exposed



Dry Corrosion or Chemical Corrosion

The diagram features two white circles on the left, each connected by a thin yellow line to a horizontal rectangular box. The top box is grey and contains the text 'Dry Corrosion or Chemical Corrosion'. The bottom box is brown and contains the text 'Wet Corrosion or Electrochemical 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

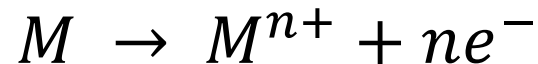
- Oxidation corrosion
- Corrosion by gases

Dry Corrosion or Chemical Corrosion

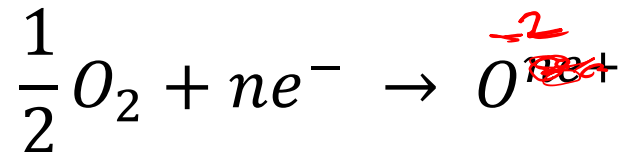
(i) Oxidation corrosion

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

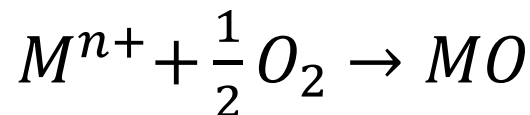
→ Metal gets oxidized to metal ions.



→ Reduce oxygen to form oxide ion.

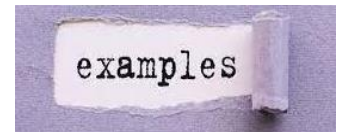
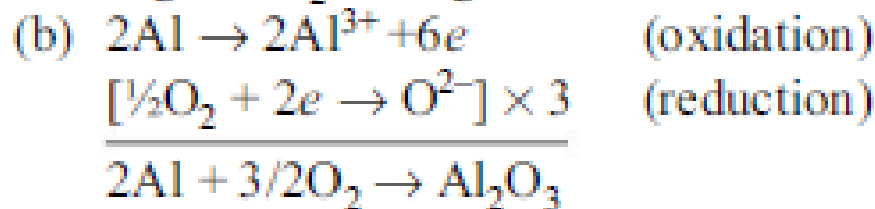
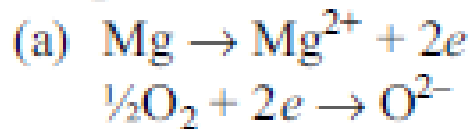


→ Metal ion and oxide ion combine to form metal oxide.

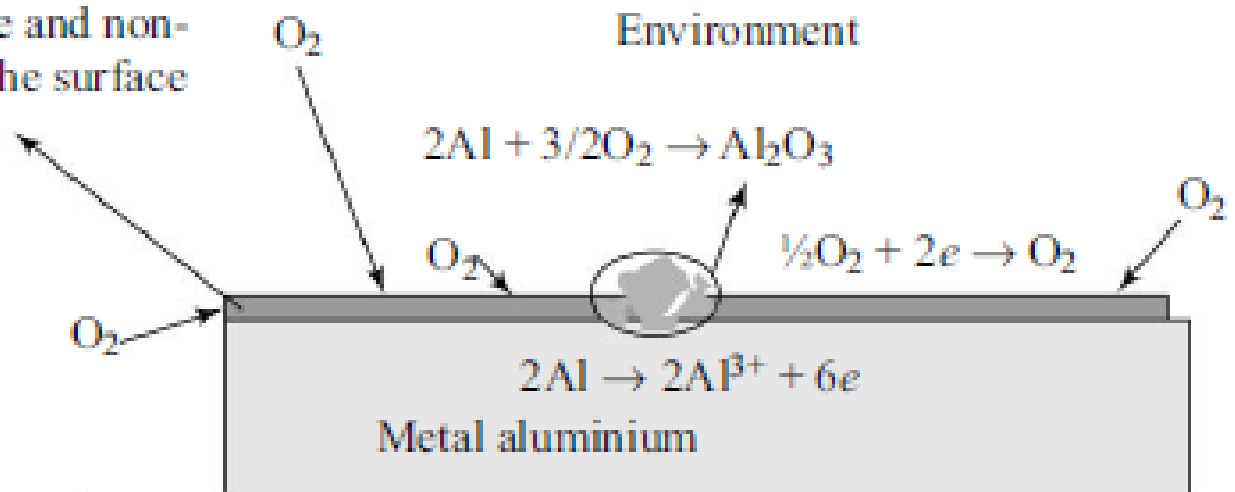


Dry Corrosion or Chemical Corrosion

(i) Oxidation corrosion

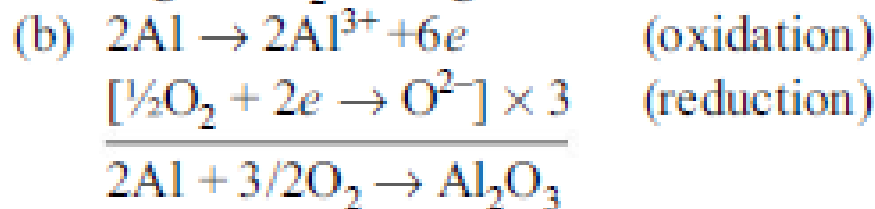
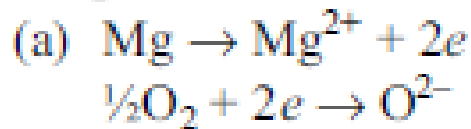


Stable protective and non-porous film on the surface of Aluminium

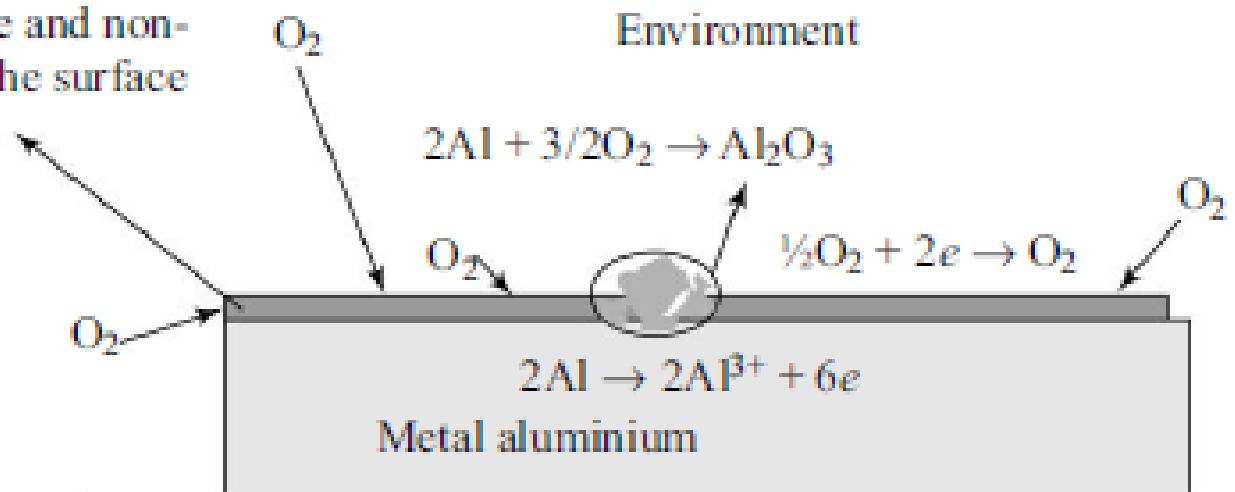


Dry Corrosion or Chemical Corrosion

(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 (O R) 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

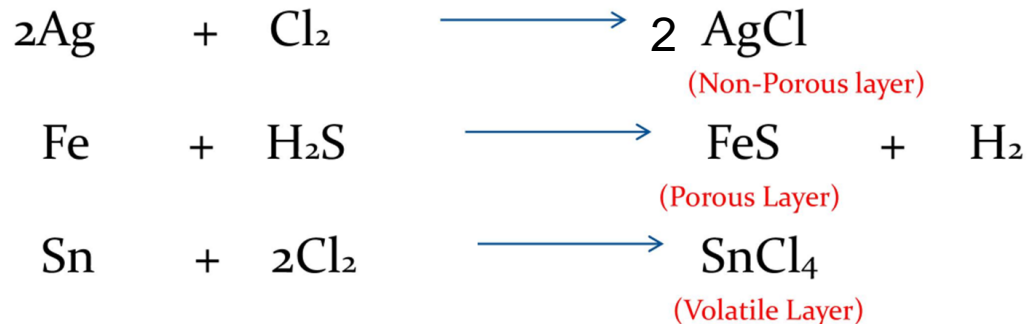
$$\text{Pilling Bedworth rule} = \frac{\text{Vol. of metal oxide layer}}{\text{Vol of metal consumed}}$$

- 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.

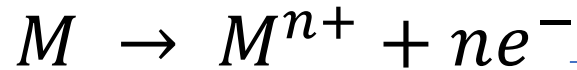
Corrosion of this type can be observed when

- 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:

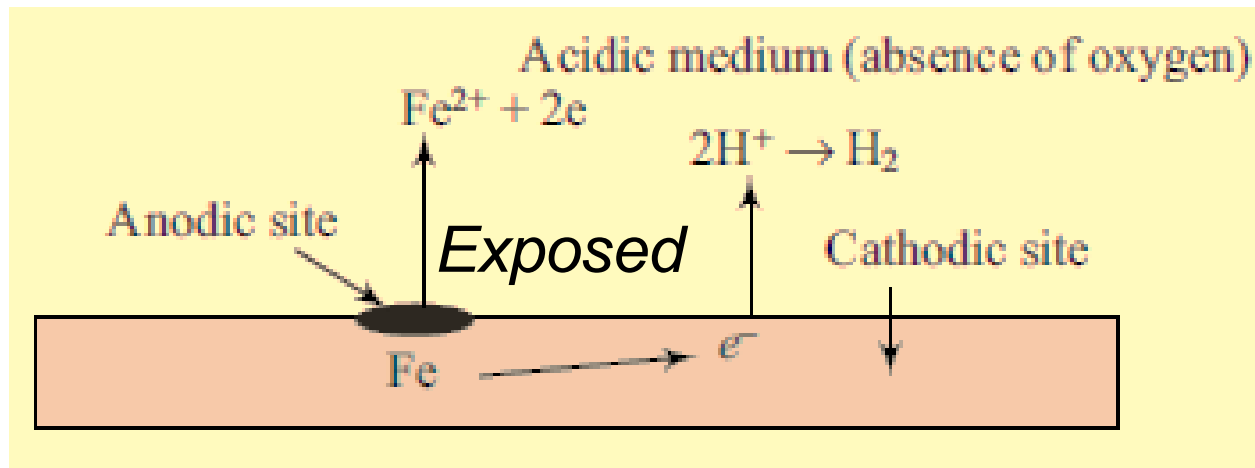
(a) Liberation of H₂

(b) Absorption of oxygen

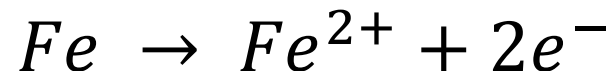
Electrochemical theory of wet corrosion

Evolution of Hydrogen type:

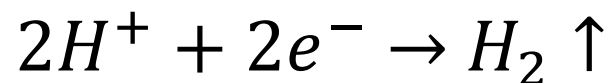
In acidic medium and in the absence of oxygen, H^+ ions are reduced to H_2 gas.



In the anodic area: Oxidation

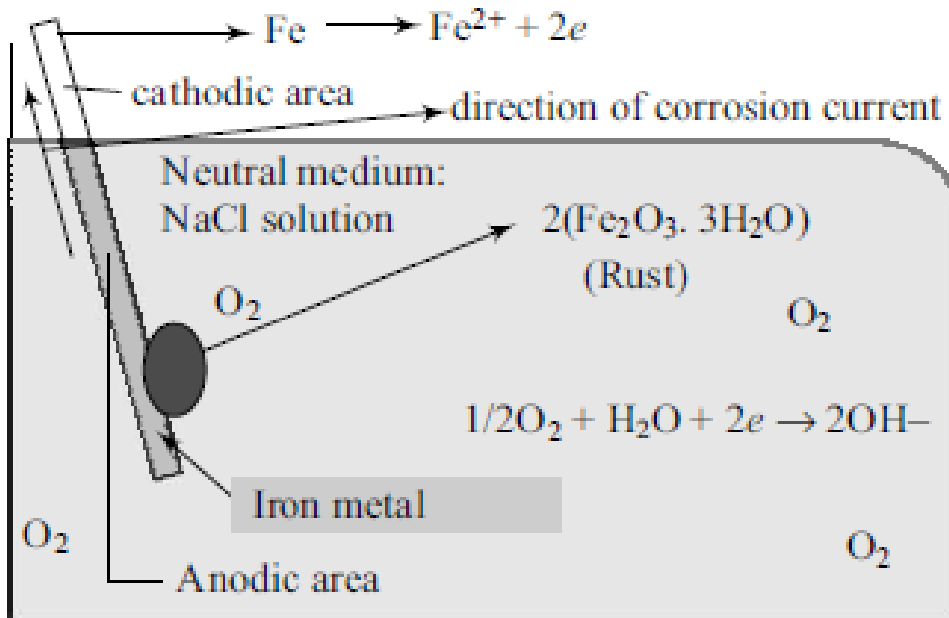


In the cathodic area: Reduction



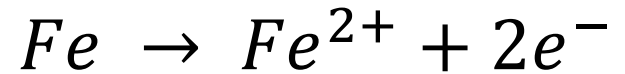
Electrochemical theory of wet corrosion

b) Absorption of Oxygen

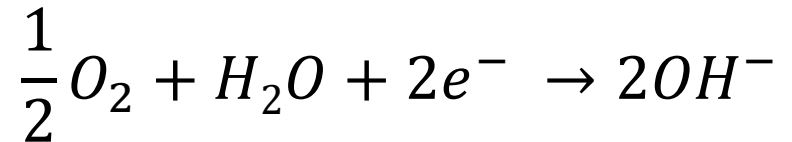


Iron rusting in oxygen-rich neutral medium

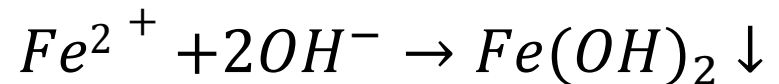
In the anodic area: Oxidation



In the cathodic area: Reduction

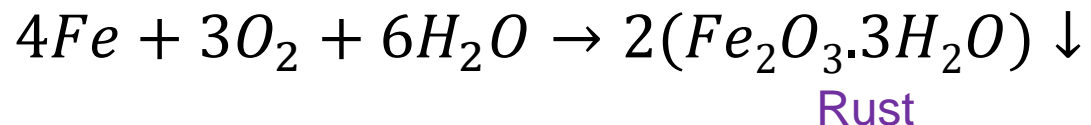


If the solution is neutral and aerated, hydroxyl ions are formed as follows.

