CORROSION :-

INTRODUCTION :-

→ Metals and alloys are used as fabrication or construction material in engineering.
→ If the metals or alloys structure are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture & other chemicals.
→ This phenomenon of destruction of metals & alloys is k/as corrosion.
→ The surface of almost all the metals begins to decay more or less rapidly when exposed to atmospheric gases, H_2O or other reactive liquid medium.

CORROSION :-

→ The process of decay of metal by env. attack is k/as corrosion.
→ Metals undergo corrosion & convert to their oxides, hydroxides, carbonates, sulphides etc.
→ eg :-

i) Rusting of iron :- When iron is exposed to atmospheric conditions, a layer of reddish scale & powder of Fe_3O_4 is formed.

ii) Formation of green film of basic carbonate :- [$CuCO_3 + Cu(OH)_2$] on the surface of Cu

when exposed to moist air containing CO_2.

→ The corrosion of metals is measured in the units of milli / inches / year or mm/year.

Metal $\underset{\text{Metallurgy - Reduction}}{\overset{\text{Corrosion - Oxidation}}{\rightleftharpoons}}$ Metallic Compound + Energy

CAUSES OF CORROSION :-

→ The metals exist in nature in the form of their minerals or ores in the stable combined forms as oxides, chlorides, silicates, carbonates & sulphides.

→ During the extraction of metals, these ores are reduced to metallic state by supplying considerable amount of energy.

→ Hence the isolated pure metals are in excited states than their corresponding ores.

→ So metals have natural tendency to go back to their combined state (minerals/ ores)

→ When metal is exposed to atmospheric gases, moisture, liquids etc, the metal surface reacts & forms more thermo-dynamically stable compounds.

EFFECTS OF CORROSION :-

→ Wastage of metal in the form of its compounds.
→ The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
→ Life span & efficiency of metallic parts of machinery & fabrications is reduced.

THEORIES OF CORROSION :-

1) Dry Corrosion
2) Wet Corrosion

(1) Dry Corrosion or chemical Corrosion :-

→ The direct chemical action of env. on the surface of metal in -nce of moisture is known as dry corrosion.
→ This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid $\bar{e}$ metal surface.

eg :-

i) Ag material undergo chemical corrosion by atmospheric H_2S gas.

ii) Iron metal undergo chemical corrosion by HCl gas.

There are 3 types of chemical corrosion :-

i) Oxidation corrosion
ii) Corrosion due to other gases
iii) Liquid metal corrosion :- oxid^n of steel in Na.

Oxidation Corrosion :-

→ Direct action of oxygen at low or high temp. on surface of metals in absence of moisture is known as oxid^n corrosion.

→ Alkali metals & alkaline earth metals are rapidly oxidised at lower temp.

→ At high temp. all metals are oxidised (except Ag, Au, Pt)

Mechanism :-

i) Oxid^n takes place at surface of metal forming metal ions M^{+2}.

ii) Oxygen is converted to oxide ions (O^{-2}) due to transfer of electrons from metals.

iii) The overall rxn^n is of oxide ion reacts c metal ions to form metal oxide film.

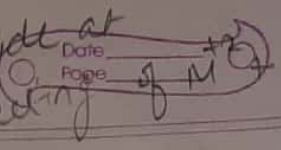
Rx^n in oxid^n Corrosion :-

$$M \rightarrow M^{+2} + 2e^- \quad (\text{Oxid}^n.)$$

$$\tfrac{1}{2} O_2 + 2e^- \rightarrow O^{-2} \quad (\text{red}^n.)$$

$$M + O_2 \rightarrow M^{+2} + O^{-2} \quad (\text{Metal oxide})$$

Form? of metal oxide at the point of melting



O^{2-}	→	←	M^+
O^{2-}	→	←	M^+ metal
O^{2-}	→	←	M^+

Oxid? mecha? of metals

→ Initially the surface of metal undergoes oxid? & the resulting metal oxide scale forms a barrier w/h restricts further oxid?

