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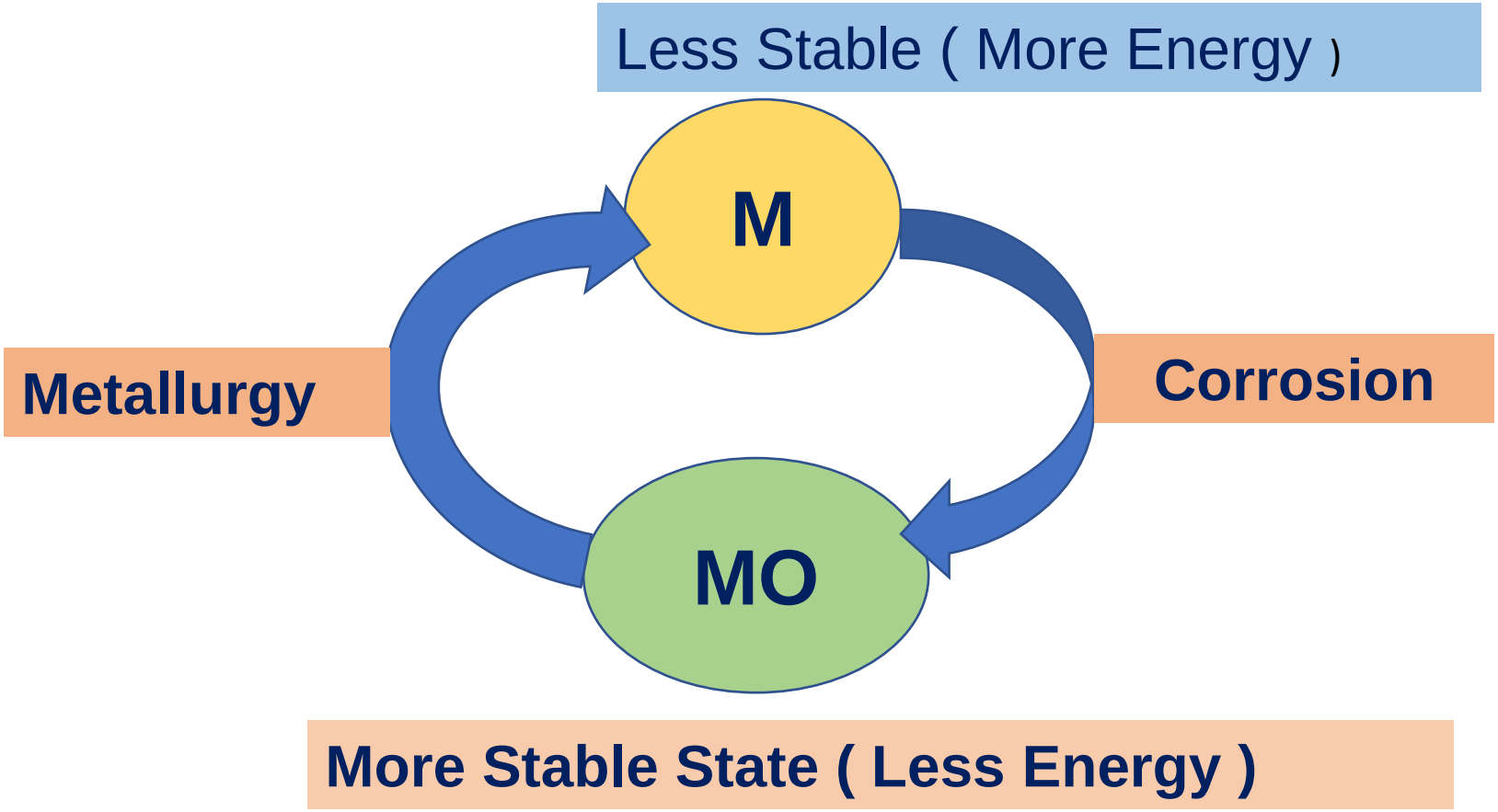
Corrosion Science

Introduction

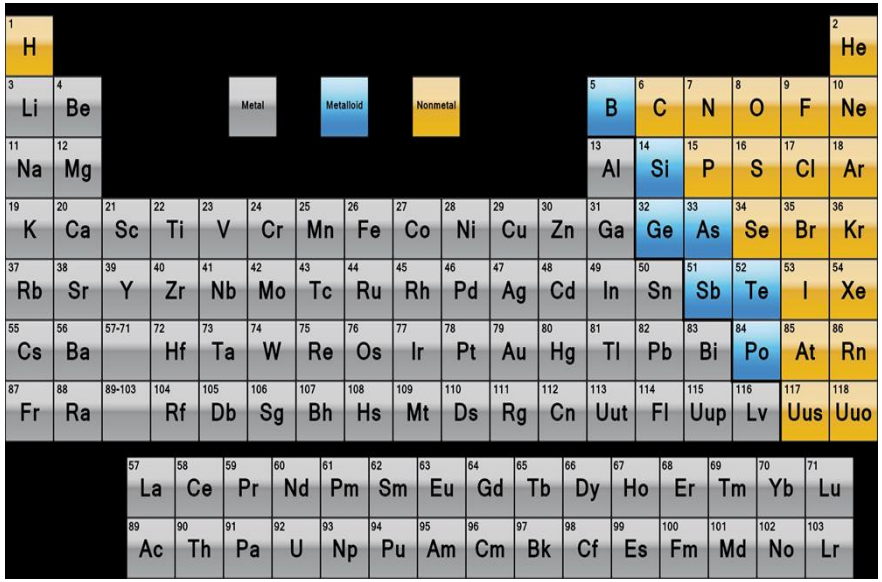
- The degradation of a material due to a reaction with its environment.
- Process of Destruction of the material through **chemical or electrochemical attack** by its environment.
- Slow process
- Measured in weight loss per unit time.
- **Corrosion is destruction of material due to chemical or electrochemical reaction occurring on its surface**

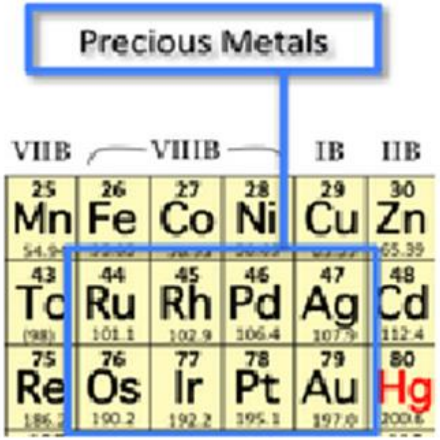
https://youtu.be/jQoE_9x37mQ?list=PLqxe1FKqykZ9IvmFCW8Tj21oJF82tPzOt

Corrosion and Metallurgy



Why Do Metals Corrode?





