

CORROSION SCIENCE

Presented by

*Dr Geetha
Associate professor
Post Graduate Department of Chemistry*

OUTLINE

■ INRODUCTION

■ IMPORTANCE OF CORROSION

■ TYPES OF CORROSION

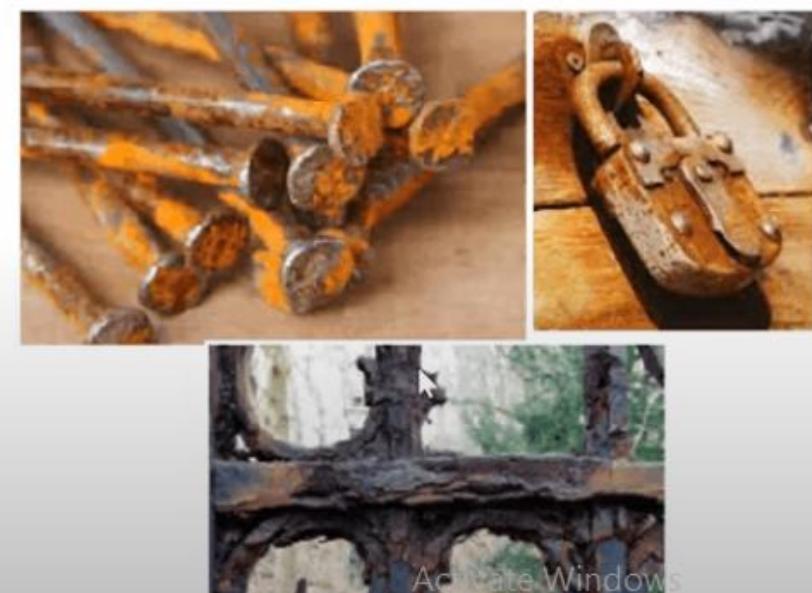
■ PREVENTION OF CORROSION

■ MEASUREMENT OF CORROSION

CORROSION

Corrosion is the process of deterioration/destruction of the metal which starts at the surface when exposed to a chemical or electrochemical environment.

Note: Corrosion may also occur in non-metallic materials such as plastics, concrete , composites etc.



Why does metal undergo corrosion???

Except noble metals, most of the metals occur in the combined form - oxides, chlorides, sulphates, carbonates etc.
- exists in the form of ores.

*Metals are more **stable** in their **combined** state*

*Even after the extraction of metals, they will always tend to revert back to their original **stable combined state***

IMPORTANCE OF CORROSION



Silver Bridge Collapse



Washington Bridge Collapse



Italy Bridge Collapse



Tacoma Bridge Collapse

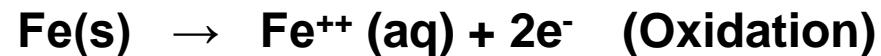


Andheri Bridge Collapse

The cost of corrosion is significant

- In 2014, the direct cost of corrosion in India was Rs. 4 lakhs crores/year!
- ~ 3 to 4% of GDP
- Up to 50% of construction budgets
- 50% of structures hit a repair in about 10 years
- 30% of steel is used for repair
- 40% of cement is used for repair

The Electrochemical theory of corrosion



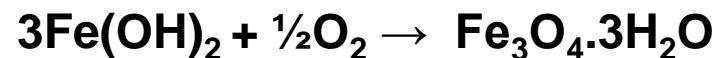
i) In acidic medium



ii) In neutral or basic medium



(Yellow rust)



(black rust)

Absorption of oxygen in the presence of oxygen

i) In acidic medium



ii) In neutral or basic medium



Liberation of hydrogen in the absence of oxygen

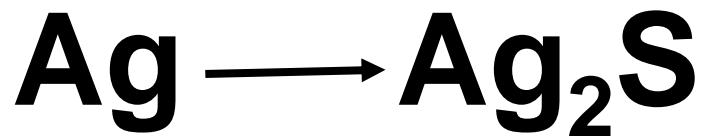
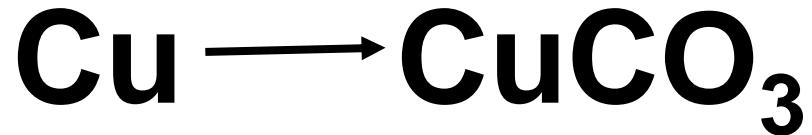
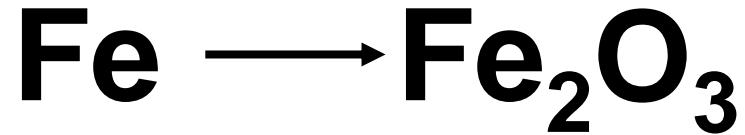
i) In acidic medium



ii) In neutral or basic medium



Have you seen any other metals undergoing corrosion?



