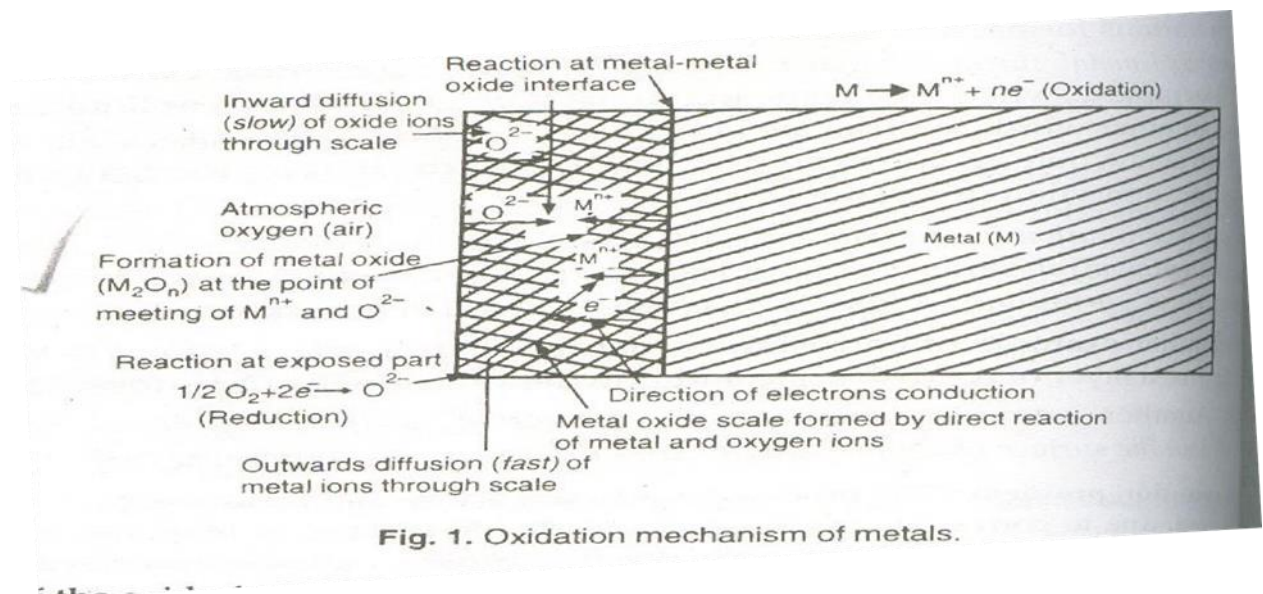
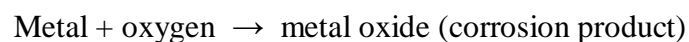


Mechanism of oxidation corrosion: - Oxidation occurs first at the surface of the metal and a scale of metal oxide is formed on the surface of the metal and it tends to act as a barrier for further oxidation.

Therefore, for oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion of the metal is generally much more rapid than the inward diffusion of oxygen. Since the metal ion is appreciably smaller than the oxide ion, therefore the metal ion has much higher mobility.



Nature of the oxide formed: - It plays an important role in further oxidation corrosion process.



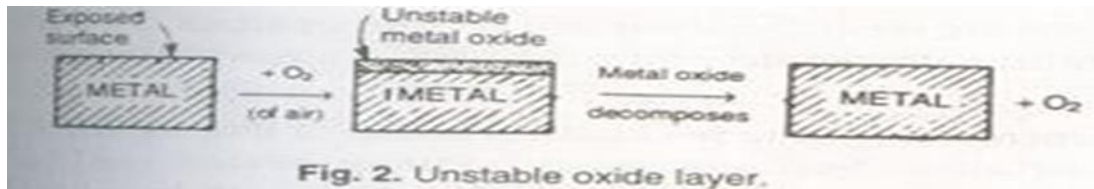
When the oxide film formed is

i) **Stable layer:** - A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

E.g.: Al, Sn, Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.

ii) **Unstable Layer**: - The oxide layer formed decomposes back into metal and oxygen
 $\text{Metal oxide} \rightarrow \text{metal} + \text{oxygen}$