Periodic Table

- Precious metals do not undergo corrosion.
- They are found in pure state in nature.
- Thermodynamically Metal oxides are more stable than pure metals

Consequences (Effects) Of Corrosion

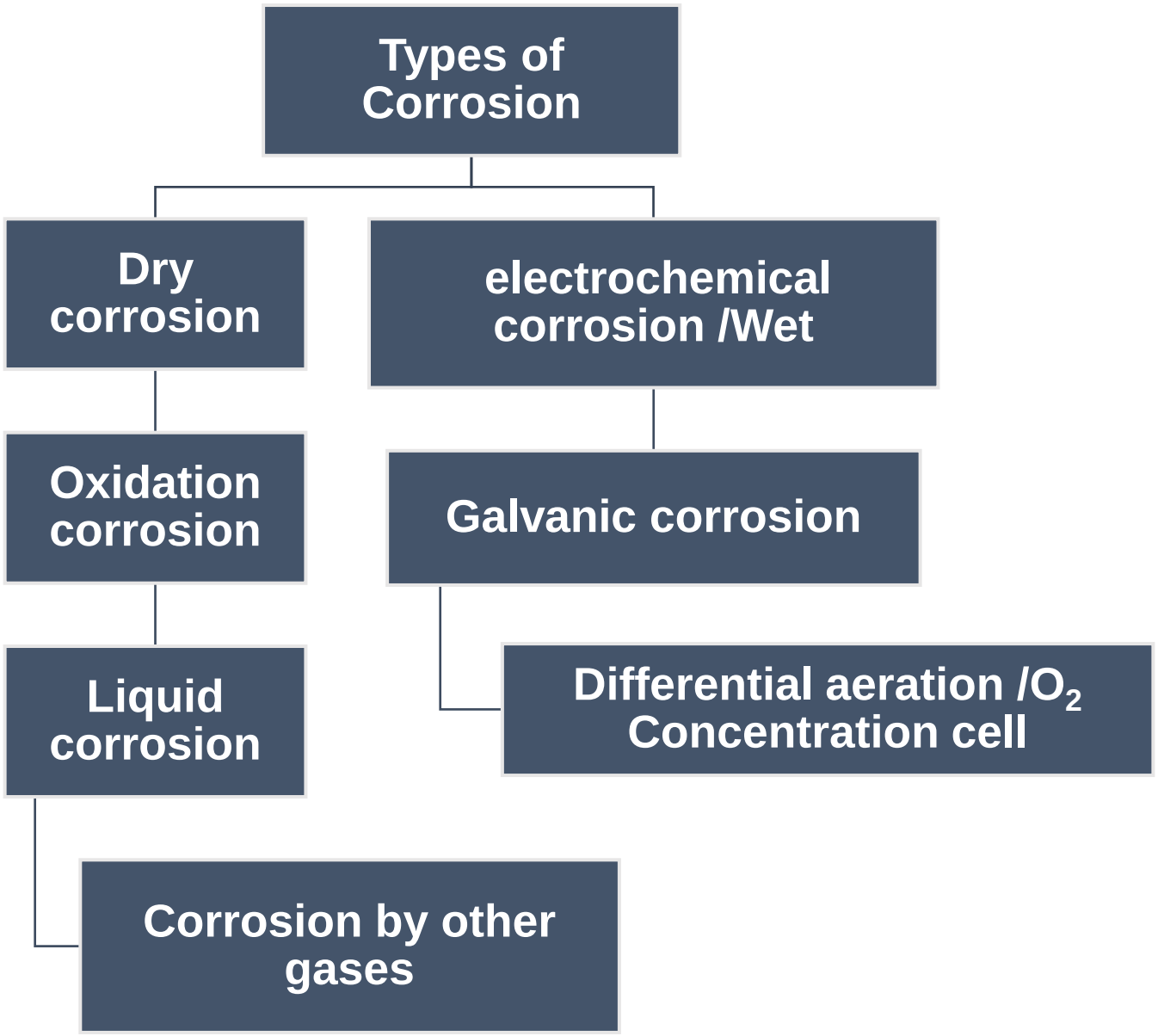
- Loss of metal or reduced thickness leading to structure failure
- Value of goods is reduced
- following Surface properties of metal are affected

I. frictional properties
II. bearing properties
III. ease of fluid flow
IV. electrical conductivity,
V. surface reflectivity
VI. heat transfer

Galvanic Series

- Metal having higher position in galvanic series has high tendency to act as **anode**
- Metal having lower position in galvanic series shows **cathodic behavior** and gets protected
- Higher difference in position of two metal will cause corrosion to greater extent

Types of Corrosion



Dry Corrosion

- Metal atom on the surface react with atmospheric oxygen to form metal oxide
- The metal oxide layer is formed perpendicular to the metal surface and forms barrier for the reduction of further metal atoms with oxygen in air
- Process of oxidation will occur only if the metal atoms from the inner layer of metal should diffuse out to the surface or oxygen atoms should diffuse in to the inner metal layers
- Metal ions are lighter and hence diffuse faster than oxide ions as oxide ions are **heavy**