Types of corrosion

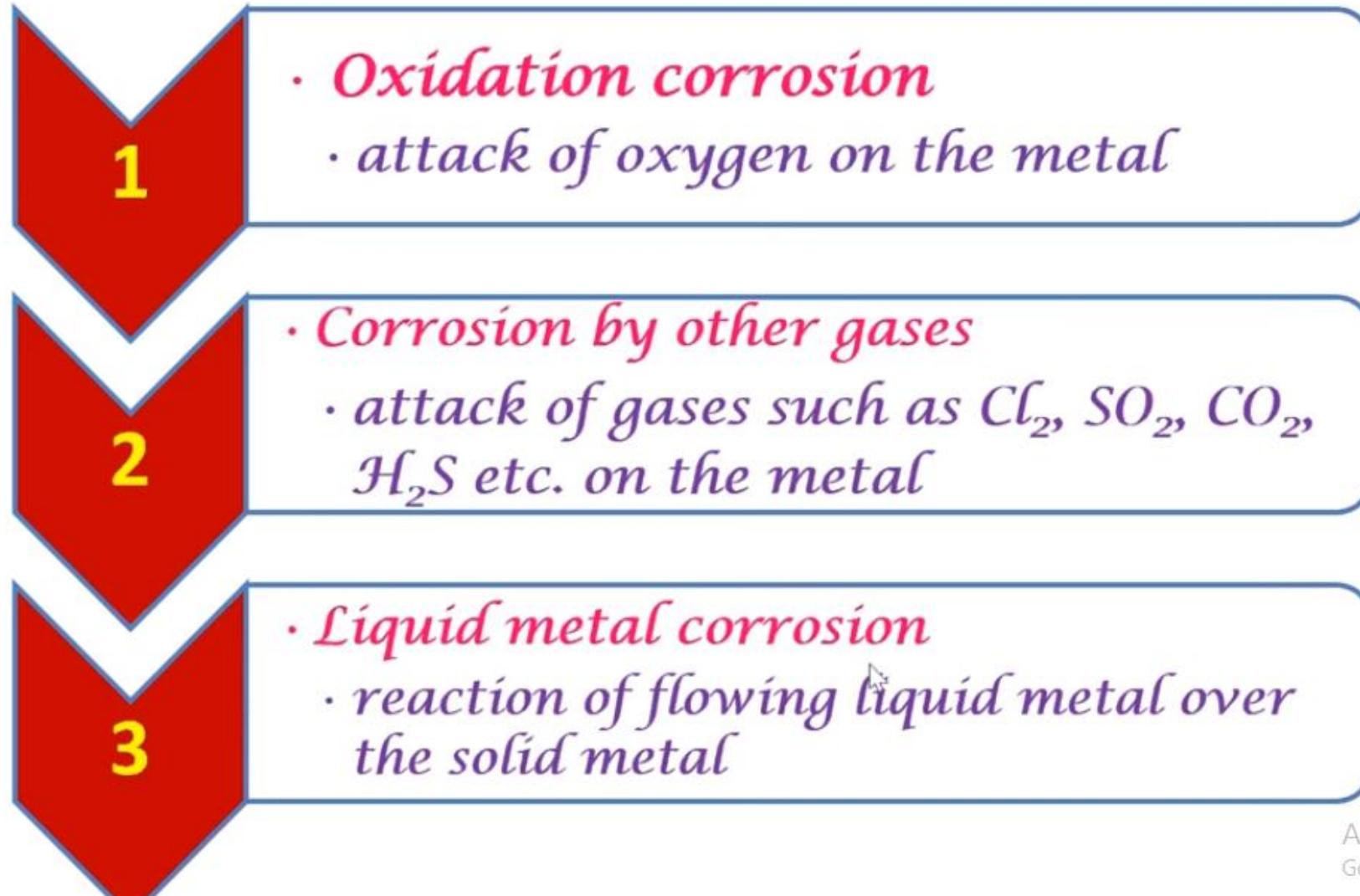
*Dry corrosion/
Chemical
corrosion*

*Wet corrosion/
Electrochemical
corrosion*

- Differential aeration corrosion
- Galvanic corrosion
- Pitting corrosion
- Stress corrosion

Activate W
Go to Settings

Dry Corrosion/ Chemical corrosion



Factors affecting Corrosion rate

Nature of metal

Difference in potential between anodic and cathodic region

The ratio of anodic to cathodic area

National Institute of Technology Karnataka(NITK), Surathkal



pH

Hydrogen overvoltage

Temperature



National Institute of Technology Karnataka(NITK), Surathkal



Electrochemical series

Metal	Electrode Reaction	E° (V)
Lithium (Li)	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.04
Potassium (K)	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
Calcium (Ca)	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
Sodium (Na)	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
Magnesium (Mg)	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
Aluminium (Al)	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
Zinc (Zn)	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
Iron (Fe)	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
Nickel (Ni)	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.25
Tin (Sn)	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
Lead (Pb)	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
Hydrogen (H)	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
Copper (Cu)	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
Silver (Ag)	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
Gold (Au)	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50

1. Nature of metal

- The metals with lower electrode potential (reduction potential) values are more reactive than the metals with higher electrode potential values.
- The active metals like Na, K, Mg, Zn with lower electrode potential values are highly susceptible for corrosion.
- The noble metals such as silver, gold, platinum etc with higher electrode potential values are less susceptible for corrosion.



National Institute of Technology Karnataka(NITK), Surathkal

2. Difference in potential between anodic and cathodic region

- Larger the potential difference between the anodic and cathodic region of the corrosion cell, higher is the corrosion rate.
- When two different metals with large difference in their electrode potentials are in contact with each other, the more reactive metal undergoes corrosion very fast.

Example: Cu & Zn



National Institute of Technology Karnataka(NITK), Surathkal

3. Ratio of anodic to cathodic area

- The rate of corrosion is more with the combination of a large cathodic region and a small anodic region.

Reason:

The greater demand for electrons at the larger cathodic region has to get a greater current density which is supplied by the smaller anodic region.

Why Iron bolts or nuts are not used in copper boilers?



National Institute of Technology Karnataka(NITK), Surathkal

4. pH

- Lower the pH, higher is the corrosion rate.

Exceptional:

Al, Zn & Pb undergo fast corrosion in highly alkaline solution



National Institute of Technology Karnataka(NITK), Surathkal



5. Hydrogen over voltage

- The difference between the actual potential at which the hydrogen evolution takes place at the electrode and the theoretical potential for the same process is called Hydrogen overvoltage.
- Higher the hydrogen overvoltage, more difficult is the liberation of hydrogen on the metal surface.
- With lower hydrogen overvoltage, hydrogen gas is liberated easily and thus the cathodic reaction rate is faster.
- When the hydrogen overvoltage on the metal is high, cathodic reaction is slower and the corrosion of the metal also becomes slower.



