

Corrosion

Definition: The surface deterioration of a metal due to its chemical reaction with the surroundings.

e.g. rusting of iron ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, $n = 1-3$)

tarnishing of silver (Formation of Ag_2S)

Why does corrosion occur? The thermodynamic stability of metals in the compound state is greater than that in its elemental state.

The extraction of metals is a non-spontaneous process, ($\Delta G^\circ < 0$), while corrosion is spontaneous ($\Delta G^\circ = -ve$)

Consequences of corrosion

- (i) loss of efficiency
- (ii) increase in maintenance cost
- (iii) plant shutdown (due to machinery failure)
- (iv) contamination of food
- (v) safety hazards

Types of Corrosion

1. Dry or Chemical Corrosion
2. Wet or Electrochemical Corrosion

① Dry or Chemical Corrosion

The corrosion that is a result of direct metal contact chemical reaction between a metal surface and surrounding gases is called dry corrosion. It is further classified into:

- A : Oxidation Corrosion
- B : Corrosion by Hydrogen
- C : Corrosion due to other gases
- D : Liquid metal corrosion

A : Oxidation Corrosion : occurs when a metal, oxygen from the surroundings react to form a metal oxide.

Process: (i) Initially, the rate of the rxn. is slow, but the rate of corrosion increases after.

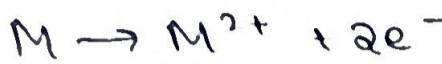
(ii) The metal atoms on the surface react with the atmospheric oxygen to form a thin oxide layer.

(iii) Further corrosion occurs when the oxide ions diffuse through the film. The metal ions also diffuse outwards. (Note: metal diffusion is faster as it is smaller) These ions meet at the interface and form products.

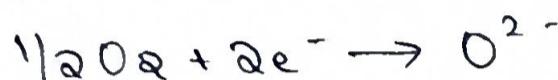
- (iv) The initial thickness formed becomes thicker due to the simultaneous chemical and physical reactions. (corrosion and diffusion)
- (v) Whether further corrosion would occur, and if there would be any influence on the physical & chemical properties, depends on the nature of the film formed.

Mechanism

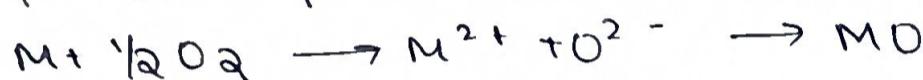
- (i) metal undergoes oxidation



- (ii) oxygen changes into its ionic form, due to the transfer of electrons from the metal.



- (iii) formation of oxide layer



B: Corrosion by Hydrogen

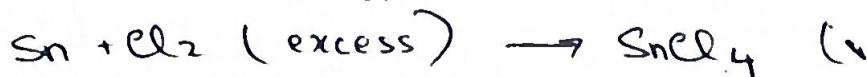
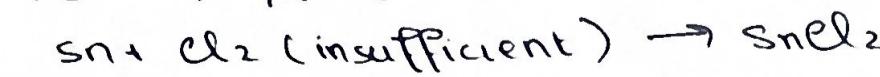
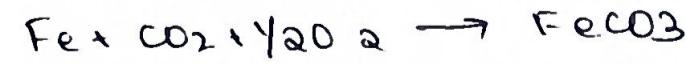
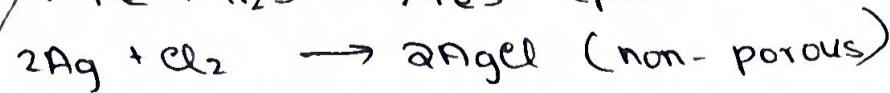
1. Hydrogen Embrittlement: The surfaces of metals are generally porous. Atomic hydrogen is small and reactive, so it is able to diffuse into the metal voids. These hydrogen atoms combine w/ each other and form molecular hydrogen. $2H(g) \rightarrow H_2$
As the volume of hydrogen increases, the pressure increases. This causes cracks and blisters on the metal surface.

2. Decarburization: Decarburization is the process by which there is a decrease in the amount of carbon, in steel, when it is exposed to an environment with hydrogen at temperatures $> 700^\circ C$. When steel is exposed to such an environment, the carbon readily reacts with the hydrogen, forming methane. The methane gas penetrates into the steel leading to cracks and blisters.



C. Corrosion by other gases

Fe + $H_2S \rightarrow FeS$ (porous) \rightarrow (found in production wells, flow lines, drilling of oil)



D. Liquid metal corrosion: Defined as the surface disintegration of a solid metal due to its dissolution in a liquid metal in the absence of any electron transfer. 3

Depends on:

- (i) temp
- (ii) ratio of surface area (SM) to volume (RM)
- (iii) flow velocity
- (iv) purity of SM and RM

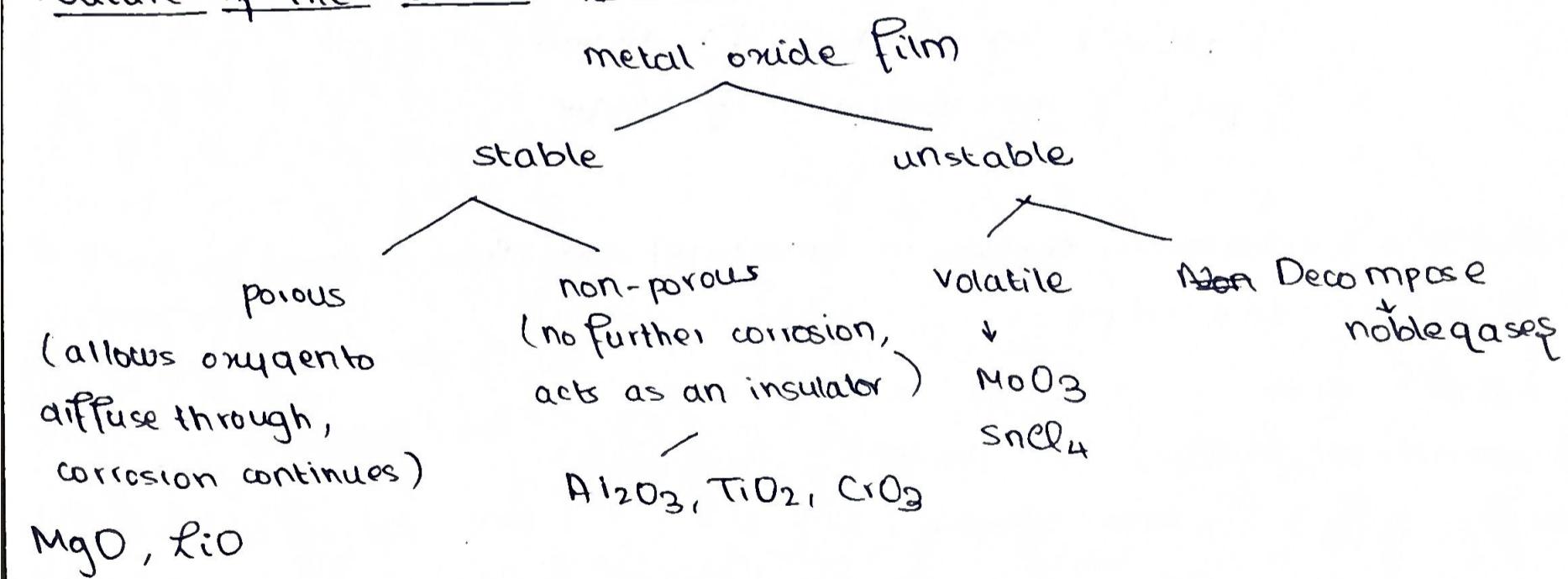
Mechanism:

