

## CORROSION AND ITS CONTROL

**Introduction:** - Many metals exist in nature in combined form as their oxides, carbonates, sulphides, chlorides and silicates (except noble metals) such as Au (gold), Pt (Platinum) etc. During extraction process these are reduced to their metallic state from their ores and during extraction of ores considerable amount of energy is required.

Compounds are in lower energy state than the metals. Hence when metals are put into use in various forms, they get exposed to environment such as dry gases, moisture, liquids etc. and slowly the exposed metal surface begin to decay by conversion into a compound.

**Definition:** - Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment at its surface is called corrosion. Thus corrosion is a reverse process of extraction of metals.

Examples:-

- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of  $\text{Fe}_3\text{O}_4$  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  $\text{CO}_2$ .

**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.

### **Dry or Chemical corrosion: -**

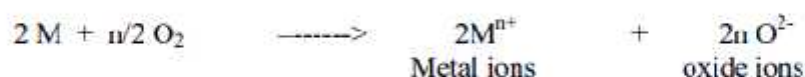
This type of corrosion occurs mainly by the direct chemical action of the environment i.e., by the direct attack of atmospheric gases such as  $\text{O}_2$ , halogens,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{N}_2$  or anhydrous inorganic liquids on the metal surface with which they are in contact. There are 3 main types of chemical corrosion.

- 1) Corrosion by oxygen (or) oxidation corrosion.
- 2) Corrosion by other gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{F}_2$  etc.
- 3) Liquid metal corrosion.

### Oxidation corrosion:-

- It is brought about by direct action of oxygen at low (or) high temperatures, usually in the absence of moisture.
- At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, and Pt.
- At ordinary temp generally all the metals are slightly attacked. However alkali metals – Li, Na, K, Rb etc. and alkaline earth metals – Be, Ca, Sr etc. are attacked very rapidly and get oxidized readily.

The reactions in the oxidation corrosion are



**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.

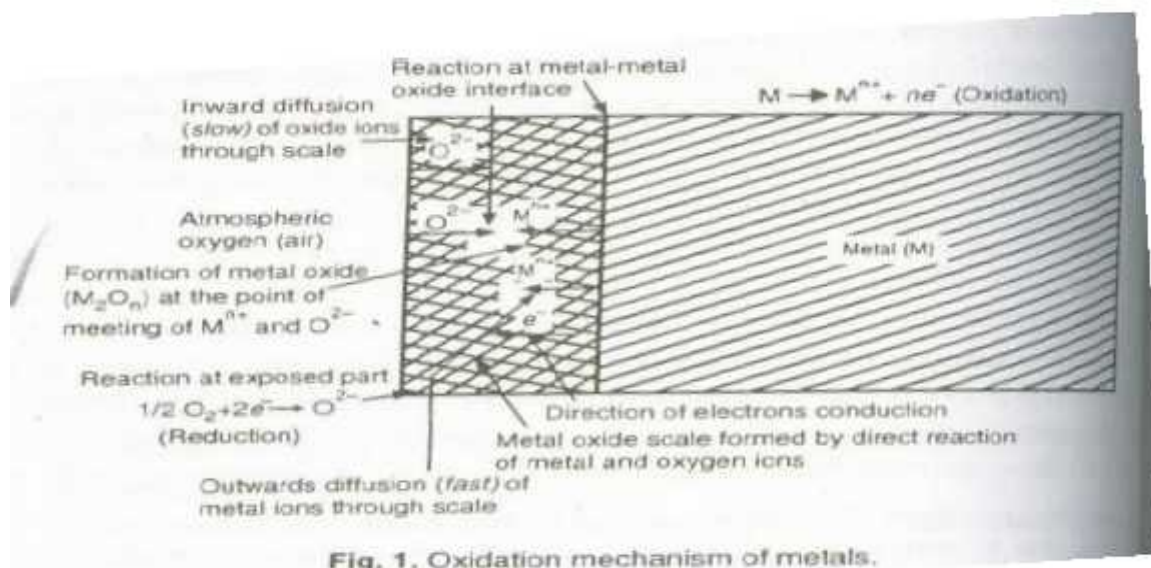


Fig. 1. Oxidation mechanism of metals.



