

Dry Corrosion Mechanism

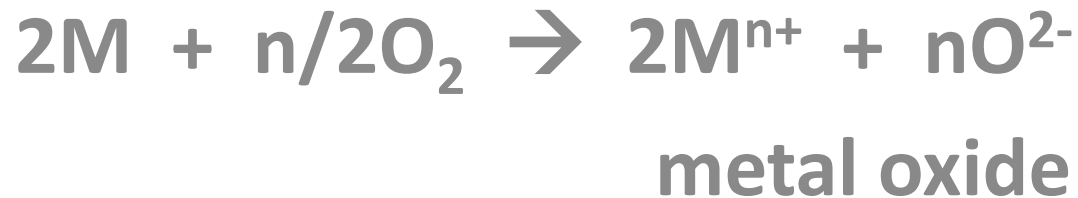
Anodic Reaction



Cathodic Reaction



Overall Reaction



Wet Corrosion (Electrochemical Corr.)

- **Electrochemical corrosion involves**
- **1. Formation of anodic & cathodic areas in conducting medium.**
- **2. Loss of electrons i.e oxidation of anode.**
- **Thus anode undergoes corrosion.**
- **3. Gain of electrons i.e reduction at cathode.**
- **4. Formation of corrosion product.**

Wet Corrosion Mechanism

- Hydrogen evolution type

Anodic Reaction



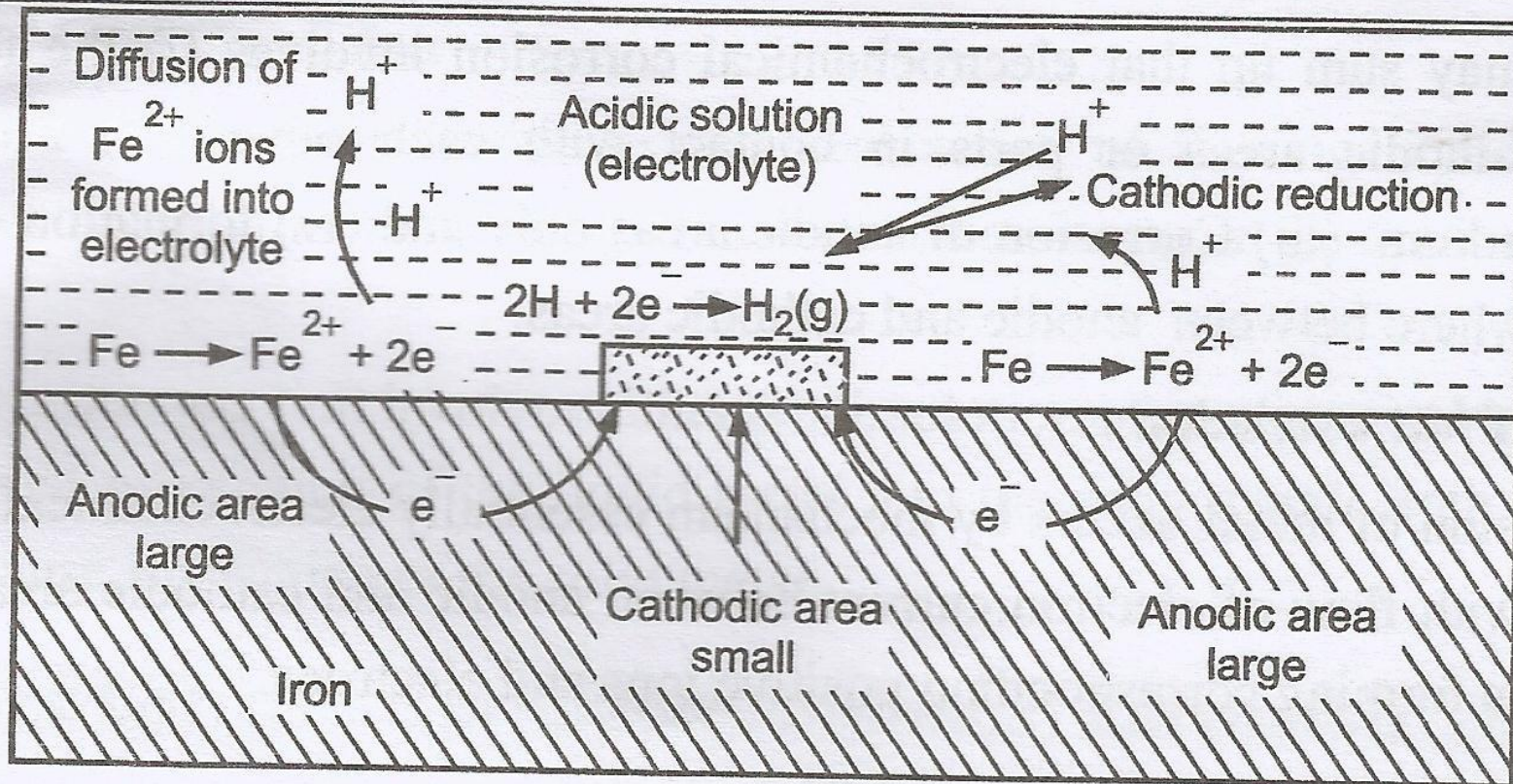
Cathodic Reaction



Overall Reaction



Hydrogen Evolution



Hydrogen evolution

- **Hydrogen evolution type of corrosion occur when**
- **i) Metals are exposed to acidic environment.**
- **li) Amount of dissolved oxygen is low.**
- **All metals above hydrogen in electrochemical series have tendency to dissolve in acidic solution with liberation of hydrogen gas.**

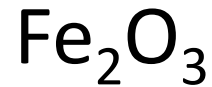
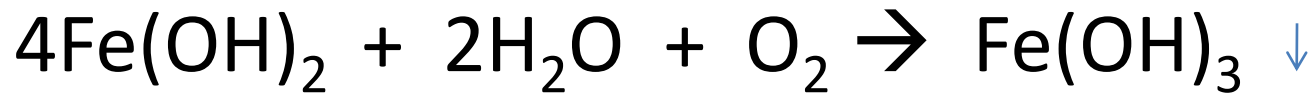
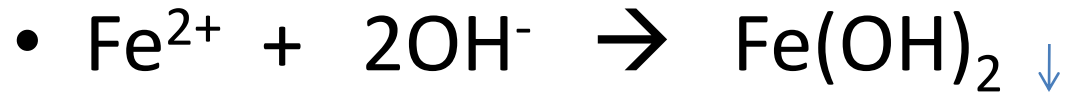
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- **E.g Acidic waste stored in steel tank.**
- **In the hydrogen evolution type the anodes are**
- **represented by large areas while cathodes are**
- **represented by small areas.**
- **Hence rate of corrosion is little slower.**
- **In this case steel becomes anodic whereas**
- **Acidic waste becomes cathodic.**

Oxygen absorption

- At anodic area, iron dissolves as ferrous ions
- With liberation of electrons.
- $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)
- These e-ns flow from anode to cathode thro' iron metal & are taken up by dissolved oxygen in the presence of water.
- $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (reduction)

Reactions



Oxygen absorption

- This type of mechanism occurs when dissolved oxygen is present in the electrolyte.

E.g rusting of iron

In neutral aqueous solution, in the presence of

- atmospheric oxygen, iron surface is coated with
- thin film of oxide.
- However if this film develops some cracks, anodic areas are developed on the surface of exposed iron metal while rest metal surface forms
- cathode.