→ The extent of corrosion depends upon the nature of metal oxide.

Nature of Oxide formed :-

It plays an important role in further oxid? corrosion process.

Metal + oxygen ⟶ metal oxide (corrosion product)

When the oxide film formed is :-

a) Stable metal oxide layer :-

→ A stable layer is fine grained in str. & can get adhered tightly to the parent metal surface.

→ Such a layer will be impervious (No pores) in nature & hence behaves as protective coatings, thereby shielding metal surface.

→ Further corrosion is prevented.

eg:- Al, Sn, Pb, Cu etc. form stable layer.

Metal + O_2 → Metal ← Stable metal oxide layer

→ No corrosion

b) Unstable metal oxide layer:-

→ The oxide layer formed decomposes back into metal & oxygen.

→ Oxid? corrosion is not possible in such cases.

eg:- Ag, Au, Pt

Metal oxide → Metal + Oxygen

c) Volatile metal oxide layer:-

→ The oxide layer formed is volatile in nature & evaporates as soon as it is formed.

→ There by leaving under lying metal surface exposed for further attack.

→ This causes rapid continuous corrosion, leading to excessive corrosion.

eg:- MoO_3 layer.

Metal + O_2 → Metal ← volatile metal oxide layer

← evaporation of metal oxide

Metal → fresh surface exposed for attack

d) Porous metal oxide layer :-

→ If the metal oxide layer is porous, the oxide layer formed has pores or cracks.
→ In this case the atmospheric O_2 penetrates through the pores or cracks & corrode the underlying metal surface.
→ This causes continuous corrosion till conversion of metal into its oxide is completed.

eg:- Alkali & Alkaline earth metals.
(Li, Na, K, Mg, Fe etc.)

Metal + O_2 → Metal → Porous metal oxide layer

↓

Further attack through pores & cracks continues

(2) Wet Corrosion or Electrochemical Corrosion :-

→ The direct chemical action of env. on the surface of metal in the presence of conducting liquid is the form of electrochemical cell.
→ It is a common type of corrosion which occurs usually in aqeous corrosive env.
→ Occurs when metal comes in contact with a conducting liquid.

→ Formⁿ of galvanic cell on the surface of metal generating anodic & cathodic areas.
→ At anode oxidⁿ takes place liberating ~~any~~ electrons.
→ Electrons at anode are transported to cathodic area where H^+ or O_2 & H_2O consumes the electrons generating non-metallic ions like OH^- or O^{-2}.
→ Metallic (M^+) & non-metallic (OH^- or O^{-2}) diffuses towards each other & results in the formⁿ of corrosion product in b/w anodic & cathodic areas.

Mechanism :-
→ Electrochemical corrosion involves flow of e^- b/w anode & cathode.
→ The anodic rxⁿ involves dissolution of metal liberating free e^-.

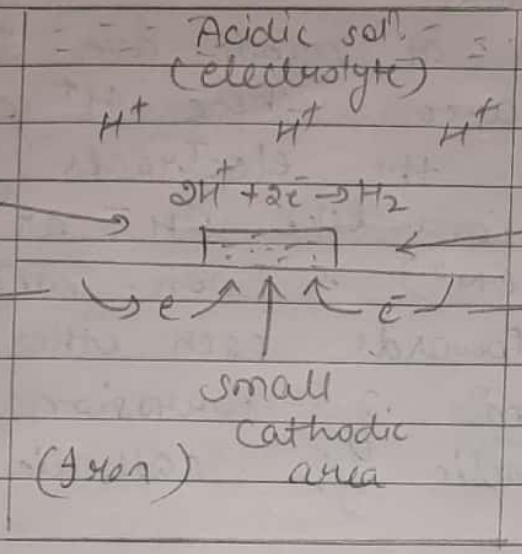
$$M \rightarrow M^{+n} + ne^-$$

→ The cathodic rxⁿ consumes e^- i.e either evolution of hydrogen or absorpⁿ of O_2 w/h depends on nature of corrosive env.