- (i) dissolution of SM into RM
- (ii) penetration of RM into SM

Example: Liquid Na in copper pipes
coolant

- results in the formation of intermetallic compounds that make Cu porous.
- reaction occurs at 900°C at about 100 hr exposure.
- results in the porous Cu pipe becoming weak, requiring replacement.
- seen in nuclear power plants where liquid sodium is used as a coolant.

Nature of the Corrosion product



MgO, LiO

Pilling Bedworth Rule / Specific Volume Ratio

Dry corrosion is governed by the Pilling Bedworth Rule. According to this:

If the volume of the metal oxide formed is greater than the volume of the metal in which it is formed, the film would be non-porous and protective. The rate of corrosion would decrease and eventually stop.

$\therefore \text{SVR} \geq 1$ e.g. Al, Cr, Ti

If the volume of the metal oxide formed, is lesser than the volume of the metal from which it is formed, the oxide layer would be porous and non-protective. (4)

e.g. Mg, Al

SVR < 1

If the PBR is very high, it causes compressive stress, causing cracks in the oxide layer. (e.g. iron)

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{1}{n} \times \frac{\text{Moxide}}{\text{Poxide}} \times \frac{P_{metal}}{M_{metal}}$$

Unstable Corrosion product: If the corrosion product is volatile / unstable, a fresh layer keeps getting exposed to the atmosphere.
⇒ The thickness of the metal keeps on reducing, and thereby its strength.

② Wet / Electrochemical Corrosion

How it occurs: when 2 dissimilar metals are in contact with each other in the presence of an aq. solution / electrolyte.

What happens: anode always undergoes oxidation.

The cathodic reaction depends on the pH.

If $pH < 7 \Rightarrow$ evolution of hydrogen

If $pH \geq 7 \Rightarrow$ absorption of oxygen

Conditions: 2 dissimilar metals in contact w/ each other exposed to an aq. solution / electrolyte.

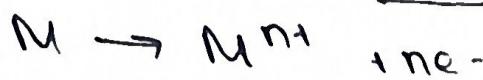
- separate anodic and cathodic regions
- potential gradient / conc. gradient
- ~ metal surface is heterogeneous.

Product Formation: The ^{metallic} ions at the anodic part and the non-metallic ions at the cathodic part diffuse towards each other to form a corrosion product.

Mobility of cation is greater, the product would be formed near / on cathode.

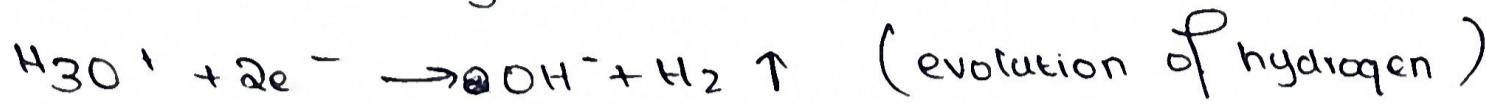
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Mechanism: at anode (oxidation)

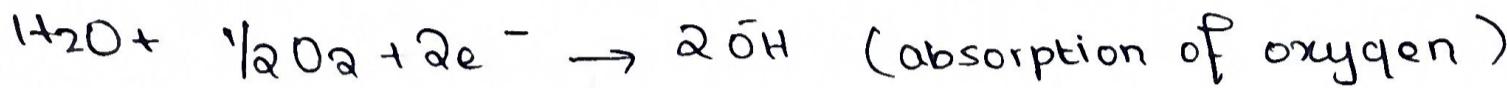


at cathode

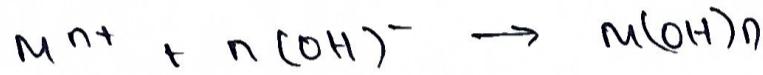
(i) in media w/ $\text{pH} < 7$:



(ii) in media w/ $\text{pH} > 7$:



Overall Reaction:



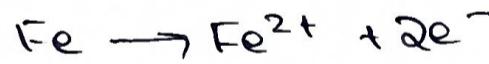
Mechanism of Rusting

Dry corrosion mechanism



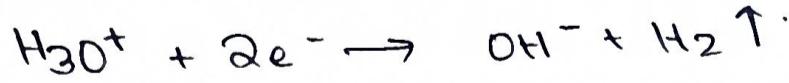
Wet corrosion mechanism

at anode:



cathode

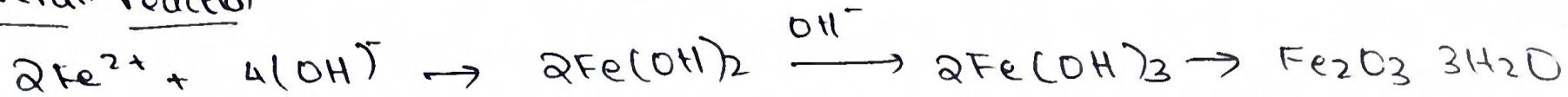
(i) acidic media



(ii) alkaline / neutral media.



overall reaction



Chemical (Dry) Corrosion

- occurs in the absence of moisture or electrolyte
- direct attack of chemicals
- 3. slow
- 4. corrosion products are formed at the site of corrosion.
- 5. process of corrosion is uniform
- 6. can happen on homogeneous / heterogeneous surface
- 7. e.g. mild scales on the surface of Fe

Electrochemical (Wet) corrosion

(6)

occurs in the presence of moisture / electrolyte

involves formation of electrochemical cells on metal surface

Fast

corrosion products always deposited on / near cathode

only happens at anode

heterogeneous surface required.

e.g. rusting of iron in a moist environment

Types of electrochemical corrosion

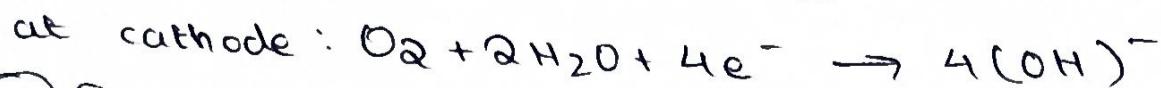
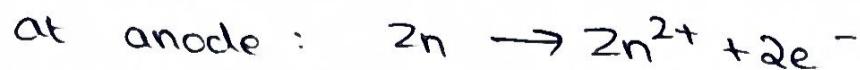
1. Galvanic / bimetallic corrosion
2. Differential Aeration

① Galvanic / bimetallic corrosion

When 2 diff. metals are in contact w/ each other, in the presence of an electrolyte/moisture, the more anodic metal corrodes preferentially.