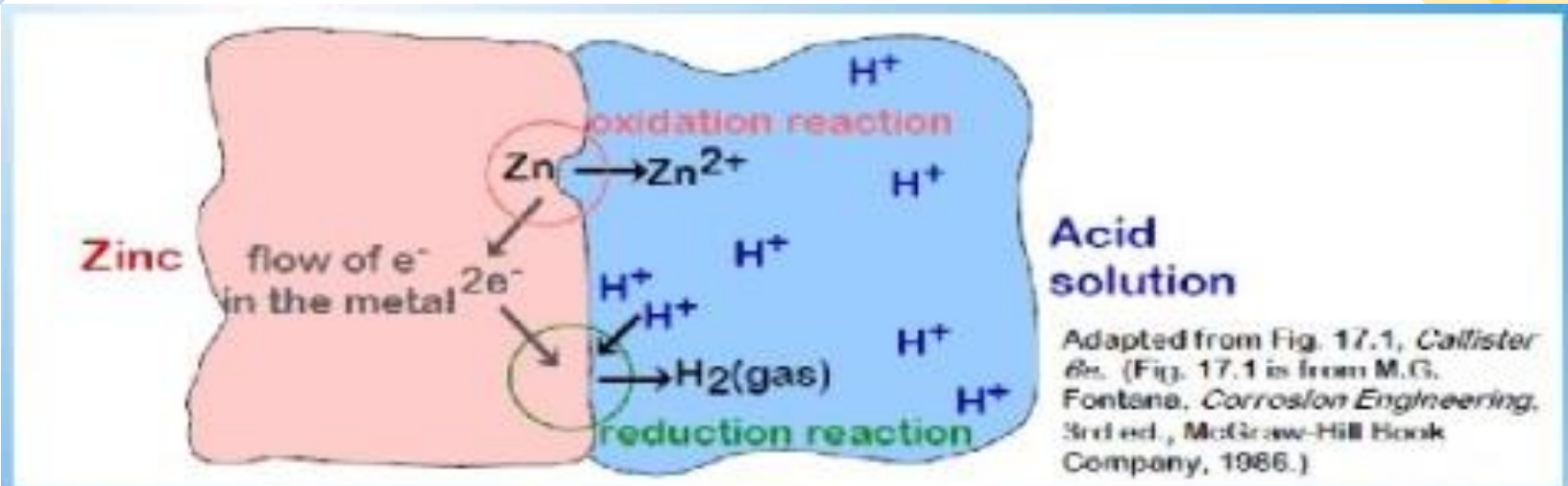


Hydroxyl ions react with metal ions and forms corrosion product.

Net corrosion reaction:



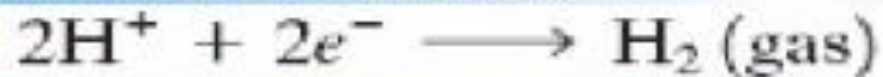
Ex. 1: Zinc metal immersed in an acid solution contain H^+



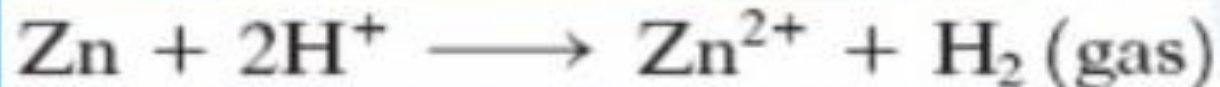
➤ zinc will experience oxidation or corrosion according to,



➤ H^+ ions are reduced according to,



➤ The total electrochemical reaction



Differences between dry and wet corrosion

Dry corrosion

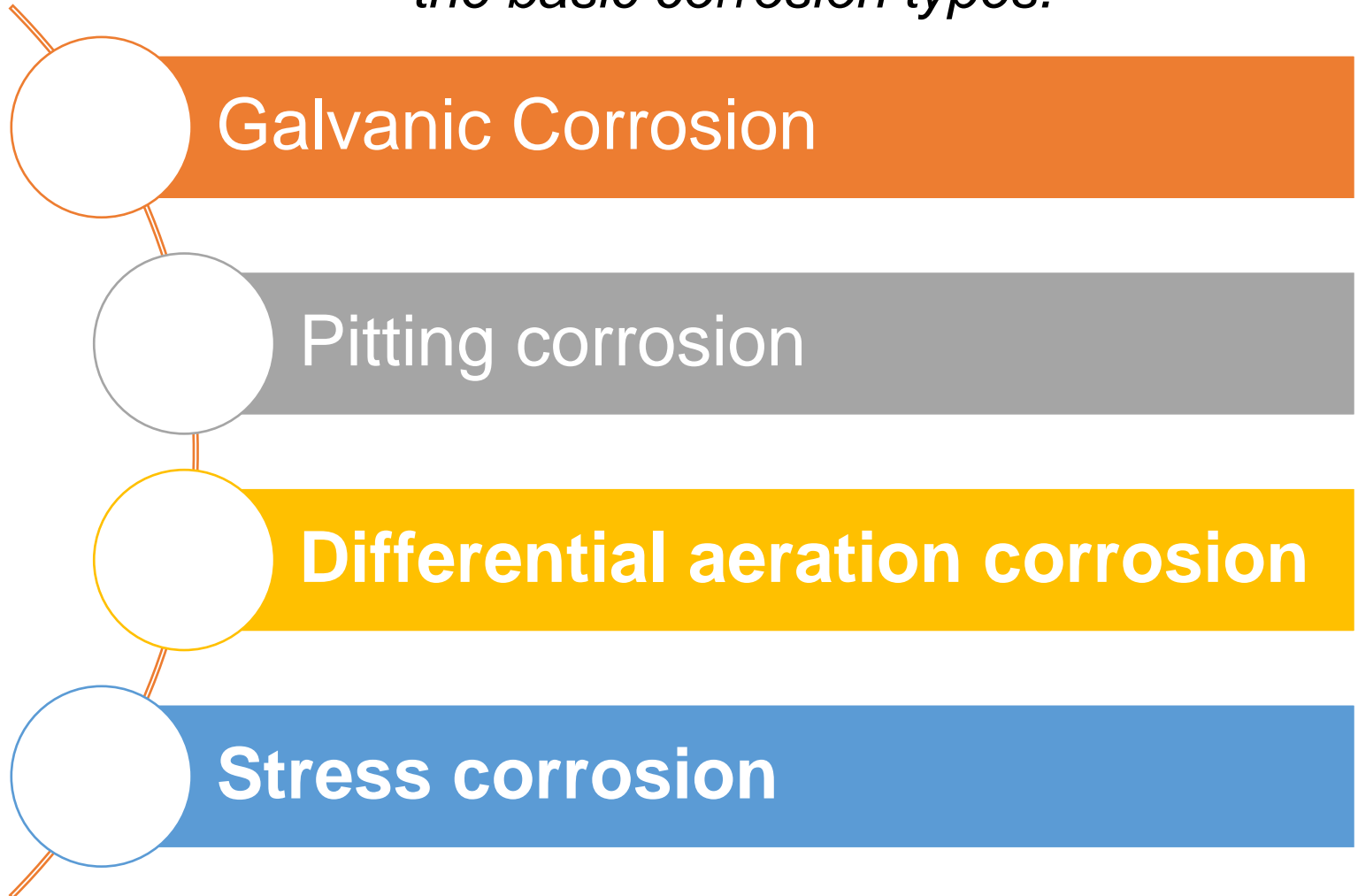
- It occurs in the absence of moisture.
- It involves direct attack of chemicals.
- It is slow process.
- Products are produced at site of corrosion.
- Process of corrosion is uniform.

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.

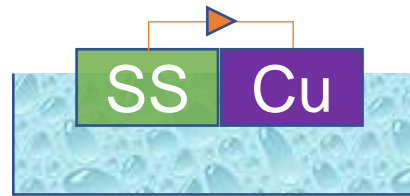
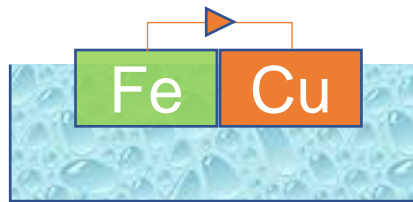
Different Forms of Wet Corrosion

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

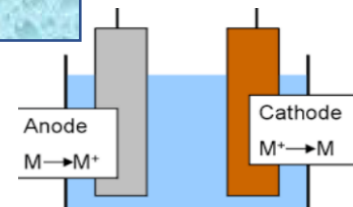


Galvanic or bimetallic corrosion

- 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.