National Institute of Technology Karnataka(NITK), Surathkal

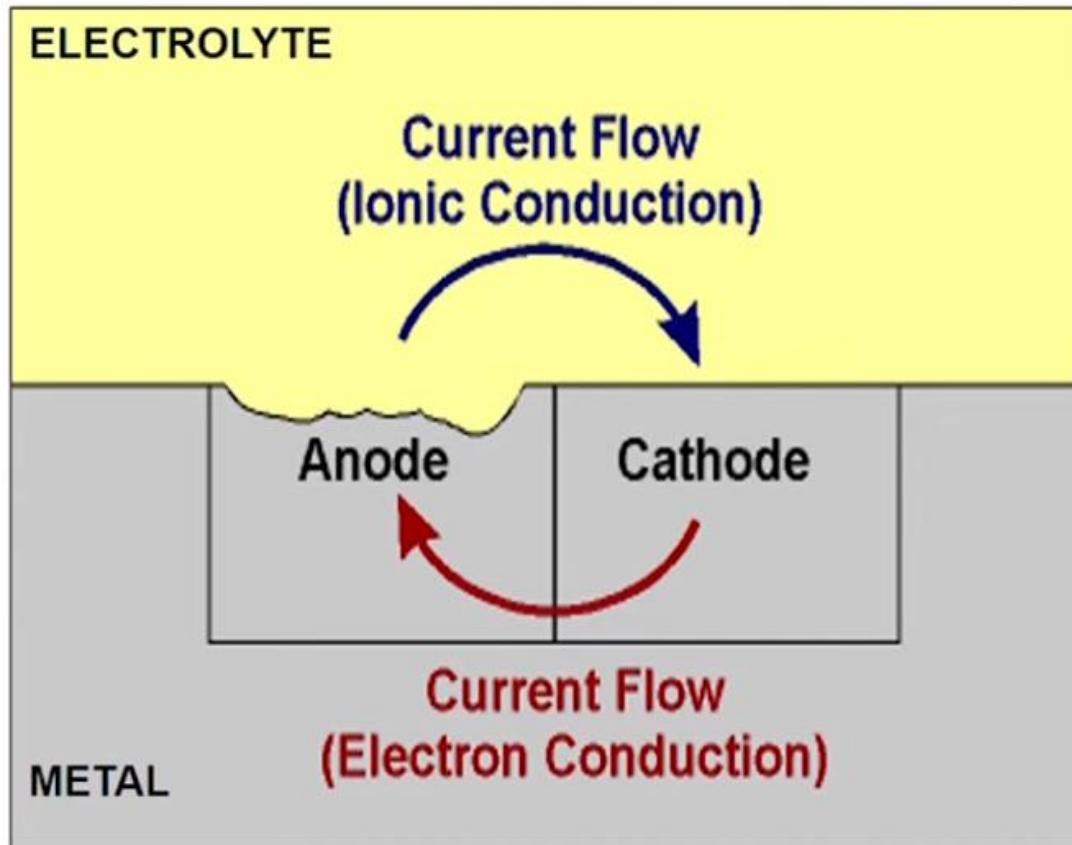
6. Temperature

The increase in temperature increases the corrosion rate

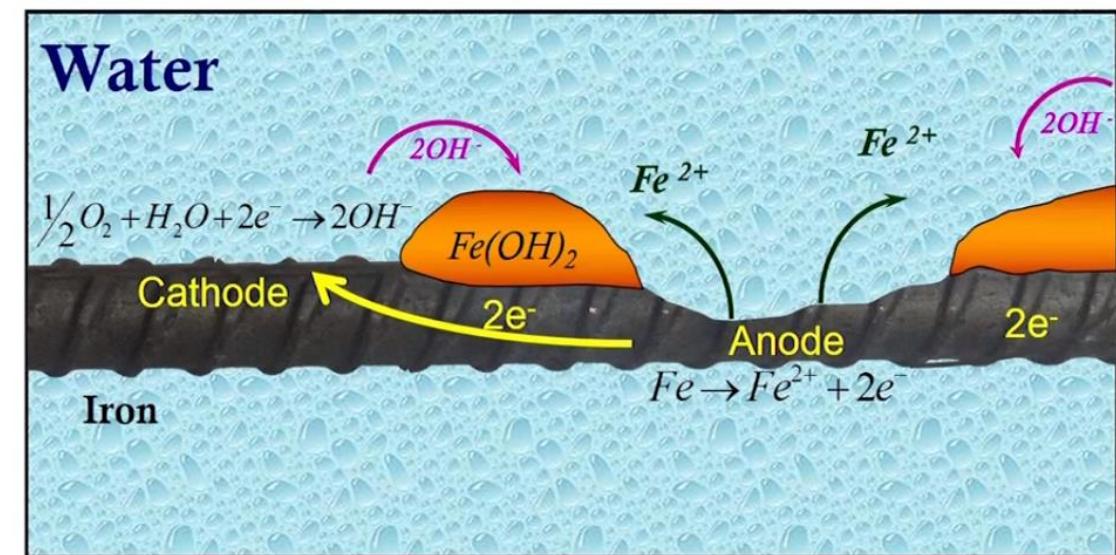


National Institute of Technology Karnataka(NITK), Surathkal

Wet Corrosion/Electrochemical theory of corrosion



Corrosion of Steel in Water with Oxygen



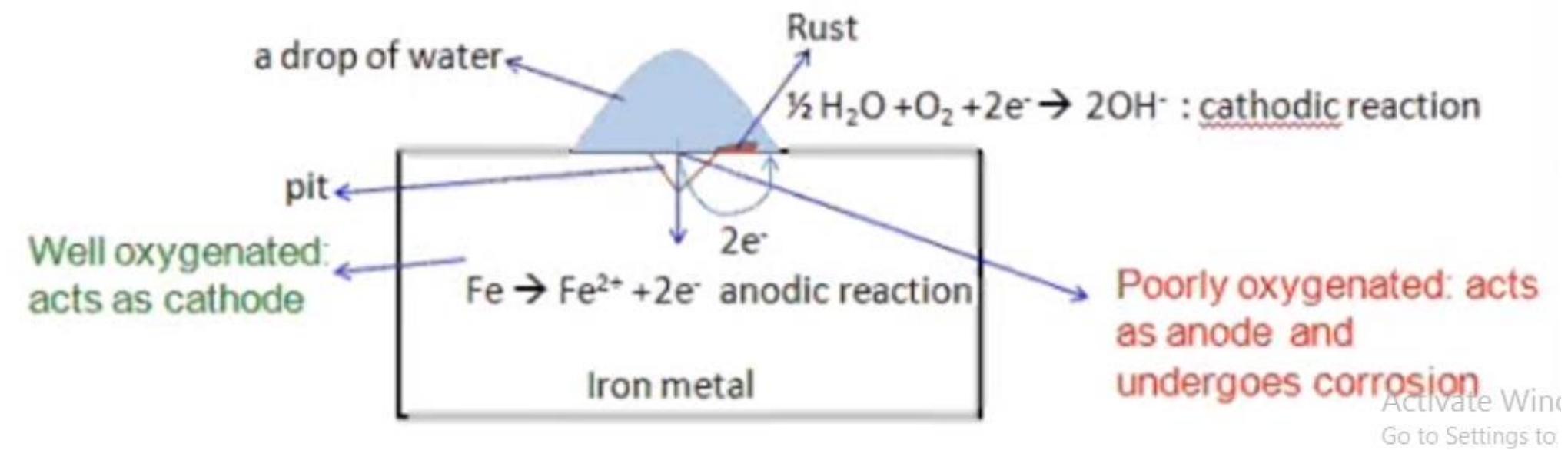
Anode & cathode coexist on the same piece of metal!