The corrosion reaction initiated due to a potential gradient is called galvanic corrosion.

For eg. ① a thermocouple made with Zn and Cu dipped in water / an electrolyte.



② For brass plates fixed w/ iron nails, a small galvanic cell is formed at the area of contact between the iron and brass. The nail is anodic w.r.t brass and undergoes corrosion: The corrosion product (rust) is visible near the brass plate.

- (1)
- ③ In an Fe - Cu couple: Fe = anode
- ④ In a Zn - Fe couple: Zn = anode
- Factors affecting galvanic corrosion
1. potential gradient (greater the potential gradient, faster is the corrosion)
 2. conductivity of electrolyte (corrosion increases w/ ↑ in conductivity)
 3. surface area of the metals: corrosion is greater at rough & uneven surfaces (increase w/ increase in SA).
 4. anode to cathode ratio: if the anode is large, cathode is small, rate of corrosion would be low.

Prevention: i) using only one metal

- (ii) selecting metals close in the galvanic series
- (iii) insulating the dissimilar metals
- (iv) using corrosion inhibitors
- (v) applying cathodic protection, by installing a third metal which is anodic to both metals in galvanic contact.

Differential Aeration / Concentration cell aeration

- How:
- conc. difference on diff parts of the metal
 - part exposed to lower conc \Rightarrow anodic
higher conc \Rightarrow cathodic
 - anodic rxn independent of pH, cathodic reaction dependent on pH

Example: Zn rod in contact with salt solution (partially immersed in it)

Part immersed : is in contact w/ less O₂ \Rightarrow anodic

Part above water: cathodic

Corrosion product: sparingly soluble Zn(OH)₂, formed at the interface of water & air

Rxns: at anode: Zn \rightarrow Zn²⁺ + 2e⁻

at cathode: H₂O + ½ O₂ + 2e⁻ \rightarrow 2OH⁻

net rxn: Zn + H₂O + ½ O₂ \rightarrow Zn²⁺ + 2(OH)⁻
 $=$ Zn(OH)₂

Types of differential aeration corrosion

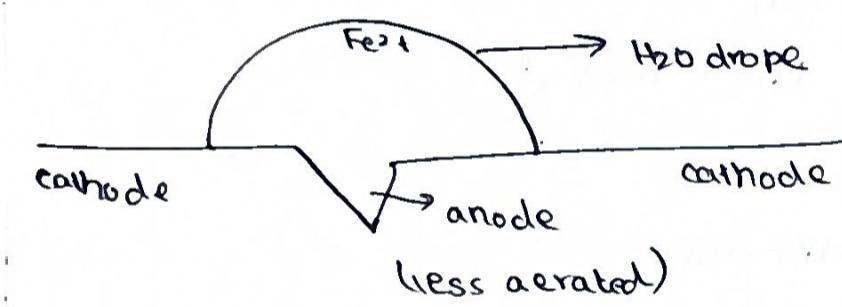
- (i) pitting corrosion
- (ii) waterline corrosion
- (iii) crevice corrosion
- (iv) pipeline corrosion

① Pitting corrosion

What: localized attack forming a pit / hole on the metal surface
when does it happen? : when there is a breaking down of the protective oxide layer due to mechanical / chemical means

which metals are prone to it? : metals with non-porous protective oxide film eg. Al, Ti, stainless steel.

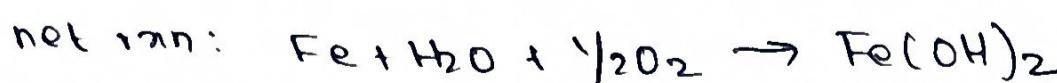
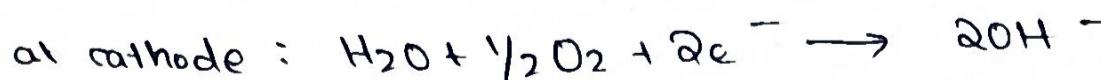
working (taking the example of ~~the~~ iron)



- consider a drop of H_2O on an iron surface.
- area under drop exposed to less O_2 \Rightarrow behaves as anode
- surrounding area \Rightarrow behaves like cathode
- the rate of corrosion is high when the area of cathode is large.
 \Rightarrow more and more corrosion happens at the same spot.
- corrosion takes place just under the impurity

Influencing factors : pH, temp. of corrosive medium

Reactions: at anode : $Fe \rightarrow Fe^{2+} + 2e^-$



Reasons for pitting corrosion : (i) non-homogeneous surface of metal
 (ii) cavities / sharp bends
 (iii) non-uniform protective film

- Prevention:
- clean metal surface
 - ensure proper design of metal
 - use a protective coating

② Crevice corrosion

where: occurs in gaps / cracks

what: corrosion occurring due to a small gap / crack / cleft is called crevice corrosion.

how: area within the crack exposed to loss O₂ \Rightarrow becomes anodic
surrounding area = cathodic

e.g. gaps and contact areas between bolts, gaskets, inside cracks, spaces filled w/ deposits

Rsns: same as that of pitting corrosion

Reasons for Crevice corrosion due to geometry of metal surface

- accumulation of impurities
- metallic parts being in contact w/ non-metallic parts e.g. plastic, rubber, glass.