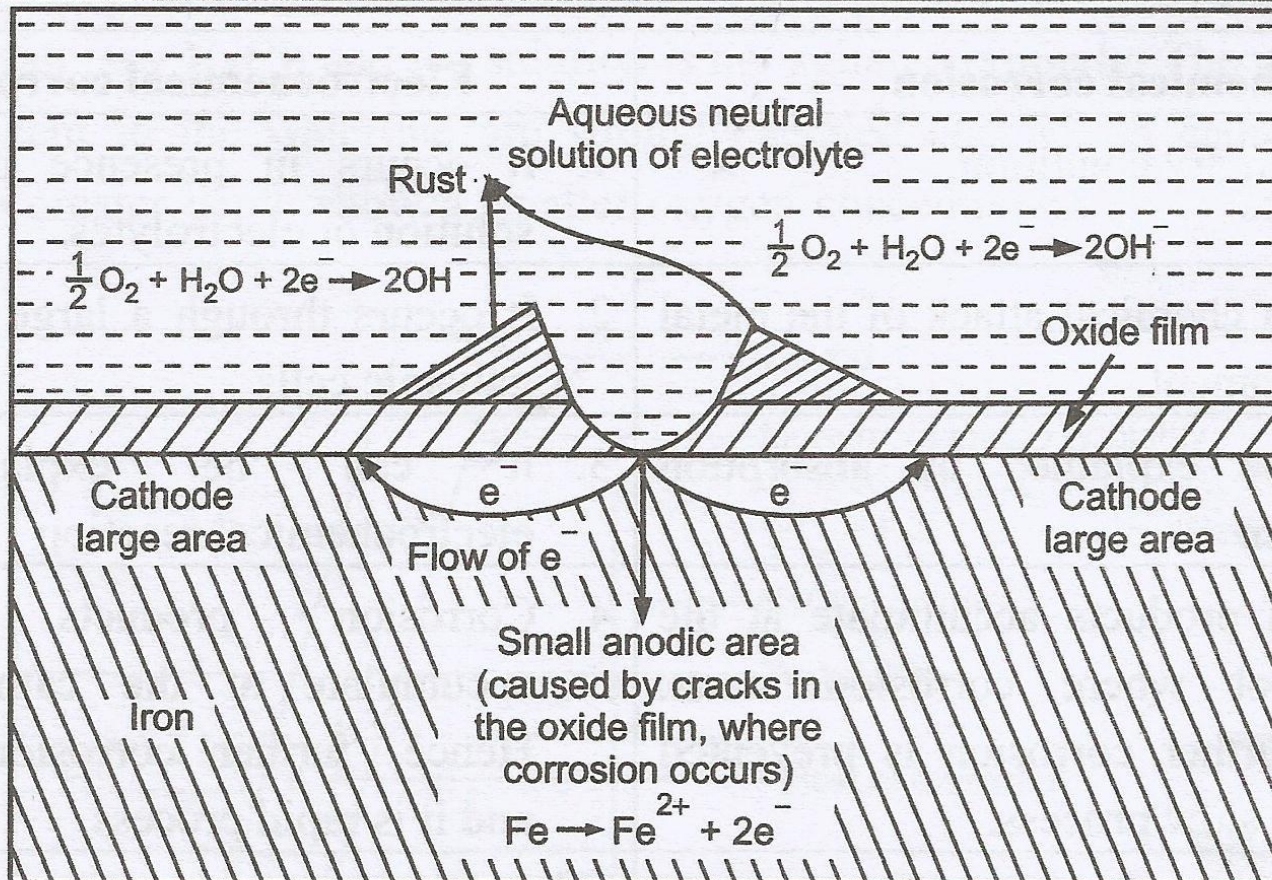
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- The Fe^{2+} & OH^- diffuse from anode & cathode respectively.
- The smaller Fe^{2+} ions move faster than larger
- OH^- ions & hence combine at cathode.
-
- Hence corrosion takes place at anode but corrosion product is deposited at cathode.

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- **An increase in O_2 content, forces cathodic reaction to the right producing more OH^- ions.**
- **It removes more electrons from Fe metal & hence accelerates corrosion at anode.**

Oxygen absorption

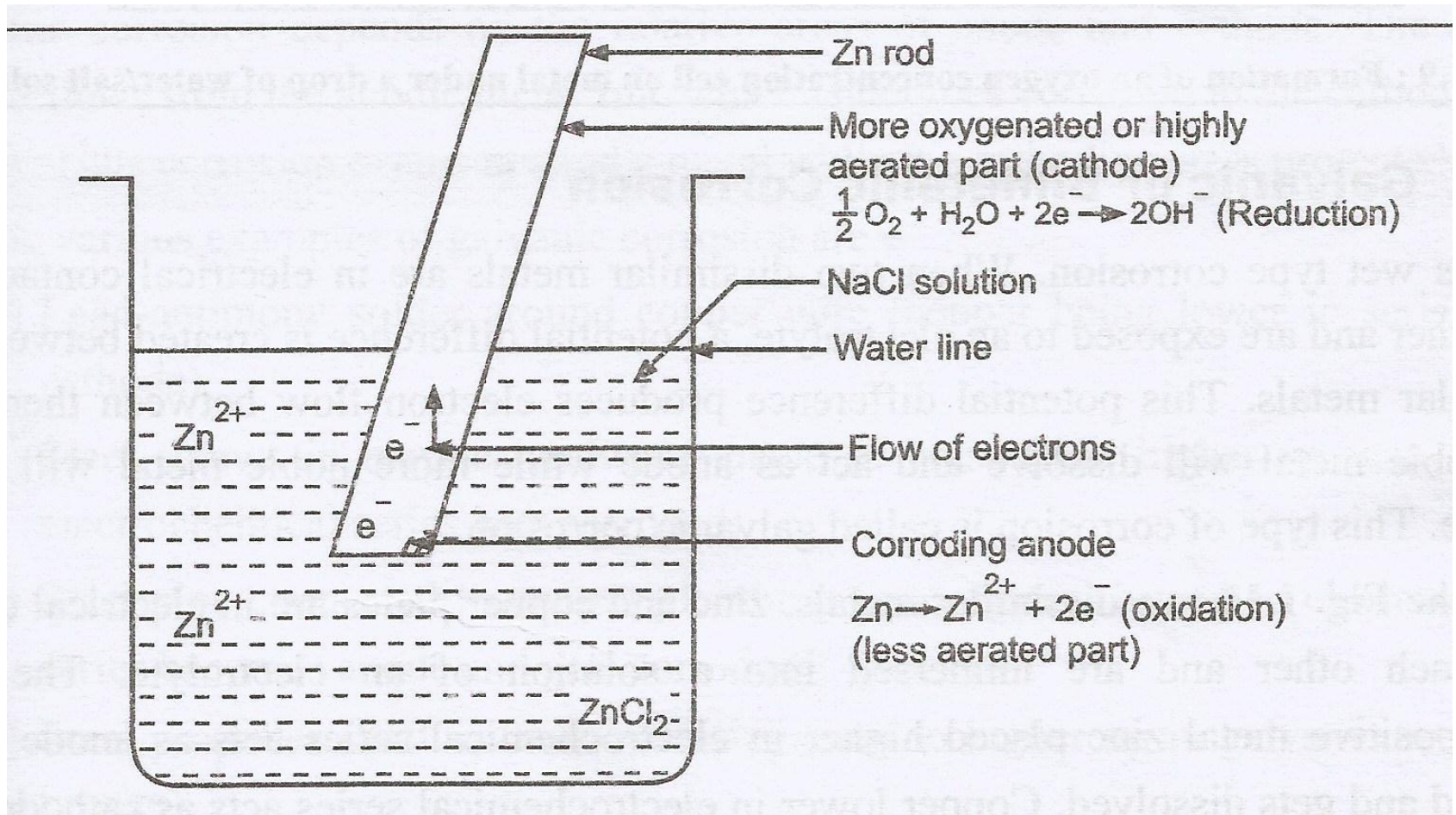


Concentration cell corrosion

This type of corrosion is due to electrochemical attack on the metal surface ,

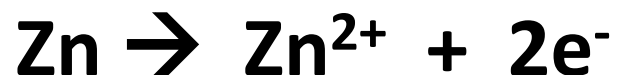
- **Exposed to**
- **a) Varying electrolyte concentration.**
- **b) difference in air or oxygen concentration**
- **over the metal surface.**

Concentration cell corrosion



Anodic & cathodic reactions

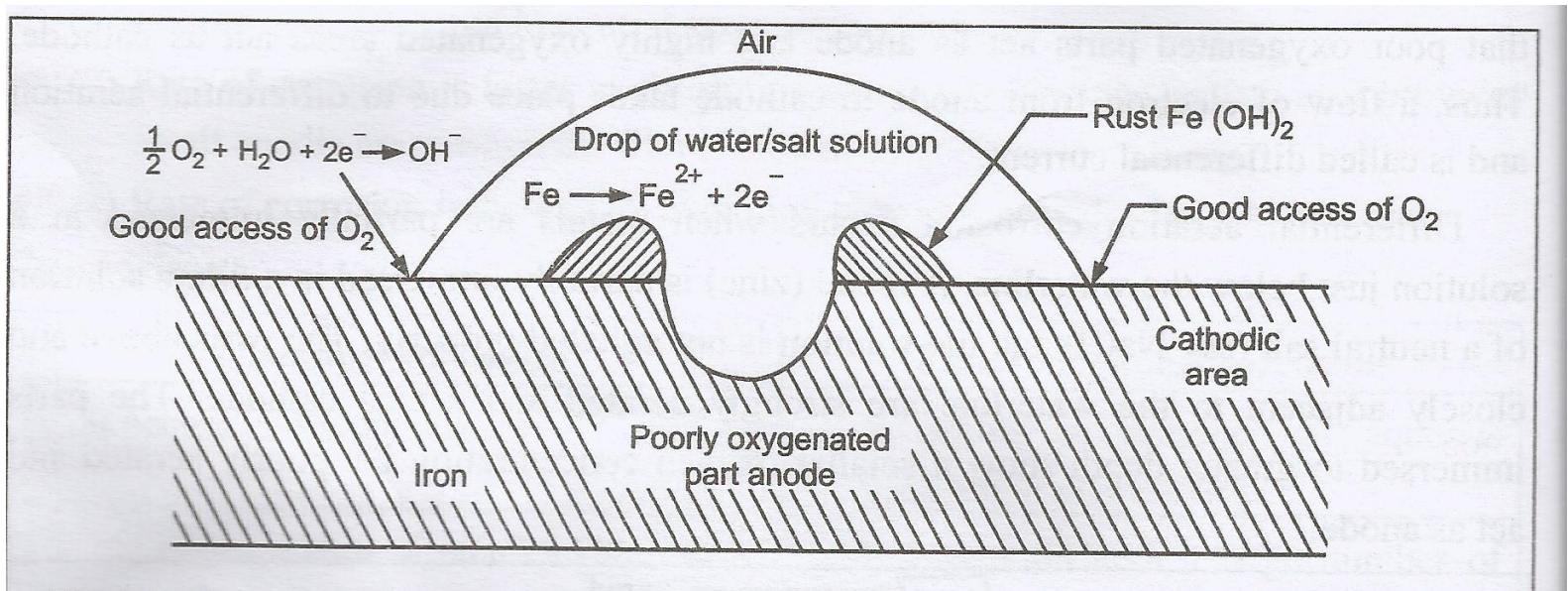
- Anodic reaction



Cathodic Reaction



Concentration cell corrosion



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- **Corrosion of iron by water drops can be easily explained.**
- **Areas covered by droplets having no access of oxygen become anodic .**
- **Whereas other areas which are freely exposed to air (highly oxygenated) become**
- **Cathodic.**
- **Hence corrosion occurs at anodic area.**