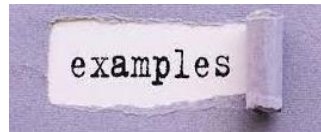
Bimetallic couples



Galvanic or bimetallic corrosion



Steel pipe connected to copper



Zinc coating on mild steel

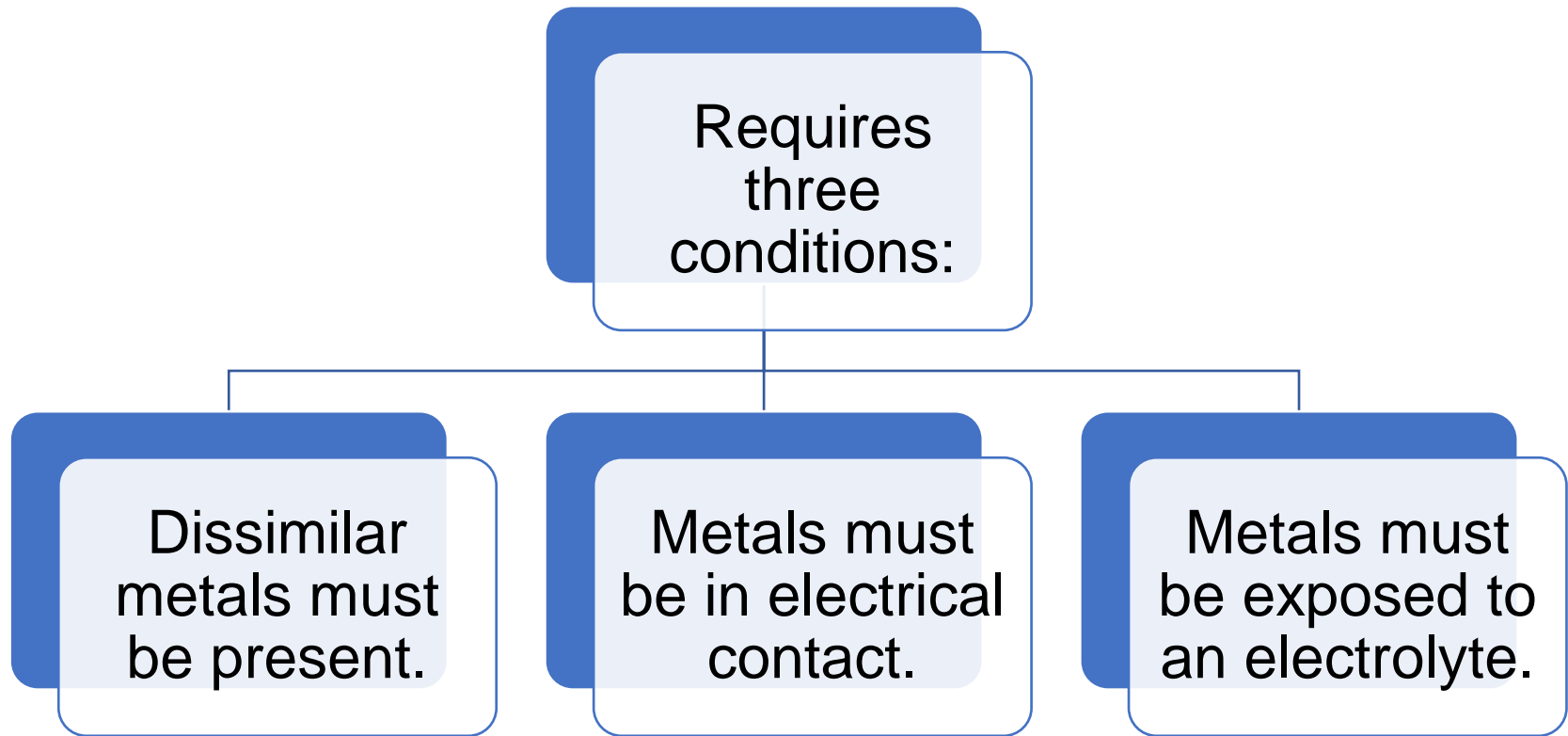


Tin coating on copper vessel



Steel propeller shaft in bronze bearing

Galvanic or bimetallic corrosion

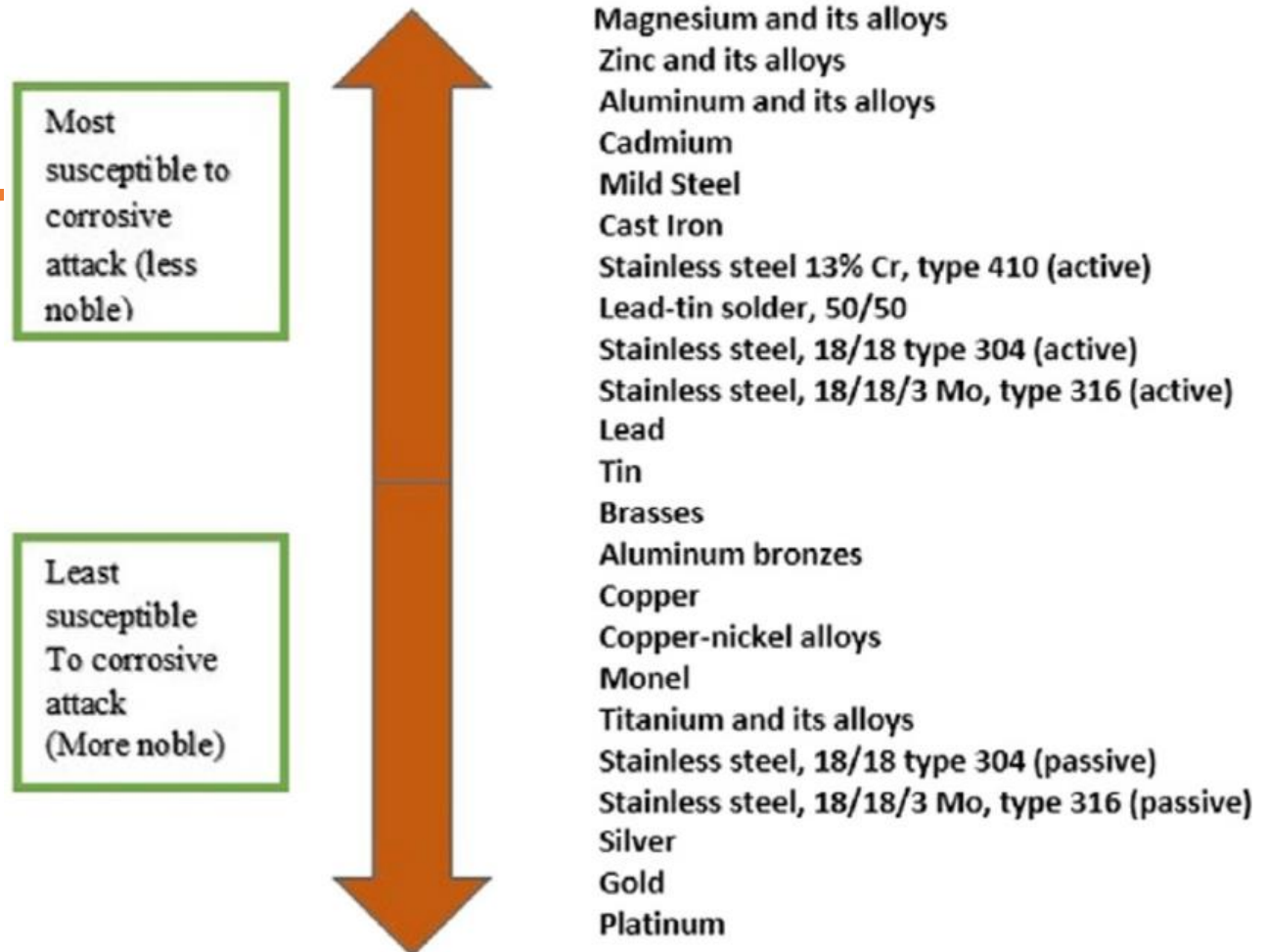


Galvanic or bimetallic corrosion

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

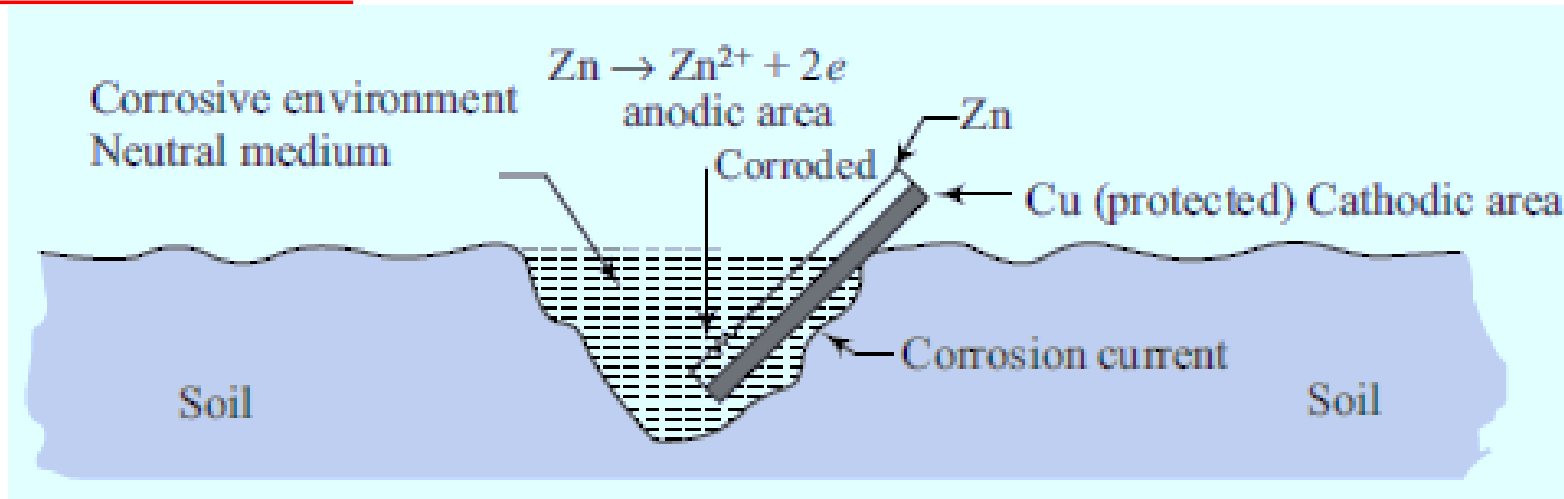
- A metal with a high standard oxidation potential acts as an anode, while a metal with a low reduction potential acts as a cathode.

Corrosion Susceptibility of metals

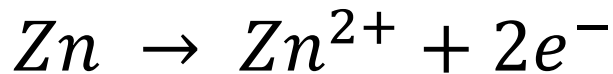


Galvanic or bimetallic corrosion

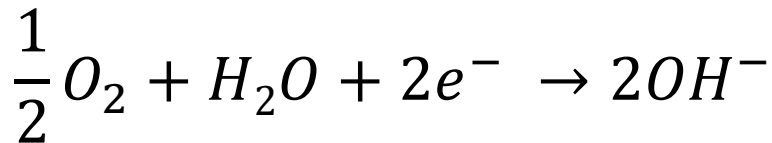
Mechanism



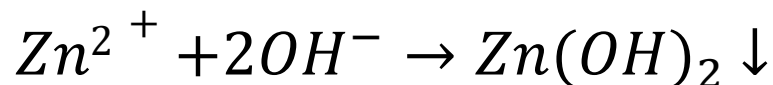
In the anodic area



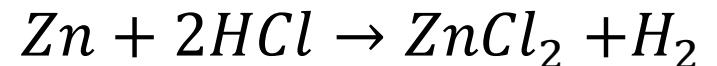
In the cathodic area



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.



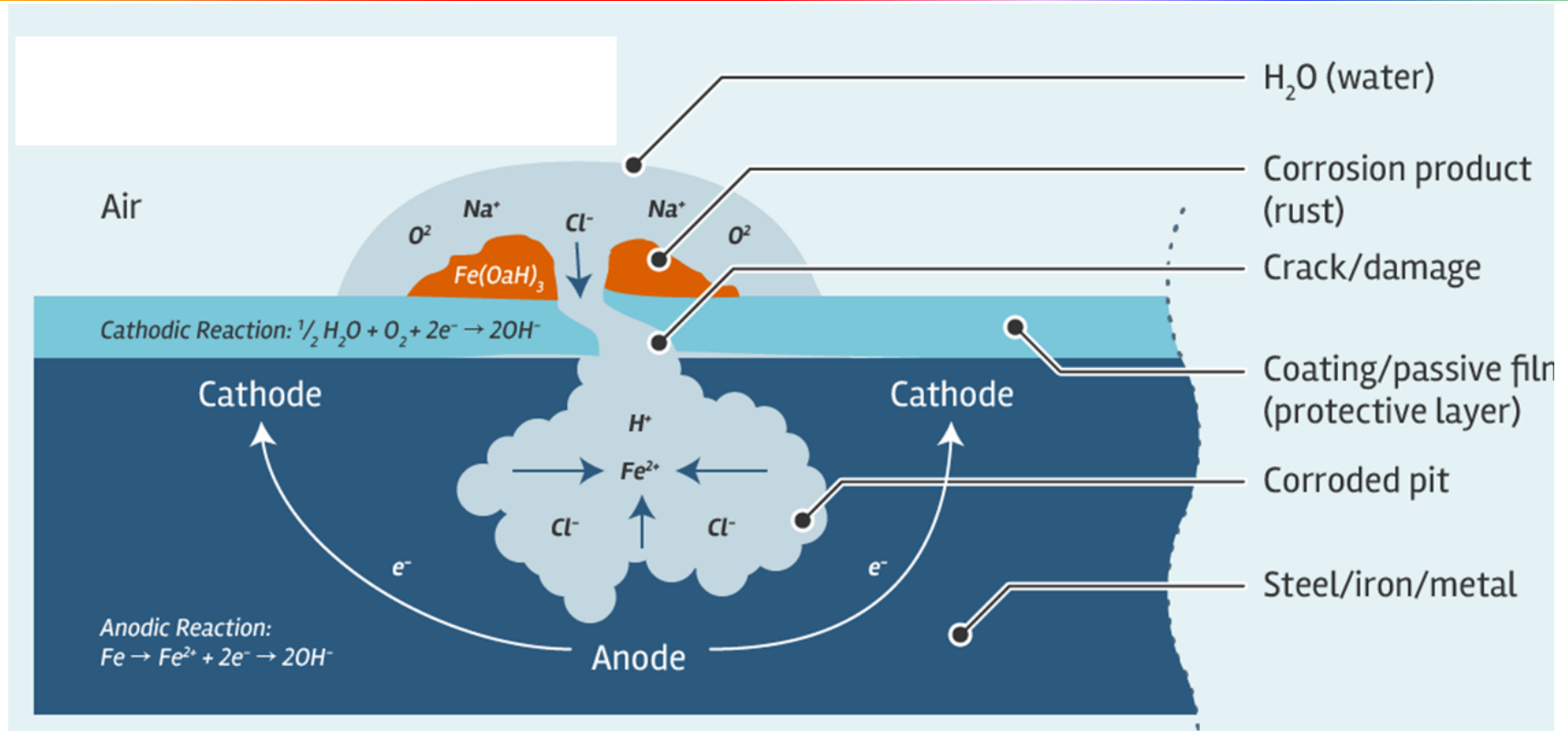
A pit or a hole forms at the anode when the anodic area and cathodic area are not equal.



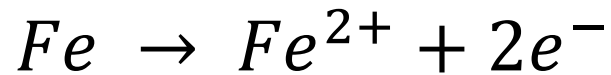
Causes of pitting corrosion

- ☞ 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).

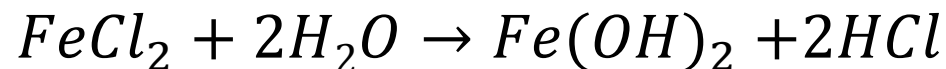
Mechanism of pitting corrosion



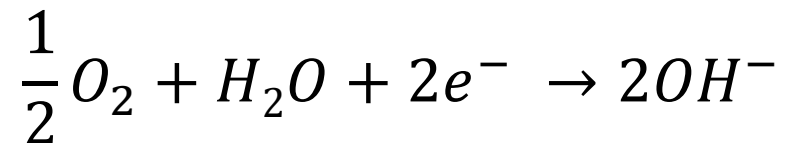
In the anodic area: Oxidation



Overall,



In the cathodic area: Reduction



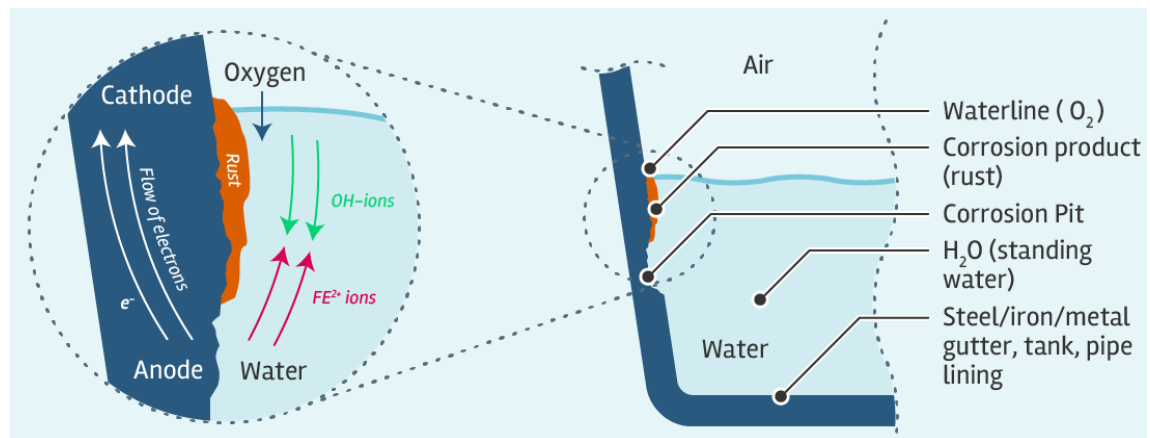
Ways to prevent pitting corrosion

- 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.

