Corrosion

When metals are exposed to atmospheric condition they react with air or water in the environment to form undesirable compound, usually oxides. This process is called corrosion. Almost all metal except the less reactive metal such as gold, platinum and Pd undergo corrosion. The produce eating away, disintegration, decaying or deterioration of a metal by chemical or electro-chemical reaction with its environment.

The Wet / Immersed / Electrochemical theory:- The tendency of a metal to pass into solution when immersed in a solution of its salt is measured in terms of electrode potential of a metal. The greater the difference in the potentials of the cathode and anode, the greater will be the corrosion. Also smaller the area of the anode as compared to the cathode, the more will be the attack.

Reaction @ Anode

$$M(s) \rightarrow M^{n+}(aq) + ne^-$$
$$Fe(s) \rightarrow Fe^{+2}(aq) + 2e^-$$
} oxidation

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

Cathode — The following reaction are involved ...

(a) hydrogen electrode or hydrogen type corrosion :-

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2$$
$$2H^+ + 2e^- \rightarrow H_2$$

ie $M \rightarrow M^{+2} + 2e^-$

ie $M + 2H^+ \rightarrow H_2 + M^{2+}$

for eg.- iron corrosion in acidic solution consists of two half cell.

$Fe \rightarrow Fe^{+2} + 2e^-$ (Anode Reaction)

$2H^+ + 2e^- \rightarrow H_2$ (Cathode Reaction)

(b) water electrode :- In oxidising acids, the cathodic reaction is the formation of water as a by-product.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

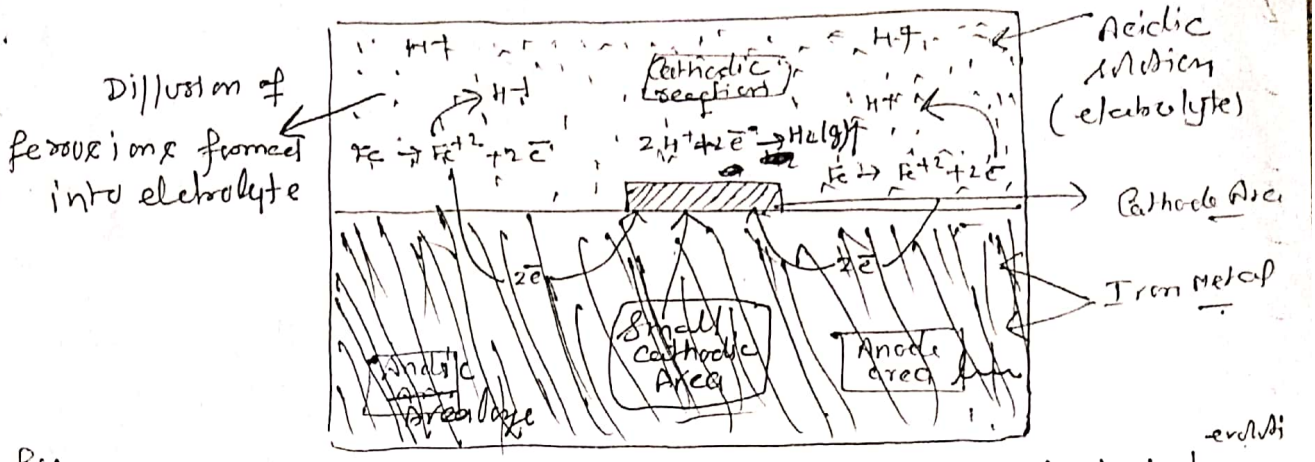


Fig: Diagrammatic representation of mechanism of wet corrosion by hydrogen evolution

(c) Oxygen electrode:-

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Corrosion of iron occurs by oxygen in the presence of aqueous solution. At anode iron dissolve to form ions as:

$$Fe \longrightarrow Fe^{+2} + 2e^- \quad \text{(Anode reaction)}$$

At Cathode: the electrons evolved by reaction will be intercepted by oxygen in presence of water.

$$2e^- + \frac{1}{2}O_2 + H_2O \longrightarrow 2OH^- \quad \text{(Cathode reaction)}$$