Wet corrosion takes place in 2 ways :-
i) Evolution of H_2
ii) Absorption of O_2

i) Evolution of H_2 :-
→ This type of corrosion occur in acidic medium.

eg:- Rusting of iron metal in acidic env. takes place in following way :-



Hydrogen evolution type corrosion.

→ At anode dissolution of iron to ferrous ion takes place & liberation of e^-.

Anode → $Fe \rightarrow Fe^{+2} + 2e^-$ (oxidn.)

→ The e^- released at anode flow through the metal from anode to cathode.

→ H^+ ions of acidic soln takes up these e^- & eliminated as hydrogen gas.

Cathode $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (redn.)

The overall rxn :-

$$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2 \uparrow$$

→ This type of corrosion causes "displacement of Hydrogen ions from acidic sol?. by metal ions.

→ In hydrogen evolution type corrosion, the anodic areas are large & cathodic areas are small.

ii) Absorption of O_2 :-

→ This type of corrosion takes place in basic or neutral medium in ↑nce of O_2.

→ eg:- Rusting of iron in neutral or basic aqueous sol? of electrolyte in ↑nce of atmospheric oxygen.

→ Usually the surface of iron is coated ⊂ thin film of iron oxide.

→ If the film develops cracks, anodic areas are created on surface & rest of the metal surface act as cathodes.

→ It shows that anodic areas are small & the cathodic areas are large.

Anode → $Fe \rightarrow Fe^{+2} + 2e^-$ (Oxid?)

The released e^- flow from anode to cathode through iron metal.

Cathode → $\frac{1}{2} O_2 + H_2O \rightarrow 2OH^- + 2e^-$ (Red?)

Overall Rn? :- $Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$

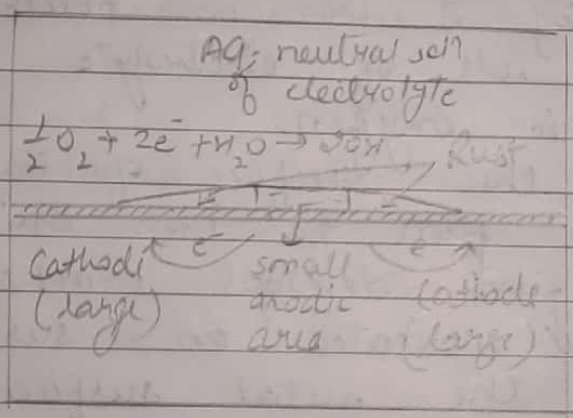
If enough oxygen is not, ferrous hydroxide is easily oxidised to ferric hydroxide & then to hydrated ferric oxide w/h is k/as rust.

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$

$$4Fe(OH)_2 + O_2 + 2H_2O \xrightarrow{\text{oxidn}} 4Fe(OH)_3 \xrightarrow{\text{oxidn}} Fe_2O_3 \cdot 3H_2O$$

(Rust)

hydrated ferric oxide



Oxygen absorption type corrosion.

CORROSION CONTROL METHODS:-

1) Proper designing
2) Using Pure metals
3) Using metal alloys
4) Use of Inhibitors
5) Modifying Environment

6) Cathodic Protection
7) Application of protective coatings.

CATHODIC PROTECTION :-

→ The method of protecting the base metal by forcibly making it to behave like a cathode there by corrosion does not occur is called as cathodic protection.

→ There are 2 types of cathodic protection.

a) Sacrificial anodic protection
b) Impressed current cathodic protection.

SACRICIFICIAL ANODIC PROTECTION :-

→ In this protection method, the metallic str. to be protected (base metal) is connected by a conducting wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.

→ The more anodic metal itself gets corroded slowly, while the parent str. (cathodic) is protected.

→ The more active metal so employed is called sacrificial anode.