Types of Electrochemical corrosion

1. Differential aeration corrosion
2. Galvanic corrosion
3. Pitting corrosion

1. Differential Aeration Corrosion

Definition: When a part of a metal is exposed to a different aeration condition than the other part of the same metal, the part of the metal which is **poorly oxygenated** acts as an **anode** and **undergoes corrosion**.



Reaction Mechanism



(Yellow rust)



(black rust)

Try to identify the part which undergoes differential aeration corrosion in the following cases

1. A metal rod partially immersed in beaker filled with water or salt solution
2. A knotted metal wire fence
3. An iron water tank or pipeline partially filled with water

2. Galvanic Corrosion

Definition

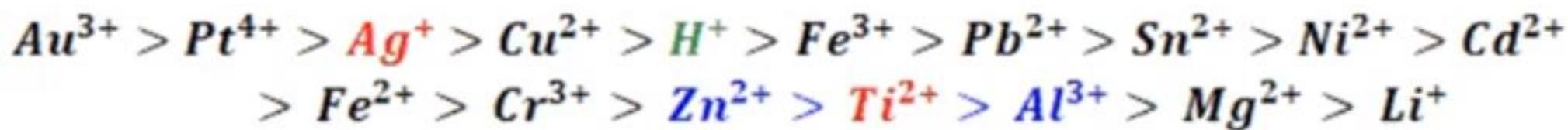
When two dissimilar metals are in contact with each other in the presence of a corrosive medium (electrolyte), the more active metal acts as an anode and undergoes corrosion.

The metal with low standard reduction potential (high std. oxidation potential), acts as anode and undergoes corrosion and the metal with high standard reduction potential acts as cathode and is protected. (electrochemical series)



ELECTROCHEMICAL SERIES

Arrangement of the standard reduction potential or standard oxidation potential of all metals *on hydrogen scale* in an *increasing or decreasing order* is known as electrochemical series.



Metal combination

$\text{Cu}^{2+} - \text{Zn}^{2+}$

$\text{Pb}^{2+} - \text{Ni}^{2+}$

$\text{Fe}^{2+} - \text{Zn}^{2+}$

$\text{Sn}^{2+} - \text{Fe}^{2+}$

$\text{Ag}^+ - \text{Ti}^{2+}$

$\text{Zn}^{2+} - \text{Al}^{3+}$

Anode

Zn

Ni

Zn

Fe

Ti

Al

Cathode

Cu

Pb

Fe

Sn

Ag

Zn

Magnesium (Mg)

Aluminium (Al)

Zinc (Zn)

Iron (Fe)

Nickel (Ni)

Tin (Sn)

Lead (Pb)

Hydrogen (H)

Copper (Cu)

Silver (Ag)

Gold (Au)

$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$

$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$

$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$

$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$

$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

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

$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$

-2.37

-1.66

-0.76

-0.44

-0.25

-0.14

-0.13

0.00

+0.34

+0.80

+1.50

EXAMPLES OF GALVANIC CORROSION

1.



Brass screw
(Cu)

Mild steel nut
(Fe)

Cathode-protected Anode - undergoes corrosion

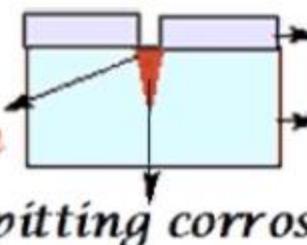
2. Mild steel pipe connected to copper plumbing

↓
(anode - undergoes corrosion)

↓
(cathode)

3. Damaged tin coated mild steel container left out in rain

damaged part (mild steel)
anode-undergoes corrosion



tin coating - cathode
mild steel container

pitting corrosion

PREVENTION

- ❖ Avoid contact of two dissimilar metals.
- ❖ For unavoidable situations
 - Anodic area should be larger than the cathodic area.
 - The two metals should be as close as possible in the electrochemical series/galvanic series.
 - An insulator may be fitted between the two metals
 - Anodic area should never be painted.
 - Avoid threaded joints between the metals.

PITTING CORROSION



Definition

Pitting corrosion is a *localized attack* in the metal resulting in the *formation* of pit, hole or cavity. (confined to point or a small area)

Reason/Cause

When the *anodic area is small* and *cathodic area is large*, it leads to *drastic corrosion* at the anode to form a pit or a hole.

The *demand for electrons by the large cathodic area could be satisfied only when the anode undergoes drastic corrosion*, as its area is very small.

CAUSES OF PITTING CORROSION

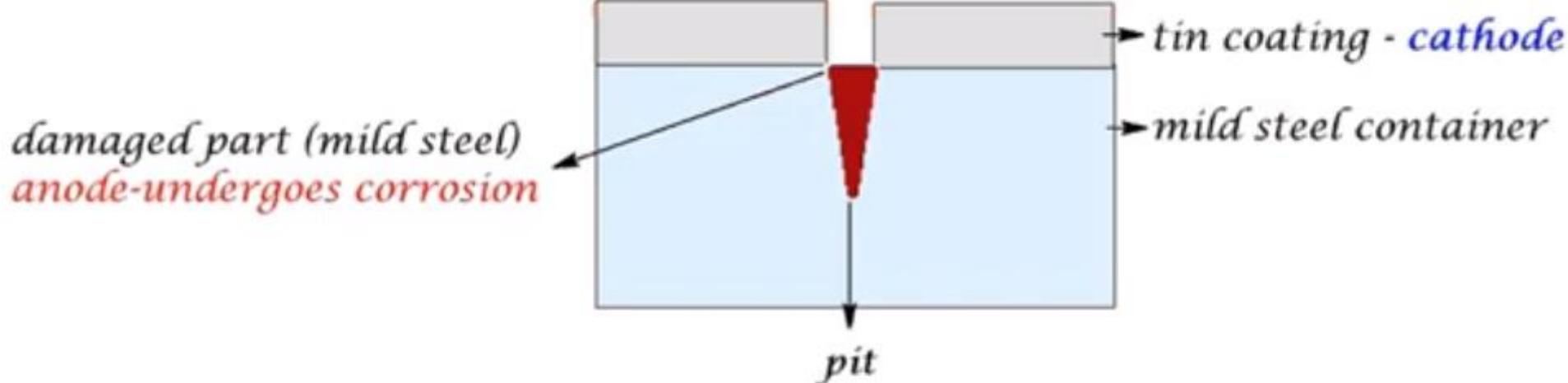
When the anodic area is small and cathodic area is large

- *Damage/cracking of the protective film over the metal*
- *Scratches/cut edges*
- *Local strain on the metal/ non-uniform stress/defects in the metal*
- *Sliding under load*
- *Chemical attack (eg. Chloride damages the protective oxide layer)*
- *Surface roughness/ non-uniform finish*
- *Turbulent flow of fluid over metal.*

