CORROSION

22/11

Corrosion and Control

Corrosion can be defined as spontaneous destruction or deterioration of a metal by chemical, electrochemical or biochemical reaction.

Examples:

Rusting of iron

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3 \cdot H_2O(s)$$

Tarnishing of silver

$$4Ag(s) + 2H_2S(g) + O_2(g) \rightarrow 2Ag_2S + 2H_2O(l)$$

Scales on copper

$$2Cu(s) + H_2O(l) + O_2(g) + CO_2(g) \rightarrow Cu_2(OH)_2CO_3(s)$$

Corrosion can be viewed as the reverse process of extractive metallurgy.

$$\underset{\text{(State of higher energy)}}{\text{Metal}} \underset{\substack{\text{Metallurgy} \\ \text{(Reduction)} \\ [e^- \text{ gained}]}}{\overset{\substack{\text{corrosion} \\ \text{(oxidation)}}\ [e^- \text{ lost}]}{\rightleftharpoons}} \underset{\text{(State of lower energy)}}{\text{Metallic compound}} + \text{Energy}.$$

$$\text{Ore} \xrightarrow{e^-} Fe \xrightarrow{H_2O,\ O_2,\ \text{oxidation}} \text{Ore}.$$

Importance: Human life & safety, Cost of corrosion, Conservation of materials, academic interest.

CONSEQUENCES OF CORROSION

- Maintenance and operating costs
- Plant shutdowns, loss of production
- Contamination and loss of valuable products.
- Effects on safety.
- Loss of aesthetic value
- Loss of technically imp surface properties.
- Loss of efficiency

Corrosion
- Dry corrosion (Chemical)
- Wet corrosion (Electrochemical)

DRY CORROSION

- Occurs due to the direct chemical reactions b/w the ~~environmentat~~ and the metals/alloys.
- Presence of an electrolyte is not at all essential for corrosion to occur.

Types:
Oxidation (due to rxn with O_2)
Other gases (CO_2, H_2S, SO_2, X_2 etc)
Liquid metal

i) OXIDATION CORROSION

When metals are attacked by dry oxygen.

Metal + oxygen → Metal oxide (corrosion product)
→ Non porous, adherent, stable, protective, continuous film.

Nature of the oxide film decides subsequent corrosion.

- If a stable film is formed.
  eg: Al, Sn, Pb and Cu.
- Unstable metal film decomposes back into metal and oxygen. eg Ag, Au, Pt
- Volatile film layer volatizes as soon as it is formed, thereby accelerating corrosion.
  eg MoO_3.

ii) CORROSION BY OTHER GASES

Due to some gases SO_2, Cl_2, CO_2, H_2S.
Depends mainly on the chemical affinity between the metal and the gas involved.
Eg: dry Cl_2 ~~g~~ attacks silver metal and forms AgCl as a thin protective and non ~~AAG~~ porous layer on the metal. As a result of this protective layer on the metal surface, the intensity of corrosion decreases.

iii) ~~&~~ LIQUID METAL CORROSION

Occurs when a molten liquid is continuously passing on a solid metal surface or on alloy. This is due to dissolution ~~or~~ ~~##~~ or due to penetration of molten liquid into the metal phase.

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WET CORROSION

This occurs due to the existence of seperate anodic (oxdn) and cathodic (redn) areas, between which current flows through the conducting soln.

At anode.

$M(s) \rightarrow M^{n+} + ne^-$

ANODE ✓
CATHODE ✓
ELECTROLYTE ✓

At cathode.

i) Hydrogen evolution.

ii) Absorption of oxygen depending upon the nature of corrosive environment.

Fe

ANODIC RXN

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

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

CATHODIC RXN.

i) Hydrogen evolution:

O_2 ✗

$2H^+(aq) + 2e^- \rightarrow H_2$ (dearated & acidic medium)

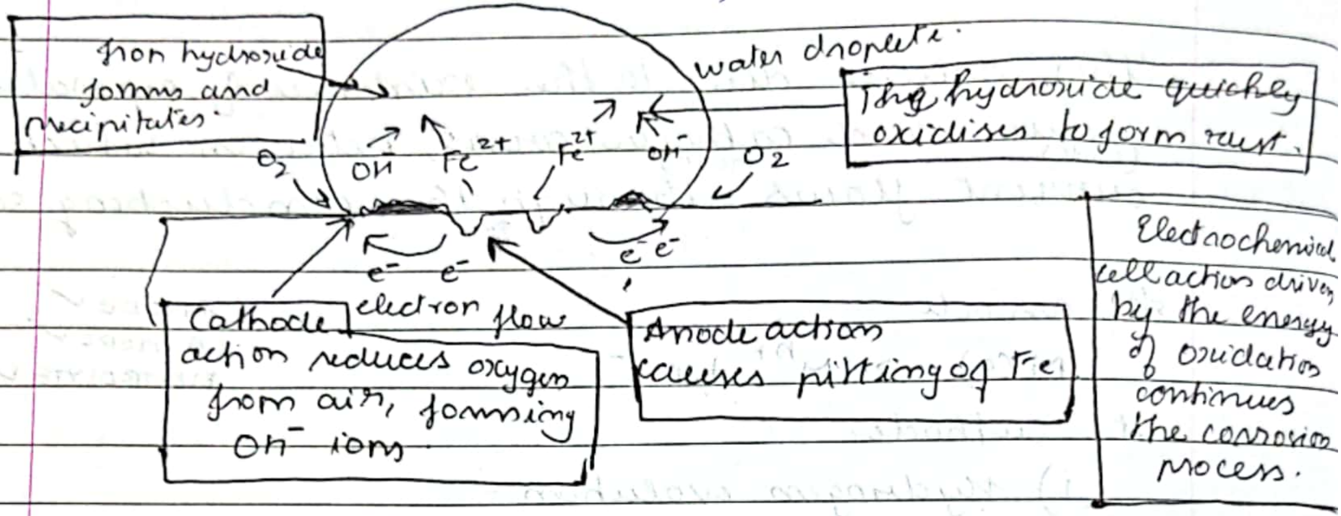
H_2 liberation along with OH^- ions formation.

$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ (~~deaer~~ dearated & neutral)

ii) Reduction of oxygen in neutral medium.

$O_2(aq) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$ (aerated & neutral)

MECHANISM OF RUSTING



At anodic sites: $[Fe \rightarrow Fe^{2+} + 2e^-] \times 2$.

At cathodic sites: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} + H_2$

Overall reaction.

$$2Fe + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 2OH^-_{(aq)} + H_2.$$

Reactions to the formation of hydrated ferric oxide (rust).

$Fe^{2+} + 2OH^-_{(aq)} \rightarrow Fe(OH)_2.$

In presence of enough oxygen, ferrous hydroxide reacts with moisture and oxygen.

$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 2[Fe_2O_3 \cdot 3H_2O]$ (Yellow rust).

If the supply of oxygen is limited, the corrosion product may be black anhydrous.

$6Fe(OH)_2 + O_2 \longrightarrow 2[Fe_3O_4 \cdot 3H_2O]$ (Black rust).