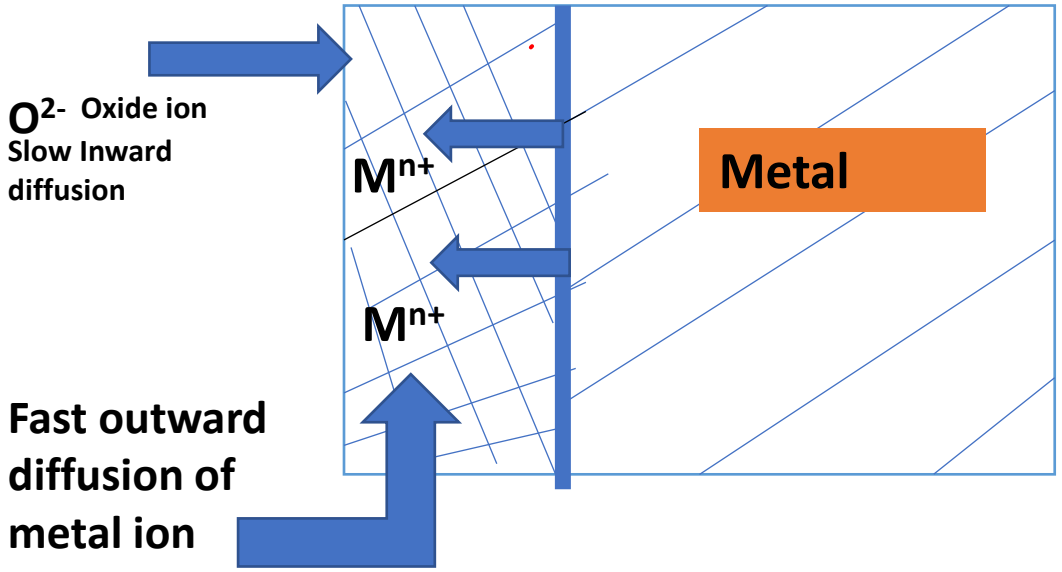
$2M \rightarrow 2M^{n+} + 2ne^-$

$n/2O_2 + 2ne^- \rightarrow nO^{2-}$

$2M + n/2O_2 \rightarrow 2Mn^+ + nO^{2-}$

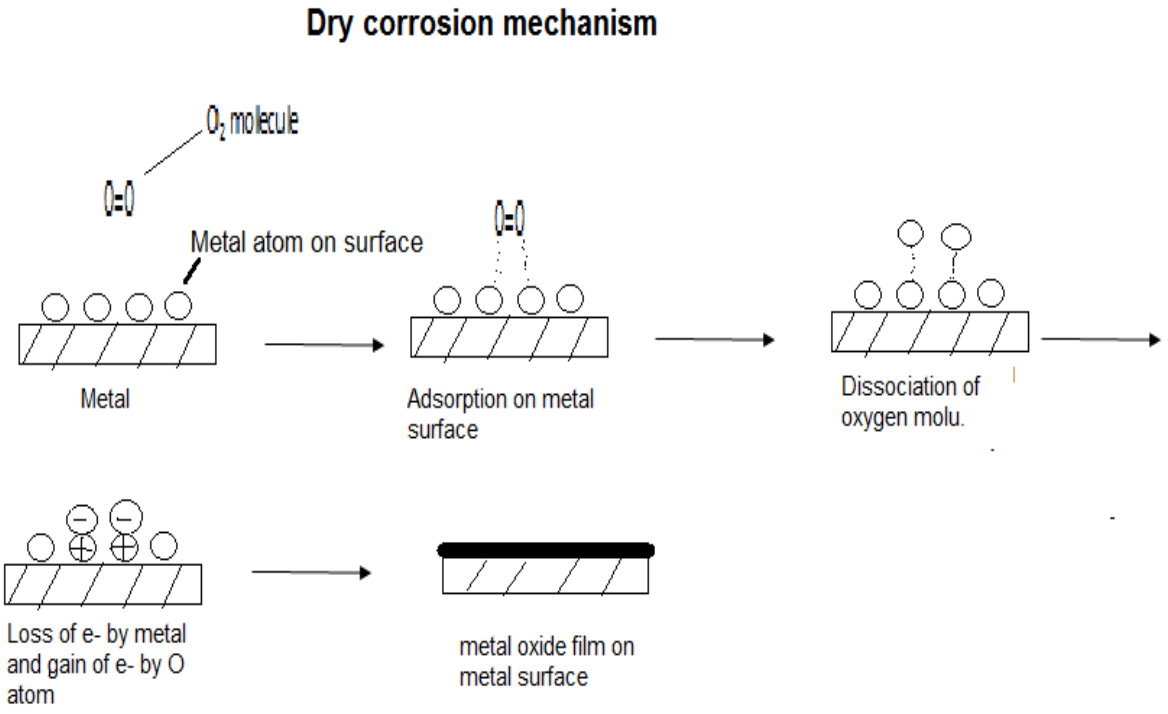
$\downarrow$

Metal oxide



Dry Corrosion Mechanism

- Adsorption
- Dissociation
- Chemisorption
- Formation of thin oxide film



Nature of Oxide Film

Nature of oxide film	Metals
Porous	Li Na K Mg Ca
Non porous	Cr Ti Al Cu Ni
volatile	Mo
Unstable	Au Ag pt

Comparison of Dry And Wet Corrosion

Dry	Wet
Direct attack of Atmospheric gases on metal in absence of Moisture	Involves Electrochemical attack on metals in Presence of Aqueous medium
Corrosive media include vapors and gases	Corrosive medium is aqueous environment
Seen in form of Oxidation corrosion	Seen in form of Galvanic or differential aeration corrosion

Pilling-Bedworth ratio (PBR)

“If the volume of oxide is smaller than the volume of metal consumed in the metal oxide formation, then the film is porous. On the other hand, the film is non-porous if metal oxide formed has greater volume than the metal consumed during corrosion.”

$$PBR = \frac{volume\ of\ metal\ oxide\ formed}{volume\ of\ metal\ consumed\ in\ forming\ oxide}$$

1) PBR <1 Oxide film formed by **Na, Mg, Li, K** (Porous)

2) 1< PBR<2 Oxide film formed by **Cr Al Ti Ni** (Non Porous)

3) PBR >2 Oxide layer gets chip off **(Nb, Si**)

Corrosion by other gases

- The degree of attack depends on the formation of protective or non-protective films.
- AgCl film, resulting from the attack of Cl_2 on Ag. Protects the metal from further attack.
- Cl_2 gas attacks on tin (Sn) forming volatile $SnCl_2$. Don't protect metal from further attack.
- H_2S at high temperature attacks steel forming a FeS scale, which is porous and don't protect metal from further attack.

Hydrogen Evolution Mechanism

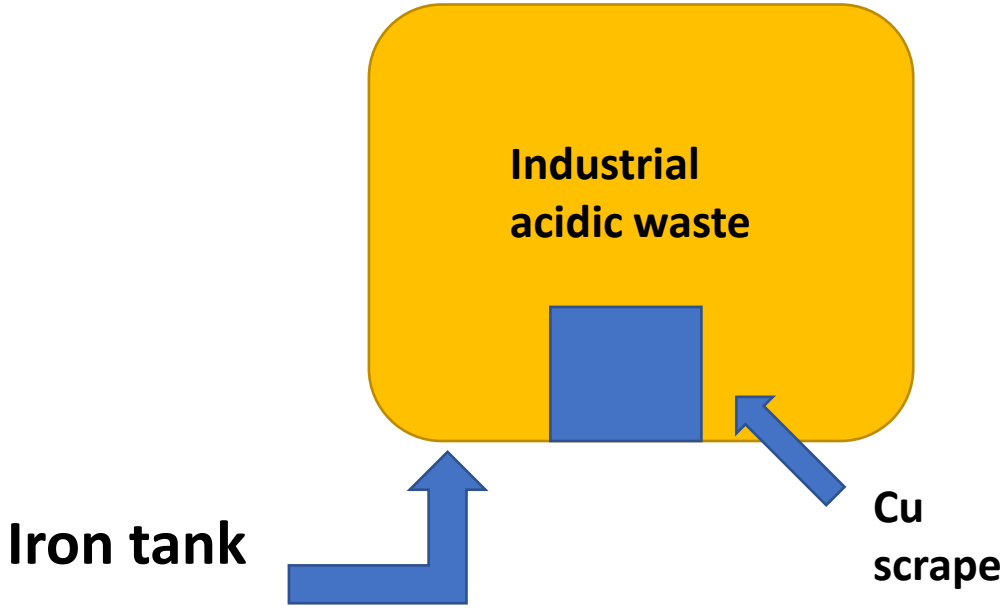
- **At anodic site** metal undergoes oxidation forming metal ions with release of electrons

