Corrosion

Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

- Corrosion is termed as the (electro)chemical reaction between a material and its environment that leads to deterioration of the material and/or its properties
- It is a <u>process</u> through which metals in manufactured states return to their natural oxidation states

$$\text{Metal ores} \underset{\text{Corrosion}}{\overset{\text{Metallurgical extraction}}{\rightleftharpoons}} \text{Metal}$$

- This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings, often by oxygen in air
- The reaction is both spontaneous & electrochemically favoured.
- Corrosion is essentially the creation of voltaic/ galvanic cells where the metal in question acts as an anode and generally deteriorates or loses functional stability.

<u>Effects of corrosion</u>

- Loss of metal/metal thickness = Loss of efficiency = Loss of time
- **Reduction in value:** Loss of valuable materials such as *blockage of pipes, mechanical damage of underground water pipes*
- **Mechanical damage:** Accidents due to mechanical loss of metallic bridges, cars, aircrafts
- **Pollution:** Causes pollution due to escaping products from corrosion (Contamination of fluids in vessels and pipes)

Common Metals/Alloys

Iron:

- Main corrosion product is rust or iron oxides
- The most familiar form of rust is the reddish coating that forms flakes on iron and steel (Fe_2O_3)
- Rust also comes in other colors, including Yellow, Brown, Orange, and even Green! The different colors reflect various chemical compositions of rust.

Steel:

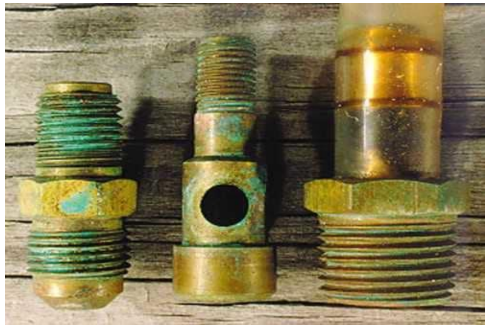
- These contain Fe, C, Cr, Ni, Mo etc.
- Main corrosion product is iron oxides – those similar to iron
- Along with iron, other alloying metals (Ni, Cr, Mo) also get corroded due the formation of corresponding oxides

Copper:

- Main corrosion products are $CuCO_3 + Cu(OH)_2$, patinas as Cu_2O

Brass and Bronze:

- Brass contains Cu, Zn
- Bronze contains mainly Cu, Sn
- Main corrosion products are similar to copper corrosion products



Reason of corrosion

- In nature, most metals (except Au, Pt, etc) prefer existing as thermodynamically more stable compounds, such as, their oxides, carbonates, chlorides, silicates etc.
- During the extraction process at high temperature, the metallic compounds are reduced to their pure metallic state which is, thermodynamically unstable state.
- The extracted/reduced pure metal will always have a strong tendency to convert itself into the more stable metallic compound oxidized state through corrosion.
- The Gibbs free energy changes of forming oxide and sulphides are negative, so oxidation reaction is usually spontaneous.

$$\text{Metal} \underset{\text{Extraction of Metals}}{\overset{\text{Corrosion (Oxidation)}}{\rightleftharpoons}} \text{metallic compounds + Energy}$$

Types of corrosion

- Corrosion is classified on the basis of nature of the Corrodent, Mechanism of corrosion, and Appearance of the corroded metal

- **Dry corrosion (chemical corrosion):**

  Classified depending on the corroding agent:

  (i) Corrosion by oxidation,

  (ii) Corrosion by gases other than oxygen

  (iii) Corrosion by liquid metals.