*Identify the place of corrosion for the following
suggest a method to prevent corrosion*

- 1. Steel screw in brass marine hardware*
- 2. Steel propeller shaft in bronze bearing*

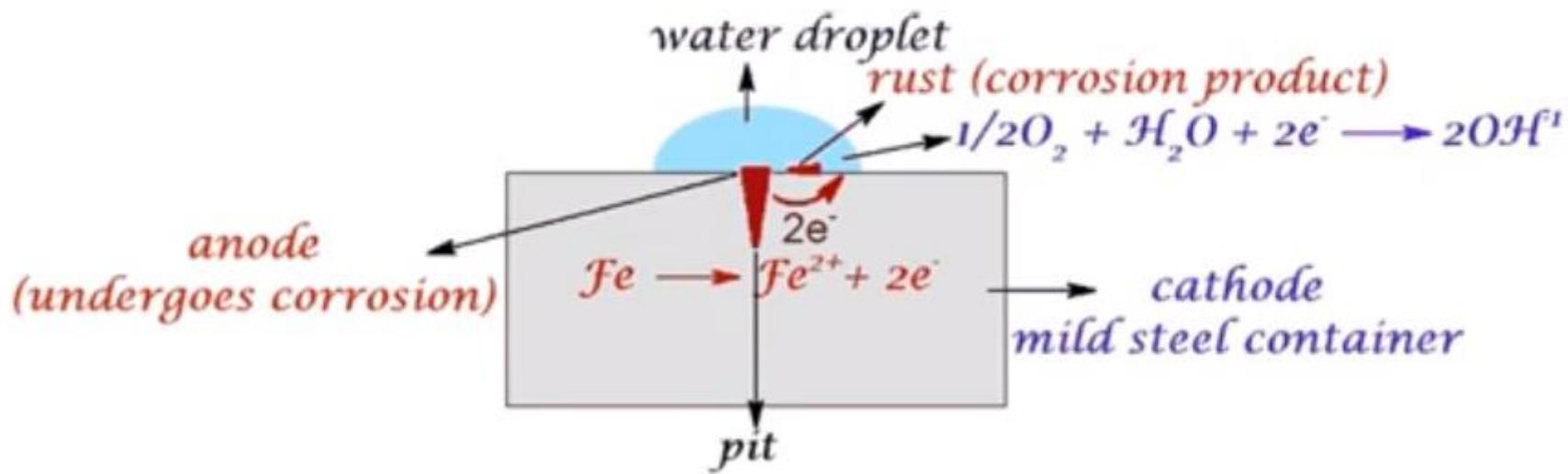
Pitting corrosion/ Galvanic corrosion



Damaged tin coated mild steel container left out in rain

Note: The same effect occurs when the protective metal oxide layer over the metal gets damaged.

Pitting corrosion/ Differential aeration corrosion





National Institute of Technology Karnataka(NITK), Surathkal



PREVENTION

- ❖ Anodic area should be larger than the cathodic area.
- ❖ Avoid cathodic protection of metals.
- ❖ Regular maintenance so that dust accumulation/moisture is minimised.
- ❖ Uniform and sufficient aeration should be maintained, so that damaged oxide layer could be regenerated.
- ❖ Control of environment (pH , temperature, chloride concentration).

i) Boiler corrosion by Dissolved gasses

Boiler corrosion caused by dissolved gases is mainly due to oxygen (O_2) and carbon dioxide (CO_2) present in feedwater.

- Oxygen corrosion:



Produces pitting corrosion, which is deep and localized.

- Carbon dioxide corrosion:

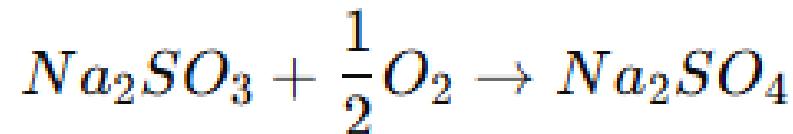
CO_2 dissolves in condensate water to form carbonic acid:



This acid lowers pH and causes uniform thinning.

Prevention:

1. Mechanical deaeration – Tray or spray deaerators to remove O₂ & CO₂.
2. Chemical removal – Oxygen scavengers:
 - Sodium sulfite:



- Hydrazine:



- Maintain feedwater pH ~8.5–9.2 to reduce CO₂ corrosion.

ii) Boiler corrosion by MgCl₂

- Source: Seawater contamination or salts in feedwater.
- Action: In boiler temperatures, MgCl₂ undergoes hydrolysis:



- The liberated HCl attacks steel:



- This causes acidic corrosion and pitting.

Prevention:

- Use demineralized / softened water.
- Add alkalinity (e.g., Na₃PO₄) to neutralize acids.

iii) Boiler corrosion by NaOH (Caustic embrittlement)

Caustic embrittlement

It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water.



- Cause: Localized high concentration of NaOH in cracks, crevices, or around rivets due to water seepage and evaporation.
- Mechanism: Concentrated NaOH attacks steel along grain boundaries, causing intergranular cracking.
- Chemical Reaction:



Internal Treatment Methods

A. Phosphate Conditioning

- Chemicals used: Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4
- Purpose: React with hardness salts (Ca^{2+} , Mg^{2+}) to form soft sludge:



- Sludge is removed by blowdown.

B. Calgon Conditioning

- **Chemical:** Sodium hexametaphosphate



- **Action:** Forms soluble complexes with Ca^{2+} and Mg^{2+} :



- Prevents scale by keeping salts in solution.

C. EDTA Conditioning

- **Chemical:** Ethylene diamine tetraacetic acid (EDTA).
- **Action:** Chelates Ca^{2+} and Mg^{2+} to form stable, soluble complexes:



(H_2Y^{2-} is the EDTA anion.)

- Works even at low concentrations; ideal for high-pressure boilers.