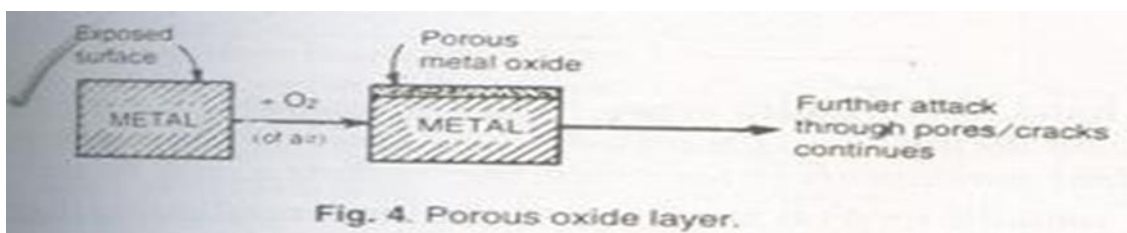
Consequently oxidation corrosion is not possible in such cases. **Eg**: Ag, Au and Pt do not undergo oxidation corrosion.



iii) **Volatile Layer**: The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion **eg**: Mo- molybdenum forms volatile MoO_3 layer.



iv) **Porous Layer**: Contains pores and cracks. In such a case the atmospheric oxygen has access to the underlying surface of the metal through the pores or cracks of the layer, there by corrosion continues until the entire metal is converted to its oxide.



Eg: Iron when attacked by H_2S at high temperature forms porous FeS layer.

Pilling – Bedworth rule: The oxide layer acts as a protective or non-porous barrier, if the volume of the oxide is at least as great as the volume of the metal from which it is formed .

On the other hand -if the volume of the oxide layer is less than the volume of metal, the oxide layer is porous and hence non-protective. Because it cannot prevent the access of oxygen to the fresh metal surface below. If the specific volume ratio is small, then rate of corrosion is

large. For eg: alkali and alkaline earth metals like Li, Na, K, Mg forms oxides of volume less than volume of metals. These layers are porous and non-protective. Hence these undergo corrosion more rapidly.

On the other hand metals like Al forms oxide whose volume is greater than the volume of the metal. Therefore Al forms a tightly – adhering non-porous protective layer.

Pilling Bedworth rule:

- To express the extent of protection given by the corrosion layer to the underlying metal Pilling Bedworth rule was postulated.
- It is expressed in terms of specific volume ratio.
- Specific Volume ratio= **Volume of metal oxide layer/ Volume of parent metal**
- Smaller the specific volume ratio, greater is the oxidation corrosion
- Eg. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten(W)
- If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous and does not allow the penetration of corrosive gases. No further corrosion.
- If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Explain the factors which influence the rate of corrosion?

Factors influencing corrosion:

- i) **Nature of metals**
- ii) **Nature of the corroding environment.**

Nature of metals:

1)*Position in galvanic series*:-The metal higher in series is more active and suffers corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

2)*Over voltage*: - when a metal, which occupies a high position in galvanic series (say Zinc), is placed in H_2SO_4 , it undergoes corrosion forming a film and hydrogen gas. The initial rate of reaction is quite slow, because of high over voltage (0.70 V) of the zinc metal, which reduces the effective electrode potential to a small value. However, if few drops of copper sulphate (CuSO_4) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal forming minute cathodes, where the hydrogen over voltage is only 0.33 V, thus, reduction in over voltage of the corroding metal/ alloy accelerates the corrosion rate. Zn has over hydrogen voltage due to which the rate of corrosion of Zn is very slow (Zn rod dipped in ZnSO_4). But when CuSO_4 solution is added to H_2SO_4 Cu gets deposited on Zn rod and acts as small cathode. For Cu higher over hydrogen voltage value is less. Hence rate of corrosion of Zn in presence of Cu becomes more. Thus metals for which over voltages are more get corrode slowly, where as those which have higher over voltages, the rate of corrosion is high.