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

- In presence of Acidic Medium

Hydrogen evolution is **seen at cathodic site**

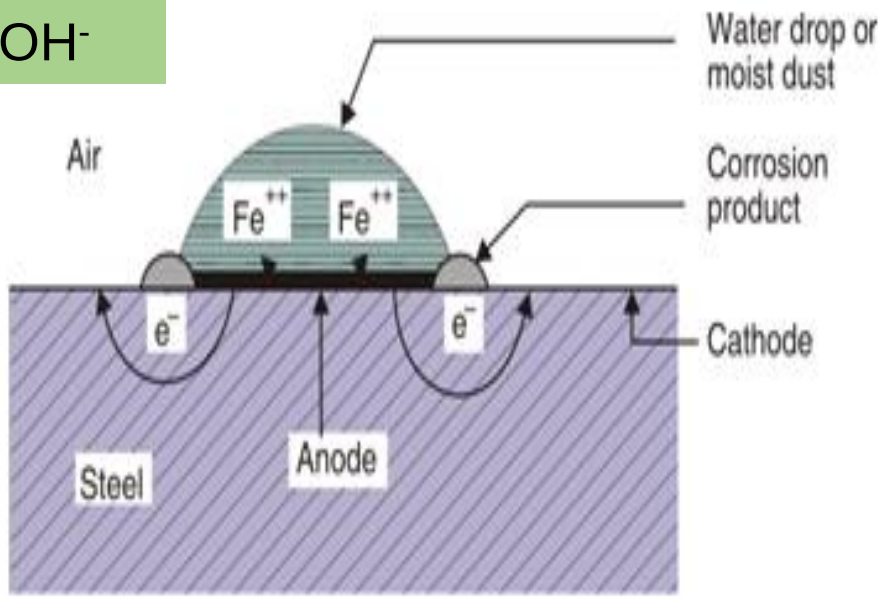
- $2H^{+} + 2e^{-} \rightarrow H_2$



Oxygen absorption Mechanism

Anode: Fe → $Fe^{+2} + 2e^-$

Cathode : $H_2O + O_2 + 2e^-$ → $2OH^-$



Forms of Corrosion

- Galvanic Corrosion
- Concentration Cell corrosion
- Pitting corrosion
- Waterline corrosion
- Stress corrosion
- Crevice corrosion

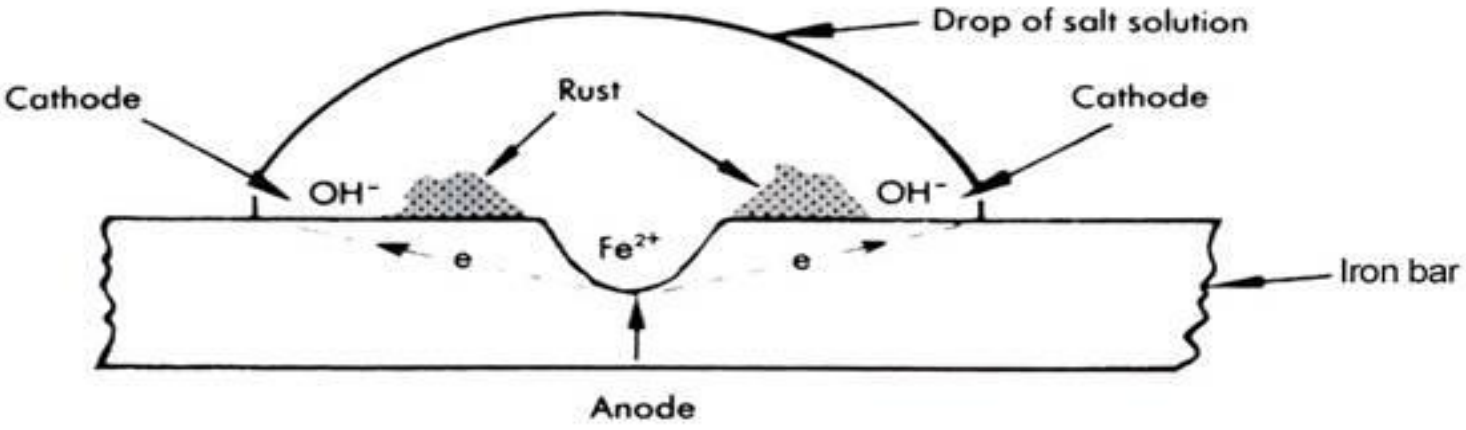
Galvanic Corrosion

- Corrosion in Presence of Two Different Metals
- Metal with higher position in Galvanic Series (with more Negative Electrode Potential) will act as Anode
- The Extent of Galvanic Corrosion depends on potential difference between two metal

stainless steel screw in contact with a cadmium plated steel washer.

Concentration Cell Corrosion

- corrosion is observed when metallic portion get exposed to varying concentration of Oxygen
- Potential difference is developed due to different exposure to O_2
- Part of metal which get more expose to Oxygen acts as cathode



Pitting Corrosion

- Observed if oxide film gets cracked or Metallic surface gets occupied by dust /sand/water drop
- Film may get rupture due to various reasons
- Small anodic areas and large cathodic areas are formed

Crevice Corrosion

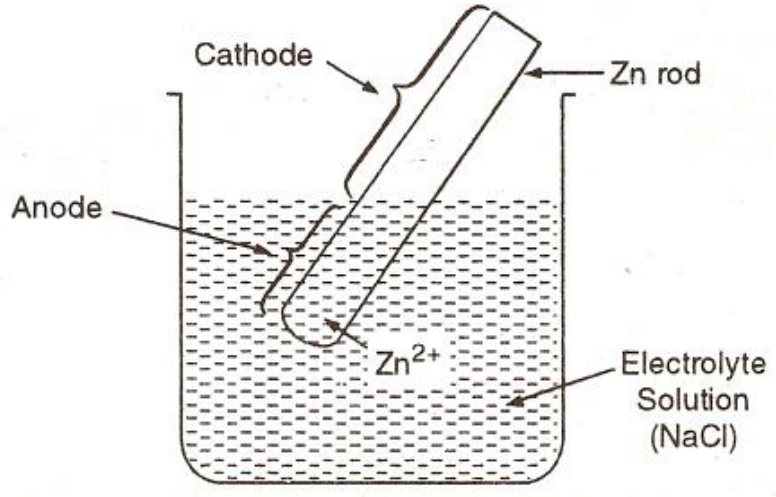
•Observed if Electrolyte gets trapped in Crevices of Bolts/**Gasket**/Nuts/washers

•Corrosion is seen as Oxygen can not cross crevice forming Oxygen concentration cell

•Corrosion seen in area with less expose to oxygen

Water-line Corrosion

- Concentration of Oxygen above the water surface is greater than that under the surface.
- Corrosion is seen due to Oxygen Concentration Cell
- metal just above the water level is cathodic w.r.t. the metal below the water level.



Factors influencing Corrosion

On the basis of Nature of metal

- **Electrode Potential /Position of Metal in Galvanic Series**
- **Purity of Metal**
- **Physical State of Metal**
- **Relative area of Anode and Cathode**
- **Nature of Oxide film**
- **Hydrogen Overvoltage**
- **Nature of Corrosion Product**

Nature of Environment

- **Temperature**
- **Humidity**
- **pH**
- **Nature of Ions Present**
- **Conductance of Corroding Medium**
- **Formation of Oxygen Concentration Cell**