- Prevention:
- clean metal surface
 - proper design + selection of materials
 - use a protective coating

③ Waterline corrosion:

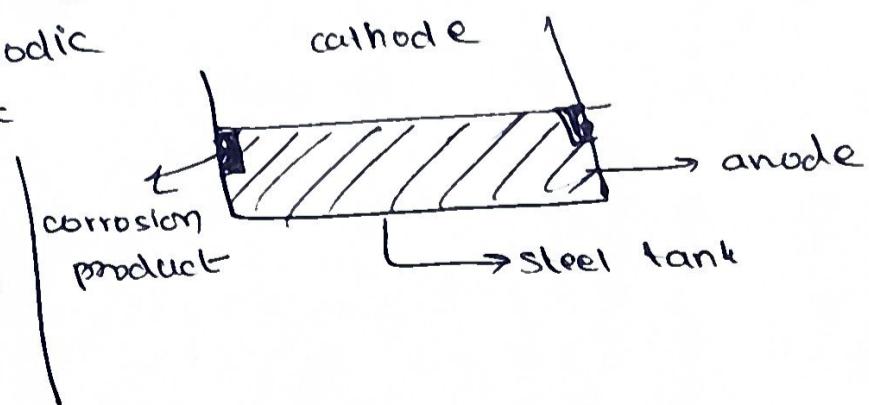
how: occurs when a metal is partially immersed in water.

working: part above H₂O \Rightarrow cathodic

below H₂O \Rightarrow anodic

• corrosion product @ ^{just below} _{waterline}

example: when water ~~heater~~ is stored
in a steel tank for a long time + in
boilers



④ Wire fence corrosion

where: places where steel wires inter cross w/ each other.

how: area under crossed places \Rightarrow anodic
surrounding parts of fence \Rightarrow cathode

⑤ Pipeline corrosion

where: external surface of underground pipes

how: underground pipes exposed to diff. types of environment.
some places may have sandy soil, others clayey soil.

- Texture + moisture levels are diff. for those 2 soil types.
- parts under sand: greater accessibility of O₂ \Rightarrow cathodic
under clay: Lesser accessibility of O₂ \Rightarrow anodic
- anodic part begins to corrode, product formed at 1 near cathode
- corrosion also accelerated if there is lots of moisture in the clay.

Factors Influencing Corrosion

Metallic Factors

1. Purity of the metal

- Greater the purity → lesser the corrosion
- Impurities lead to heterogeneity and enhance corrosion
- Rate of corrosion increases under cathodic impurities + areas under stress } anode corrodes

2. Relative areas of cathode and anode

- Corrosion of area of cathode
- Eg: Intense rusting of steel tap attached to a copper tank. Copper acts as cathode, its area is very large compared to steel tap.

3. Physical State of the Metal

- Smaller the grain size of a metal, greater is its solubility
⇒ heterogeneity also decreases
⇒ resistance towards corrosion increases

4. Position of the metal in the galvanic series

- Higher the position of the metal / alloy in the galvanic series, greater is its tendency to corrode.
- When 2 metals are in electrical contact, the more active metal corrodes. Greater the potential diff. between them, greater is the corrosion.

Ex1: When Zn & Cu are in contact : Zn corrodes

Ex2: Zn & Ag : Zn corrodes (to a much greater extent)

(1)

Corrosion (contd.).

Factors influencing corrosion

A. Metallic Factors

1. Purity of metal

- greater the purity of the metal, lesser the corrosion
- impurities lead to heterogeneity on the metal surface, and the anodic part corrodes
- greater is the cathodic impurity. The rate of corrosion increases in the presence of a cathodic impurity
- Even pure metals, areas under stress tend to be anodic, and corrode

2. Relative areas of cathode & anode

- Rate of corrosion \propto area of cathode

$$\propto \frac{1}{\text{area of anode}}$$

- For eg, intense corrosion is observed on steel taps attached to a large copper vessel. Steel is anodic w.r.t copper, and its surface area is less. \Rightarrow Intense corrosion occurs.

3. Physical State of metal : The smaller the grain size of a metal / alloy, greater is its solubility. An alloy with all its constituents having such small grain size behaves like a homogenous solution.

Reduction in the heterogeneity increases the resistance towards corrosion

4. Position of alloy / metal in the galvanic series

- The position of an alloy / metal in the galvanic series represents its tendency to corrode.
- The higher up that an alloy / metal is in the galvanic series, greater is its tendency to corrode.
- When 2 metals are in contact, greater the potential diff. between them, larger will be the extent of corrosion

For e.g. when Zn and Cu are in contact : Zn corrodes
when Zn & Ag are in contact : Zn corrodes, but to a larger extent as
the potential diff. between Zn & Ag $>$ Zn & Cu.

5. Nature of the surface film

- Greater is the specific volume ratio, lesser is the corrosion. However, this is not the only deciding factor as MoO₃ has a SVR of 2.3 but still corrodes.
- Ni, Cr, W have SVRs of 1.6, 2.0 & 3.6. W resists corrosion even at elevated temperatures.

6. Solubility of the corrosion product

- If the corrosion product is soluble in the corrosive medium, without chemically reacting, then corrosion proceeds unabated. (e.g. Zn in HCl)
- However, if the corrosion product is insoluble, then it acts as a physical barrier between the metal and the surroundings. If a sufficient amount of corrosive product formed coats the metal surface, then further corrosion does not occur. e.g. Pb in H₂SO₄

7. Volatility of the corrosion product

- If the corrosion product formed is volatile, then corrosion proceeds unabated. e.g. NO₃, SnCl₄

8. Over-Voltage / Over-Potential

The difference in the electrode potential of an electrode / cell under the passage of current and the thermodynamic value of electrode potential, under the same ~~non~~ experimental conditions in the absence of electrolysis is called over-voltage.

Mathematically,

over voltage = Theoretical potential at which evolution of the gas is supposed to occur - actual potential at which the evolution of the gas happens.

Greater the over voltage, lesser the corrosion.
For e.g. When a Zn rod is dipped in HCl, theoretically evolution of H₂ should be at 0V, but experimentally, it begins only at 0.7V.

$$\therefore \text{Over potential} = 0 - 0.7 \\ = -0.7V$$

This over potential can be reduced by adding a drop of CuSO_4 soln to H₂ gas. This leads to the formation of a tiny electrochemical cell at the pt of contact of Zn & Cu, which accelerates the formation of H₂. (3)

B. Environmental Factors

1. Temperature

rate of corrosion \propto temp.

temp. increases the rate of diffusion of ions in wet corrosion, activates metal surface in dry corrosion

2. Humidity

increase in humidity \propto corrosion

The relative humidity above which corrosion increases rapidly is called critical humidity

It is a characteristic property of metals, and is a fn. of pH.
For iron critical humidity = 58% in an unpolluted atmosphere
= 45% in a polluted atmosphere

3. Impurities in the environment

Corrosion is less in a pure environment.