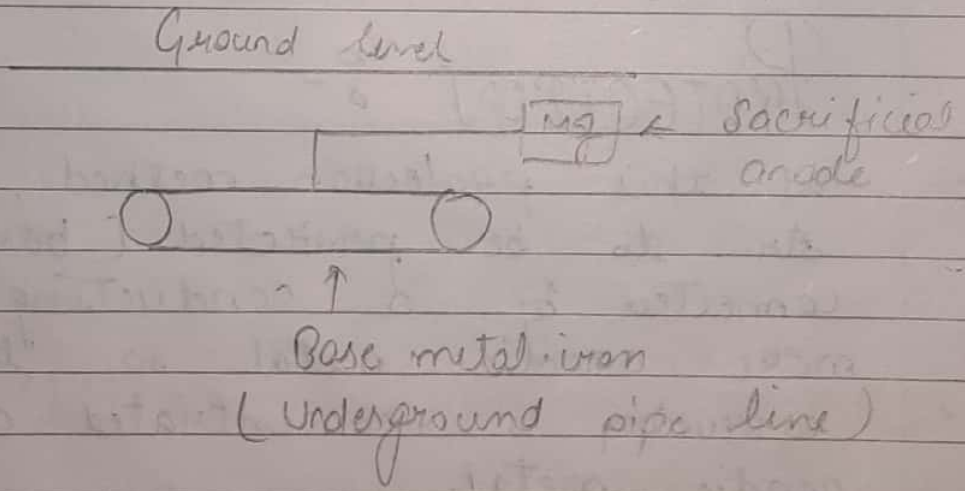
→ The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

→ The artificially made anode gets corroded gradually protecting the original metallic str.

→ The process is klas sacrificial anodic protection.

→ Metals commonly employed as sacrificial anode are Mg, Zn, Al & their alloys w/h possess low red. pot. & occupies higher end in electrochemical series.

eg:- A ship - hull is made up of steel is connected to sacrificial anode (Zn - blocks) w/h undergoes corrosion leaving the base metal protected.



Buried pipe line protected to Mg block

Applications of sacrificial anode protection:-

By referring the electrochemical series, the metal c low red. pot. is connected to base metal w/h act as anode :-

1) To protect underground pipelines → Burried pipe line protected by connecting to Mg block
2) Protection of ship hull & other marine devices.
3) Protection of H_2O tank → by suspending Zn or Mg rods, body of tank made cathode & protected.

Advantages :-

1) It is simple method.
2) It does not require external power.
3) It has low maintainance & installation cost.
4) Cathodic interferences are minimum.

Disadvantages :-

1) More than one anode is required some times.
2) It does not work properly in high corrosive env.
3) Sacrificial anode must be replaced periodically as & when it is consumed.

PROTECTIVE COATINGS :-

METALLIC COATINGS :-

→ The surface of the base metal coated c another metal (coating metal) is called metallic coatings.

→ Metallic coatings are classified into 2 :-

a) Anodic coatings.

b) Cathodic coatings.

(a) Anodic Coatings :-

→ The metal used for the surface coating is more anodic than the base metal w/h is to be protected.

→ eg :- Coating of Al, Cd, Zn on steel surface are anodic bcoz their electrode pot. are lower than that of base metal iron, therefore anodic coatings protect the underlying base metal sacrificially.

→ The form? of pores & cracks over metallic coatings exposes base metal & a galvanic cell is formed b/w base metal & coating metal. The coating metal dissolves anodically & base metal is protected.

(b) Cathodic Coatings :-

→ Cathodic coatings are obtained by coating a more noble metal (i.e metals having higher electrode pot. like Sn, Au, Ag, Pt etc.) than base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.

→ Cathodic coating protects the base metal only when the coating is uniform & free from pores.

→ The formn. of pores over the cathodic coating exposes the base metal (anode) to env. & a galvanic cell is set up. This causes more damage to the base metal.

LUBRICANTS :-

→ Any substance introduced b/w the moving & sliding surfaces ∈ a view to reduce frictional resistance.

→ The process of minimising frictional resistance between moving or sliding surfaces by the introduction of lubricants in b/w them is called lubrication.