Cathodic Protection

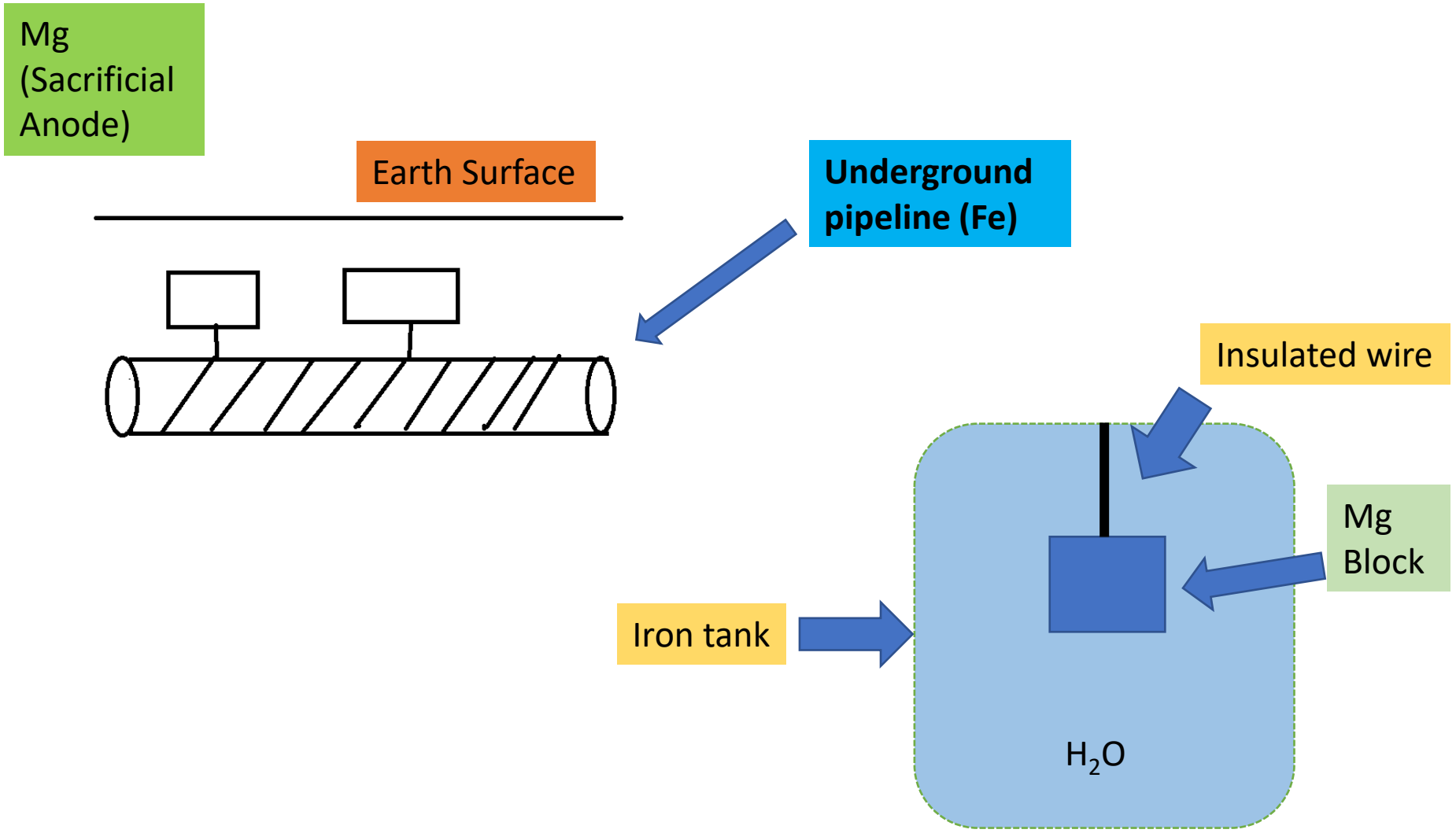
- The principle involved is that the metal to be protected is made to **behave like a cathode**
- Alloys/metals like steel, brass, copper and lead can be protected in all types of soils and almost all sorts of aqueous media by cathodic protection method
- This technique is also employed to prevent pitting corrosion in stainless steel or aluminium and can also be used to prevent stress corrosion cracking in brass, mild steel, stainless steel, magnesium and alumin**ium**

Cathodic protection using Sacrificial Anode

- Metallic structure to be protected from corrosion is attached to **more active metal (Zn/Mg)**
- More active metal behave as anode
- Corrosion is **concentrated on active metal only**
- Main metallic structure acts as cathode and gets protected

https://youtu.be/RAlC75xG4qU?list=PLqxe1FKqykZ_vOORtJL4z7OIxiHhMqXlb

Sacrificial Anodic Protection



Examples of Sacrificial Anodic Protection

Aluminium sacrificial anodes *(light colored rectangular bars)* mounted on a steel jacket structure.

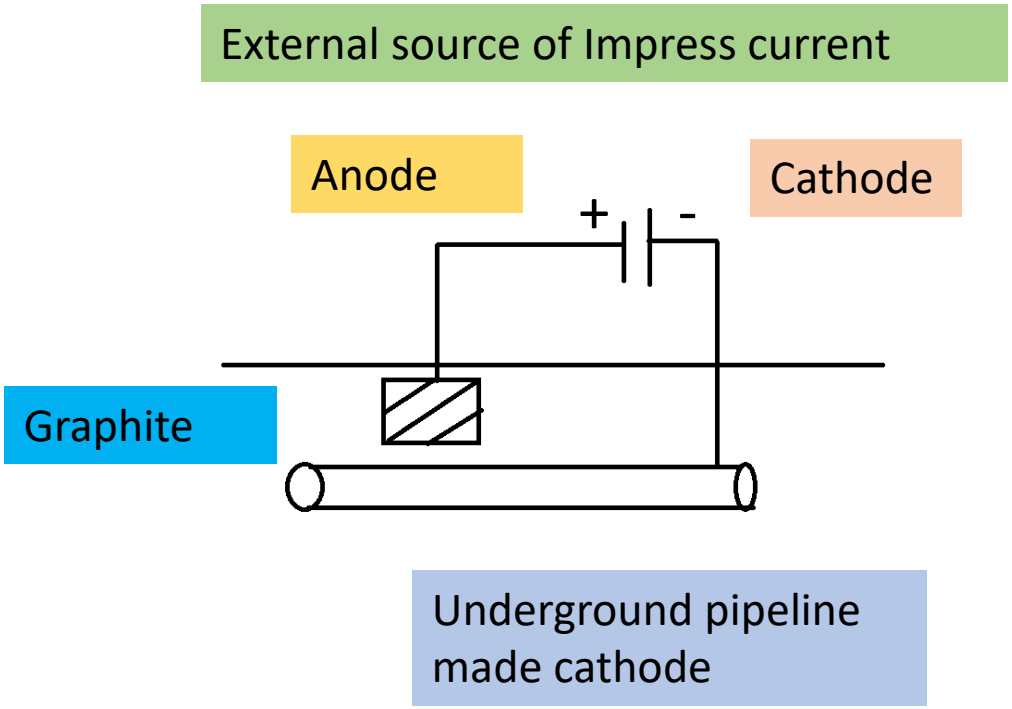
Sacrificial anode attached to hull of Ship showing Corrosion

Using Impressed Current

- An impressed current is applied in opposite direction to nullify the corrosion current
- Conversion of the corroding metal from anode to cathode.