**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



Consequently oxidation corrosion is not possible in such cases.

Eg: Ag, Au and Pt do not undergo oxidation corrosion.

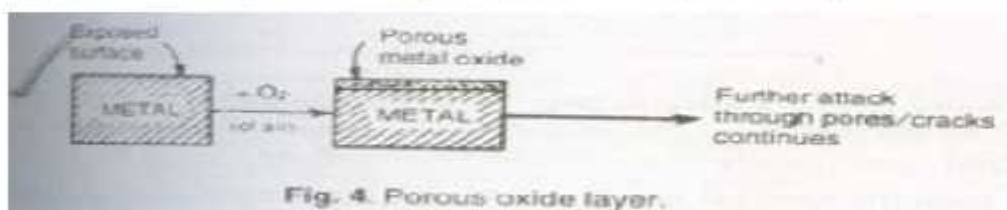


- iii) **Volatile Layer:** The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile  $\text{MoO}_3$  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  $\text{H}_2\text{S}$  at high temperature forms porous  $\text{FeS}$  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.

### ***Wet (or) electrochemical corrosion:-***

This type of corrosion is observed when

- A conducting liquid is in contact with a metal (or)
- When two dissimilar metals (or) alloys are either immersed (or) dipped partially in a solution.
- The corrosion occurs due to the existence of separate anodic and cathodic areas or parts between which current flows through the conduction soln.
- In the anodic area oxidation reaction takes place so anodic metal is destroyed by dissolving (or) forming a compound such as an oxide.
- Hence corrosion always occurs at anodic areas

∴ At Anode



∴ At cathode



- In cathodic area, reduction reaction (gain of  $e^{-}$  s) takes place. The metal which is acting as cathode is in its reduced form only. Therefore it cannot be further reduced. Therefore cathodic reactions do not affect the cathode.
- So at cathodic part dissolved constituents in the conducting medium accept the electrons to form some ions like  $OH^{-}$ ,  $O_2^{-}$  etc.
- The metallic ions from anodic part and non-metallic ions from cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.
- The  $e^{-}$  s which are set free at anodic part flow through the metal and are finally consumed in the cathodic region.

Thus we may sum up that electrochemical corrosion involves:

- i) The formation of anodic and cathodic areas.
- ii) Electrical contact between the cathodic and anodic parts to enable the conduction of electrons.
- iii) An electrolyte through which the ions can diffuse or migrate this is usually provided by moisture.
- iv) Corrosion of anode only
- v) Formation of corrosion product is somewhere in between cathode and anode.

***Mechanism of wet or electrochemical corrosion:-***

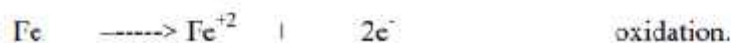
In wet corrosion the anodic reaction involves- the dissolution of metal as corresponding metal ions with the liberation of free electrons:



Whereas the cathodic reaction consumes  $e^{-}$ s either by a) evolution of hydrogen b) or by absorption of oxygen depending on the nature of the corrosive environment.

***Evolution of hydrogen:*** occurs

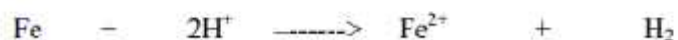
- In acidic environments.
- For eg in the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of  $e^{-}$ s.



- These electrons flow through the metal from anode to cathode (acidic region) where  $H^{+}$  ions are eliminated as  $H_2$  gas.



- The overall reaction is



- This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.
- In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.