Ex: corrosion of Zn rod dipped in H_2SO_4 is very slow. When small amount of CuSO_4 solution is added to H_2SO_4 , Cu gets deposited on the Zn rod and acts as cathode and the rate of corrosion of Zn increases. (Over voltage of Zn metal is 0.73)

3)*Purity of metal*: - Impurity of a metal generally causes heterogeneity and form minute electrochemical cells and the anodic part gets corroded. For eg: Zn metal containing impurity such as Pb (or) Fe undergoes corrosion. The rate and extent of corrosion increases with extent of impurities.

4)*Nature of the surface film*: - when metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For **eg**: the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Consequently the rate of oxidation corrosion is least for (w) tungsten.

5)*Nature of the corrosion product*:- a) Solubility of corrosion products : If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed **e.g**: PbSO_4 formation in case of Pb in H_2SO_4 .

b)*Volatility of corrosion products* : - If the corrosion product is volatile, it evaporates as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack.

This causes rapid and continuous corrosion. For **eg**: Mo forms MoO_3 volatile oxide.

Nature of the corroding environment:-

i) *Temperature*: With increase of temperature, the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosion medium increases.

ii) *Humidity*: The higher the humidity of the atmosphere the greater is rate and extent of corrosion because the moisture acts as medium for O₂ in air and behaves as an electrolyte.

For eg: atmospheric corrosion of iron is slow in dry air compared to moist air. Iron combines with O₂ and water to form ferrous hydroxide which combines with atmospheric CO₂ to form ferrous bicarbonate.



iii) *Effect of pH*: - Generally acidic media are more corrosive than alkaline and neutral media. Hence metals may be virtually classified according to pH range in which they will be affected (or) resistant. However atmospheric metals like Al, Pb etc. are corroded in alkaline medium and the corrosion rate of iron in O₂ free water is slow, until the pH is below Zn is rapidly corroded in weakly acidic solutions.

(iv) *Presence of impurities in atmosphere*: Atmosphere, in the vicinity of industrial area, contains corrosive gases like CO₂, H₂S, SO₂ and fumes of HCl, H₂SO₄ etc. In presence of these gases, the acidity of the liquid, adjacent to the metal surface, increases and its electrical conductivity also increases. This consequently results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.

(v) *Presence of suspended particles*: suspended particles are chemically active in nature [Like NaCl, (NH₄)₂ SO₄] absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.

(vi) *Nature of ions present*: Presence of anions like silicate in the medium leads to the formation of insoluble reaction products (e.g. silica gel) which inhibit further corrosion. On the other hand Cl⁻ ions present in the medium, destroy the protective and passive surface film, thereby exposing the metal/ alloy surface for fresh corrosion.

(vii) *Conductance of the corroding medium*: Conductance of dry sandy-soils is lower than those of clayey and mineralized soils. Consequently, stray currents will cause more severe

damage to the metallic structures, buried under clayey and mineralized soils than those under dry sandy –soils.

(viii) *Polarization of electrodes:*

- (i) If the cathode area is larger than the anode area, then the anodic current density, I_a (current flowing per unit surface area of anode) is greater than the cathodic current density, I_c evidently, the corrosion current (I_c) will be larger and hence, the anodic material undergoes accelerated corrosion.
- (ii) The greater the extent of polarization of either anode or cathode or both, the smaller is the corrosion current and hence, lower is the corrosion rate.
- (iii) If mainly anode, undergoes polarization, the corrosion current and corrosion rate is controlled by only anodic control polarization.
- (iv) If mainly cathode, undergoes polarization, the corrosion current and corrosion rate is controlled by only cathode control polarization.
- (v) If both the electrodes get polarized, the corrosion current and corrosion rate is controlled by both the electrodes.

GALVANIC SERIES:

In the electrochemical series, (reduction electrode potential arranged down in an increasing order), a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example, Li corrodes faster than Mg; Zn corrodes faster than Fe; corrodes faster than Sn; Cu corrodes faster than Ag and so on

Galvanic series give real and useful information for studying the corrosion of metals

Active (Or) **anodic**

↓↑

Mg
Mg alloys
Zn
Al
Cd
Al alloys
Mild steel
Cast iron
High nickel cast iron
Pb-Sn solder
Pb
Sn
Inconel
Ni-MO-Fe alloys
Brasses
Monel (7=Ni, 30=Cu, rest =Fe)
Silver solder

Cu
 Ni
 Cr stainless steel
 18-8 stainless steel
 18-8 MO Stainless steel
 Ag
 Ti
 Graphite
 Au
 Pt

Noble (Or cathodic)

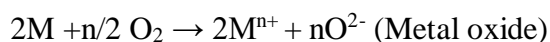
Corrosion: Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, is called corrosion.