Applications

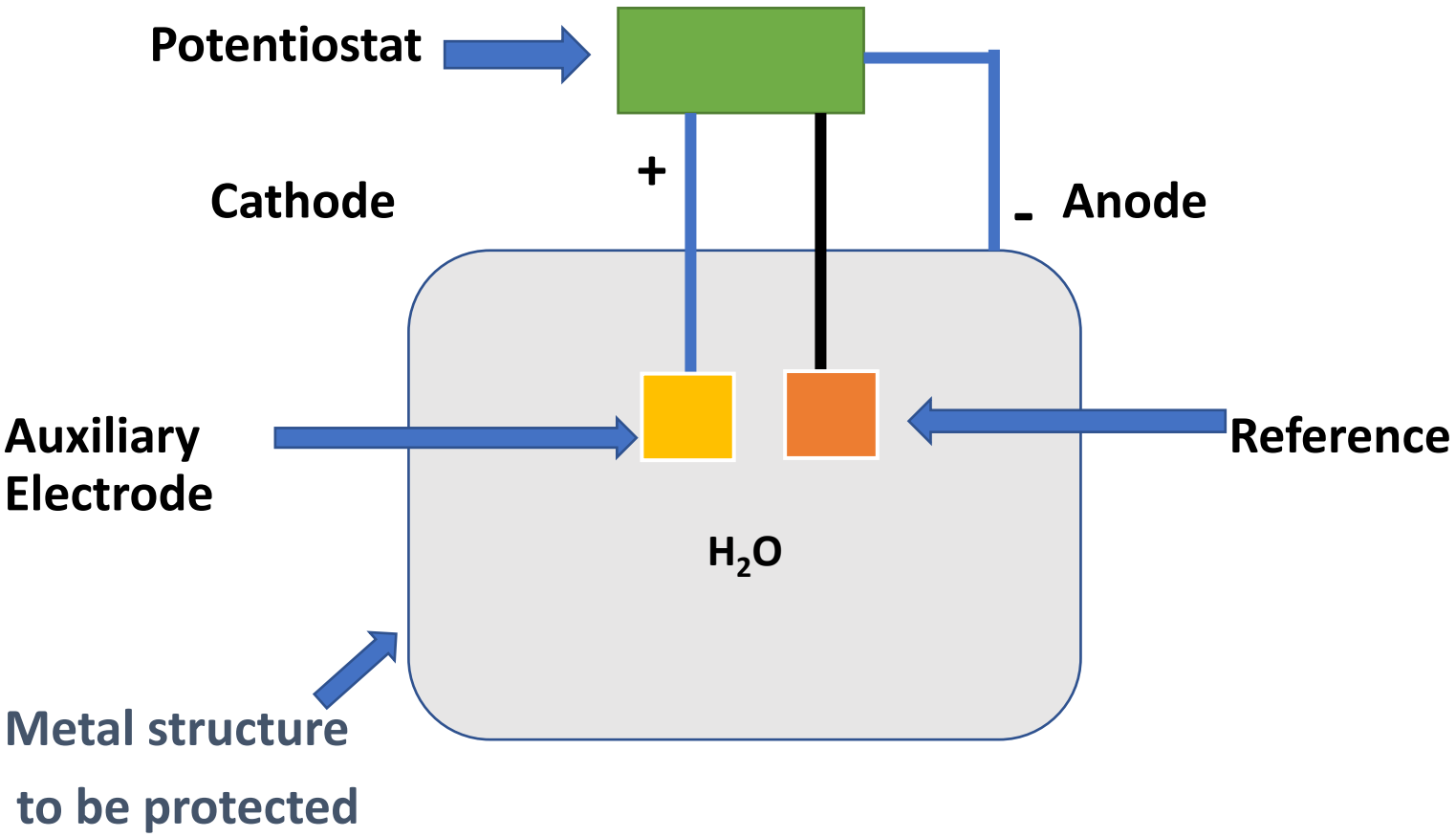
- Open water box coolers
- water tanks
- condensers
- transmission line towers



Anodic Protection

- Applicable for metals which shows active passive behavior **(Al + Cr + Ti + Ni)**
- Metallic structure to be protected is made **more Anodic** by applying External current
- **Formation of thin oxide film** prevents corrosion of Metallic Structure

Anodic Protection



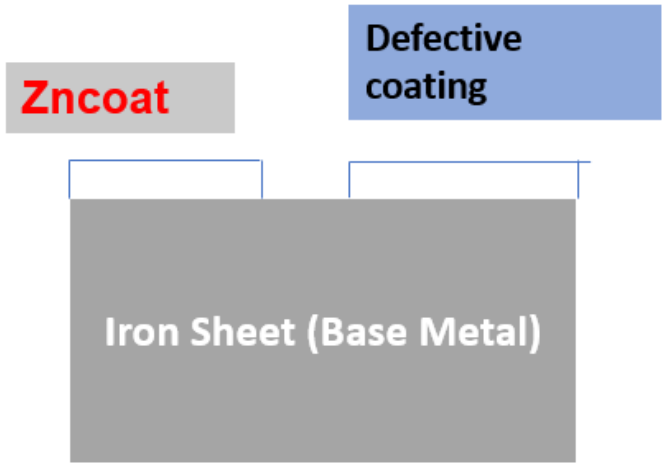
Anodic Protection

Applications

1. **Chemical reactors**
2. **Industrial metal condensers**
3. **Pipe lines for carrying corrosive liquids or solutions**

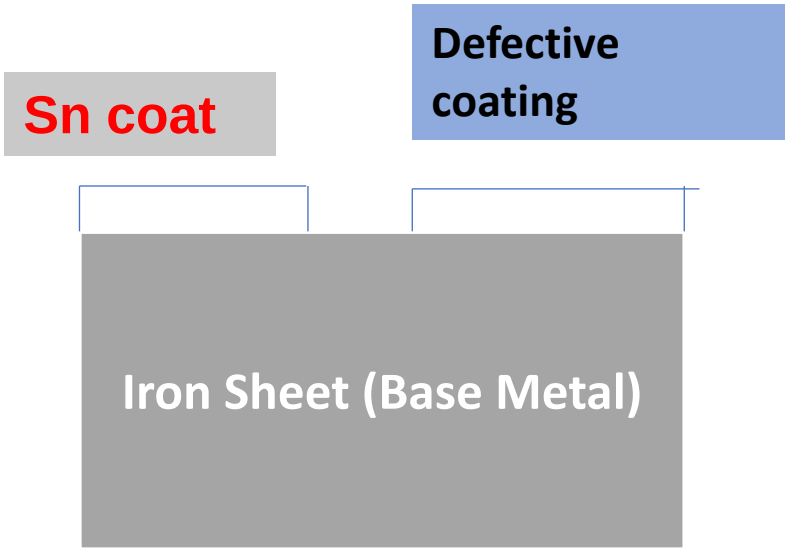
Anodic Coating

- Coating metal is higher placed in galvanic series than the base metal
- If coating gets break then base metal is protected until coating metal is present
- Anodic coating is mostly preferred.
- Coating of Zn, Al, Cr on steel
- Galvanizing is an example of anodic coating



Cathodic Coating

- coating metal used for coating has lower position in Galvanic Series
- If coating gets rupture than Base metal undergoes corrosion
- Cathodic coating is less preferred.
- Tinning is an example of Cathodic coating