IMP. FUNCTIONS OF LUBRICANTS :-

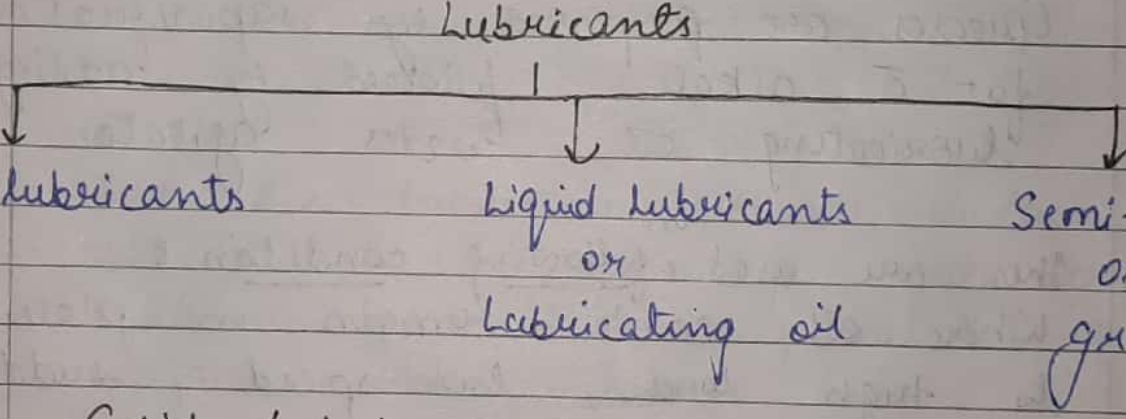
1) Lubricants avoids direct contact b/w the rubbing surfaces & reduces surface deform., wear & tear.
2) It acts as a coolent by reducing loss of energy in the form of heat.
3) Lubricants enhances effeciency of a machine by reducing wastage of energy & expansion of metal by local frictional heat.
4) It avoids relative motion of moving surfaces, such that running cost of

the machine.

5) The lubricants used b/w piston & the cylinder wall of an internal combustion engine acts as a seal & can prevent the leakage of gases from cylinder under high pressure.

6) It prevents from corrosion also.

CLASSIFICATION OF LUBRICANTS



(1) Solid Lubricants :-

eg:- Graphite

MoS_2 → Molybdenum disulphide

Graphite is better than MoS_2 bcoz graphite can be used at high temp. as lubricants while MoS_2 oxidises above 350°C temp.

→ These are used in foll. cond?

→ where operating temp. & load is too high.

→ There is a need to avoid combustible lubricants.

(2) Liquid lubricants or Lubricant oils :-

eg :- → Animal & vegetable oils
→ Mineral or petroleum oils
→ Blended oils.

Properties of Good lubricant oils

→ Low pressure → stability
→ Low freezing point → Non-corrosive Property

(3) Semi-solid lubricants or Greases :-

Greases are prepared by saponification of fat & alkali, followed by adding hot lubricating oil under agitation.

These are used in following condition :-

→ Where oil can't remain in place due to high load, low speed, sudden jerks etc.

eg :-

→ Calcium based greases or cup-greases
→ Soda base greases
→ Lithium base greases
→ Axle greases.

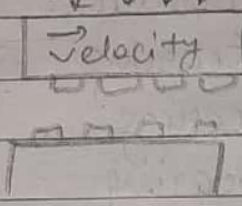
LUBRICATION TECHNIQUES OR TYPES OF LUBRICATION :-

3 Mech: / 3 types :-

a) Thin layer / Boundary Lubrication
b) Fluid Film / Hydrodynamic Lubrication
c) Extreme Pressure Lubrication

(a) Thin layer / Boundary Lubrication

→ A thin film of lubricant is absorbed on the surface & held by Vander Waals forces.



→ When the lubricant is not viscous enough to generate a film of sufficient thickness for the separation of surfaces under heavy load, friction is reduced by this method.

solid lubricants
Animal oil

→ It is applied when the speed is very low, the loading heavy, the oil has low viscosity.

→ Some peaks may have higher thickness than the film of lubricant w/h results in wearing & tearing.