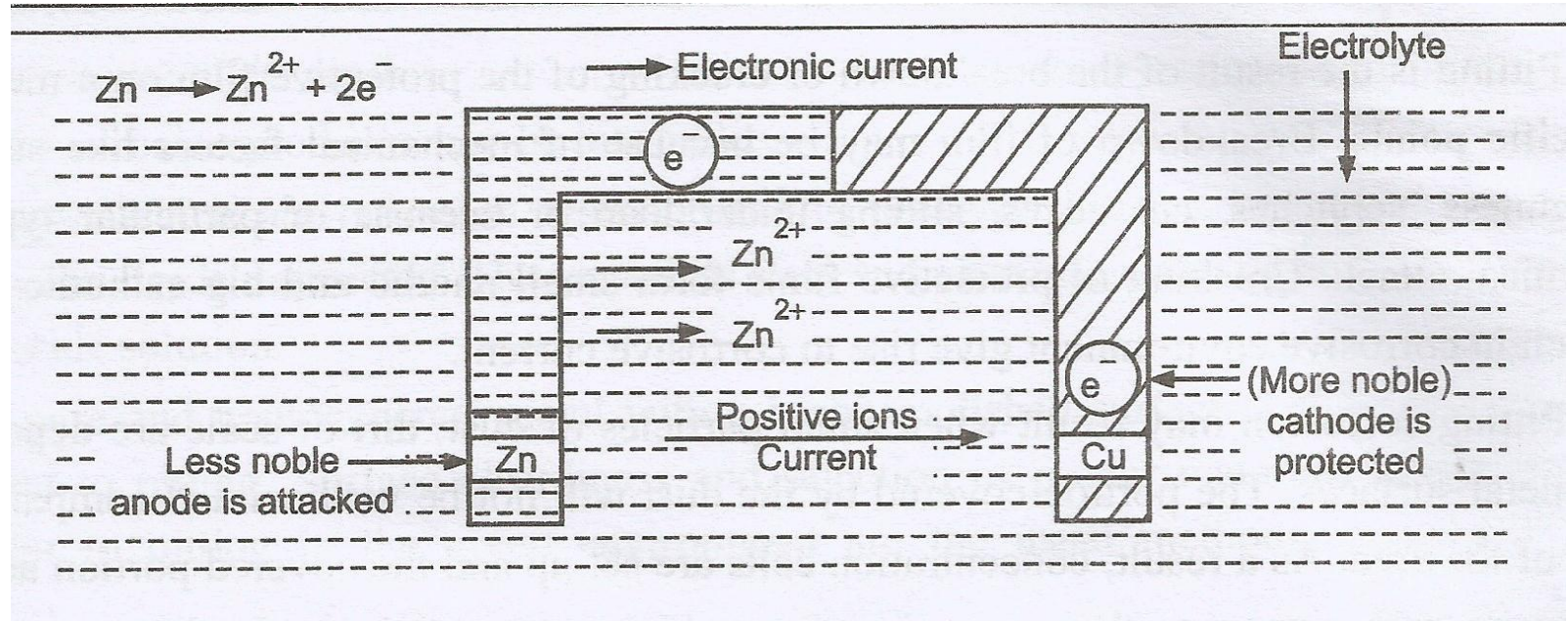
Galvanic or bimetallic corrosion

- When two dissimilar metals are in electrical
- Contact with each other & are exposed to an electrolyte, a potential difference is created between two dissimilar metals.
- The more electropositive metal placed higher in electrochemical series acts as anode & loses electrons.(undergo oxidation)

contd

- **Whereas metal lower in electrochemical series acts as cathode & undergo reduction.(gain e⁻s)**
- **Hence there is flow of electrons from anode to cathode.**
- **E.g steel screws in marine hardware made up of brass.**
- **Steel pipe connected to copper plumbing.**
-

Galvanic or Bimetallic corrosion



Pitting corrosion





Pitting Corrosion

- Pitting corrosion is extremely localized attack
- Resulting in the formation of cavities or holes.
- Pitting penetrate deep into metal & ruin the metal.

Cause of pitting corrosion

- **Pitting is the result of breakdown or cracking of the protective film on metal at specific points.**
- **Breakdown of film may be because of surface roughness, sliding under load or due to chemical attack.**

Mechanism

- **Pitting corrosion may happen when dust, dirt or scale are deposited on metal surfaces.**
- **The portion covered with dust is poorly oxygenated as compared to the rest area.**
- **Hence oxygen concentration cells are formed & poorly oxygenated area acts as anode & undergo corrosion.**

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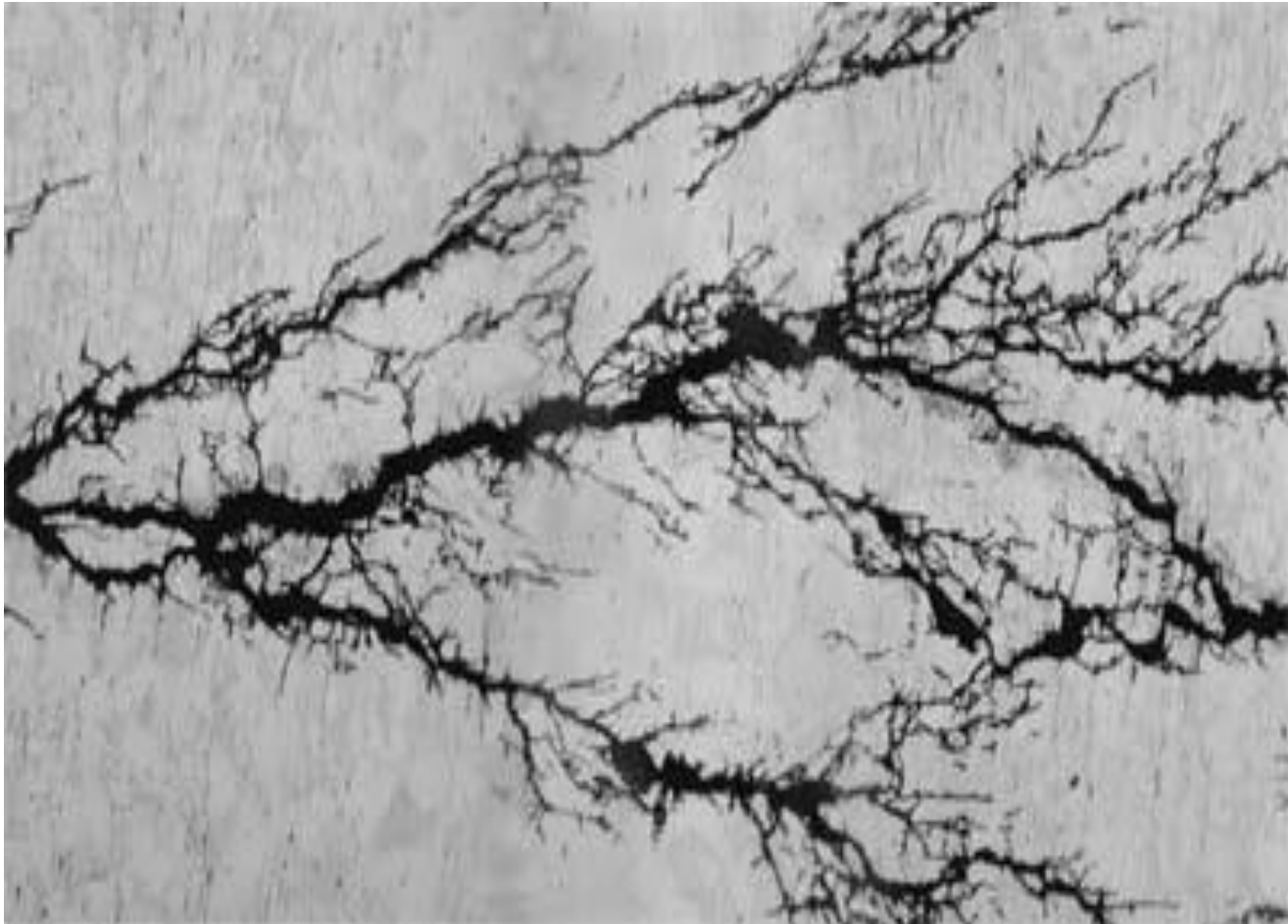
- Once pit or cavity is formed, rate of corrosion increases due to small anodic area compared to large cathodic area.
- This type of corrosion is highly dangerous & cause damage & destruction of pipes, tubes & reaction vessels.