Overall reaction -

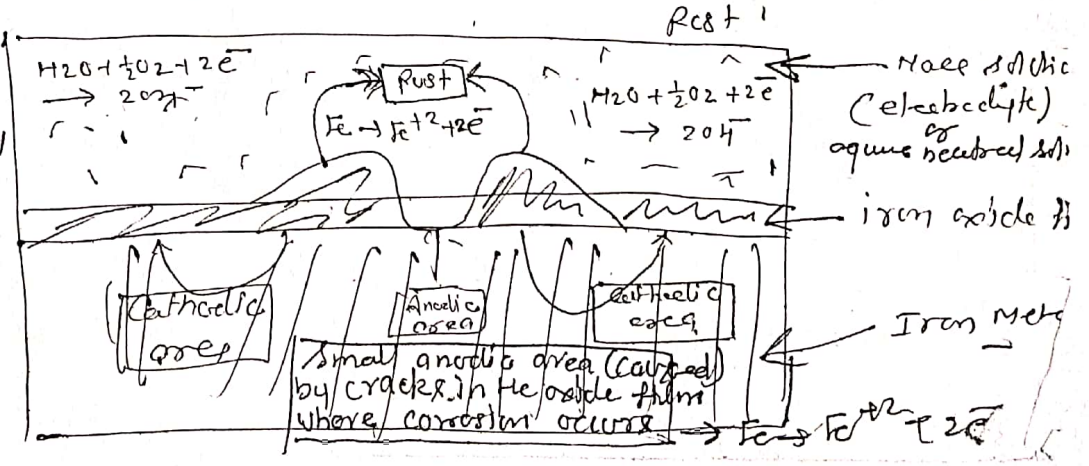
$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{+2} + 2OH^-$$

The OH^- ions produced reacts with the newly formed Fe^{+2} ion forming $Fe(OH)_2$ or rust. this process is known as rusting of iron.

$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow$$

Rust

Fig: Diagrammatic representation of wet corrosion mechanism by absorption of oxygen type corrosion.



(i) If enough oxygen is present

$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$ → yellow rust.

Fe^{+2} & Fe^{+3}

(ii) If the supply of oxygen is limited →

$6Fe(OH)_2 \longrightarrow Fe_3O_4 \cdot 6H_2O$ (black)

$Fe_2O_3 \cdot H_2O$

$(Fe_2O_3 \cdot FeO) \cdot 6H_2O$

Chemical Corrosion or Dry Corrosion or Direct chemical Attack Theory

It is type of corrosion which occurs through the action of atm. gases such as, O_2, X_2, SO_2, H_2S, N_2 etc. on the metal surface. A solid film of corrosion product is formed on the surface of the metal which resists further corrosion. However, if a liquid corrosion product is formed, then the metal is exposed to further attack. for eg, Cl_2 and I_2 attack silver, generating a protective film of silver halide. The three main type of...

(1) Oxidation Corrosion → that is direct chemical action of oxygen at low & high temperature on metals generally in the presence of moisture. Alkali & Alkaline metals (Mg, Ca, Ms etc) suffer extensive oxidation even at low temp., whereas high temp; practically all metals except Ag, Au and Pt are oxidized.

$$2M \longrightarrow 2M^{n+} + 2n\cdot e^- \quad (oxi.)$$

$$nO_2 + 2ne^- \longrightarrow 2nO^{2-} \quad (red.)$$

$$2M + nO_2 \longrightarrow 2M^{n+} + 2nO^{2-}$$

In high temp. oxidation of iron in dry air, three distinct metal oxide layers are formed on iron. Fe_2O_3 is the outermost layer, FeO is the innermost & Fe_3O_4 is the intermediate.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$
$$3Fe + 2O_2 \rightarrow Fe_3O_4$$
$$2Fe + O_2 \rightarrow 2FeO$$

Metal + oxygen → metal oxide (compound)

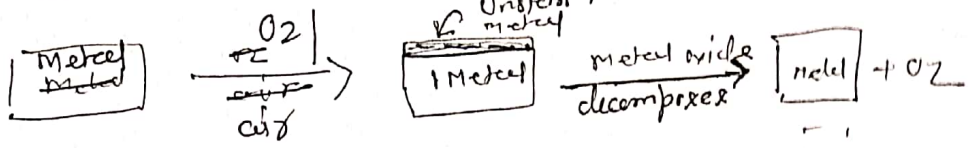
are thin they are

(i). Stable :- Such a film is protective in nature, thereby shielding the metal surfaces. The oxide films on Al, Sn, Pb, Cu and Pt etc. are stable, tightly adhering and impervious in nature.

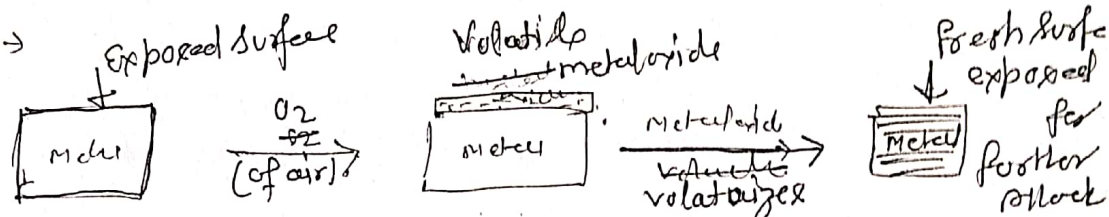
(ii) Unstable —

Metal oxide ⇌ Metal + oxygen

⇒ Ag, Au & Pt do not undergo.