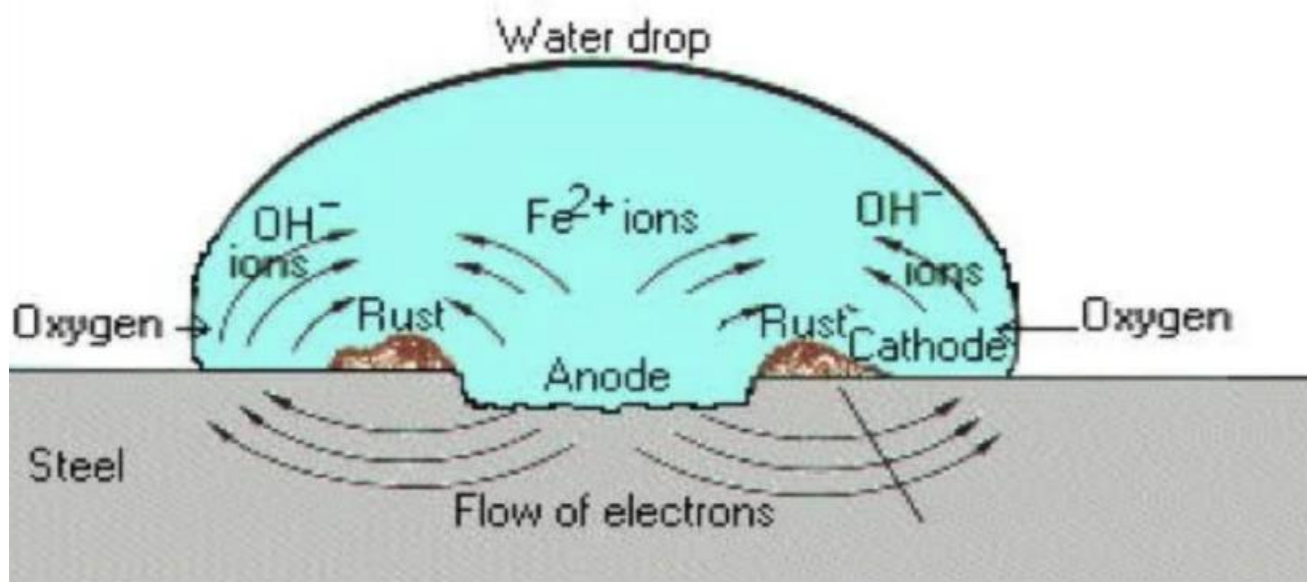


Differential aeration corrosion

- 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



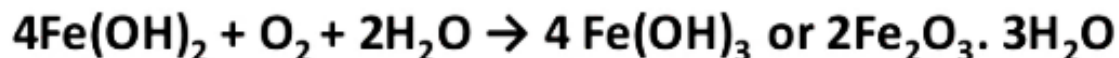
In case of Iron metal

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

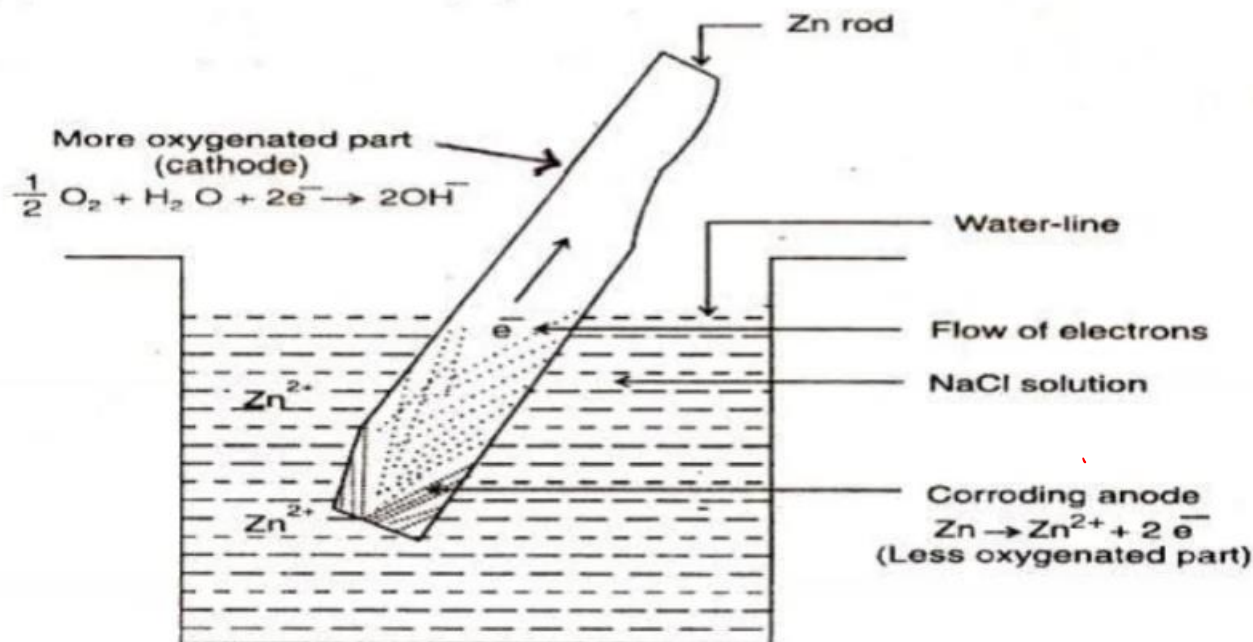
Reaction at cathode:- $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (Reduction)

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

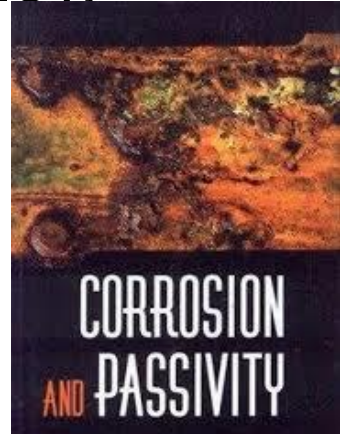
There is a phenomenon known as passivity or passivation when a metal or alloy exhibits a much higher corrosion resistance than would be expected based on its chemical composition.

Passivity is the result of the formation of a

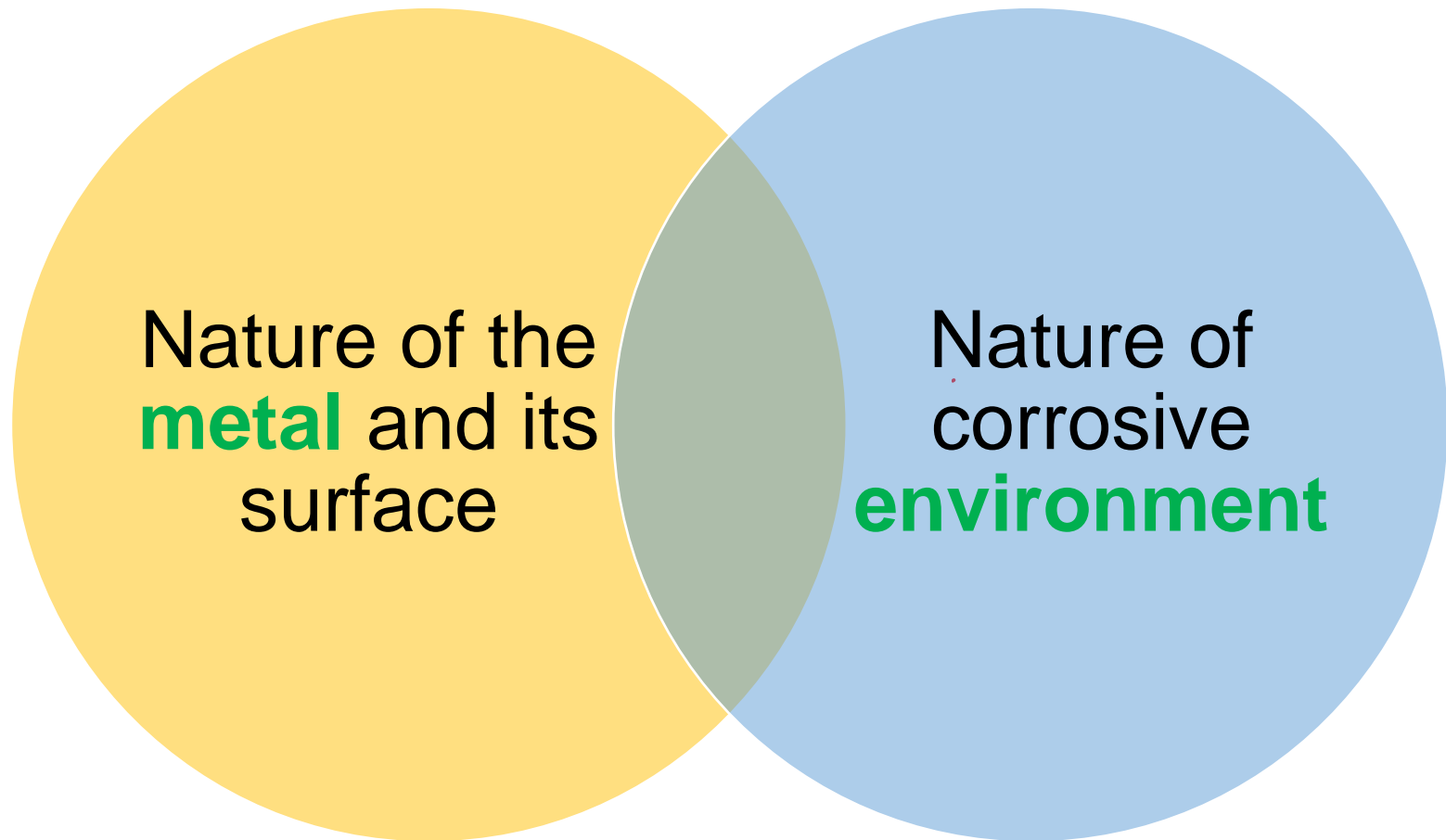
- Highly protective.
- Very thin (0.0004mm)
- Quite invisible film on the surface of metal or alloy.
- makes it more noble.

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*

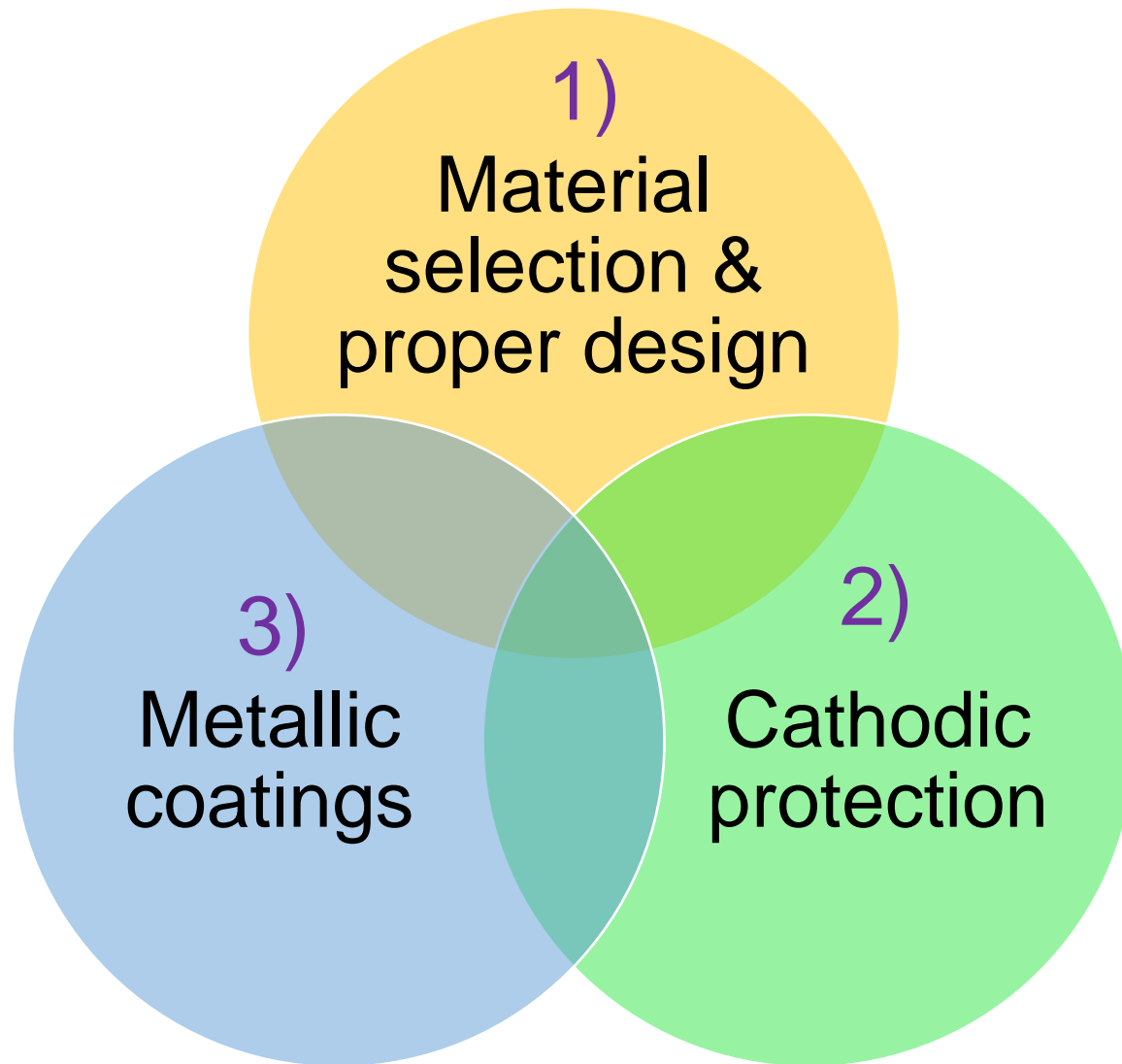
4) Effect of P^H :

- 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

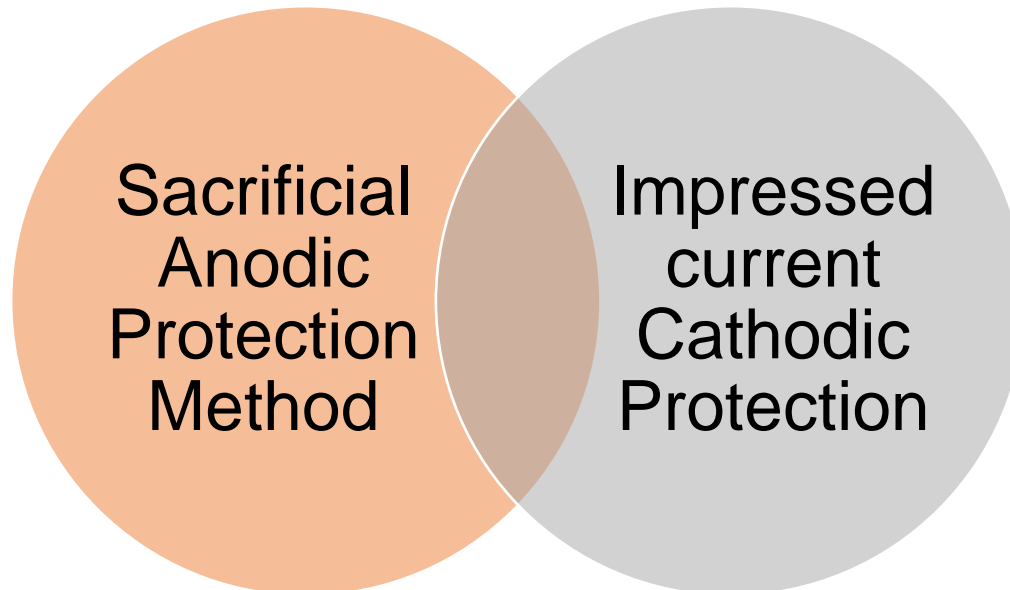
- Using pure metal
 - Corrosion is accelerated by metal impurities.
- Using metal alloys
 - A homogeneous alloy reduces corrosion rates.
- In a corroding environment, **avoid contacting** dissimilar metals.
- A dissimilar metal should have **more anodic surface** area than a cathodic surface.
- An **insulating 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.