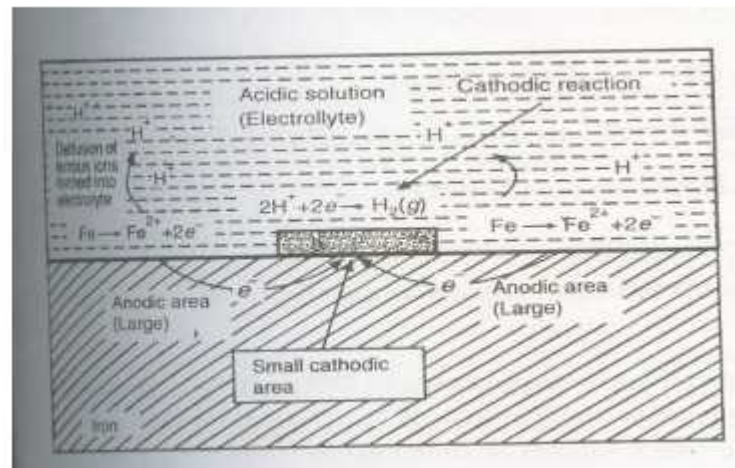


Fig. 5. Mechanism of wet corrosion by hydrogen evolution.

**Absorption of oxygen type corrosion:** Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.

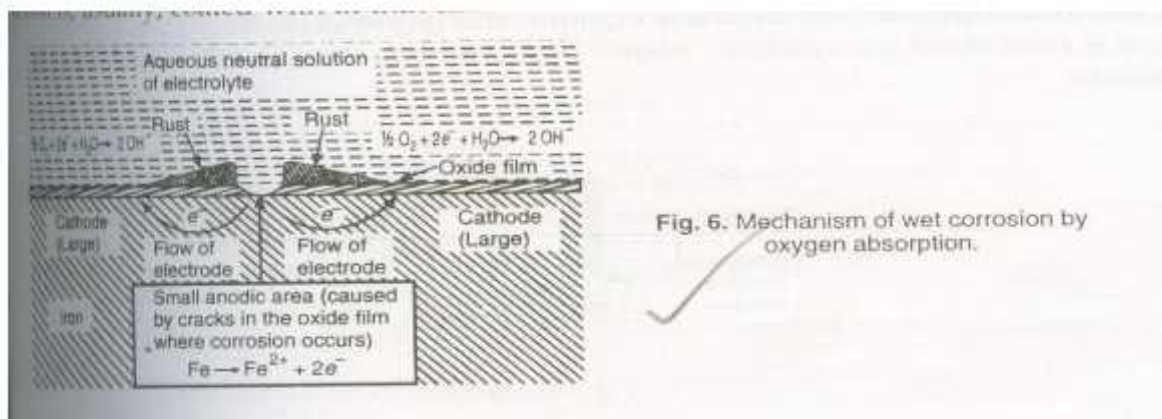
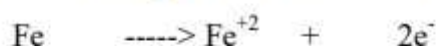


Fig. 6. Mechanism of wet corrosion by oxygen absorption.

- The surface of iron will be usually coated with a thin film of iron oxide. However if this oxide film develops some cracks, anodic areas are created on the surface.
- While pure metal parts act as cathode.
- Thus anodic areas are very small surface parts.
- The rest of the surface of the metal forms cathodes.
- Thus at the anodic part iron metal dissolves as  $\text{Fe}^{+2}$  ions with the liberation of  $\text{e}^-$  s.



- The liberated  $\text{e}^-$  s flow from anodic to cathodic areas through iron metal during which they interact with dissolved oxygen and moisture.



- The  $\text{Fe}^{+2}$  ions and  $\text{OH}^-$  ions diffuse and form ferrous hydroxide precipitate when they meet with each other



- If enough  $\text{O}_2$  is present  $\text{Fe}(\text{OH})_2$  is easily oxidized to  $\text{Fe}(\text{OH})_3$  (ferric hydroxide)



The product called yellow rust actually corresponds to  $\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$ .

- If the supply of  $\text{O}_2$  is limited, the corrosion product may be even black anhydrous magnetite  $\text{Fe}_3\text{O}_4$ .