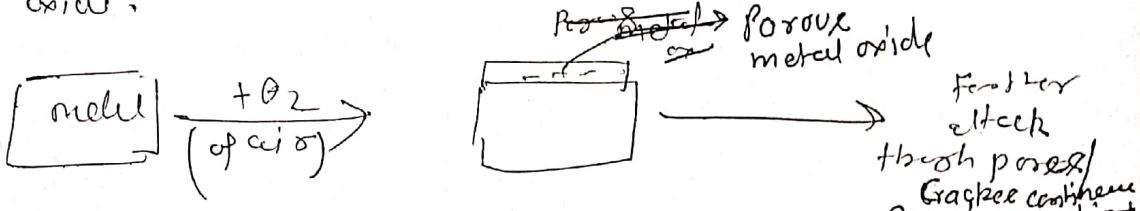


(iii) Volatile →



(iv) Porous :- The oxide film formed is having pores or cracks. MoO3

In such a case, the atmospheric oxygen have access to the underlying surface of metal through the pores or cracks of the layers, thereby the corrosion continues unobstructed till the entire metal is completely converted into the oxide.



(2) Corrosion by other gases :- Gases like CO_2, SO_2, Cl_2, H_2S & F_2 etc also cause corrosion of metals. The extent of corrosion depends mainly upon the chemical affinity between the metal and the gas involved. The degree of attack depends upon the formation of protective (non-porous) or non-protective (porous) films on the metal surfaces.

for eg. Ag cl layer formed from the attack of chlorine on silver metal is protective and non-porous. Therefore, the intensity of the attack decreases and protects the silver metal from further attack. In petroleum industry steel is attacked by H_2S gas at

at high temp. and FeS scale is formed. The silver metal also get tarnished by H_2S gas in presence of moisture.

$$Fe + H_2S \longrightarrow FeS + H_2$$

$$2Ag + H_2S \xrightarrow{H_2O} Ag_2S + H_2$$

(3) Liquid Metal Corrosion → This type of corrosion is due to the chemical action of flowing liquid metal at high temp. on solid metal or alloy. It occurs in devices used for nuclear power. The corrosion involves dissolution of a solid metal or intergranular penetration of the liquid metal into solid metal.

ATMOSPHERIC CORROSION :→ (1) Temp. → with increase of temp of environment the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosive medium increase. But the solubility of gases (like O_2) decrease with temp.

(2) Humidity → The higher the moisture content of the atmosphere, the greater is rate and extent of the corrosion because the moisture acts as medium for oxygen in air and behaves as electrolyte in air.

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

$$Fe(OH)_2 + CO_2 \longrightarrow Fe(HCO_3)_2O_2 \text{ and } CO_2Fe_3O_4 \cdot 3H_2O$$
(rust)

Like H_2O, CO_2, SO$_2$ and H_2S make the moisture acidity which consequently increases the corrosion rate. Similarly, in the marine atmosphere, the presence of sodium and other chlorides lead to increased conductivity of the liquid layer in contact with the metal surface, thereby corrosion rate is more.

(d) Nature of ions present:- due to the presence of ions, which accelerate the corrosion.

(e) Effect of pH:- Generally, acidic media are more corrosive than alkaline and neutral media.

(f) Conductance of the medium:- The greater the conductance, the more is the corrosion, eg:

(g) formation of oxygen concentration cell:- The rate of corrosion increases with increasing supply of oxygen or air to the moist metal surface.

PREVENTIVE METHOD & CORROSION CONTROL

The most important methods are:

(a) Proper design:- Proper design means the metals should keep contact with the corroding agents to a minimum and it is so designed that corrosion should be uniform localized and least intense.

(b) Joints should be properly designed to reduce the tendency for liquids to enter and be retained

(c) Contact between dissimilar materials for apart in the electrochemical series should be avoid.

(d) Using of high purity metal:- Always use pure metal, but it is difficult to prepare pure metal. Mechanical strength of pure metal is less.

(e) Use of Alloy conditions:- (a) Alloy should be completely homogeneous. Stainless steel contains chromium oxide films which protects further corrosion.

(f) Cathodic protection:- This method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.

(g) Using special heat treatment:- Heat treatment which leads to homogenisation of solid solutions, especially in cast alloys that are subject to coring, tends

to improve corrosion resistance. Heat treatment like annealing ⑦ helps to remove residual stresses which is carried out temps. below the lower critical line (1000 to 1200°F).

⑥ Use of Inhibitors ↦ Corrosion inhibitors are chemicals which when added to the corrosive solution in small quantities, effectively reduce or decrease its corrosive effect. In most cases the inhibitor will form a protective layer on the metal surface. The various inhibitors are:

⑦ Surface Coatings:- Surface coatings includes paints, salt and oxide films and metallic coatings. A coated surface isolates the underlying metal from the corroding environment. The only limitations of this method is the service behaviour of the protective coatings as the coating applied must be chemically inert to the particular environment.

⑧ Environment Modification:- The corrosive effect of the environment can be modified by removing the corrosive agents from the environment or by neutralising their corrosive effect by addition of specific substances.