Protective coatings

Metallic coating

1. Hot dipping
2. Electroplating
3. Metal cladding
4. Cementation
5. Electroless plating

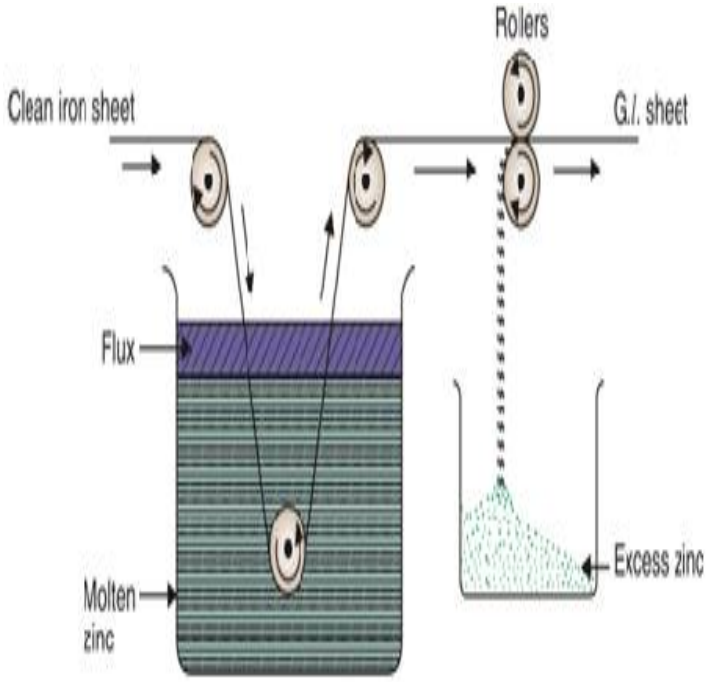
Non Metallic Coating :

Inorganic Coating (Chemical conversion Coating)

1. Phosphate Coating
2. Chromate Coating
3. anodizing

Galvanizing

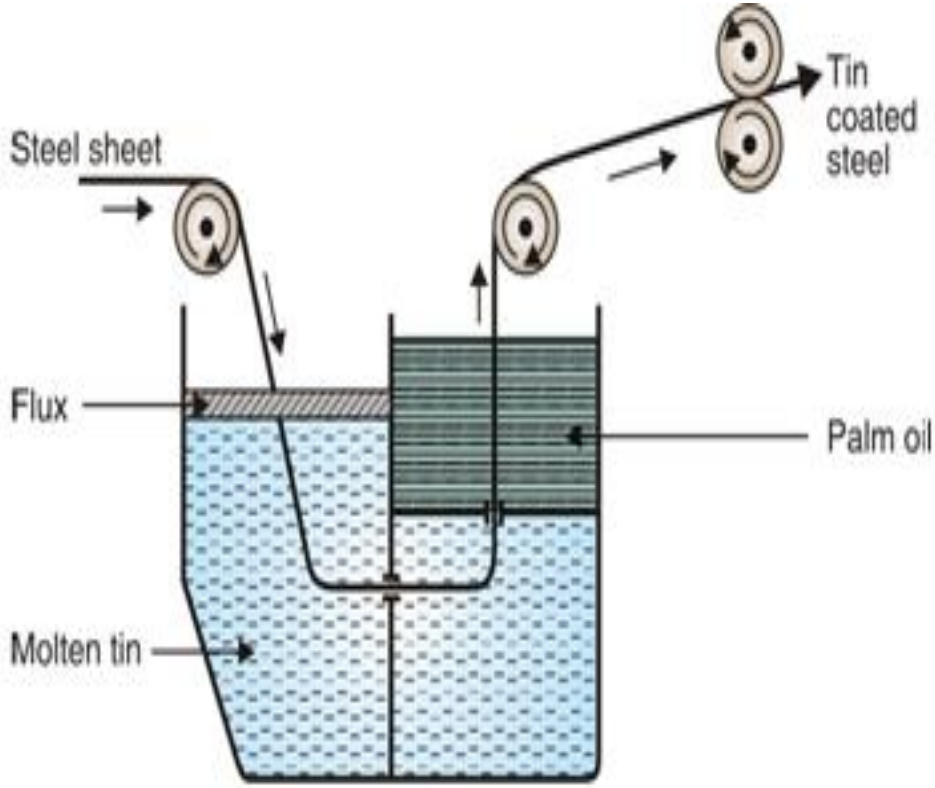
- Coating of Zinc on Iron Sheet
- **Anodic coating**
- **Precleaned iron sheets** are passed through bath of molten metal
- Metallic surface is prevented from oxidation using flux
- Sheets are finally annealed



https://youtu.be/UE7zY9JoVIc

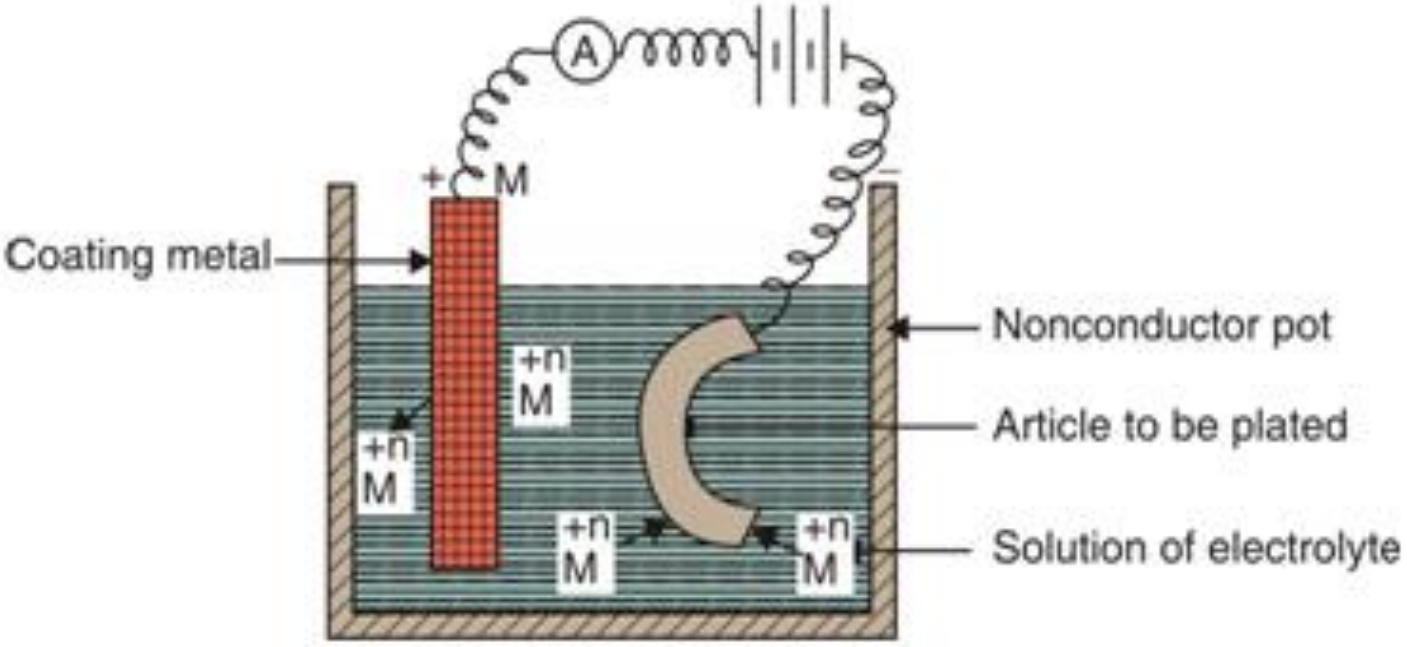
Tinning

- Coating of tin on iron sheet
- Cathodic coating
- Tinned containers can be used for storing foods, ghee, oils, pickles etc.