(crevice)

Areas in the vicinity of an industrial area have gass like $\text{CO}_2, \text{HCl}, \text{H}_2\text{SO}_4, \text{H}_2\text{S}$.
In addition to this, there may be suspended particles like C, Si. (inert)

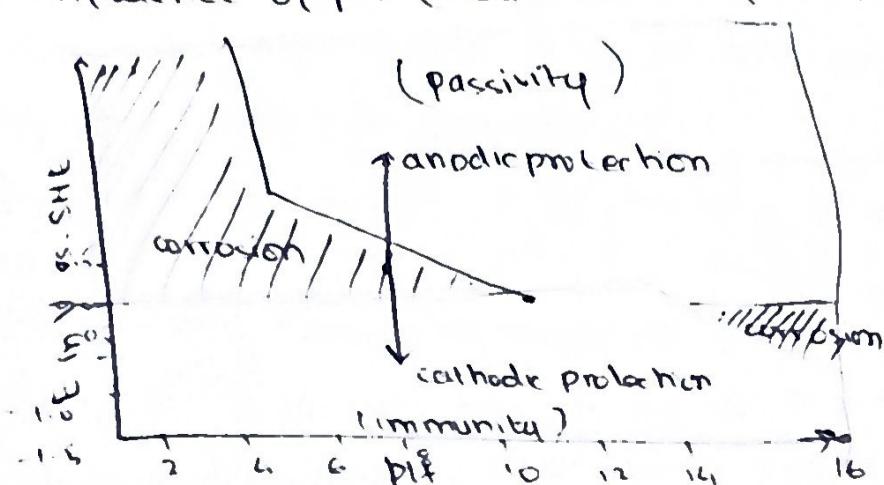
$\rightarrow \text{SO}_2$ is the leading pollutant, that contributes to the corrosion of metals.

\rightarrow In marine environments, there is NaCl in the air, which contributes to corrosion.

\rightarrow C, Pb from exhaust fumes: C is inert, but may lead to a crevice situation if it is on a metal

Pb, if deposited on metal surfaces, would form a galvanic cell.

4. Influence of pH (Pourbaix diagram)



- A Pourbaix diagram provides information about the stability of a metal as a function of pH and EMF.
- The rate of corrosion is greater in acidic media ($\text{pH} < 7$), than in neutral or alkaline media ($\text{pH} > 7$).
- A simplified Pourbaix diagram shows regions of immunity, corrosion and passivity.

Immunity \Rightarrow metal does not undergo oxidation in that region.

Corrosion \rightarrow metal reacts and undergoes corrosion at a measurable rate

Passivity \Rightarrow metal forms a passive & stable coating of oxide on its surface

For e.g. Fe becomes passive between pH 8 & 12.

5. Nature of anions present

- Presence of silicate anions \Rightarrow an insoluble product is formed, inhibits any further corrosion.
- Chloride ions destroy passive layer, accelerate corrosion.
- Chloride ions in acidic media (HCl) are more detrimental than when they are in alkaline or neutral media (NaCl)

6. Conductivity of the corrosive medium.

- Conductance of the corrosive medium plays an important role when the medium is submerged / underground.
- Conductivity of dry sandy soil $<$ wet clayey soil. (This has moisture in it)

7. Presence of oxygen

- The amount of oxygen in the air also influences corrosion.
- For highly anodic materials, even the slightest amount of O_2 can promote oxidation.
- If the amt of oxygen at the surface increases, an oxygen concentration cell may be formed, promoting corrosion.

Corrosion Control

By modifying the metal or the environment

i. Control of corrosion by proper design

- ① Use noble metals : like gold & platinum, which do not corrode.
can be used to make needle tips, surgical instruments, are expensive, can be used only for special purposes

② use pure metals: pure metals are more resistant to corrosion than a combination of metals. with pure metals, potential gradient can be avoided.

③ use alloys: many alloys have constituents that help inhibit corrosion.
For eg. stainless steel has chromium which creates a protective oxide layer.

④ use adjacent metals in the galvanic series: if multiple metals have to be used, use metals close to each other in the galvanic series to minimize potential gradient.

⑤ increase the size of the anode: make area of the cathode small.

For eg. ~~a nut~~, a nut can be made of steel, and the bolt of copper.

⑥ avoid sharp corners: sharp corners lead to accumulation of dust/dirt, cause internal stress.

⑦ apply protective coating: the coating acts as a barrier between the metal surface and the surroundings.

Organic coating: paints, varnish

Inorganic coating: galvanizing → coating w/ Zn

tinning → coating w/ Tin

⑧ encourage proper design: avoid sharp corners
insulation & welding are helpful
ensure proper drainage of water (stagnant water can lead to wet corrosion)

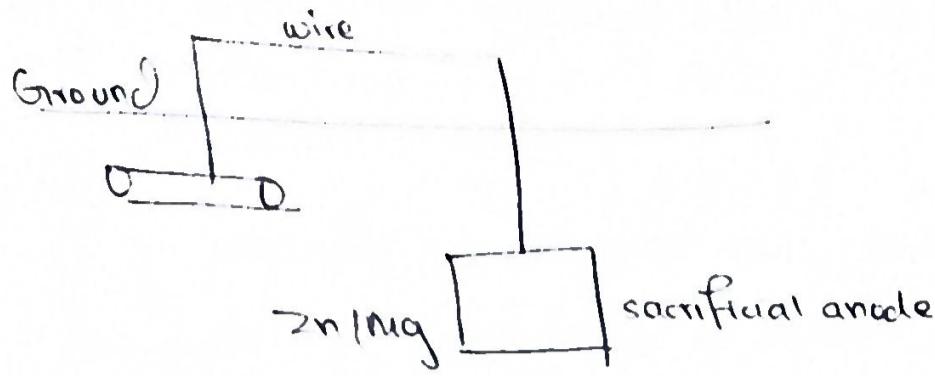
Q. Electrochemical protection

done by forcing the metal to behave like a cathode

It can be done in 2 ways:

A. Sacrificial anode protection method

- The metal is made to behave like a cathode by connecting it to a more anodic material.
- Corrosion thus occurs only on the active metal, and the original metallic structure does not corrode.
- Since a galvanic cell is deliberately constructed, it is called galvanic protection as well.
- The sacrificial anode is regularly inspected and replaced if needed.
- For eg. Mg/Zn is connected to Fe pipes as they are more anodic w.r.t Fe.



applications: to protect water pipes, hulls of ships, water tanks, marine structures etc

advantages: (i) no power requirements

- (ii) no regulations
- (iii) easy to set up
- (iv) easy to maintain

disadvantages: (i) poorly coated structures may require multiple anodes.