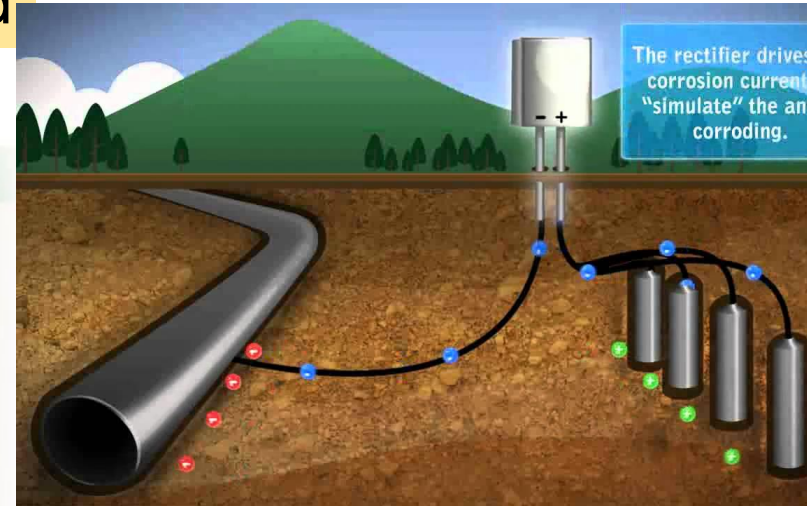
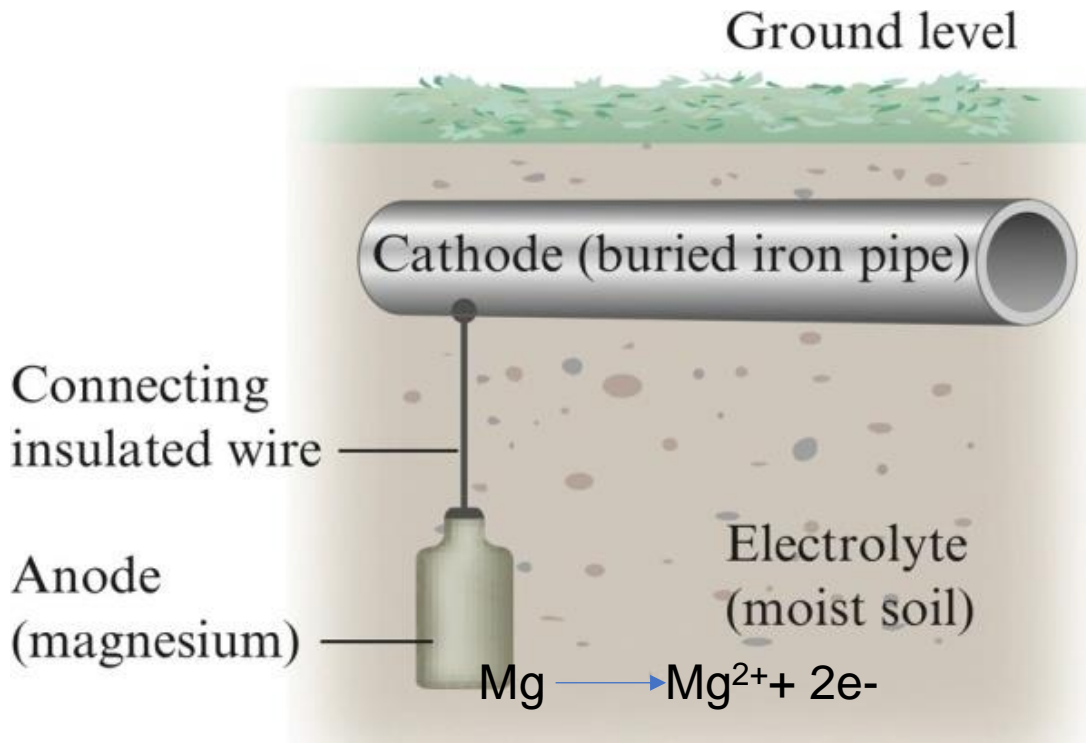
As a result, more anodic metal corrodes while more parent metal is protected during corrosion.

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.

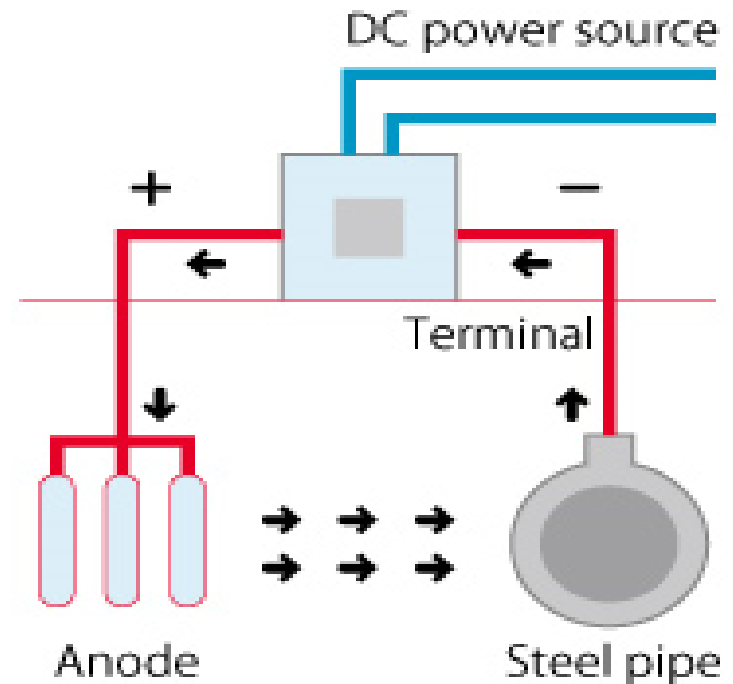
Protection methods of corrosion

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)

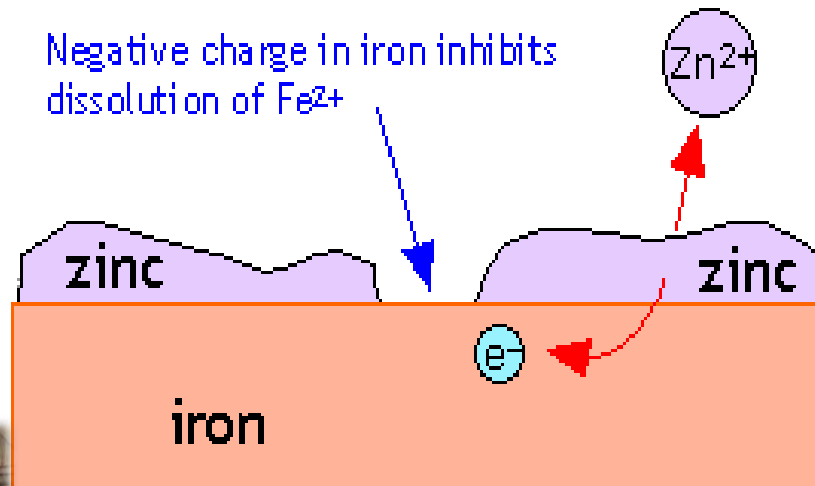


Protection methods of corrosion

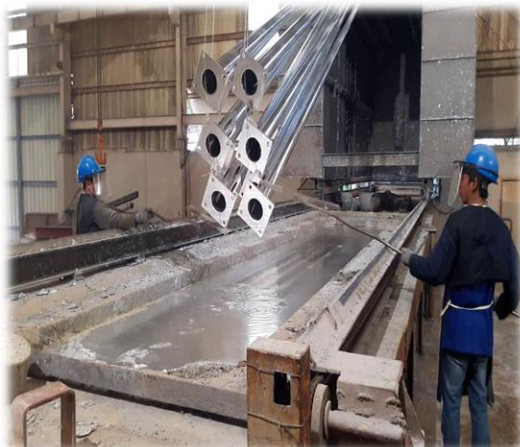
2) Metallic coatings: a) Anodic Coatings: (Sacrificial Coating):

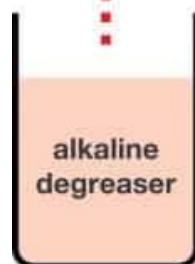
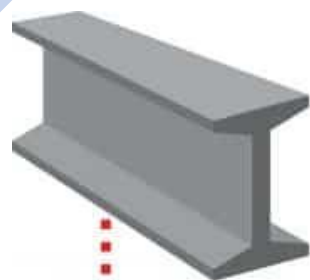
- Ex: Steel (Iron) is coated with Zinc.

Zinc serves as anode and Iron serves as cathode.

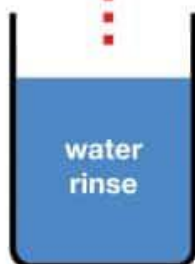


Sacrificial coating

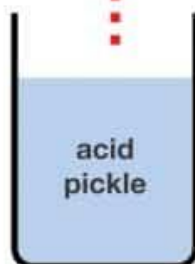




paint and oil removed

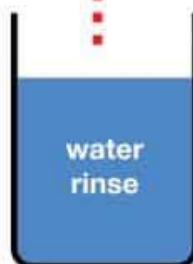


water
rinse



acid
pickle

rust and mill
scale removed



water
rinse



hot
flux

ZAC to activate
steel surface



hot air
dry

reduces splash
and increases
dip speed



molten
zinc

galvanize at
450°C



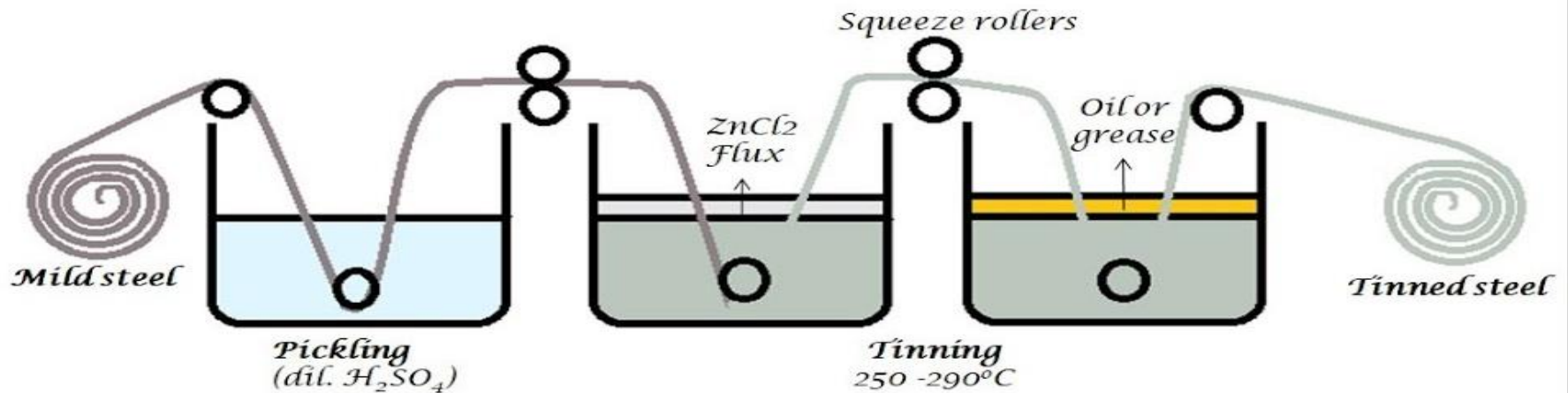
quench and
passivate

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.