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

  (i) Evolution of hydrogen-type corrosion,

  (ii) Consumption of oxygen-type corrosion,

  (iii) Galvanic or bimetallic corrosion,

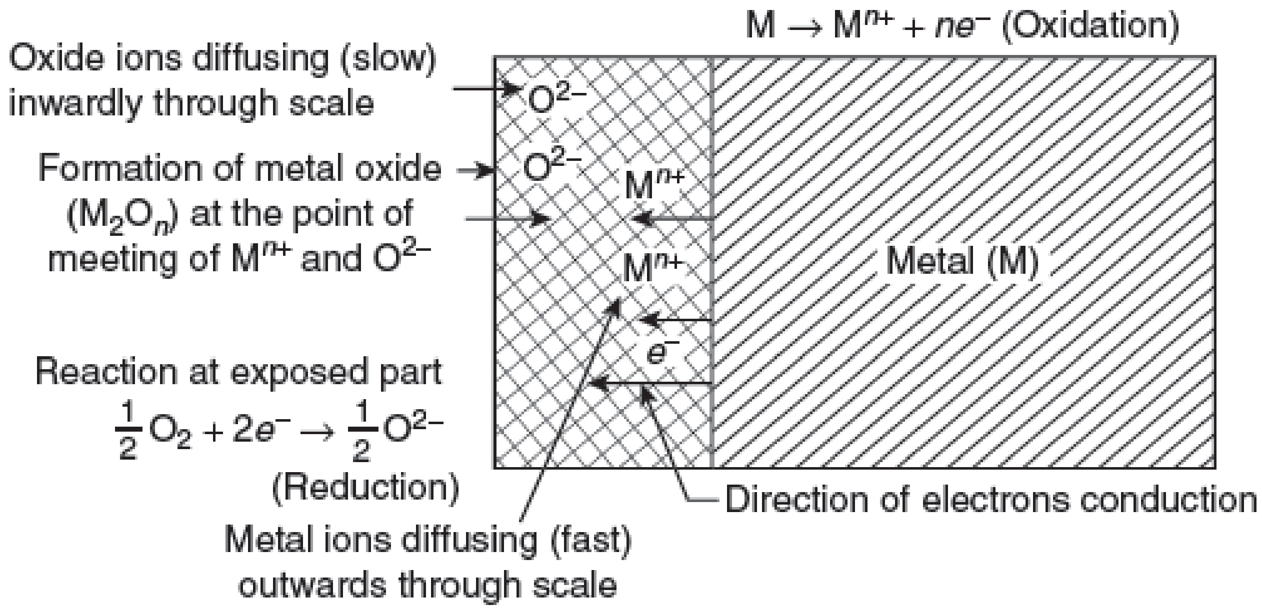
  (iv) Concentration cell corrosion (or water line corrosion).

Dry Corrosion

- This corrosion occurs due to the direct chemical attack of atmospheric gases such as O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquids on the metal surface.
- Dry corrosion occurs when there is no moisture or water to aid corrosion
- This process is very sensitive to temperature. Under hot conditions, dry corrosion occurs at a much faster rate
- Corrosion is due to adsorption & the corrosion products, generally, accumulate in the same spot where corrosion occurs
- Main types of dry corrosion are
  - Corrosion by oxygen/oxidation corrosion
  - Corrosion by other gases like H_2S, SO_2, N_2, CO_2, F_2 etc.
  - Liquid metal corrosion/Erosion Corrosion

Oxidation Corrosion

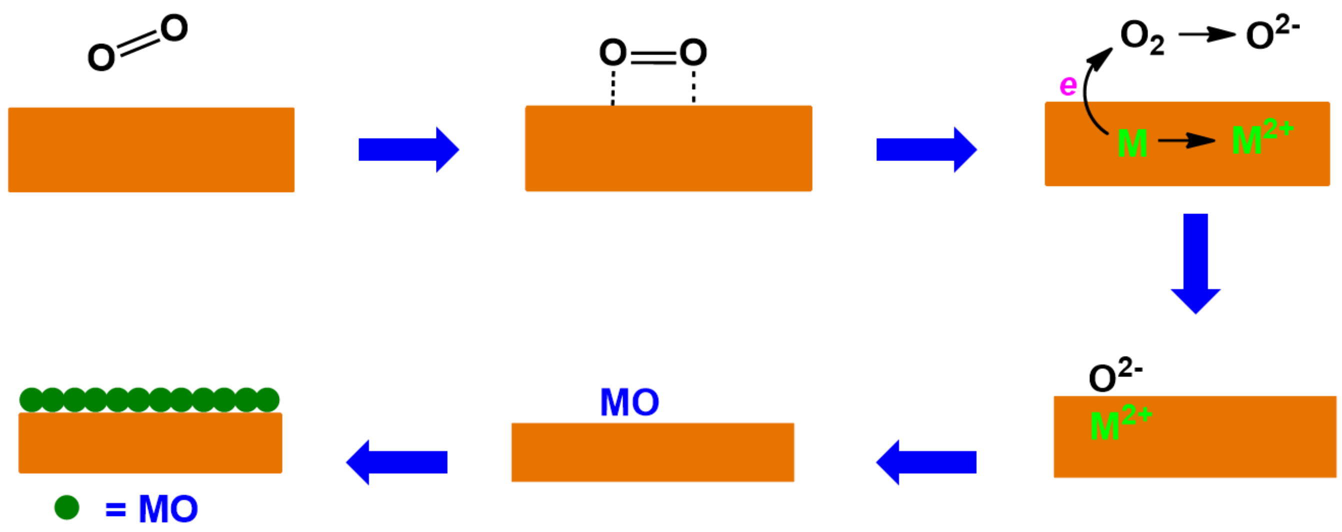
- Direct action of oxygen in the absence of moisture at high/low temp. leads to oxidation corrosion
- At high temp. all metals are attacked by oxygen – except noble metals like Ag, Au, Pt. At ambient temp. generally metals are slightly attacked
- Alkali metals & alkaline earth metals get oxidized readily