- **Passive metals (corrosion resistant) exhibit pitting corrosion when passivity is destructed.**
- **The stainless steel & aluminium show pitting in the presence of chloride solution.**

Stress corrosion



Hair cracks in reactor



Cause of stress corrosion

- **Stress corrosion is the combined effect of**
- **Static tensile stress &**
- **Corrosive environment on metal**

- Tensile stress may result from :
- Poor design
- Riveting
- Welding
- Bending
- Pressing
- Quenching
- Thermal treatment etc.

- **For this type of corrosion, the corrosive agents**
- **Are highly specific & selective as**
- **A) Acid chloride solution for stainless steel.**
- **B) Traces of ammonia for brass.**
- **C) Caustic alkali & strong nitrate solution for mild steel.**

Examples of stress corrosion

- 1. **Caustic embrittlement in boilers**
- **This corrosion occurs in mild steel reactors used as boilers, When exposed to alkaline solution at high temperature.**
- **Boiler water contains sodium carbonate added for softening of water which at high temp breaks up to give sodium hydroxide.**
- **$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$**

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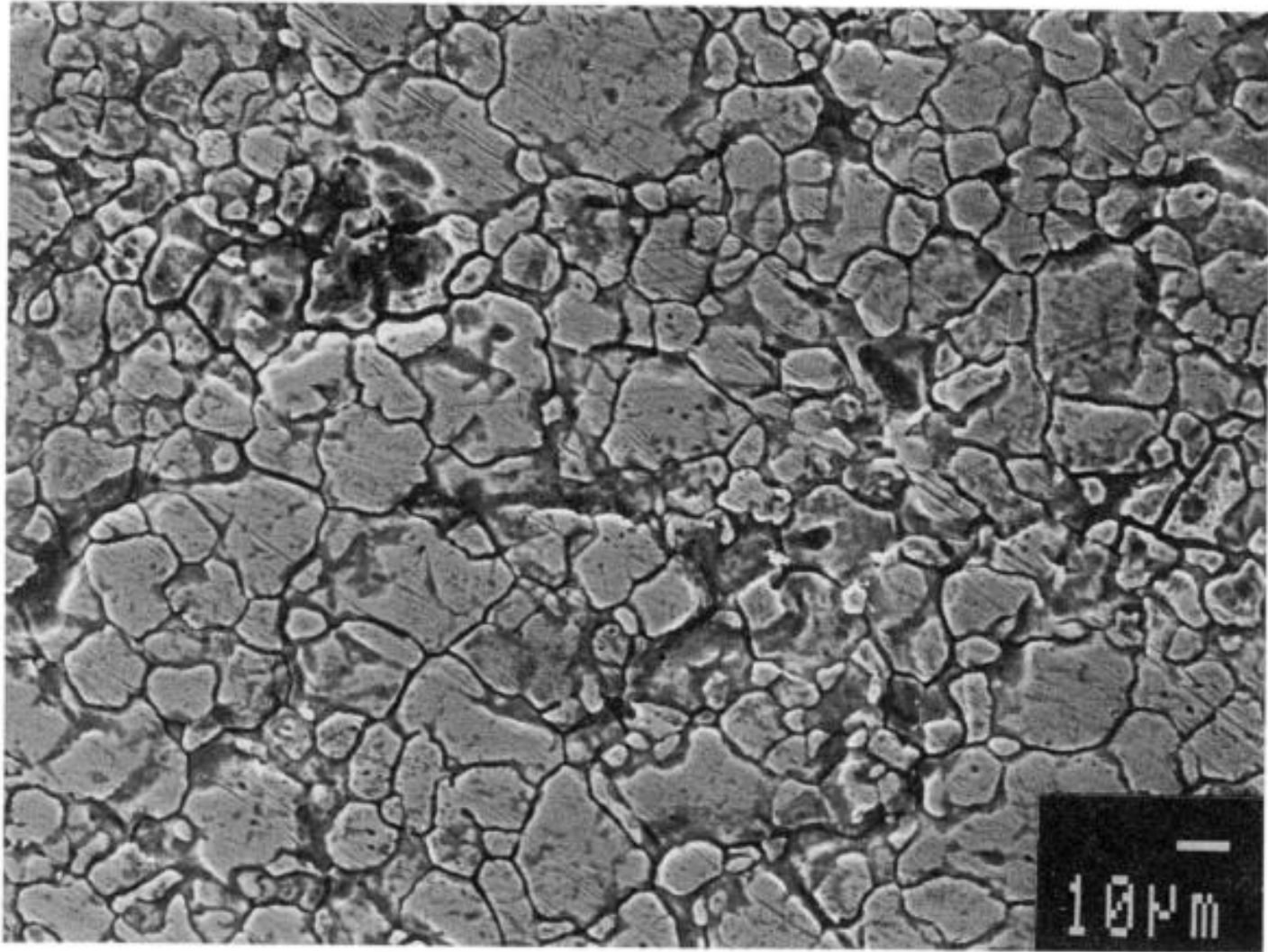
- This alkali goes into minute hair cracks of the reactor & becomes concentrated as water evaporates.
- This concentrated alkali dissolves iron as sodium ferroate in crevices, cracks where metal is stressed.

How to control stress corrosion

- **Caustic embrittlement can be prevented by blocking hair cracks of the reactor with sodium sulfate or tannin.**

- **Stress corrosion can be minimized by**
- 1. Suitable treatment to relieve internal stress.
- 2. Heat treatment to prevent heterogeneity.
- 3. Removing the critical environment.
- 4. Selecting a better resistant material.
- Adjusting the composition & eliminating certain impurities

Intergranular Corrosion



- When molten metal is cast, the solidification starts at many randomly distributed nuclei.
- Due to random nucleation, planes of atoms in neighbouring grains do not match up. Such areas of mismatch between the grains are called **grain boundaries**.

- **Intergranular Attack of Austenitic Stainless Steels:**

With austenitic stainless steels, intergranular attack is usually the result of chromium carbide precipitation (Cr_{23}C_6) at grain boundaries, which produces a narrow zone of chromium depletion at the grain boundary. This condition is termed sensitization

Sensitization involves the precipitation of chromium carbides at grain boundaries, which results in a narrow zone of chromium depletion at the grain boundary.

- Because the chromium is the primary alloying element that makes stainless steel corrosion resistant, the chromium-depleted regions are susceptible to preferential corrosion attack. It is believed that this occurs because the chromium content immediately adjacent to the carbide may be below that required for the stainless steel alloy.
- Hence the area adjacent to grain boundary acts as anode & corrosion occur at this place.

- The chromium carbides tend to precipitate at the grain boundaries of austenitic stainless steels in the 950 to 1450°F temperature range. Any exposure or thermal excursion into this temperature range during metal manufacture, fabrication, or service could potentially sensitize the steel.
- Common practices such as welding, stress relief, and hot forming can expose the steel to the sensitizing temperature range.

Remedies for intergranular corrosion

- The formation of chromium carbides is readily reversed by a solution anneal heat treatment.
- When stainless steel assemblies are too large,
- To be heated, the prevention of chromium depletion can be avoided by using 18/8 stainless steel containing less than 0.03% carbon or by adding titanium to 0.08% carbon in steel.

Factors affecting rate of corrosion

- **Nature of metal**
- **Nature of environment**

Nature of metal

- 1. Position of metal in galvanic series
- 2. Relative area of anode & cathode
- Corrosion Rate $\propto \frac{\text{Cathodic area}}{\text{Anodic area}}$
- 3. Purity of metal

- **4) Physical state of the metal**

- **a) Grain size**
- **b) Orientation of crystal**
- **c) Stress**

- **5) Nature of oxide film**

- **A) Porous**
- **B) Non-porous**
- **C) volatile**
- **D) Unstable**

- **6) Solubility & volatility of corrosion products**

- Soluble corrosion product
- Insoluble corrosion product
- Volatile corrosion product

7) Passivity of metal

- Certain metals like Cr, Ni, Al, Co are corrosion resistant than expected from their position in galvanic series due to self healing protective film formed on their surface.

Overvoltage

- Overvoltage is defined as the difference between the theoretical reversible electrode potential & the actual electrode potential at which evolution of gas occurs (in H₂ evolution).

- E.g If pure Zn metal rod is placed in H_2SO_4 , it undergoes corrosion forming a film due to H_2 gas bubbles. Due to this initial rate of reaction is slow & occurs at high overvoltage (0.7V) of a Zinc metal.
- However if few drops of CuSO_4 are added, the corrosion rate of Zn is accelerated as some copper gets deposited on the zinc metal forming minute cathode & hydrogen overvoltage drops to 0.33 V.