Electroplating

- Electroplating is the method in which coating metal is coated on a base metal on the basis of electrolysis principles.



Reactions involved in Electroplating

At anode

$Cr \longrightarrow Cr^{+3} + 3e^-$ (if chromium anode)

$Ag \longrightarrow Ag^+ + e^-$ (if silver anode)

At Cathode (article)

$Cr^{+3} + 3e^- \longrightarrow Cr$ (if chromium plating)

$Ag + e^- \longrightarrow Ag$ (if silver plating)

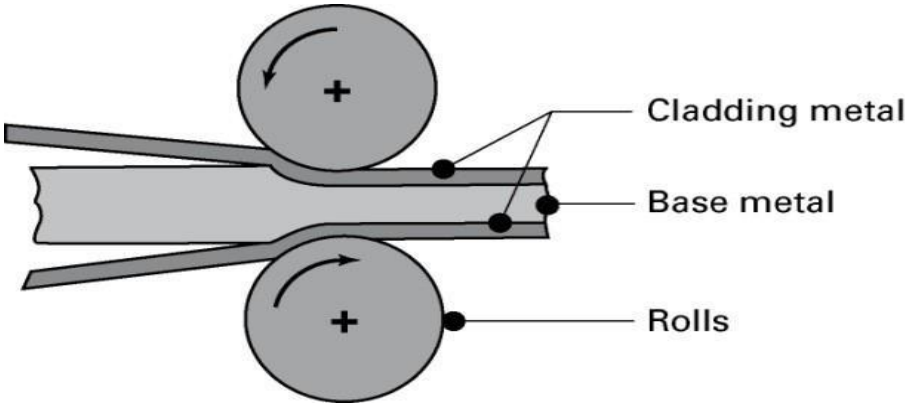
https://youtu.be/aDkpbB31lek

Applications of electroplating

- Corrosion protection
- Decoration or better appearance
- To have surface of plastic, glass, wood conducting.
- For electroforming of many parts of machines by electro deposition of thick layer

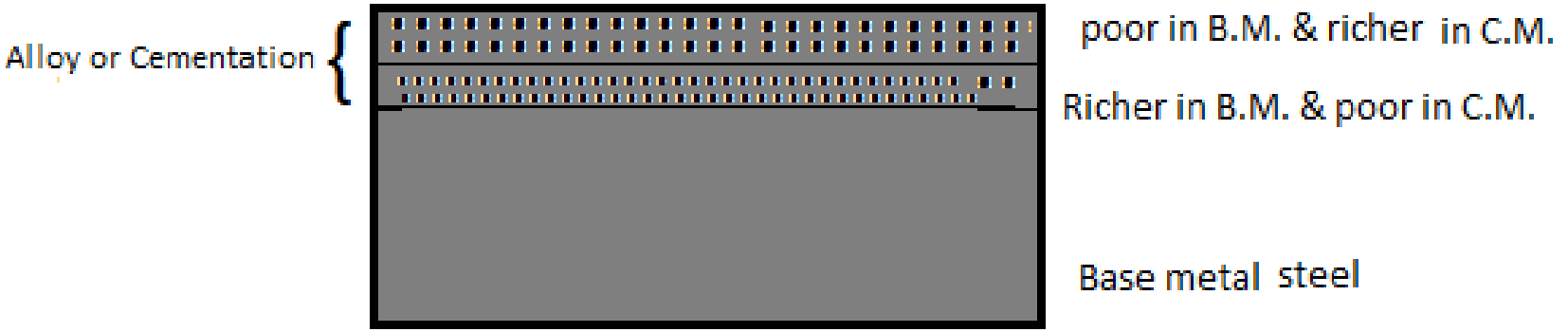
Metal Cladding

- process of sandwiching the base metal between two thin layers of coating metal by hot-rolling the composite to produce a firm bonding.
- The coat metals are usually metals of least reactivity (Cu, Ni, Ag, Pt, Ti)
- This is done base metal like Al, Cu
- Theses corrosion resistant materials are used in aircraft industry



Cementation

- Involves formation of **strong layer of alloy** of coating metal and base metal on the surface of base metal
- Used for coating small articles line nuts, bolts, screws, spanners, screw drivers, tools furnace parts, and turbine blades
- Coating of Fe by Zn is refer as **sherardizing**
- Al on Fe is refer as **Colorizing**



Electroless Plating

- Metal is deposited on any other material by using **reducing Agent**
- Based on **catalytic reduction of metal ion** on the surface of substrate
- No Need of **external electric current**
- **Nonconductive surfaces** can be metallized

- **Copper Electroless Plating:**

At Anode:

$$2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$$

At Cathode : $Cu^{+2} + 2e^- \rightarrow Cu$

Nickel Electroless Plating

Coating Bath Composition for Ni Electroless Plating :

- Coating Solution = 20 g/lit $NiCl_2$
- Reducing agent : Sodium Hypophosphite
- Complexing agent :15 g/L Sodium succinate
- Buffer : 10 g/l Sodium acetate
- pH = 4.5
- Temp = 93 ^0C

Reaction :

Anode: $H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ 2e^-$

At Cathode: $Ni^{+2} + 2e- \rightarrow Ni$

Nonmetallic Coating

- **Inorganic coatings form chemical bonds with the base metal and provide protection against oxidation at high temperature, weathering and corrosion.**
- **phosphate coatings and chromate coatings are mostly prefer**

Phosphate Coating

- A thin film of metal phosphate coating gets deposited on the metal surface due to interaction of surface atoms of the base metal and certain metal phosphates in aqueous solution of phosphoric acid

- Chemical or electrochemical reaction between phosphating solution and base metal result into surface film consisting of Zn /Mn phosphates
- Phosphate coatings are adopted as excellent base for paints
- Coating is usually carried out by immersion or spraying or brushing

- Base Metal (Fe) + Zn Phosphate + H_3PO_4 → Fe-Zn Phosphate (film)

Chromate Coating

- coatings also provide the **base for paints**
- These coatings are formed by the reaction between the **base metal** with **sodium dichromate** and **dilute sulphuric acid**
- At a particular pH, basic chromium chromate ($Cr_2O_3 .CrO_3 . x H_2O$) gets precipitated on the metal surface
- The primary function of **chromate coating** is to render the base metal passive, thereby acting as a corrosion inhibitor
- applied on aluminium, zinc, cadmium, copper, silver, manganese and tin metal substrates

Anodizing

- Coating is produced by anodic oxidation process on metal such as Al ,Zn Mg etc
- In anodizing **base metal acts as anode** in electrolytic bath and by passing direct current
- **Steel or copper** acts as cathode
- Chromic acid or H_2SO_4 are prefer as electrolyte
- Bath temperature is maintained at 35 ^0C
- **Al exhibits high anodic passivity** by developing its oxide layer and hence prevent corrosion when coated on other metals
- Anodic current density is maintained at 10-20 mA /cm^2
- Anodized articles are used as soap boxes ,tiffin carriers ,window frames