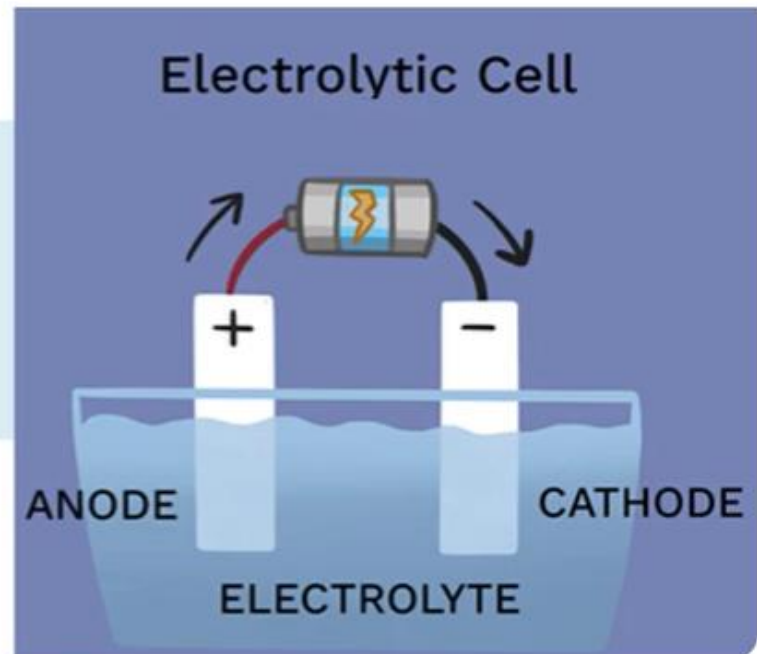
Electroplating

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)

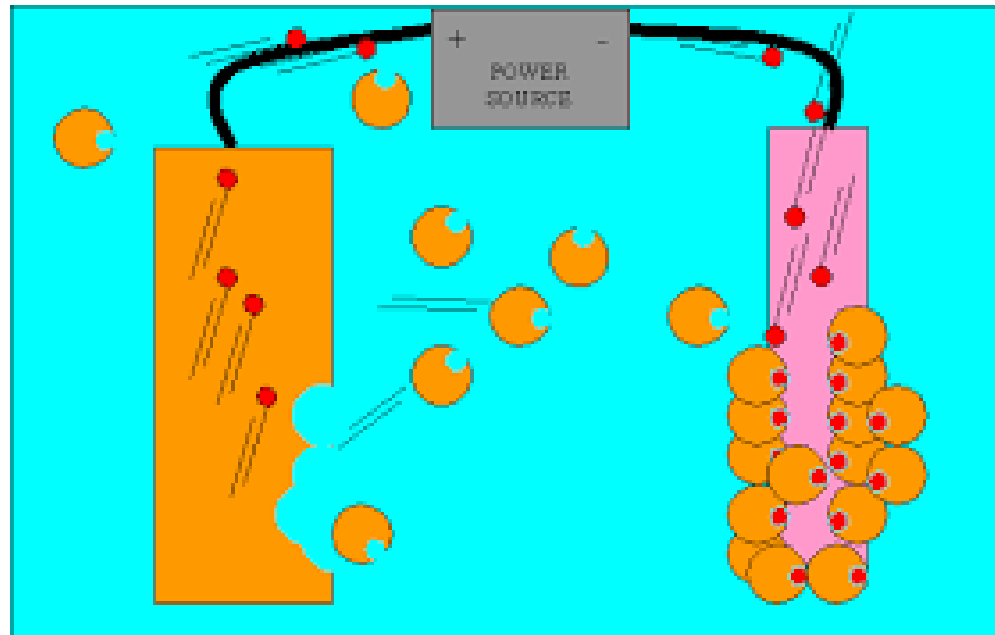


Electroplating

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:

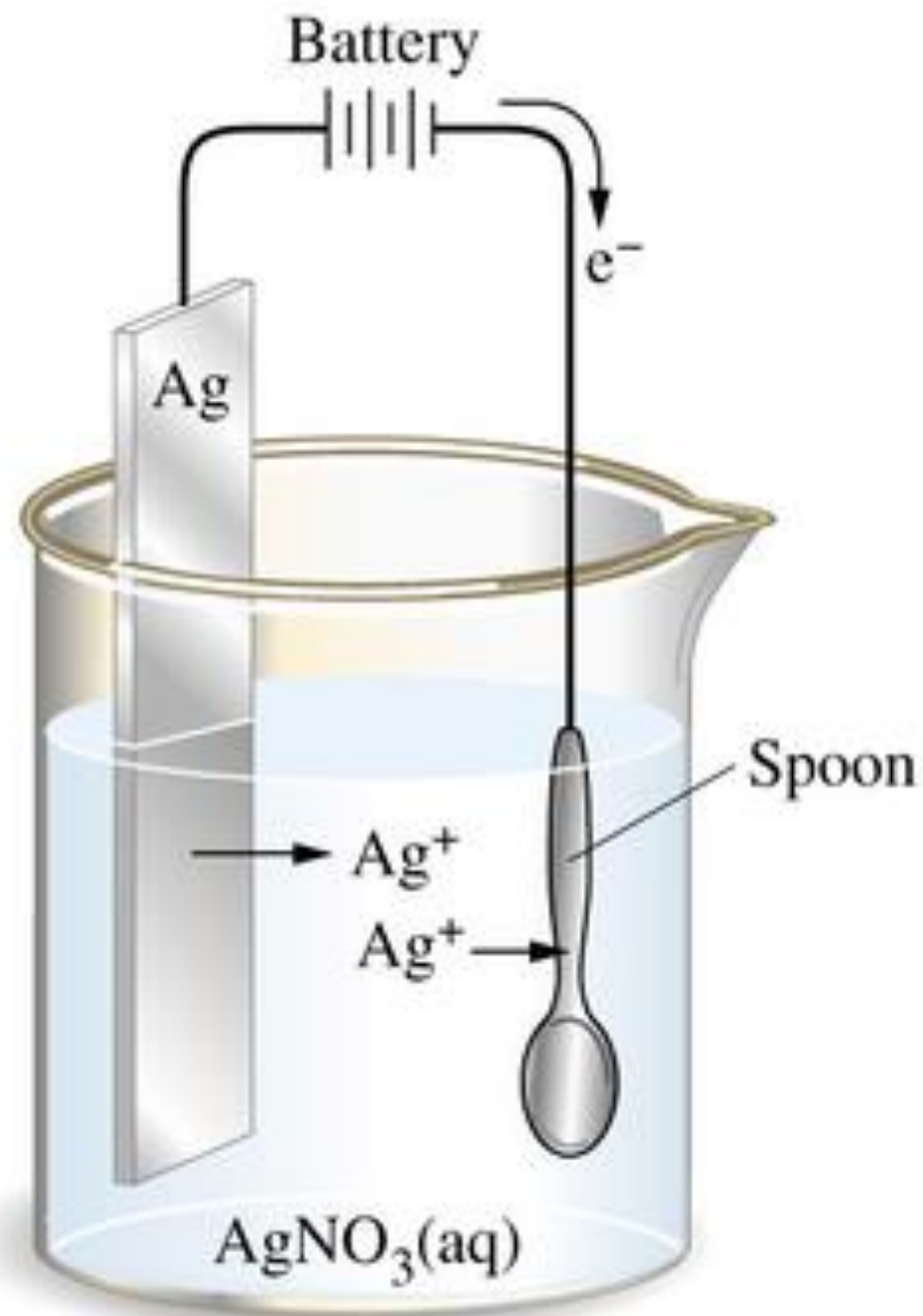
- ✓ Oils, Fatty substances and greases are removed by Solvents wash (CCl_4 , & acetone)
- ✓ metal surface is washed with hot water

Electroplating

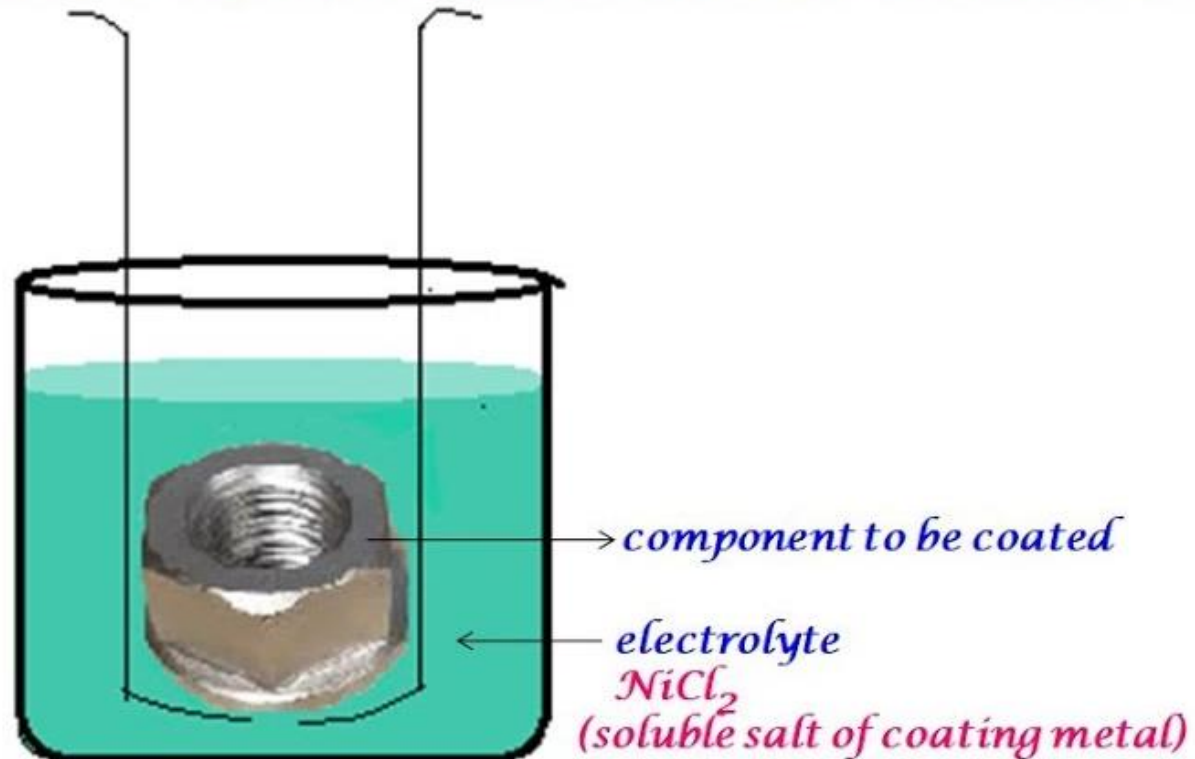
1) *Electro-deposition:*

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?**

CORROSION

INTRODUCTION

- ✦ Definition: Corrosion refers to the degradation or deterioration and ultimate destruction of metal due to its reaction with the surroundings.

Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$] on the surface of copper.
- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.

Why study corrosion?

Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety. Decisions regarding the future integrity of a structure or its components depend upon an accurate assessment of the conditions affecting its corrosion and rate of deterioration. With this information an informed decision can be made as to the type, cost and urgency of possible remedial measures.

- ◆ In a modern business environment, successful enterprises cannot tolerate major corrosion failures, especially those involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination. For this reason considerable efforts are generally expended in corrosion control at the design stage and in the operational phase

CAUSE OF CORROSION

- All the metals exist in nature in combined forms as oxides, carbonates, sulphides etc.
- High amount of energy is required to extract the metal from ore.
- Thus, the metal is in thermodynamically unstable state.
- It is the natural tendency of metal to revert back to thermodynamically stable state when it comes in contact with the elements in the environment.

CONSEQUENCES OF CORROSION

- ♠ Enormous waste of machineries and different types of metallic materials
- ♠ It leads to sudden failure of machines.
- ♠ It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is an expensive.
- ♠ It may leakage of inflammable gas from the corroded pipe lines resulting into fire accidents etc.
- ♠ It causes contamination of potable water.
- ♠ It has been estimated that 25% of annual world production of iron is wasted due

to corrosion.

THEORIES (OR) MECHANISM OF CORROSION

There are Two theories of corrosion

- * Dry or Chemical Corrosion
- * Wet or Electrochemical Corrosion

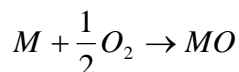
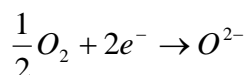
1) Direct Chemical Attack (Or) Mechanism Of Dry Corrosion

- ♦ The direct chemical action of atmosphere gases like oxygen, halogen, H₂S etc in a dry environment on metals, a solid film of the corrosion product is formed on the surface of the metal.

- ♦ This is known as chemical corrosion.

a. Oxidation Corrosion (Reaction With Oxygen)

- ★ Some of the metals directly react with oxygen in the absence of moisture.
- ★ Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- ★ The metal ion and oxide ion combine to form metal oxide on the metal surface.



- ★ The nature of metal oxide layer formed plays an important role in determining further corrosion.

1) 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.

2) Unstable oxide film: Au & Pt develop unstable oxide film which instantaneously decomposes to form metal & oxygen.

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

4) 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.

Pilling Bedworth rule: The protective or non protective nature of oxide film is determined by this rule. The ratio of volume of oxide film to the volume of metal consumed is known as Pilling-Bedworth rule.

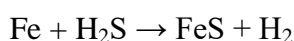
- ★ If the ratio is <1, the metal oxide layer is porous and non protective. Ex:-Oxide layer on alkaline metals
- ★ If the ratio is ≥1, the metal oxide layer is non porous protective layer. It stops

further corrosion of metal. Ex:-Oxide layer on Al, Cr, Cu, W.

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

b. Corrosion By Other Gases:

- ✦ This type of corrosion is due to the attack of other gases like Cl_2 , SO_2 , H_2S , NO_x in dry atmosphere on the metal.
- ✦ The corrosion products may be protective or non-protective.
- ✦ Dry Cl_2 reacts with Ag and forms AgCl which is protective layer, Eg: $2\text{Ag} + \text{Cl}_2 \rightarrow 2\text{AgCl}$ (protective),
- ✦ where as SnCl_4 is volatile, $\text{Sn} + 2\text{Cl}_2 = \text{SnCl}_4$
- ✦ H_2 Embrittlement: Formation of cracks and blisters on metal surface due to high pressure of H_2 gas.



c. Liquid Metal Corrosion:

- * This type of corrosion takes place, when molten metal passes through metallic pipes due to dissolution of solid metal by liquid molten metal or due to internal penetration of solid metal into liquid metal.
- * For example: Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.
- * Coolant (sodium metal) leads to corrosion of cadmium (moderator) in nuclear reactors.

2) Electrochemical Corrosion (or) Wet Corrosion

- ✦ This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- ✦ At anodic area, oxidation reaction occurs, thereby destroying the anodic metal due to dissolution. Hence, corrosion always occurs at anodic parts.
- ✦ At cathodic area, reduction reaction occurs.
- ✦ These anodic and cathodic regions are formed due to several factors like
 - On a metal surface if the concentration of oxygen is different
 - Due to contact of two different metals
 - If metal surface is subjected to stress

Anodic Reaction:

- ✓ At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons.
- ✓ These electrons migrate towards cathode.



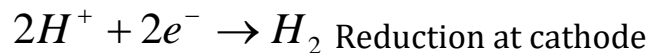
Cathodic Reaction:

- ✓ At cathode reduction takes place. Depending upon on the nature of the corrosive environment cathodic reaction takes place in the following way:

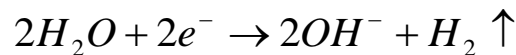
- Evolution of hydrogen.
- Absorption of oxygen depending upon the nature of corrosion environment.

a) Evolution of Hydrogen type:

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

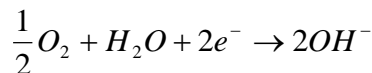


- ★ In basic medium and in the absence of oxygen, the cathodic reaction is,



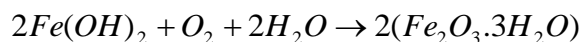
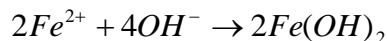
b) Absorption of oxygen:

- ★ In neutral and aerated medium: If the solution is neutral and aerated, hydroxyl ions are formed as follows.