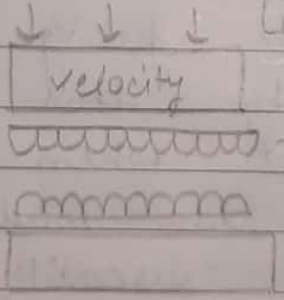
→ Hence the chemical or physical forces on some metal surfaces would avoid the direct contact of metals & absorb a thin layer of lubricating oil.

→ The co-efficient of friction is reduced

due to oiling.

(b) Fluid film / Hydrodynamic Lubrication :-

→ Also has thick film lubrication.
→ Carried out with help of liq. lubricants.
→ The sliding surfaces are separated by a thick film of abt 10000 Å which is applied to prevent direct surface to surface contact.
→ Wearing & tearing of metal is minimized.
→ In ball bearing, the irregularities of shaft & bearing surfaces are covered by a thick film of lubricants.
→ It is useful in delicate & light machines like watches, clocks, guns etc



(c) Extreme Pressure Lubrication :-

→ Under heavy load & high speed condn, high local temp. is generated.
→ The liq. film may not stick, it may decompose & vaporise.
→ So special additives called extreme

* contain active radicals/groups like Cl, P, S.

pressure additive are blended ∈ lubricating oil to form more durable film to withstand high temp. & pressure.

→ eg :- Chlorinated esters, sulphurised oils & tricresyl phosphates.

semi solid lubricants

PROPERTIES OF LUBRICANTS :-

(a) Cloud point :-
The temp. at w/h the impurities begin to separate from the soln & lubricating oil becomes cloudy or hazy in appearance. (wax crystals)

(b) Pour Point :-
The temp. at w/h the oil ceases to flow & pour.

(c) ~~Flash~~ fire point :-
The lowest temp. at w/h the vapour of that fuel will continue to burn for at least 5 seconds after ignition by an open flame.

(d) Flash point :-
The lowest temp. at w/h vapours of the volatile material will ignite given an ignition source.

(e) Viscosity :-

→ Property of a fluid that determines its resistance to flow.

→ It is an indicator of flow ability of lubricating oil.

→ If temp. ↑es, viscosity of lubricating oil b

→ If pressure ↑es, " " ↑es.

(f) Viscosity Index :-

→ Rate at w/h the viscosity of oil changes c̄ temp. is measured by an emperical no. k/as viscosity index.

→ A relatively small change in viscosity c̄ temp. is indicated by high viscosity index.

→ A low viscosity index shows a relatively large change in viscosity c̄ temp.

=x=

REFRACTORIES :-

→ Inorganic materials w/h can withstand very high temp. ẽout softening or suffering deformation.
→ Used for construction of kilns, ovens, furnaces, crucibles etc.
→ Main func? of refractories ~~are~~ varies depending on the purpose to w/h they are subjected like confining heat ẽ the furnace, transmitting or storing heat in refrigerators.

CHARICTRISTICS OF REFRACTORIES :-

→ High temp. resistance under working cond?
→ Good abrasions resistance by dusty gases & melt on metals.
→ Low ability to contain heat.
→ High mechanical strength.
→ Thermal strength to ẽ stand shock due to rapid & repeated temp. fluctuations

CLASSIFICATION OF REFRACTORIES :-

→ Classified into 3 categories on the basis of their chemical nature.

a) Acidic Refractories :-

→ Made from acidic materials such as Al & silica (oxides)
→ They are resistant to acid slags but attacked by basic materials.
→ eg :- Silica, Alumina & fire clay refractories.

b) Basic Refractories :-

→ Consist of basic materials, but attacked by acidic materials.
→ They find extensive used in steel making open - hearth furnaces. eg :- Magnesia.

Neutral Refractories :-

→ Completely neutral in chemical sense.
→ They consist of weakly acidic / weakly basic materials like Zirconia (ZrO_2), Chromites ($FeO(CrO_2)$), graphite & Silicon carbide.