Corrosion control

1. Electroplating
2. Cathodic protection
3. Anodic protection
4. Inhibitors

1. Electroplating

ELECTROPLATING OF COPPER

Anode

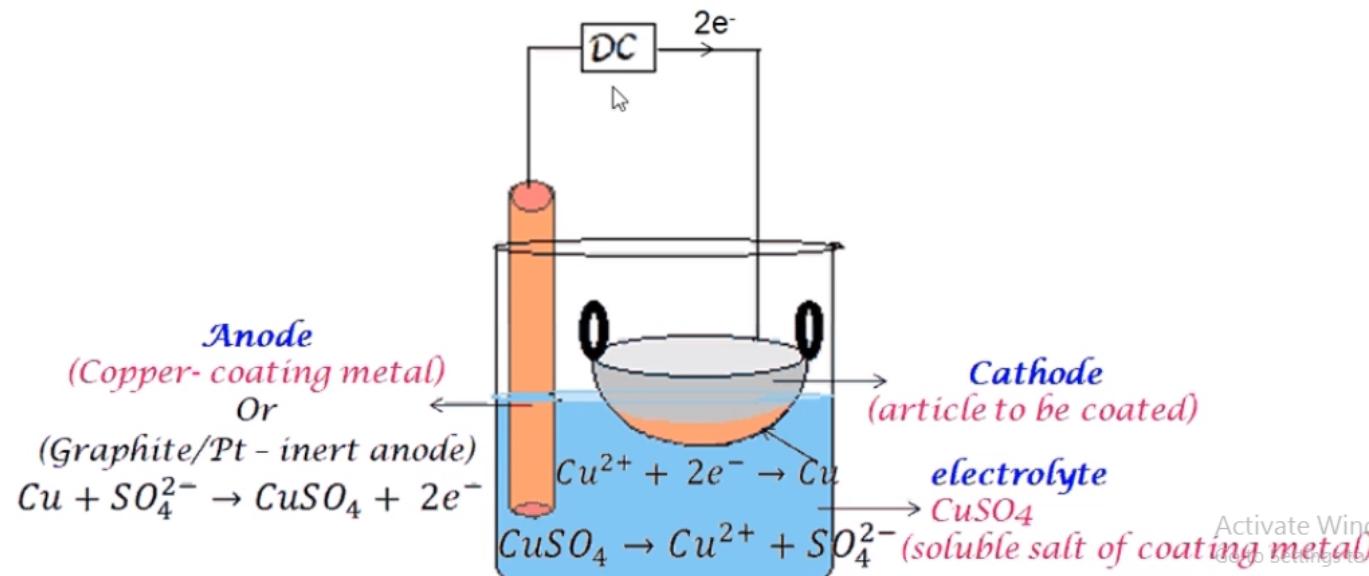
Coating metal (Cu) or inert metal

Cathode

Article to be coated

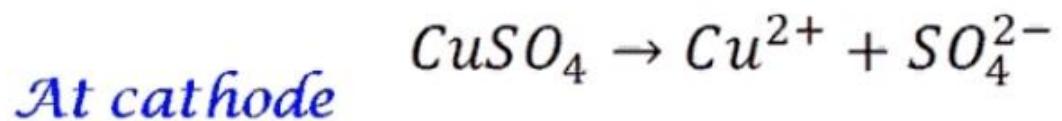
Electrolyte

$CuSO_4$ (solution with soluble salt of coating metal)

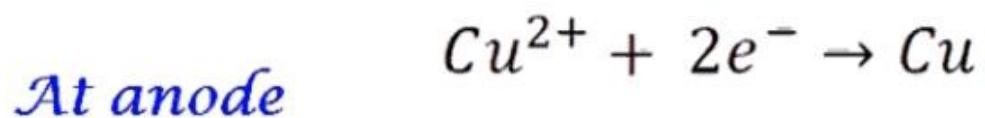


PROCESS (ELECTROPLATING OF COPPER)

When direct current is passed through $CuSO_4$ (electrolyte), it decomposes to its ions

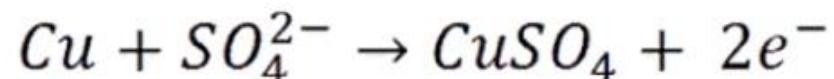


Cu^{2+} ions gets reduced to Cu and gets deposited on the article



Case-I - Anode is the coating metal (Copper)

Copper gets oxidised to form Cu^{2+} ions and reacts with SO_4^{2-}



Case-II - Anode is the inert metal (Pt, Graphite etc.)

Electrolyte has to be added to maintain the concentration of $CuSO_4$.

Metal coatings

2 types

- Anodic coating
- Cathodic coating

1. Anodic Coating

Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal.

Example : Iron is coated with anodic and more active metals such as zinc, magnesium and aluminium.



Advantages of Anodic Coating:

Even if the coating is ruptured, the base metal does not undergo corrosion.

The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion.

Galvanisation is an example of anodic coating.

What is Galvanisation???????

Galvanisation is a process of coating a base metal surface with zinc metal

Galvanised steel is not used to store foods??

Zinc dissolves in dil acids to produce toxic zinc compounds



National Institute of Technology Karnataka(NITK), Surathkal



2. Cathodic coating

- Cathodic coatings are produced by coating a base metal with a more noble metal which is cathodic.
- The metals such as copper, nickel, tin, silver are commonly used as cathodic coatings on steel.
- These coating metals are less reactive than the base metal & are less susceptible for corrosion.

Disadvantages of cathodic coating.....

When coating is damaged, an intense localised corrosion occurs due to setting up of a galvanic cell that consists of large cathodic area & a small anodic area.

Tinning is an example

What is tinning????

Coating a base metal with tin.

Tinning involves following steps

- 1.The sheet is first washed with organic solvents to remove rust and scale deposits
- 2.Then treated with dilute sulphuric acid to remove rust and scale deposits. Finally washed with water and air dried.
- 3.The clean & dry sheet is passed through molten stannous chloride flux. The flux helps molten metal to adhere on the metal surface
- 4.It is then passed through a tank that contains molten tin.
- 5.Finally passed through a series of rollers immersed in palm oil. The oil prevents the oxidation of tin coated surface.