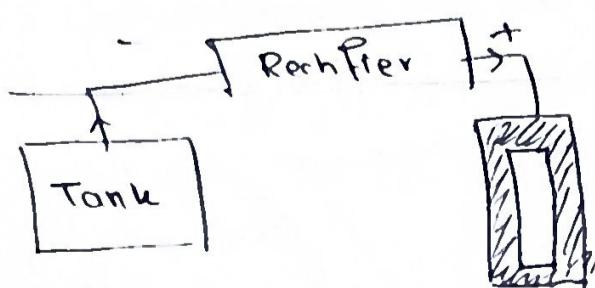
- (ii) anodes need to be regularly replaced
- (iii) installation can be expensive if installed after construction

B. Impressed Current Cathodic Protection (ICCP)

- In this method, corrosion is inhibited by impressing (applying) DC current on the base metal.
- The metal structure to be protected is connected to the -ve terminal of the rectifier.
- The +ve terminal is connected to an inert material like graphite, which is immersed in a back fill with coke breeze & sodium chloride.
- The backfill helps increase the conductivity of the soil. The coke breeze helps absorb moisture from the soil, the NaCl dissolves in it.

applications

- This method of protection can be applied to large stationary structures, like pipe lines, transmission towers, buildings.



advantages

- (i) can protect a large area
- (ii) can support varied voltage & current
- (iii) little to no maintenance required.

disadvantages:

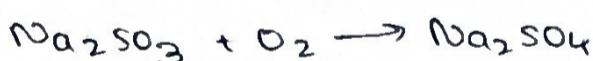
- (i) power failure may occur
- (ii) requires a power supply \Rightarrow monthly costs incurred
- (iii) capital investment is high

Differences between sacrificial anode method and impressed current cathodic protection method	
Sacrificial anode	ICCP
1. no power supply required	power supply required
2. anode needs to be periodically replaced	anodes are stable & do not disintegrate
3. low investment	high investment
4. economical for short term protection	suitable for large structures & long term protection
5. can be used when current requirements & resistivity of the electrolyte are low	can be used when current requirements & resistivity of the electrolyte are high

3. Control of corrosion by modifying the environment

- ① Decreasing dissolved oxygen: by mechanical / chemical methods
- ② Mechanical method: solubility of gases decreases w/ an increase in temp.
∴ By increasing the temp. of the electrolyte, and by continuous agitation, oxygen can be driven out. Deaeration is done in deaerators by ~~by~~ electrically floating the electrolyte, and the usage of paddles

③ Deaeration : The process of removing dissolved oxygen using chemicals like hydrogen & sodium sulphite.



④ Dehumidification : removal of moisture from the air using alumina/silica gel

⑤ Alkaline neutralization : dissolution of gases like $\text{HCl}, \text{H}_2\text{S}, \text{SO}_2, \text{CO}_2$ make the medium acidic, that can promote corrosion. This can be neutralized by spraying alkaline neutralizers like NH_3 .

4. Corrosion Inhibitors

- Corrosion inhibitors are substances, which when added in small quantities to the medium reduce the rate of corrosion.
- They work b/c are inorganic / organic compounds which when added in small quantities, dissolve in the medium, and eventually form a protective coating on the anodic / cathodic region.
- Corrosion inhibition is achieved without disturbing a process.

There are 3 types of corrosion inhibitors

- (i) Anodic inhibitors (chemical passivity)
- (ii) Cathodic inhibitors (adsorption inhibitors)
- (iii) Vapour phase inhibitors (volatile corrosion inhibitors)

Anodic inhibitors

- prevent corrosion reaction happening on anode
- forms a protective coating (mostly an oxide layer) on anode
- causes a large anodic shift in corrosion potential
- forces metal into passivation region \rightarrow These inhibitors are sometimes called passivators.
- if some areas are left unprotected by inhibitors, severe localized corrosion occurs in those regions.

Uses: to limit pitting corrosion

Inhibitors used : chromates, nitrates, phosphates, tungstates of transition metals.

Cathodic Inhibitors

- Cathodic inhibitors work by:
 - (a) slowing down the cathodic reaction
 - (b) precipitating on the surface of cathodic areas to limit the diffusion of reducing species onto the surface.

Cathodic inhibitors can work using 3 different mechanisms:

- Cathodic poisons: make the recombination & discharge of H_2 more difficult
- cathodic precipitators: they are precipitated out forming a protective oxide layer on the surface.
- Oxygen scavenger: prevents the cathodic depolarization caused by oxygen.

In an acidic solution : • slow down diffusion of H^+ to cathode
Inhibitors used : amines, urea

- retard evolution of H_2 gas

Inhibitors used : antimony / arsenic oxide

In a neutral solution : • eliminate O_2 from cathodic areas / retard its formation
Inhibitors used : sodium sulphite

Zn, Ru react w/ hydroxyl ions, form hydroxide layers, form impermeable self-barriers

Vapour Phase Inhibitors (VPI)

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- VPIs are materials that have significant vapour pressure, which allows for the vaporization of molecules, and subsequent adsorption on the metal surface, forming a protective layer.
- It is the organic portion of the VPI that provides volatility.
- Usage: protection of storage containers, packing materials
- Protection of ferrous metals: Diethylhexyl ammonium nitrate is used
- copper & alloys : benzotriazole

Advantages of VPI

- (i) environmental friendly
- (ii) easy to use
- (iii) comes as powders, sprays, liquids
- (iv) surface coating can be removed by conventional cleaning methods

PROTECTIVE COATINGS

Electroplating

Electroplating is the process of depositing a layer of metal on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the metal.

The metal which gets deposited is called the coating metal (CM) or protective metal (PM), and the metal on which the coating is done is called the base metal.