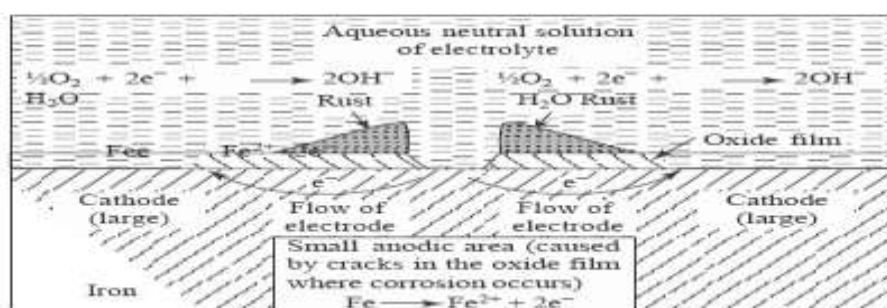
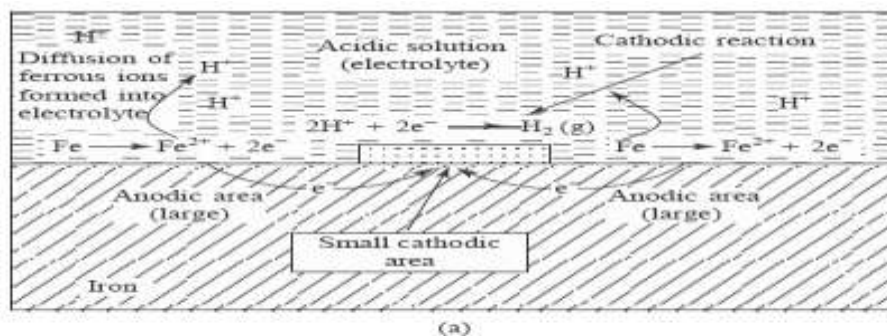


Formation of corrosion product:

- ✓ The hydroxyl ions react with metal ions and forms corrosion product.
- ✓ In case of iron, hydroxide ions react with ferrous ions and forms insoluble hydrated ferric oxide called Brown rust.



- ✓ If the supply of oxygen is limited, the corrosion product may be black magnetite
- ✓ Fe_3O_4 .



.Wet Corrosion: or Electro Chemical Corrosion:

Wet corrosion of metals occurs through electron transfer, involving two processes, oxidation and reduction. In oxidation, the metal atoms lose electrons. The surrounding environment then gains the electrons in reduction. The metal, where electrons are lost, is called the anode. The other metal, liquid or gas which gains the electrons is called the cathode.

Eg: $\text{Fe} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2$

Mechanism:

At Anode: Oxidation occurs $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

At Cathode: Reduction occurs and it depends on nature of the environment

Acidic environment:

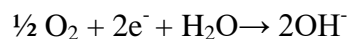
Hydrogen evolution: All metals above H_2 in electrochemical series undergo this type of corrosion

Example: Iron metal in contact with HCl .

($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$)

Neutral or basic environment:

Absorption of oxygen: or Formation of hydroxide ion type corrosion.



Example: Iron metal in contact with a neutral solution.

Net Corrosion is $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_3 \rightarrow [\text{Fe}_2\text{O}_3, 2\text{H}_2\text{O}] \text{ Rust}$

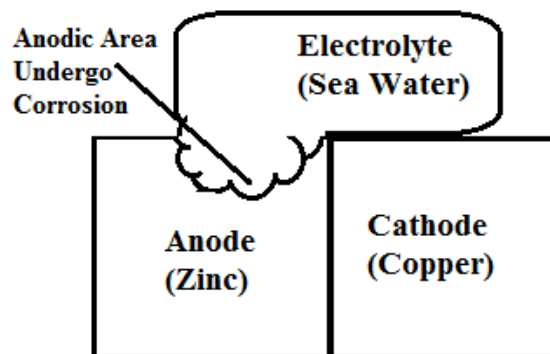
An example of wet corrosion is copper fitting on a steel pipe carrying water. Steel pipe acts as the anode, copper fitting, the cathode. The pipe is in direct contact with the fitting for the connection.

Water acts as electrolyte, allowing for migration of the ions, and completion of the circuit.

TYPES OF CORROSION

1. Galvanic Corrosion:

- When two dissimilar metals are connected in presence of a corrosive environment, then the metal higher in electrochemical series undergoes corrosion.
- This type of corrosion is also called galvanic corrosion or bimetallic corrosion.
- For example, zinc and copper constitute a galvanic couple, where zinc acts as anode and undergo corrosion and copper behaves as cathode and get protected from corrosion.
- The extent of corrosion depends on the potential difference between the two metals.
- This galvanic corrosion can be minimized by
 - Avoiding galvanic couple
 - Selecting metals closely placed in electrochemical series as galvanic couple
 - Providing an insulating material between the two metals

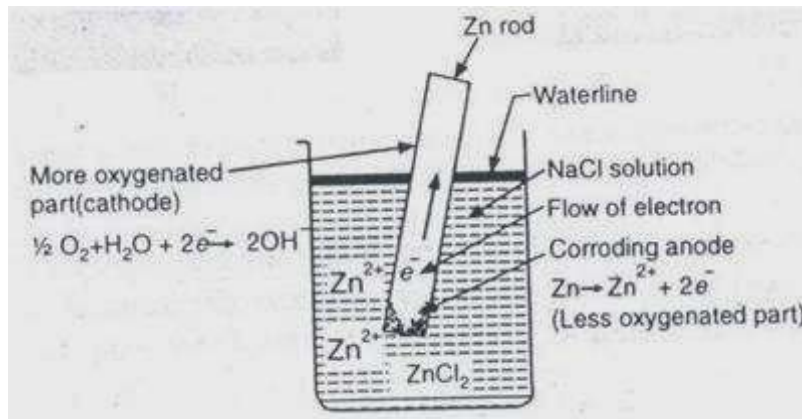
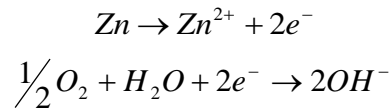


2. Concentration Cell Corrosion (Differential Aeration Corrosion)

- This type of corrosion arises due to exposure of metal to varying concentration of electrolyte or of varying aeration.
- Differential aeration corrosion occurs when one part of metal is exposed to a different air concentration from the other part.
- Then, part of the metal exposed to **less concentration of oxygen acts as anode** and other parts exposed to **high concentration of oxygen act as cathodes**.
- Anodic part undergoes corrosion.
- Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline.

Example:

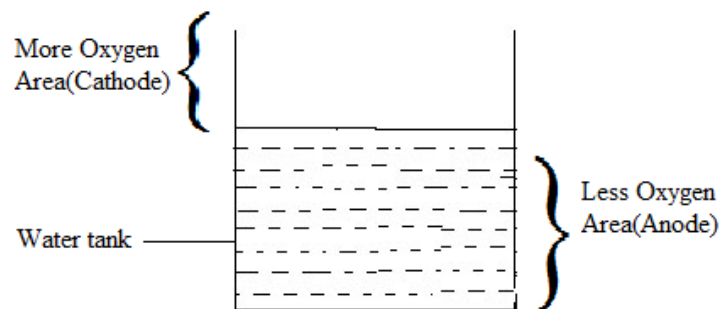
- If a metal is partially immersed in a dilute solution of a neutral salt solution, then the parts above the solution are more strongly aerated hence, become cathodic.
- If a metal part immersed to greater depth show a smaller oxygen concentration and thus become anodic.



Examples: Water line corrosion, Drop corrosion

Water Line Corrosion:

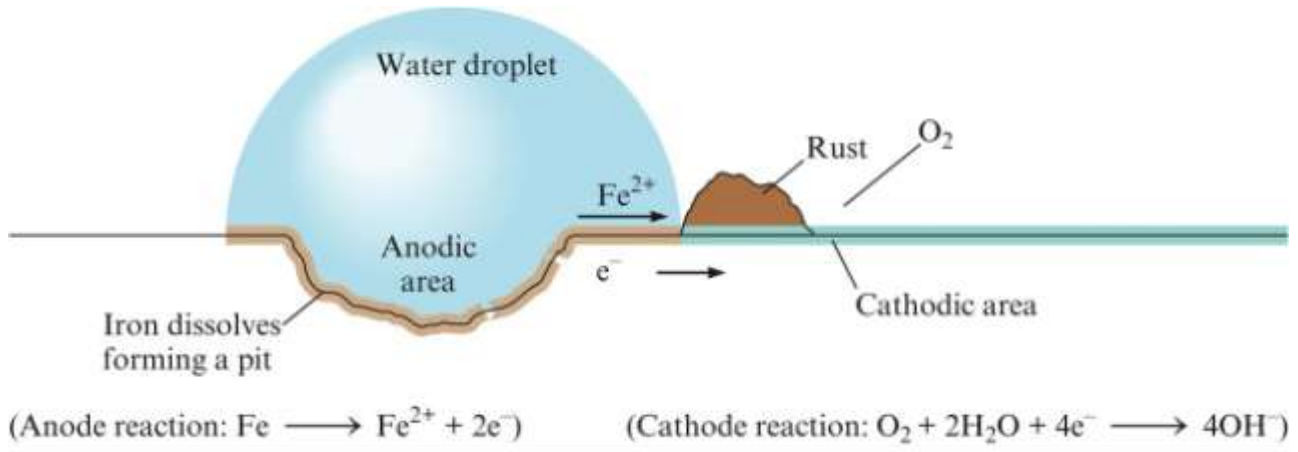
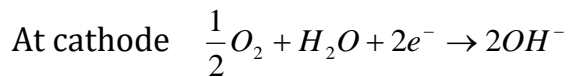
- * It has been observed in rusting of an iron tank takes place along the line just beneath the level of water in it.
- * It is also due to differential aeration.
- * The area above the waterline (well aerated) acts as cathode where as the area below the waterline (less aerated) acts as anode and is corroded.



Drop Corrosion:

- For instance iron metal surface is covered with a drop of water.

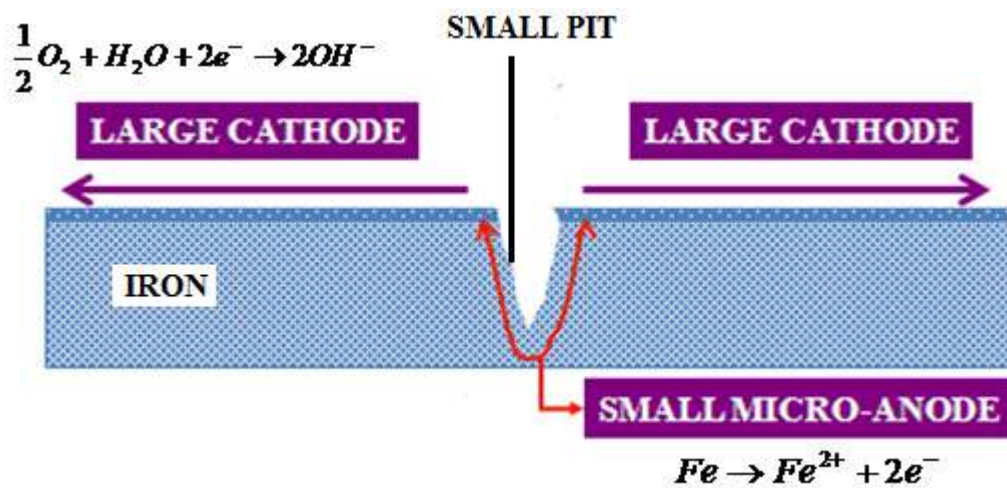
- The area covered by a drop has low oxygen concentration and thus acts as an anode and suffers corrosion, the uncovered area of the metal acts as large cathode due to high O₂ concentration.



3.Pitting Corrosion:

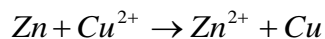
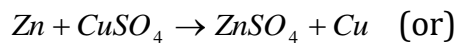
- * Pitting of metal occurs where there is a break in the protective layer.
- * Pitting corrosion is a non uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin holes in the metal.
- * This gives rise to the formation of small anodic and large cathodic areas.
- * The presence of the impurities (like sand, dust, scale etc) on the surfaces of metals also leads pitting.
- * A part below the impurity become the anodic area undergoes corrosion and the surrounding part become the cathodic area.
- * Once a small pit is formed, the rate of corrosion will be increased.





GALVANIC SERIES

- ✓ Electrochemical reactions are predicted by electrochemical series.
- ✓ A metal having higher position can replace (reduce) other metals that have lower position in the series.
- ✓ For example:



- ✓ Or in other words, zinc will corrode faster than copper.
- ✓ Some exceptions have been observed in this generalization. For example, Ti is less reactive than Ag.
- ✓ Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e., sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble character.

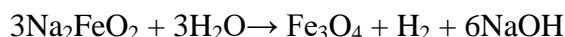
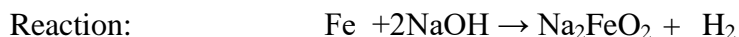
More anodic: **Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni-Mo-Fe alloys, Brasses, Cu, Ni, Cr-alloy, Ag, Ti, Au, Pt** towards noble nature.

From **left to right, anodic nature decreases**, corrosion tendency decreases.

Stress corrosion: In a metallic structure, if there is a portion under stress, it acts as anode and rest part of the structure acts as cathode. It is now a galvanic system and hence anodic part which is small in area would corrode more. Stress corruptions are observed in the following systems:

(i) Caustic embrittlement is a type of stress corrosion occurring in steel tank (Boiler) at high temperature and in alkaline medium. Boiler water has Na_2CO_3 ; it will be hydrolysed at high temperature to give NaOH. It flows into hair cracks and crevices. There it reacts with

iron and forms Na_2FeO_2 (sodium ferroate) which decomposes to give Fe_3O_4 (ferric oxide) and NaOH . NaOH thus formed further reacts with iron to cause corrosion. It is called caustic embrittlement.