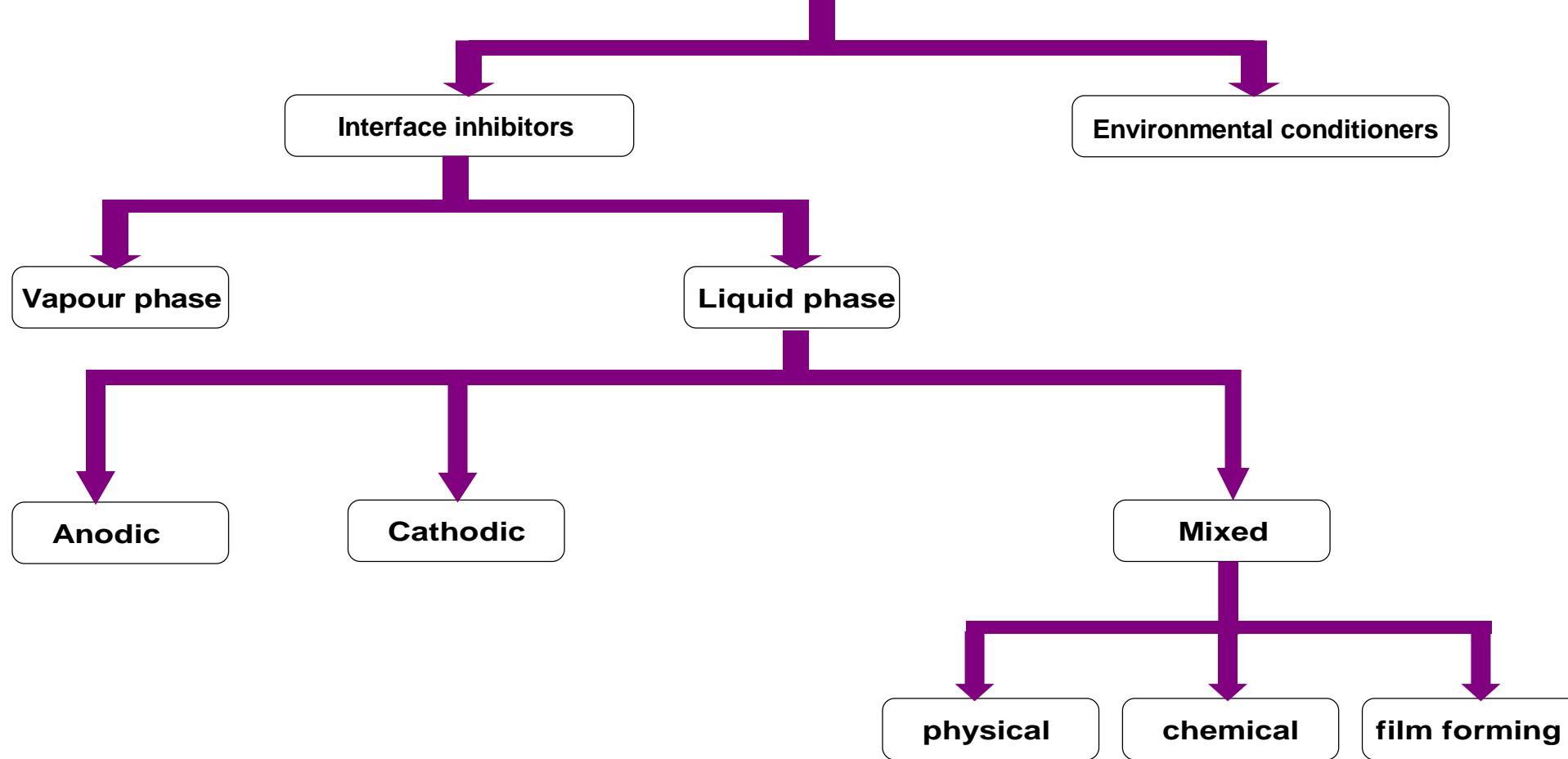
Corrosion control by INHIBITORS

- An **INHIBITOR** is a substance that when added in small concentration to an environment, decreases the corrosion without significant reaction with the components of the environment.
- An efficient inhibitor is compatible with the environment, economical for application and produces desired effects when present in small concentration.
- Inhibitor efficiency **P** is given by

$$P = \frac{w_0 - w}{w_0} \times 100$$

- - w_0 is the corrosion rate in the absence of inhibitor and w is the corrosion rate in the presence of inhibitor.

Classification of inhibitors



Vapour phase inhibitors

- **Volatile corrosion inhibitors (VCI)** are a type of corrosion inhibitor that are used to protect ferrous materials and non ferrous metals against corrosion or oxidation where it is impractical to apply surface treatments.
- They slowly release chemical compounds within a sealed airspace that actively prevents surface corrosion
- VCI chemicals are often added to paper and plastic substrates as a medium to deliver the protective chemical compounds for use in automotive packaging
- Dicyclohexylammonium Nitrite