- When oxidation starts, a thin layer of oxide film will be formed on the surface and the nature of the film decides the further action (Porous/non-porous film)

Oxidation Corrosion

Mechanism



- Oxidation takes place first at the surface of the metal
- Adsorption of oxygen on to the metal surface
- Loss of electron from the metal and gain of electron by oxygen
- Dissociation of oxygen
- <u>Formation of oxide layer onto the metal surface</u>

- For oxidation, either the metal must diffuse outwards through the oxide layer to the surface or the oxygen must diffuse inwards through the oxide layer 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.
- This diffusion is driven by the <u>size of metal and oxide ion</u>

- <u>Types of oxide layers:</u> Nature of the oxide formed plays an important part in oxidation corrosion process. As the oxide layer grows the rate of electron transfer decreases. The corrosion can be stopped and the metal can be passive
  - Stable: Oxides of Al, Cu, Pb, Sn
  - Unstable: Ag, Pt, Au
  - Volatile: Molybdenum oxide
  - Porous: Oxide of Li, Na, Mg

Oxide Layers

Stable (protective) oxide layer

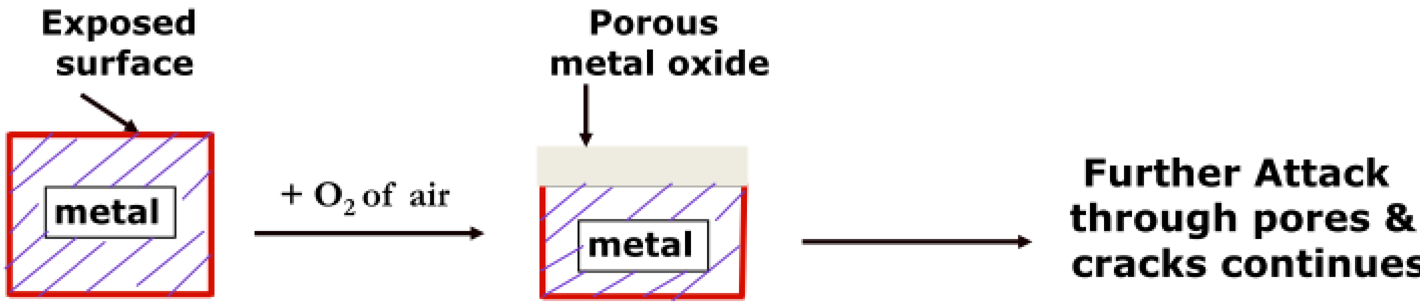
- It is a fine grain of oxide layer which is non-porous and adheres strongly to the metal. Oxides of Al, Pb, Cu, Ni and Cr which form stable, non-porous & tightly adhering impervious metal-oxide films (~ 30 nm thick) to the pure metallic surface.
- Such layers prevents oxygen from diffusing through the metal and further attack is stopped. Further oxidation corrosion is stopped

Unstable oxide layer

- Oxide layers produced on noble metal surfaces (Pt, Ag etc.) immediately decompose back into the metal and oxygen, thereby preventing oxidation corrosion

$$\text{Metallic oxide} \rightleftharpoons \text{Metal} + \text{Oxygen}$$

Porous oxide layer:

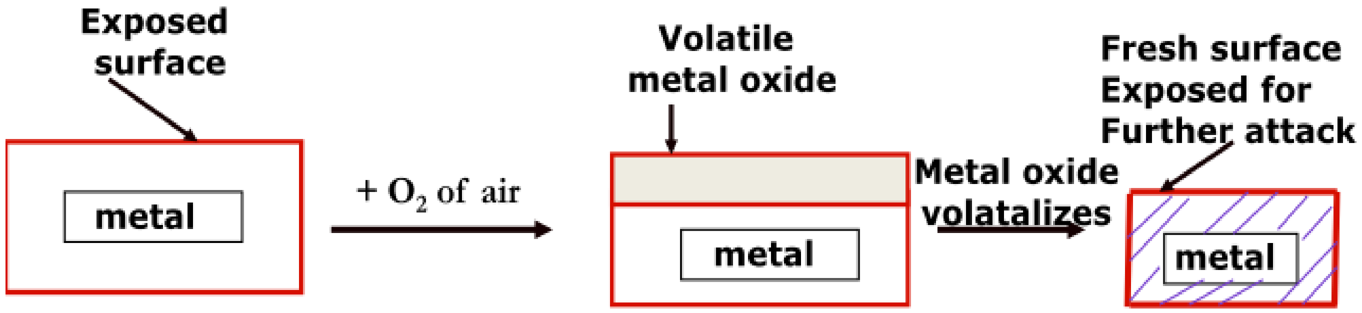


Porous oxide layer

- These oxide layers have minute pores.
- Oxygen will diffuse through these pores and cracks promoting further corrosion.
- ✓ Fe is a good example of this type of corrosion. Iron when attacked by H_2S at high temperature forms porous FeS layer

Oxide Layers

❑ Volatile oxide layer



Volatile metal oxide

- These are oxide layers which evaporate as soon as they are formed and hence further corrosion is facilitated.
- The underlying metal surface is exposed for further corrosion. After some time the metal itself will disappear.
- ✓ Molybdenum (Mo) is an example of volatile oxide layer corrosion. MoO_3 is volatile (*MoO_2 is non-volatile*).

❑ Pilling – Bedworth rule

- The protective/non-protective nature of the oxide film is determined by Pilling-Bedworth rule
- The ratio of the volume of the oxide formed to the volume of the metal consumed is called as Pilling-Bedworth ratio

$$\boxed{R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}}$$

R_{PB} = Pilling–Bedworth ratio, M = Atomic/Molecular mass, n = number of atoms of metal per 1 molecule of the oxide, ρ = density, V = volume.

- If $V_{oxide} > V_{metal}$: The oxide layer is protective and non-porous
  - ✓ Aluminium forms Aluminium oxide whose volume is greater than the volume of the metal (Al). These do not undergo corrosion rapidly. Other metals: Cu, In, Al, Ni, Cr
- If $V_{oxide} < V_{metal}$: The oxide layer is non protective and porous
  - ✓ Alkali and alkaline earth metals like Li, Na, K – these undergo corrosion more rapidly

Corrosion by other gases

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- **Main types of dry corrosion are**
  - Corrosion by oxygen/oxidation corrosion
  - **Corrosion by other gases like H_2S, SO_2, N_2, CO_2, F_2 etc.**
  - Liquid metal corrosion/Erosion Corrosion

⇒ **In dry atmosphere CO_2, Cl_2, SO_2, F_2, NO_x etc. are gases which can attack the metal and corrode**

⇒ **Extent of corrosion depends on the affinity of the metal to the gas.**

⇒ **These gases chemically react with the metal forming either porous or non-porous layers of films**

⇒ **Protective/non-porous layer prevents from further attack, whereas non-protective/porous layer expose the underlying fresh metal surface for further attack.**

⇒ **H_2S gas attacks steel and make them brittle**

$2\,Ag + Cl_2 \rightarrow 2\,AgCl$ non-porous layer

$Fe + H_2S \rightarrow FeS + H_2$ porous layer

$Sn + 2\,Cl_2 \rightarrow SnCl_4$ volatile layer

- **Liquid metal corrosion/Erosion Corrosion**

- **Liquid metal (Hg, Zn, Sn, Pb, Cd etc.) flowing at high temperature over the solid metal or alloy can result in**

⇒ **dissolution of solid metal by liquid metal**

⇒ **internal penetration of the liquid metal into the solid metal**

This type of corrosion is experienced in pipe lines used in oil and refineries. Liquid mercury dissolves most metals by forming amalgams, thereby corroding them.

In devices used in nuclear power plants – it causes brittle failure of metal structure