Comparison Between Galvanic Series And Electrochemical Series

Galvanic series	Electrochemical series
<ul style="list-style-type: none"> • It predicts the corrosive tendencies of metal alloys. • Calomel electrode is used as a reference electrode. • Position of metal or alloy may change. • This series was developed by the studying corrosion of metals and alloys in unpolluted sea water without their oxide film. • Electrode potentials are measured for both metals and alloys. 	<ul style="list-style-type: none"> • It predicts the relative displacement tendencies of metal. • Standard hydrogen electrode is used as a reference electrode. • Position of metal is fixed. It cannot be change. • This series is developed by dipping pure metals in their salt solution of 1M concentration with out any oxide film on them. • Electrode potentials are measured only for metals and non metals.

FACTORS INFLUENCING THE RATE OF CORROSION

1. Nature of The Metal And Its Surface

a. Position of metal in galvanic series:

- It determines the extent of corrosion.
- The metal higher in the electrochemical series acts anode which undergoes corrosion easily, the metals lower in the series acts as cathode which is protected from corrosion due to their higher oxidation potentials.
- The greater difference in their electrode potential faster is the rate of corrosion.

b. Over voltage:

- Over voltage decreases rate of corrosion increases.

(Hydrogen overvoltage/over voltage is the potential difference that can be found between an electrode and a reversible hydrogen electrode within a single solution. This is where hydrogen (H₂) undergoes formation from ions of hydrogen.)

c. Purity of the metal:

- The impure metals are prone to corrosion than the pure ones.
- Impurities cause heterogeneity and form tiny electrochemical cells where anodic part gets corroded.
- The effect of even traces of impurities on the rate of corrosion will be as follows.

Metal	% purity	Corrosion rate
Zinc	99.999	1
Zinc	99.99	2650
Zinc	99.95	5000

d. Surface of metal:

- A rough surface metal readily undergo corrosion due to collection of more dirt.
- A polished surface does not corrode easily.

e. Stressed part of a metal:

- Stress in metal surface is produced by mechanical operations such as welding bending, pressing etc.
- The portion subjected to more stress acts as anode and other portion acts as cathode.

f. Ratio of anodic area to cathodic area:

- The rate of corrosion increases with decrease in the ratio of anodic area to cathodic area.
- The smaller the ratio larger is the cathodic area and higher is the demand for electrons i.e. Rapid corrosion of small anodic area.
- For example, steel rivets (anode) are in copper sheets, steel rivets are completely corroded.

g. Physical state of the metal:

- ✓ The rate of corrosion is influenced by the physical state of a metal.
- ✓ For instance, the smaller the grain size of the metal or alloy, the greater will be the rate of corrosion.

PASSIVITY

- ✓ Passivity or passivation is the phenomenon in which a metal or an alloy exhibits a much higher corrosion –resistance than expected from its position in the electrochemical series.
- ✓ Passivity is the result of the formation of a highly protective, but very thin (0.0004mm) and quite invisible film on the surface of metal or alloy, which makes it more noble.
- ✓ Passive film is insoluble, non-porous and self healing nature (when broken, it will repair itself).
- ✓ Examples of passive metals and alloys are Ti, Al, Cr and wide variety of stainless steel alloys, containing Cr.
- ✓ Passivation is not a constant state, but exists only in certain environment condition, which tend to maintain thin protective oxide films on their surfaces.
- ✓ In presence of oxygen, the oxide film is automatically repaired, whenever any damage occurs, but in oxygen absence, the passive metals and alloys become chemically active and are rapidly corroded.
- ✓ Fe and Al produce a thin protective oxide layer with action of concentrated HNO_3 . In case of stainless steels and titanium, the protective oxide film is maintained, even in dilute HNO_3 .
- ✓

2. Nature of Corrosive Environment

a. Temperature:

- Temperature increases the rate of almost every chemical reaction.
- Thus, the rate of corrosion also increases with increase in temperature.

b. Humidity of air:

- Corrosion increases with increase in humidity of air.
- This is due to the fact that humidity acts as solvent for oxygen which is essential for setting up a corrosion cell.

c. Nature of atmosphere:

- ♦ Corrosion increases if the air is polluted by smoke or gases like H_2S , SO_2 and electrolytes like NaCl and $(\text{NH}_4)_2\text{SO}_4$.

d. Effect of P^{H} :

- In general, acidic media are more corrosive than alkaline or neutral media.
- Low P^{H} accelerates corrosion by providing more hydrogen ions.

e. Conductance of the corroding medium:

- ✓ It plays an important role in corrosion.
- ✓ Dry sandy soils have lower conductance than clay or mineralized soils.

- ✓ Hence, the metallic parts submerged in clay or mineralized soils undergo faster corrosion than in dry sandy soils.

f. Nature of corrosion product:

- The formation of stable protective oxide films reduces the corrosion rate of metals where as the formation of volatile, non porous and non protective oxide films prolong the corrosion.

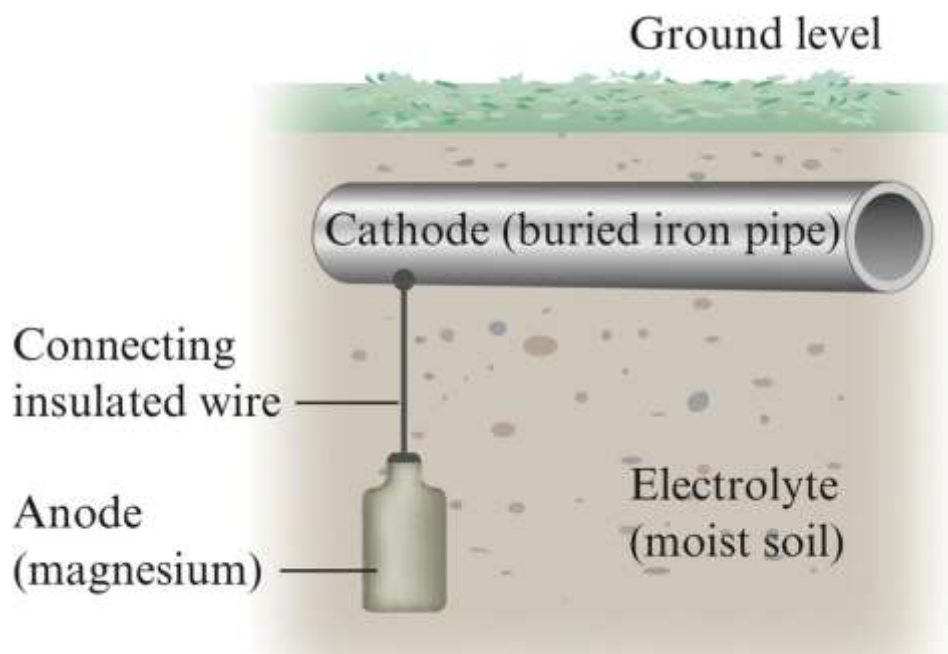
PROTECTION METHODS OF CORROSION

1. CATHODIC PROTECTION:

- ⬆ The principle involved in this method is to force the metal to be protected to behave like a cathode, there by corrosion does not occur.
- ⬆ There are two types of cathodic protection.

a) Sacrificial Anodic Protection Method:

- ♠ In this method, the metallic structure to be protected is connected by a wire to a more anodic metal.
- ♠ Thus during corrosion more anodic metal gets corroded while the parent metal is protected.
- ♠ The more active metal used is known as sacrificial anode which is replaced from time to time by fresh one.
- ♠ Metals commonly used as sacrificial anode are magnesium and zinc.
- ♠ This method is used for the protection of ships and boats. Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium undergo corrosion.



Sacrificial anodic protection

b) Impressed Current Cathodic Protection:

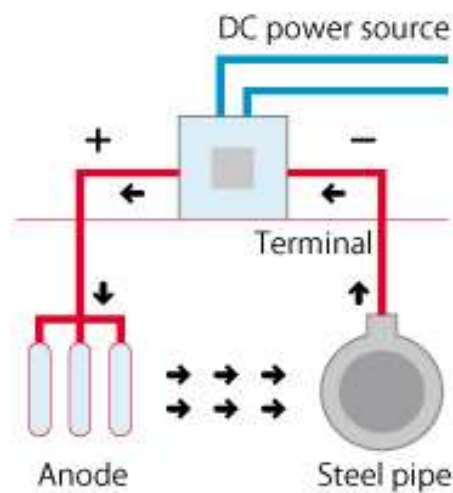
- ♣ In this method, the metallic object to be protected is made cathode by connecting it with the negative terminal of the DC source.
- ♣ The positive terminal is connected to an insoluble anode like graphite, scrap iron or platinum.
- ♣ The impressed current nullifies the corrosion current.
- ♣ The electrons flow to the metallic object as a result it acts as cathode and is protected.

Applications:

- ☞ These methods are used for the protection of buried pipelines, under ground cables, water tanks etc.

Problems and limitations:

- ✓ Capital investment and maintenance costs.
- ✓ Chemical reactions taking place at the surface of protected structure.
- ✓ Possibility of soil and microbiological corrosion.



Impressed current cathodic protection

ELECTROPLATING

- It is widely used to coat the base metals with protective metallic coatings of copper, nickel, zinc, lead etc.

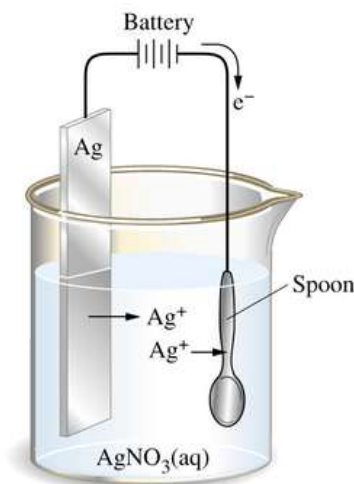
Process:

- Before electroplating, the metal surface is cleaned thoroughly.
- The article to be electroplated is made cathode since metallic ions are positive and thus get deposited on the cathode.
- The anode is made of pure metal, which is to be coated on the article.
- The electrolyte is the salt of the metal to be coated on the article.

- A direct current is passed through the electrolyte.
- The anode dissolves, depositing the metal ions from the solution on the article.

Electroplating With Gold:

- **Cathode:** Article to be electroplated (Spoon)
- **Anode:** Block of gold metal
- **Electrolyte:** Aqueous solution of AuCl_3 or Potassium auro-cyanide $\text{K}[\text{Au}(\text{CN})_2]$



ELECTROLESS PLATING

- ◆ In this process, the base metal article is dipped in a bath of a noble metal salt which is used for coating.
- ◆ The noble metal forms a layer on the base metal article by displacement of base metal by noble metal.
- ◆ This process is also called as 'immersion plating' or 'displacement plating'.
- ◆ For example, **Nickel coating on base metal:** The base metal article is dipped in a bath of nickel sulphate and sodium hypophosphite kept at temperature of 100°C and at pH from 4.5 to 5. Nickel ion from solution reduces to nickel phosphide, which forms a strong adherent thin film.

Electroplating: It is an electrochemical process in which a base metal is coated by Zn, Ag, Cr, Au, Sn, etc. to protect it from corrosion and also to make it shining and decorative. The base metal is made cathode, dipped in a suitable electrolyte, and the metal to be deposited is made the anode. Anodised coating is done for non-ferrous metals, such as Zn, Mg and Al. They not only protect from corrosion but also give a good look to the metal. Organic coats must have chemical inertness, good surface adhesiveness and non effectiveness towards inorganic chemicals and water. The object before subjecting to electroplating process, it is essential to clean the surface of

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object. The following methods are used to clean the metal surface. Solvent cleaning: Organic solvents such as Trichloro ethylene and methylene chloride are used to remove organic matter and grease on the surface of cathode. Trichloro ethylene is used to remove paint varnishes, films, resins etc. Per chloro ethylene is used to remove high melt waxes and cleaning PCB. The above process is called solvent cleaning. Alkali cleaning: After solvent cleaning the metal is cleaned with alkali solution. Alkali cleaners

such as soaps, detergents, sodium carbonate, sodium hydroxide, sodium phosphate etc are commonly used. iii) Mechanical cleaning: The object is subjected for mechanical cleaning to remove oxide scales, rust and other impurities on the metal surface. The mechanical cleaning methods involves, cleaning with Bristle brushes, mechanical polishing, grinding using polishing machines, and sand blasting. Pickling: In this method the oxides scales are removed by dipping the base metal in a dilute acids. Pickling of steel involves dipping in dilute HCl or dilutes H_2SO_4 to remove rust and other oxide scales. Rinsing with water: After surface cleaning process the metallic surface is thoroughly rinsed with water, dried and subjected for electroplating process. Procedure: Cathode: the cleaned article is made as cathode. Anode: the anode is the coating metal itself Or an inert material of good electrical conductivity like graphite. Electrolyte: the electrolyte is a solution of a soluble salt of the coating metal. The anode and cathode are dipped in the electrolyte. When direct current is passed, coating metal ions migrate to the cathode and get deposited there. A thin layer of coating metal is obtained on the article made as cathode. For brighter and smooth deposits, low temperature, medium current density, low metal-ion concentration are used.

Electroplating of Copper:

Step 1:

The article to be electroplated is first treated with organic solvents like CCl_4 (Carbon tetra chloride) to remove oils, greases etc.,

Step2:

The metal to be coated i.e. the base metal after step-1 is cleaned with Dil HCl to remove scales or the oxide layer.

Step3:

Anode – pure copper, Cathode – base metal

Electrolyte is $CuSO_4$ solu. Taken in an electrolytic tank.

Anode and Cathode immersed in the electrolyte.

Reactions:

At anode: $\text{Cu(s)} \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation) Copper is dissolved.

At cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu(s)}$ (Reduction) Copper is deposited

	Sulphate bath	Cyanide bath
Plating bath solution	200-250 g CuSO_4 , 50-75 g H_2SO_4 , per L of	40-50 g CuCN , 20-30g KCN , 10 g K_2CO_3 per L
Operating temperature	20-40°C	40-70°C
Current density	20-50 mA/cm^2	10-40 mA/cm^2
Addition agents	Gelatin, dextrin, sulphur containing brighteners, sulphonic acids	Sodium thiosulphate
Current efficiency (%)	95-99	60-90