National Institute of Technology Karnataka(NITK), Surathkal

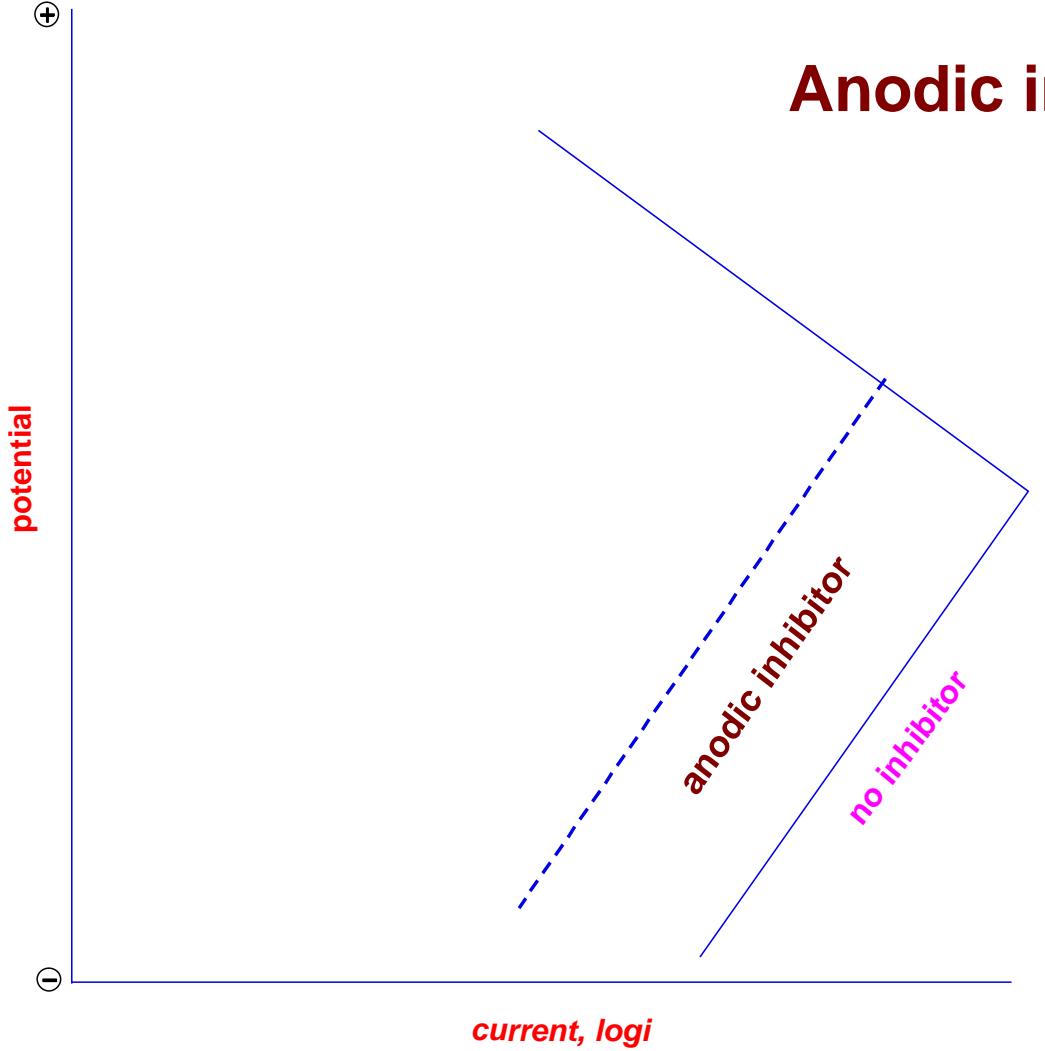


Anodic inhibitors

- These inhibitors selectively cover the anodic sites of the metal surface.
- During the addition of anodic inhibitor, the potential versus log(current density) diagram promotes a shift of the anodic polarization curve from the solid line to the dashed line with little or no effect on the cathodic polarization curve.
- The net effect is an increase in the corrosion potential E_{corr} and decrease in the corrosion rate.



National Institute of Technology Karnataka(NITK), Surathkal



National Institute of Technology Karnataka(NITK), Surathkal



Cathodic inhibitors

- In acid solution the cathodic reaction is the reduction of hydrogen ions to hydrogen atoms which combine hydrogen molecule.



- In alkaline solution the cathodic reaction is oxygen reduction



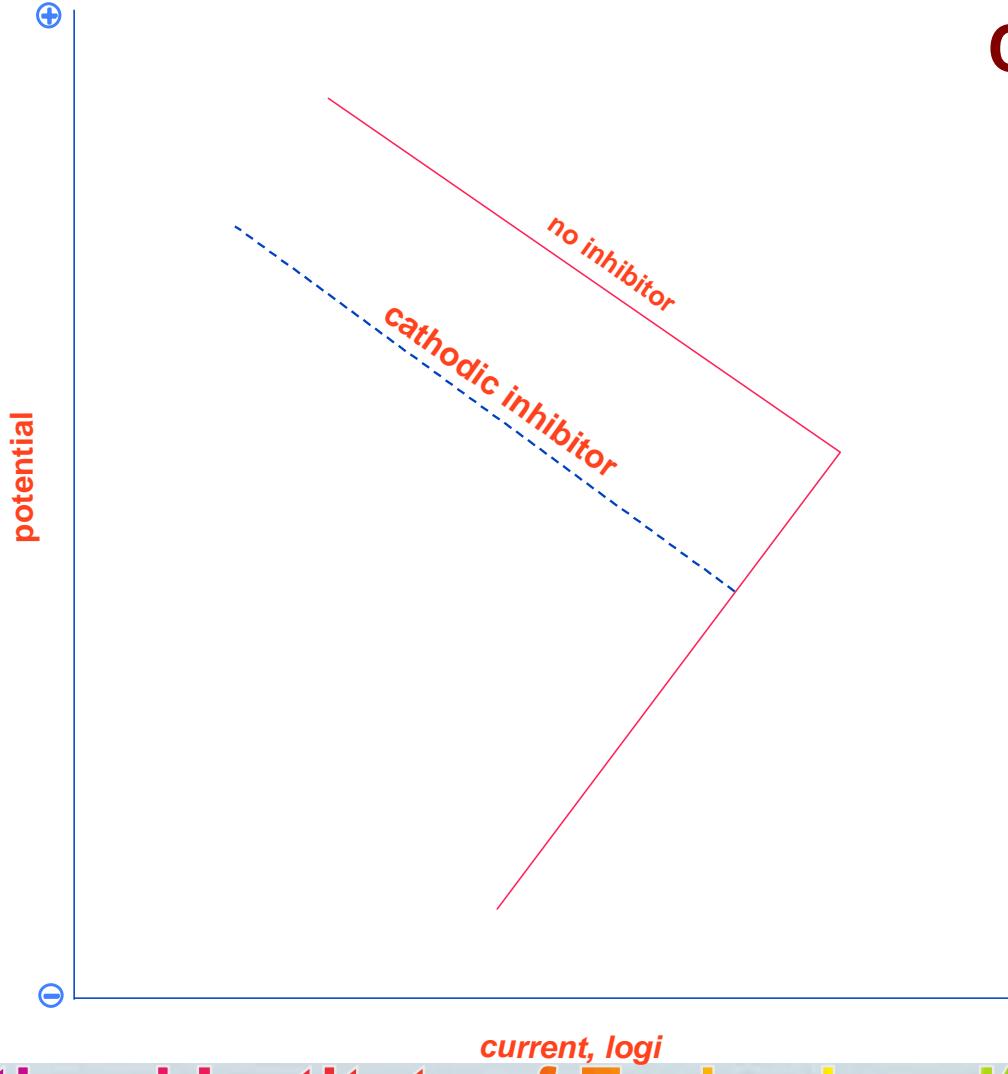
Cathodic inhibitor impedes reduction reaction.



National Institute of Technology Karnataka(NITK), Surathkal



Cathodic inhibitors



National Institute of Technology Karnataka(NITK), Surathkal



Weight Loss Method of Corrosion

Principle

- Corrosion causes **loss of metal mass** over time. By measuring the **difference in weight before and after exposure**, the **corrosion rate** can be calculated.

Procedure

- **Prepare metal specimen** (known surface area and initial weight).
- **Clean and dry** the specimen.
- **Immerse** the specimen in a corrosive medium (acid, saltwater, etc.) for a known duration.
- **Remove**, clean (to remove corrosion products), dry, and **reweigh**.
- Calculate **weight loss** = Initial weight – Final weight.

$$\text{Corrosion Rate (mm/year)} = \frac{87.6 \times W}{D \times A \times T}$$

Where:

- W = Weight loss in mg
- D = Density of metal in g/cm³
- A = Area of the specimen in cm²
- T = Time of exposure in hours
- **87.6** = Conversion factor to get mm/year