Examples:-

- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.
- ii) Formation of green film of basic carbonate- $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of copper when exposed to moist air containing CO_2

Corrosion is an oxidation process and it is reverse of metal extraction.

The reactions in the oxidation corrosion are:



Causes of corrosion: 1. The metals exist in nature in the form of their minerals or ores in the stable combined forms as oxides, chlorides, silicates, carbonates and sulphides.

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

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

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

5. When metal is exposed to atmospheric gases, moisture, liquids etc, the metal surface reacts and forms more thermodynamically stable compounds.

Effects of corrosion: 1. Wastage of metal in the form of its compounds.

2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced

Disadvantages of corrosion: The process of corrosion is slow and occurs only at surface of metals but the losses incurred are enormous. Destruction of machines, equipment, building materials and different types of metallic products, structures etc. Thus the losses incurred are very huge and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over the world.

Theories of corrosion: - Corrosion can be explained by the following two theories .

1. Dry or chemical corrosion.
2. Wet or electrochemical corrosion.

Q1. Explain dry corrosion in detail.

Dry or Chemical corrosion: -

This type of corrosion occurs mainly by the direct chemical action of the environment i.e., by the direct attack of atmospheric gases such as O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquids on the metal surface with which they are in contact. There are 3 main types of chemical corrosion.

- 1) Corrosion by oxygen (or) oxidation corrosion.
- 2) Corrosion by other gases like SO_2 , CO_2 , H_2S and F_2 etc.
- 3) Liquid metal corrosion.

Wet Corrosion or Electrochemical Corrosion

- The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electrochemical cells.
- It is a common type of corrosion which occurs usually in aqueous corrosive environment
- Occurs when metal comes in contact with a conducting liquid.
- Formation of galvanic cell on the surface of metal generating anodic and cathodic areas
- At anode oxidation takes place liberating electrons.

- Electrons at anode are transported to cathodic area where H^+ or O_2 and H_2O consumes the electrons generating non-metallic ions like OH^- or O^{2-}
- Metallic (M^+) and non metallic (OH^- or O^{2-}) diffuse towards each other and results in the formation of corrosion product in between the anodic and cathodic area.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

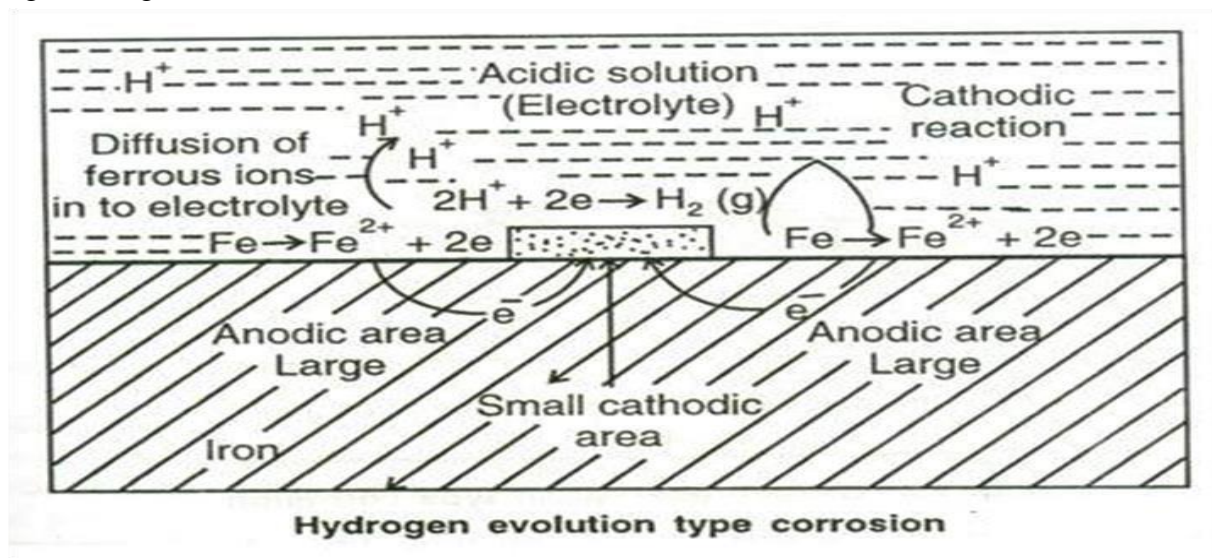
Wet corrosion takes place in two ways.