- Thus Corrosion rate is inversely proportional to overvoltage.

NATURE OF ENVIRONMENT

- **Temperature:**
- As rate of all chemical reactions & rate of diffusion increase with temperature, rate of corrosion is high at higher temperature.
- This is due to increased ionization & mobility of ions & diffusion of ions

However in differential aeration corrosion, rate of corrosion decreases due to less solubility of oxygen at high temperature

- **Humidity Or moisture in air**
- **Rate of corrosion increase in the presence of moisture as moisture dissolves atmospheric gases & acts as electrolyte in the reaction which helps in conduction of ions.**

Effect of PH

- Acidic media are more corrosive than alkaline & neutral media.
- However amphoteric metals like Zn, Al, Pb form complex ions in alkaline solution & go into solution at higher PH.

Presence of impurities in the atmosphere

- Atmosphere in the vicinity of industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 & fumes of HCl & H_2SO_4 which increases acidity & electrical conductivity of liquid surrounding metal surface. This consequently increases corrosion rate

contd

- Suspended particles present like NaCl , $(\text{NH}_4)_2\text{SO}_4$ absorb moisture & act as strong electrolyte & thereby increase rate of corrosion.
- Particles of charcoal even though inactive adsorb gases like SO_2 , SO_3 & Moisture & enhance rate of corrosion.

Nature of ions present.

Anions

Presence of anions like silicate form an insoluble reaction product & inhibit corrosion.

On the contrary chloride ions destroy protective passive film of Al, stainless steel & increase corrosion rate.

- **Cations :**
- Many metals corrode rapidly in the presence of Na^+ ions & NH_4^+ ions.
- Presence of minute Cu ions in mine water accelerate the corrosion of iron pipes used for carrying such water.

Conductance of corroding medium

- If soil contains moisture & soluble salts, it increases conductivity of soil which as a result increase stray current corrosion.
- (Stray current is that direct current which has leaked from an electric power circuit & flows thro' metallic structures in earth.)

Contd.

- The point at which stray current leaves the metallic structure becomes anodic & gets dissolved.
- Stray current damage underground structures in clayey & mineralised soil than those under sandy soils.

Formation of oxygen concentration cells

- Formation of oxygen concn cell increase corrosion rate.
- Highly oxygenated area behaves as cathode whereas poorly oxygenated area behaves as anode.

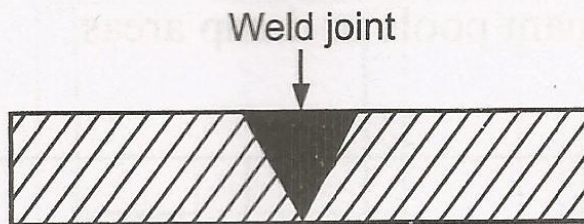
Methods to control corrosion rate

- **1. Design & material selection**
- **Selection of appropriate material for manufacturing machine parts or joining different parts helps to control corrosion.**

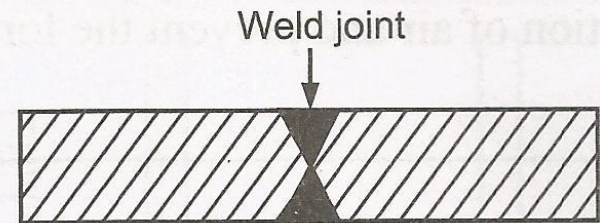
- **Proper design**
- **Proper design should avoid inhomogenities**
- **Thus proper design should avoid the presence of crevices to avoid the formation of oxygen concentration cells.**
- **Thus the use of rivets & bolts is undesirable & it should be replaced by butt weld.**

Methods to control corrosion rate

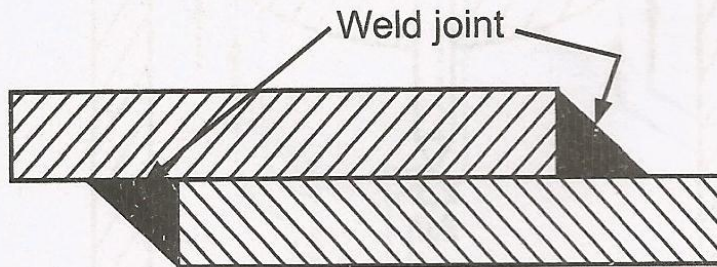
Proper design



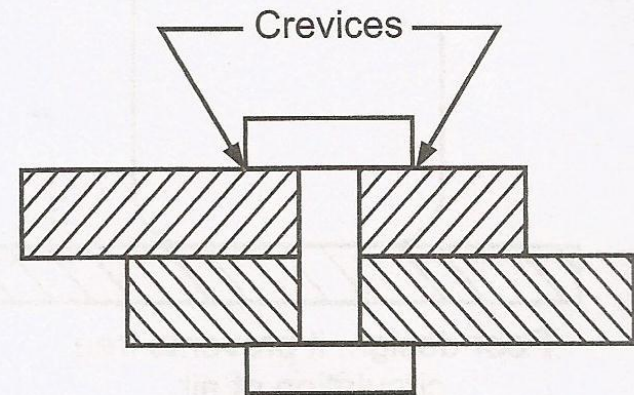
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(Best design)

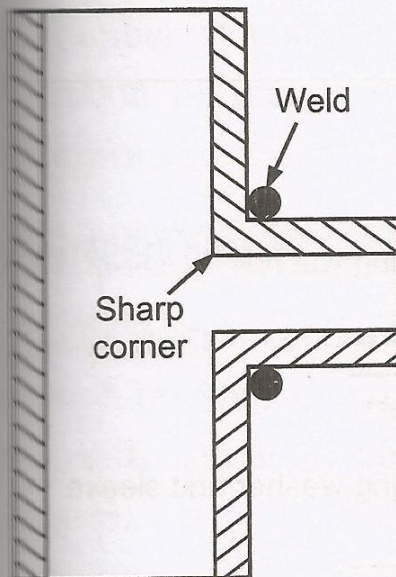


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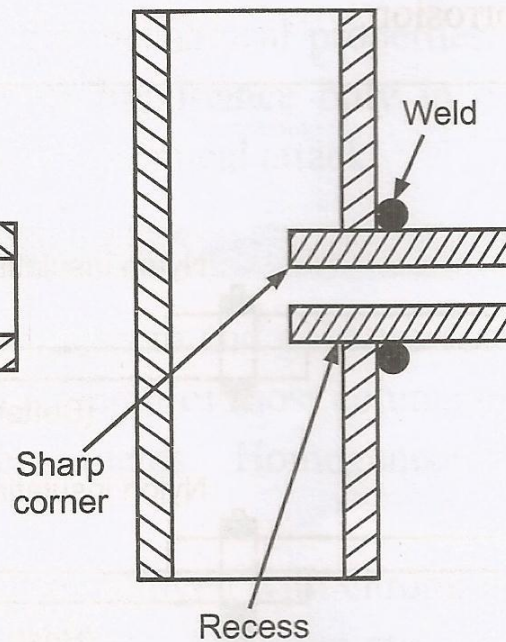


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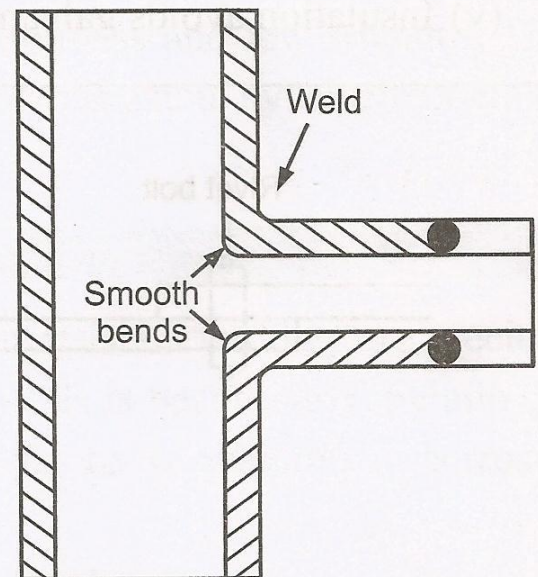
- However when crevices cannot be avoided, they should be painted or coated with impervious material.
- 2. Sharp corners & recesses should be avoided as they create stagnant areas where dirt, dust can accumulate which can give rise to corrosion.