Objectives of electroplating

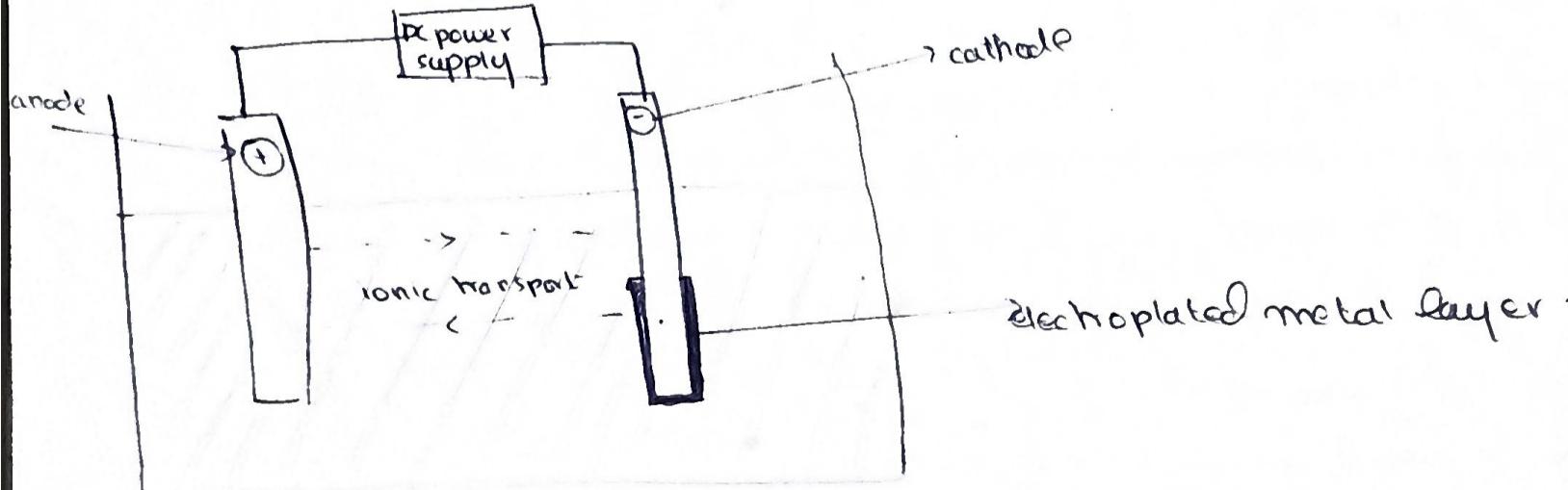
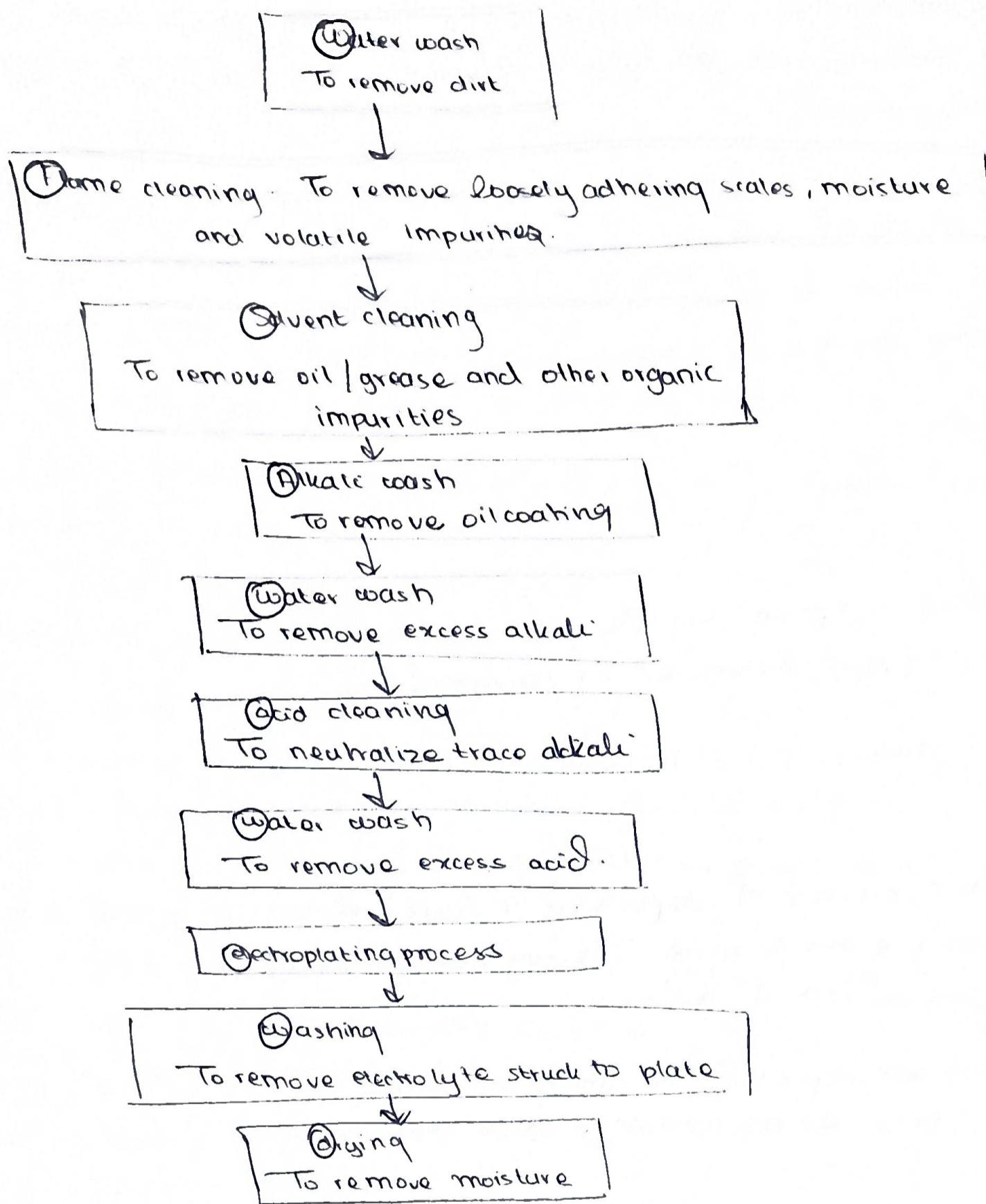
- increase wear resistance
- increase decorative and commercial value
- resistance towards corrosion
- increase hardness & improve physical strength

Mechanism of electroplating

Electrodeposition is carried out by directly passing current through an electrolyte containing the soluble salt of the metal

The base metal to be coated is made the cathode (-ve) and the coating metal is the anode (+ve)

Process of electroplating



Factors influencing thickness of the film

(i) Current density

high current density \Rightarrow coarse coat

very low current density \Rightarrow insufficient coating

Greater is the current density, poorer is the quality of plating

- current density should be moderate

(ii) Concentration of the electrolyte : concentration of the electrolyte should be uniform throughout the process of electroplating.

(iii) Time of contact : thickness of the film is dependent on the time for which electroplating is done.

Time of contact \propto thickness

(iv) Throwing power = capacity of an electrolyte to give a uniform coat

Throwing power of thickness

- For decorative purposes: a thin film would suffice

- For corrosion resistance: the thickness should be more.

(v) Temperature : The temp. of the electrolyte should be close to room temp. In some cases electroplating happens at higher temperatures.

(vi) pH of bath : pH is low \Rightarrow hydrogen gas evolves at cathode

pH is high \Rightarrow metal hydroxides are precipitated.

Optimum pH to be maintained using buffers

(vii) Active surface: the ^{base} metal should be free from any sort of impurity prior treatment to be done.

Uses

(i) Cu electroplating in PCBs, increases conductivity

(ii) Ni, Cr plating on automobile parts so that they are hard & resist corrosion

(iii) Ag on radar components to increase range of scanning.