1. Evolution of Hydrogen
2. Absorption of Oxygen

Evolution of Hydrogen:

This type of corrosion occurs in acidic medium.

Eg: Rusting of iron



At Anode dissolution of iron to ferrous ion takes place with the liberation of electrons

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)

The electrons released at anode flow through the metal from anode to cathode, where as H^+ ions of acidic solution take up these electrons and eliminated as hydrogen gas

Cathode: $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (Reduction)

The overall reaction is: $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow$

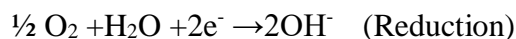
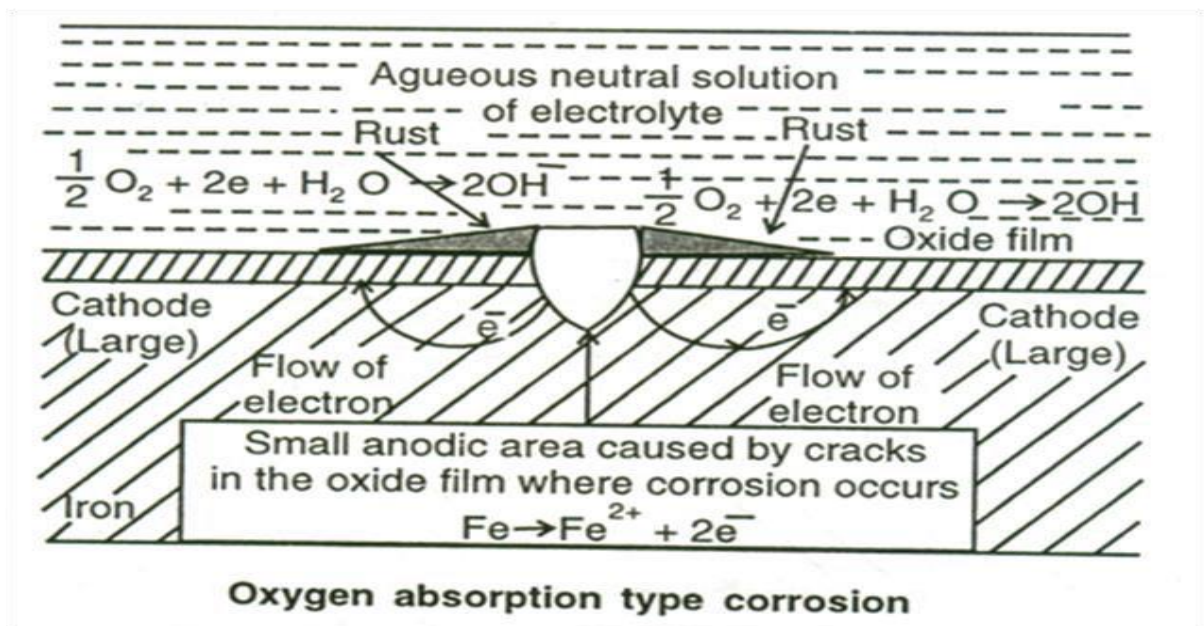
This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.

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

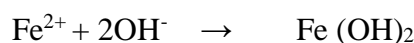
Absorption of Oxygen:

- This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- For example, rusting of iron in neutral or basic aqueous solution of electrolyte in presence of atmospheric oxygen.
- Usually the surface of iron is coated with a thin film of iron oxide.
- If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
- It shows that anodic areas are small and the cathodic areas are large.

Anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)



The Fe^{2+} ions and OH^- ions diffuse and when they meet, ferrous hydroxide is precipitated.



If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide