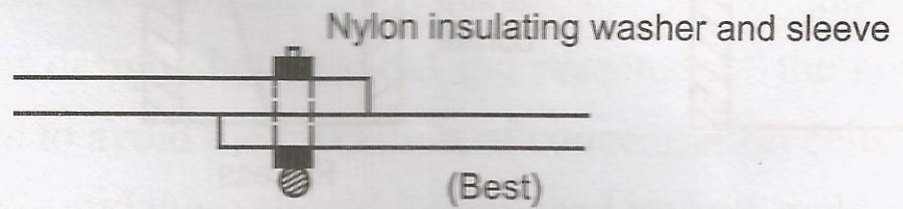
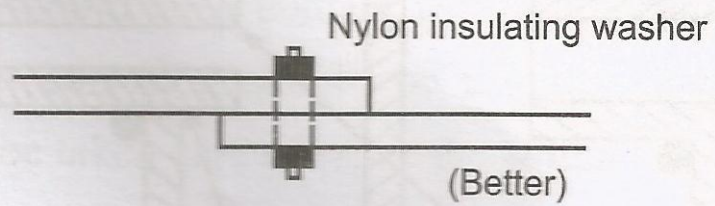
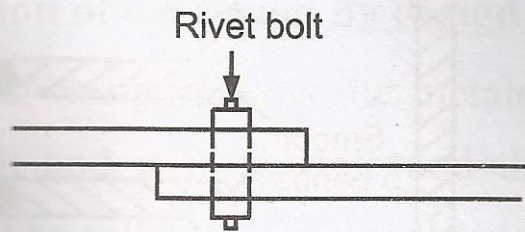
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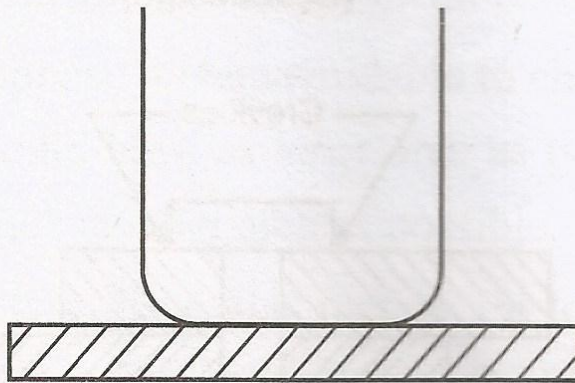
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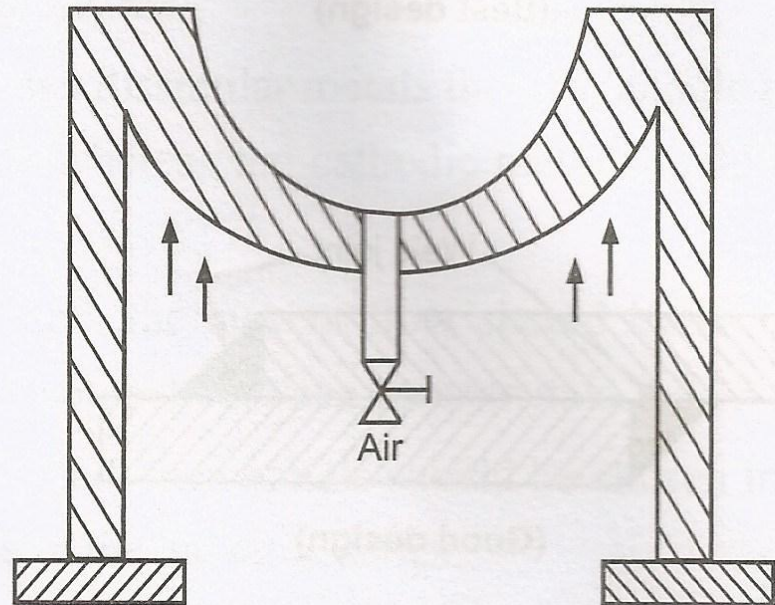
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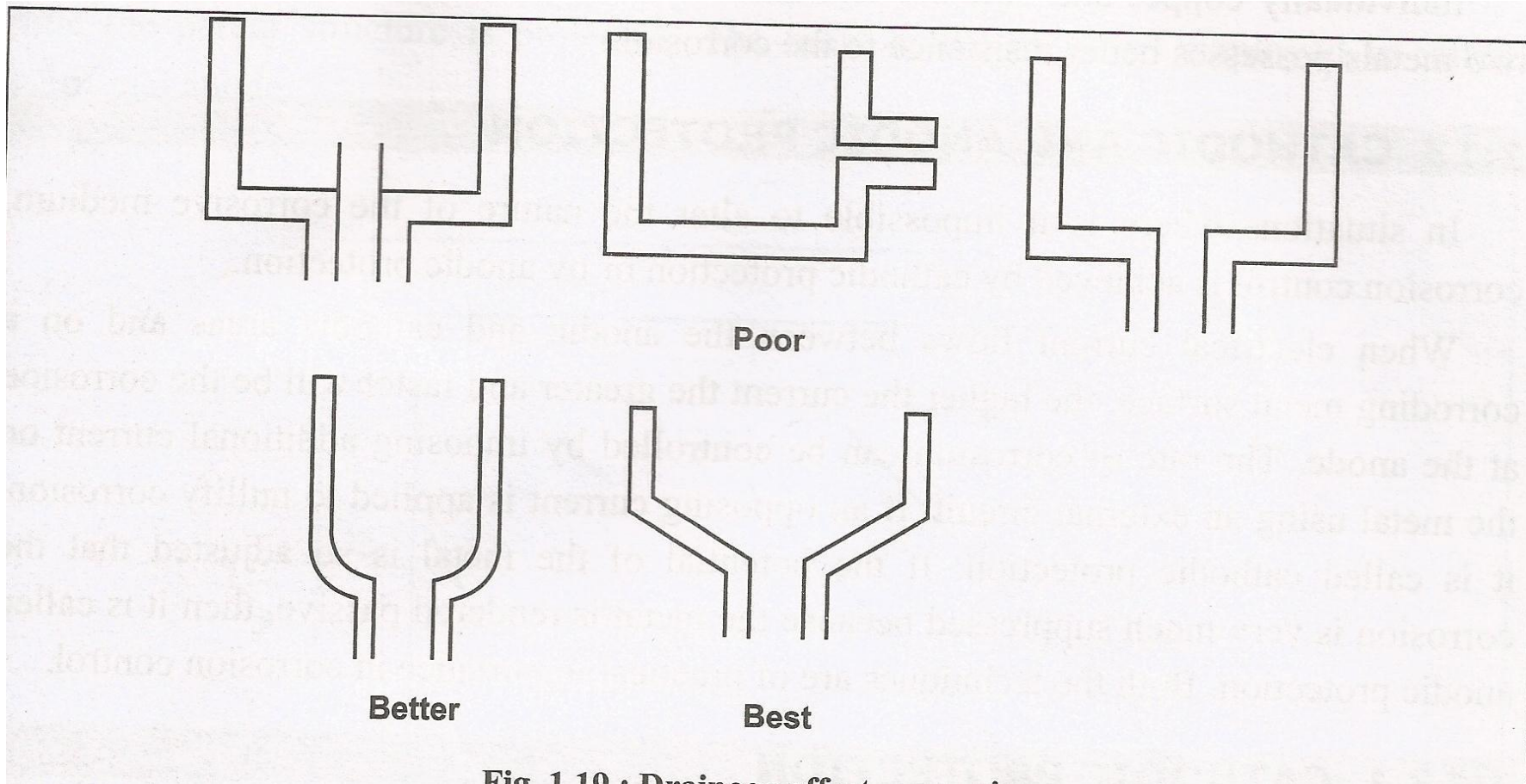
- Whenever possible, the equipment should be supported on legs to allow free circulation of air & prevent the formation of stagnant areas.
- The design should be such which allows uniform flow of corrosive liquid as stagnant areas, highly turbulent flow & high velocity can cause accelerated corrosion.
- Insulation avoids galvanic corrosion.



Poor design, it prevents free circulation of air



Best design, it allows free air circulation, proper drainage and easy washing



Material selection

- Avoid contact of dissimilar metals in the presence of corroding medium. If this principle is not followed, corrosion is localized on more active metal.
- If it is unavoidable to use dissimilar metals then the anodic material should have larger area as compared to cathodic material.

- If two dissimilar metals are to be used, they should be insulated to avoid direct contact.
- Metals should be chosen in such a way that their position in galvanic series is close.
- The anodic metal should not be painted or coated as any break in coating would lead to rapid localized corrosion.
- Metal alloys should preferably be used for better corrosion resistance & strength.

Using high purity metal

- Corrosion resistance of pure metal is more as compared to impure metal specifically in electrochemical corrosion as impurity of traces of other metal forms galvanic cell & increase corrosion rate.

Using metal alloys

- Corrosion resistance of metals can be increased by using metal alloys.
- E.g, In stainless steel chromium metal imparts corrosion resistance to steel as chromium metal has tendency to form an oxide which gets adhered to the surface, also this oxide film if broken gets held immediately.

- Another example is of brass which is more corrosion resistant as compared to Cu & Zn.

Cathodic Protection

- 1. Sacrificial anode method
- 2. Impressed current method

Cathodic protection

- **Principle**
- **The principle involved in cathodic protection is to force the metal (to be protected) to behave as cathode & since there will not be any anodic area on the metal, corrosion does not occur.**

Sacrificial anode method

- In sacrificial anode method (galvanic protection), a more active metal is connected to metal structure to be protected so that all the corrosion is concentrated at the more active metal & thus parent metal structure is protected.
- The corroded sacrificial anode block is replaced by a fresh one when consumed completely

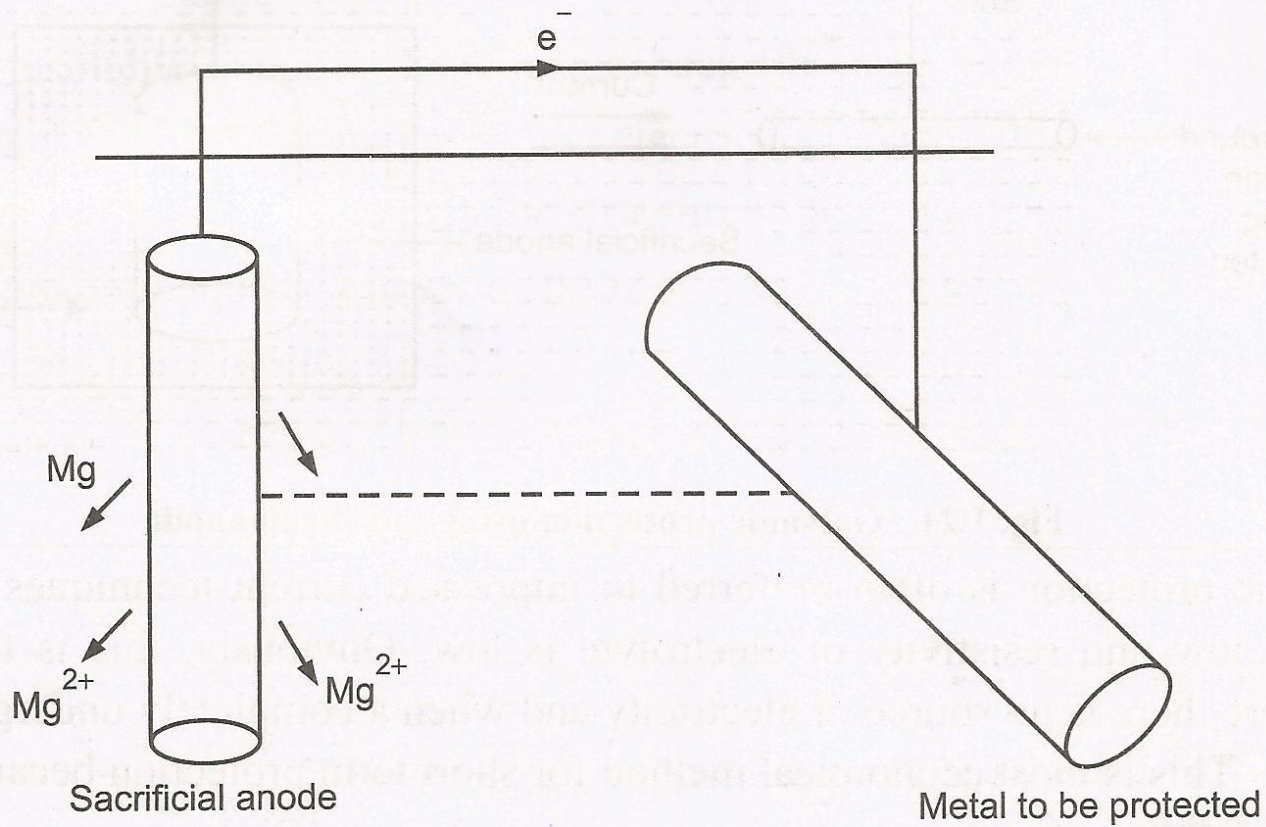


Fig. 1.20 : Cathodic protection using sacrificial anode

- Metals commonly used as sacrificial anodes are Mg, Zn, Al & their alloys.
- Mg has the most negative potential & can provide better protection & hence used in high resistivity electrolytes such as soils.
- Zn is generally used in good electrolytes such as sea water.
- Al anodes have limited use as they form protective oxide film (passivity).

Applications of sacrificial anode

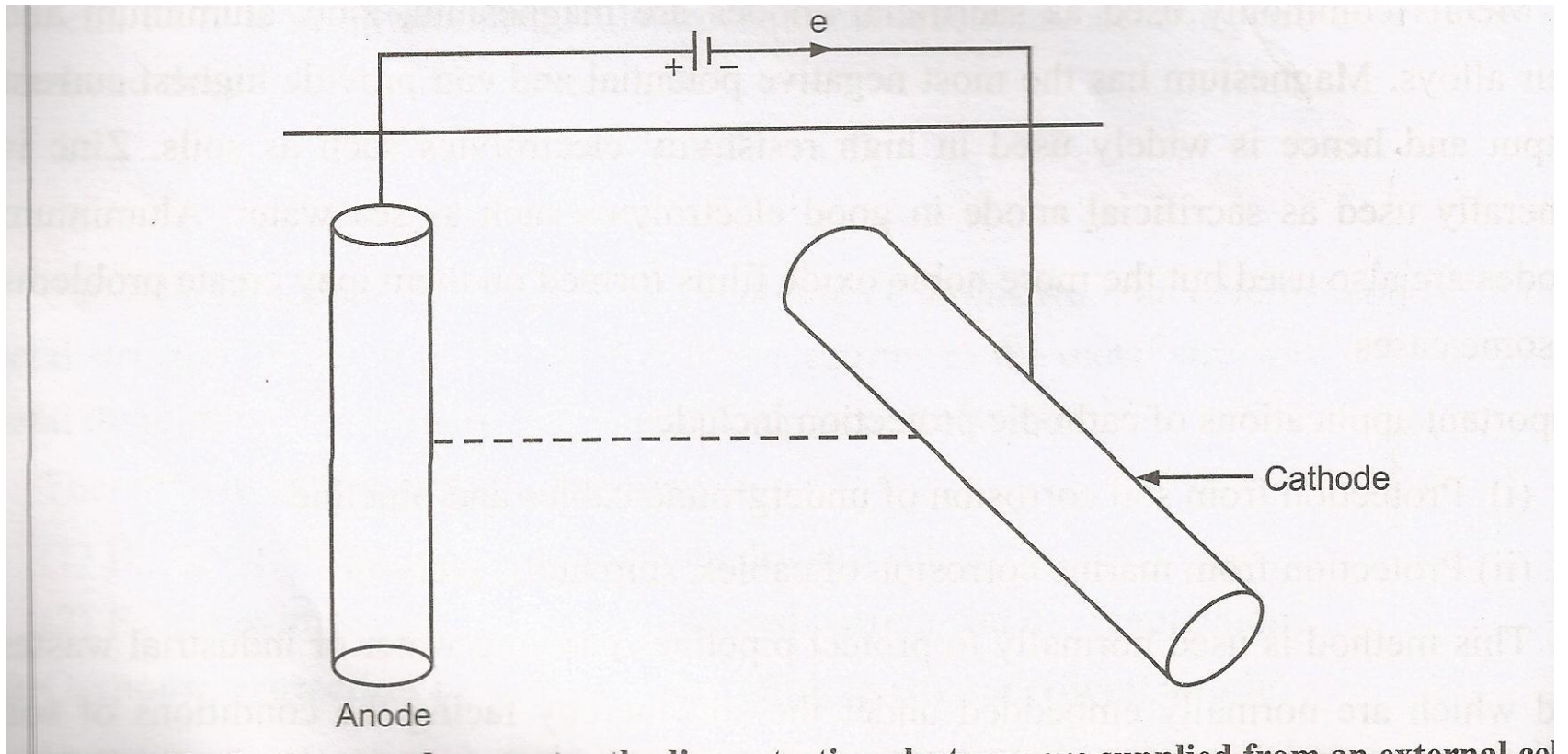
- 1. Protection from soil corrosion underground cables & pipelines.
- 2. Protection from marine corrosion of cables, ship hulls, piers etc.

Impressed current method

- In this method , a current is applied in the opposite directions to that of corrosion current, thereby converting the base metal (to be protected) to cathode from anode. Such an impressed current can be obtained by using d.c.source such as battery or dry cell with an insoluble anode such as platinum, graphite, stainless steel.

- In this method, the insoluble anodic metal used(platinum, steel, scrap iron) is normally embedded underground. To this with the help of d.c. current source, the impressed current is applied & whole of this assembly is connected to the metallic structure to be protected. The connections are done by using wires.

- The insoluble anode is kept inside back-fill made up of gypsum or any such material which can help in increasing the electrical contact with soil.
- In case of larger structures, many such anodes are connected in series.



Impressed current method

Under i.e. long pipeline etc.