Electroplating of gold

(write general intro)

anode : gold

cathode : metal to be plated

electrolyte : $K[Au(CN)_2]$

optimum temperature : 60 - 70°C

anode reaction : $Au(s) \rightarrow Au^{3+} + 3e^-$

cathode reaction $Au^{3+} + 3e^- \rightarrow Au$

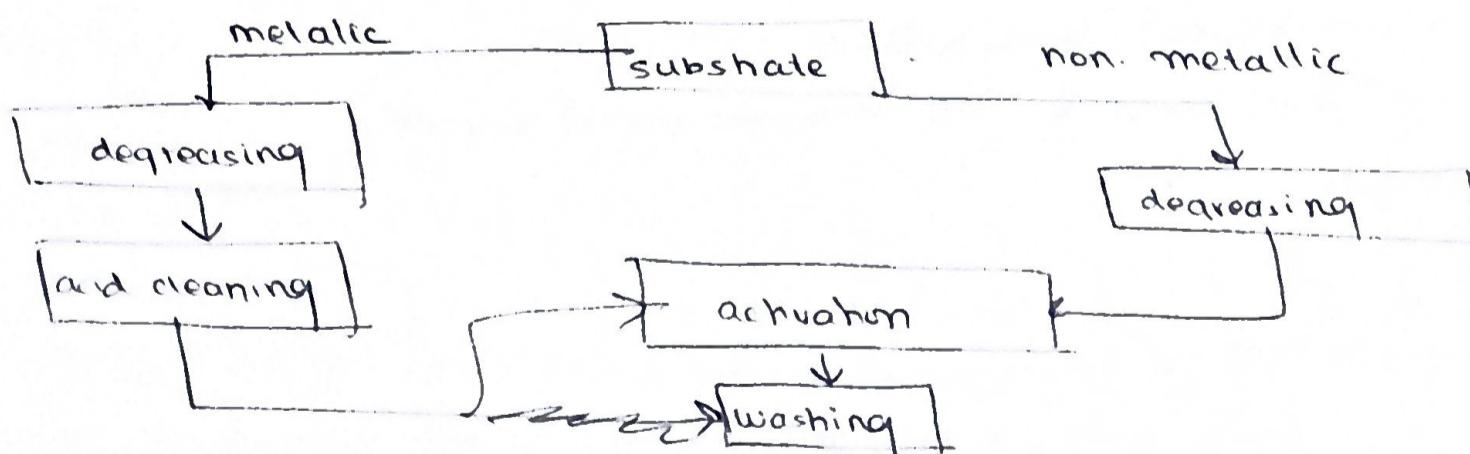
applications : (i) decorative and ornamental purposes
(ii) electronics , printed circuit

Electroless Plating : electroless plating is a technique of depositing a noble metal from its salt soln on a catalytically active surface of a metal by using a suitable reducing agent.

The reducing agent reduces the metallic ions to metal , which gets deposited on the catalytically active surface , giving rise to a uniform coating .

Metal ions + reducing agent \rightarrow metal (deposit) + oxidized products

pretreatment has to be done before carrying out electroless plating to ensure that the surface is homogenous .



Pretreatment for metals & alloys

- 1 Degreasing to remove ~~scales~~ & grease
- 2 acid cleaning to remove scales
- 3 weak acid etching or nickel strike to activate

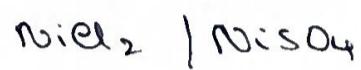
Pretreatment of non-metals

- 1) degreasing to remove oil and grease
- 2) activation is done by dipping the substrate in SnCl_2 - HCl , and then in PbCl_2 soln

Electroless nickel plating

- It is a technique to deposit a Ni-C-P alloy on a solid work piece
- It is an autocatalytic method, i.e. once a layer of Ni is formed, it initiates catalyses the rxn. to form a thick coating.
- The plating can be done on Al, Cu, Fe and also on non-metals like glass, quartz

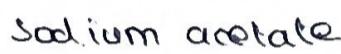
coating soln.



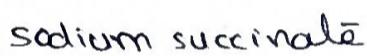
reducing agent



buffer



complexing agent



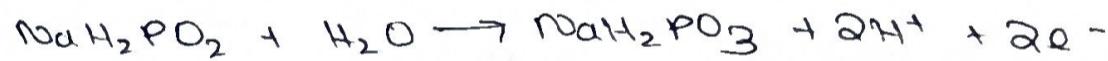
optimum pH

4.5

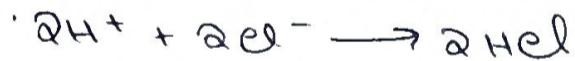
optimum temperature

93°C

rxn at anode



rxn at cathode



overall rxn



Applications

(i) electronic devices

(ii) jewellery

(iii) components in oil field, marine aviation, aerospace & industry

Advantages

(i) coating can be done on metals & non-metals

(ii) the surface need not be uniform

(iii) no electricity needed

(iv) can obtain matte, semi-bright & bright finishes

Disadvantages

(i) life time of chemicals is short

(ii) waste treatment cost is high.

Differences between Electroplating & Electroless plating

Electroplating

- (i) requires current
- (ii) separate anode is used
- (iii) object coated by making it cathode
- (iv) anode rxn: $M \rightarrow M^{n+} + ne^-$
- (v) not suitable for irregular surfaces

Electroless plating

- (i) no current
- (ii) catalytic surface of substrate is anode
- (iii) object coated after surface activation
- (iv) reducing agent: $O^{2-} + ne^-$
- (v) can be used for irregular & complicated parts.

Non-metallic coatings

- Paint is a dispersion of pigment in medium oil.
- It is a thick liquid used to decorate & protect wood, metal etc.
- The oil carries the various ingredients of the paint. It acts as a vehicle / carrier and leaves behind a non-porous protective film on drying.
- When paint is applied on a surface, the solvent evaporates. The drying oil slowly oxidizes forming a pigmented film that saves the surface from corrosion.

A good paint should have the following properties:

- should have high covering power
- spread easily,
- good adhesive power
- should not crack on drying
- should provide corrosion & water resistance

Ingredients of Paint

1. Pigment
2. Vehicle / drying oil
3. Thinner
4. Extender / Filler
5. Driers
6. Plasticizers
7. Anti-sludging agents

Ingredients of paint

Pigments : fine powdered color producing substances in paint
can be natural or synthetic

Mineral pigments : Fe ore, chalk, mica, clay

Synthetic pigments : Lead, Lead oxide

Reactive pigments : red lead, zinc oxides

Functions : • gives color, texture & opacity

- durability
- protects metal from destructive ultraviolet rays
- covers manufacturing defects