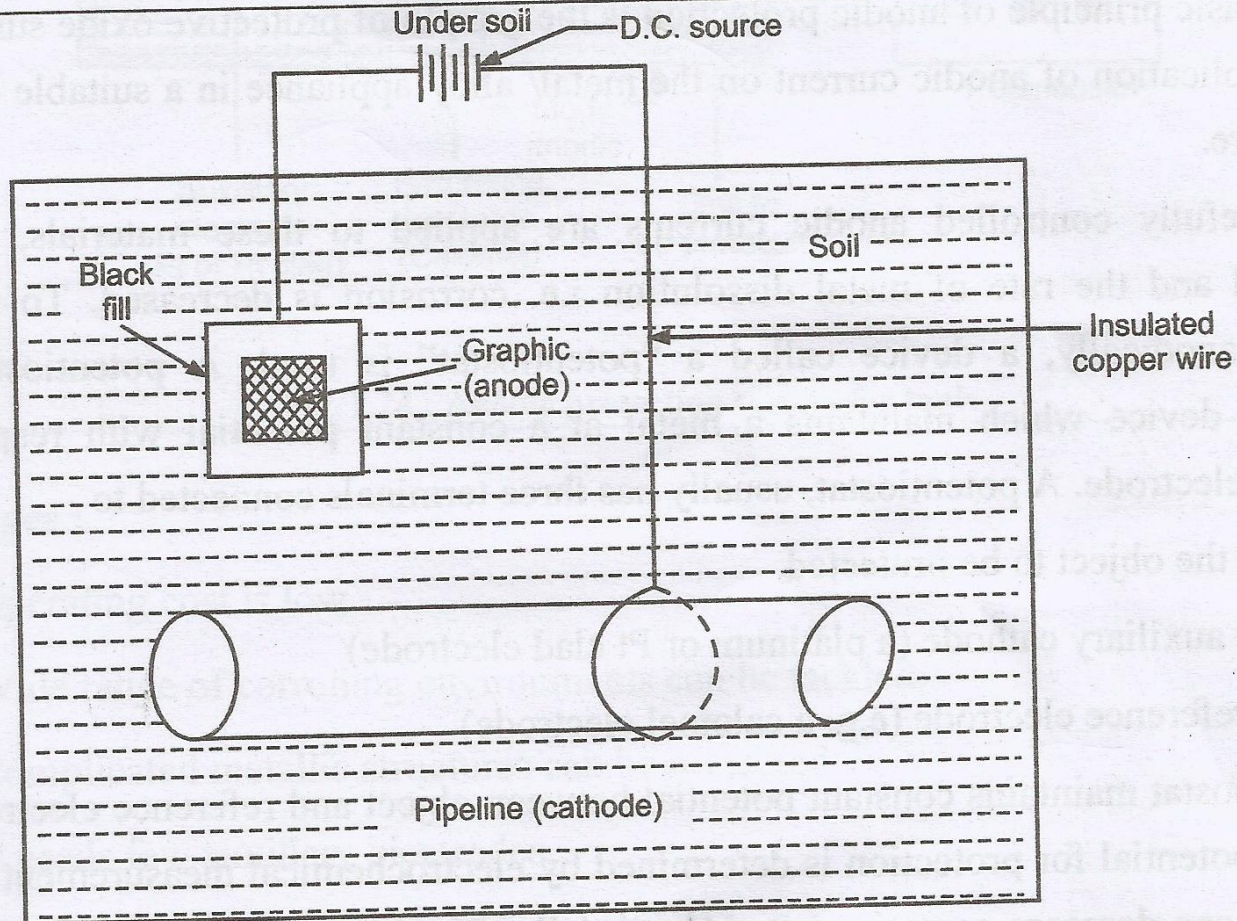


Fig. 1.23 : Corrosion control by impressed current

- **Applications of impressed current method**
- **This type of protection has been applied to buried structures such as tanks, pipelines, transmission line towers, marined piers, ships, etc.**
- **This method is particularly useful when current requirements & electrolyte resistivity are high.**

- Impressed current method is well suited for large structures & long term operation.
- It can be automatically controlled which reduces maintenance & operating cost.

- **Metallic coatings**
- **Objective of coating surfaces:**
 - **1) To prevent corrosion of metals**
 - **2) To enhance wear & scratch resistance**
 - **3) To increase hardness**
 - **4) To enhance oxidation resistance**
 - **5) To insulate electrically & thermally**
 - **6) To impart decorative colour.**

Types of metallic coatings

- 1) Anodic coatings e.g galvanizing (Zn coating)
- 2) Cathodic coatings e.g tinning (Sn coating)

- **Anodic coating:**
- **Anodic coatings are produced from coating metals which are more anodic to the base metal. E.g coating of Zn, Al on iron/steel.**
- **In this case even if coating breaks underlying metal is protected as the coating metal is more anodic it gets attacked first & also as anodic area is greater than cathodic area corrosion rate is less.**

Cathodic coating

- In this method base metal is coated with cathodic metal. E.g tinning on iron
- AS the coating metal is cathodic , it has high corrosion resistance than base metal & thus protect base metal.
- If the crack appears on the coating, corrosion become intense since cathodic area is larger than anodic area.

Methods of application of metal coatings

- 1. Electroplating
- 2. Metal cladding
- 3. Metal spraying
- 4. Diffusion or Cementation
 - (sherardising, calorising, chromising, siliconising)
- 5. Hot dipping
 - (galvanizing, tinning)

HOT DIPPING

- In hot dipping process, metal to be coated is immersed in a bath of molten coating metal.
- It is used for making coating of low melting metals such as Zn, Sn Pb, Al on iron steel & copper which have relatively higher melting point.

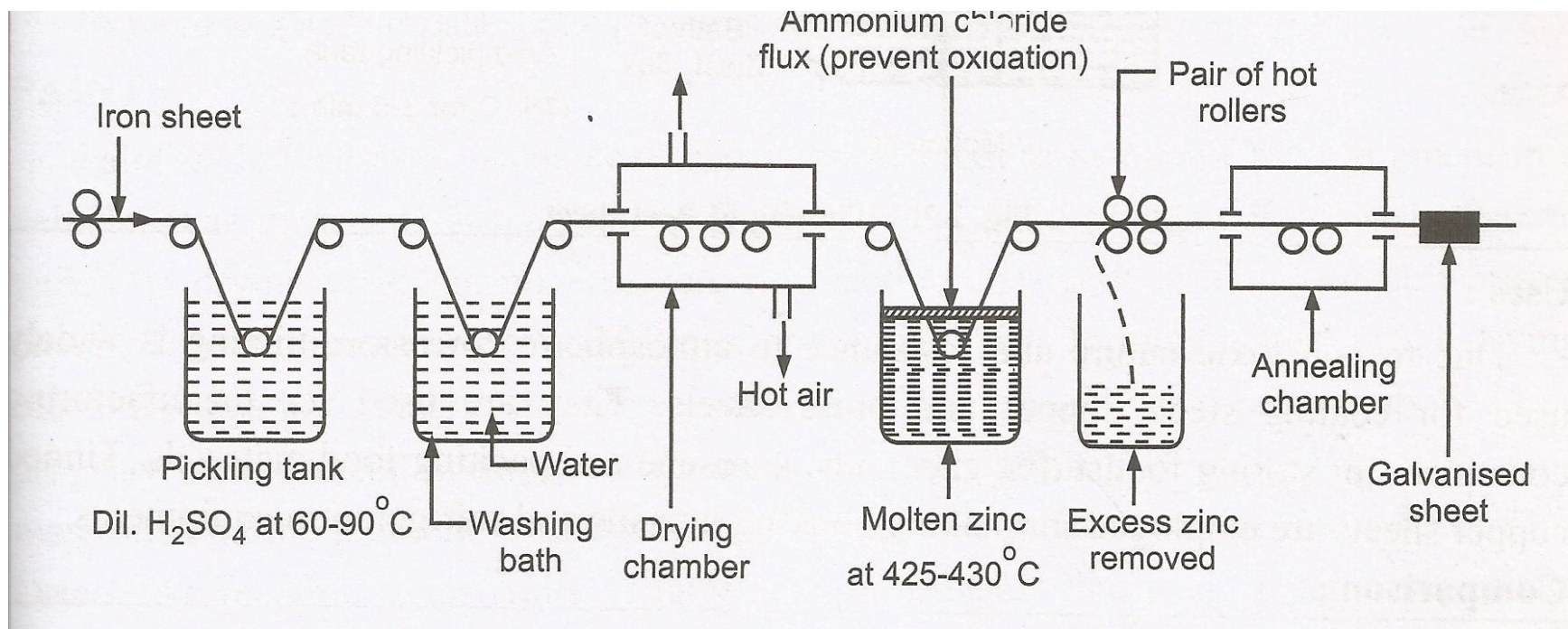
Galvanizing

- In this process, iron or steel article is first cleaned by pickling with dil HCl or dil H_2SO_4 solution for 15-20 minutes at $60-90^\circ\text{C}$. This removes scale, rust & other impurities.
- The pickle article is washed with water & dried.

- The article is dipped in a bath of molten zinc maintained at 425-430⁰C.
- The surface of bath is covered with flux of ammonium chloride to prevent oxide formation.
- The coated sheets are passed thro' a pair of hot rollers which removes excess of Zn deposited & makes the coating uniform & adhering.

- Finally sheet is annealed at a temperature of 650°C & cooled slowly.

GALVANIZING



Tinning

RP

HOT DIPPING: TINNING PROCESS

