

Introduction

- ❖ A pure metal exists in nature as more stable forms such as oxide, sulphides, carbonates etc..
- ❖ For getting pure metals these more stable forms are reduced where in large amount of energy is required.
- ❖ Thus metals can be considered as being present in their excited state.
- ❖ Therefore most metals have a tendency to revert back to their more stable (low energy) state.
- ❖ Hence when a metal surface is exposed to environment such as gases, liquids, moisture etc, it starts to react and begin to decay leading to its destruction.

Definition of Corrosion

Any process of destruction and consequent loss of solid metallic material, through the unwanted chemical or electrochemical attack by its environment , starting at its surface is called as corrosion.

Types of Corrosion

- ❖ Dry or chemical Corrosion
- ❖ Wet or electrochemical Corrosion
 - ❖ Galvanic corrosion
- ❖ Concentration cell corrosion
 - ❖ Pitting Corrosion
- ❖ Intergranular corrosion
- ❖ Waterline corrosion
- ❖ Stress corrosion

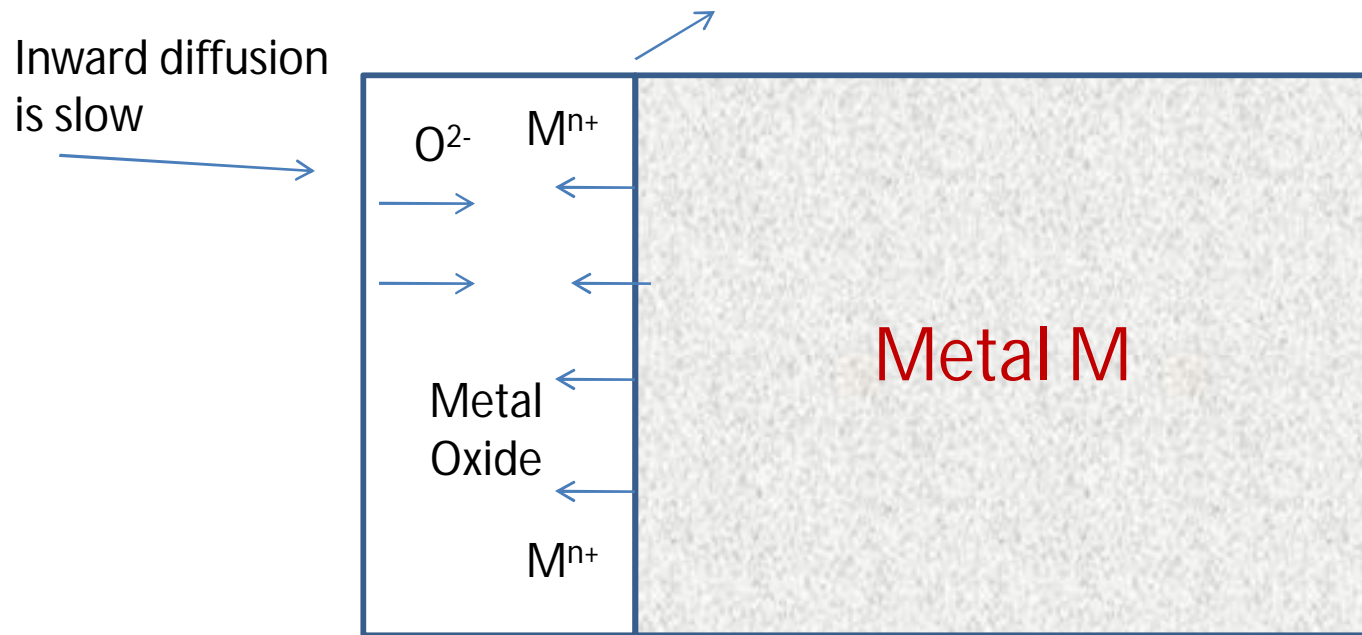
Dry or Chemical Corrosion

1. Oxidation Corrosion
2. Corrosion due to other gases like SO_2 , CO_2 , Cl_2 , H_2S etc.
3. Liquid metal corrosion

Oxidation Corrosion

- ❖ Takes place by direct reaction of oxygen with metal at low or high temperatures.
- ❖ Normally at low temperatures only a few metals such as Li, Na, K are attacked.
- ❖ At high temperatures almost all except Ag, Au and Pt are attacked.





The formation of metal oxide is in the form of a thin film in the beginning. The nature of this thin layer decides further course of corrosion

- ❖ Stable film: Acts as a protective coating. This shields the remaining metal from corrosion.
- ❖ Unstable: The formed layer decomposed back into metal and oxygen. Therefore no corrosion takes place.
- ❖ Volatile: Leads to rapid corrosion.
- ❖ Porous: Also leads to faster corrosion.

Pilling Bedworth Rule:

"An oxide is protective or non porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed".

OR

"If the volume of the oxide is less than the volume of the metal then the oxide layer is porous and hence non protective because it can not prevent the access of oxygen to fresh metal surface below."

Corrosion due to other gases like SO_2 , CO_2 , Cl_2 , H_2S etc.

- ❖ Depends on the chemical affinity between the metal and gas involved.
- ❖ Formation of protective (AgCl) or non protective film (SnCl_4) on metal surface.

Wet or Electrochemical Chemical Corrosion

The conditions under which wet corrosion takes place are

1. When a conducting liquid is in contact with a metal
2. When two dissimilar metals or alloys are in dipped partially in a solution.

Under such conditions separate anodic and cathodic regions are created between which current can flow through conducting liquid.

At anodic area oxidation takes place i.e. liberation of free electrons and metal is destroyed by either dissolving or having a combined state like forming an oxide etc.

Corrosion always occurs at anodic areas.

At anode:



Mechanism of wet corrosion

- ❖ It involves current flow between anodic and cathodic regions.
- ❖ At anode dissolution of metal forming corresponding metal ions and liberation of free electrons takes place.
- ❖ These liberated electrons are consumed in the cathodic reaction by two possible ways.
 - ❖ 1. Evolution of hydrogen or,
 - ❖ 2. absorption of oxygen

Evolution of Hydrogen type corrosion

- ❖ Evolution of hydrogen type corrosion takes place normally in acidic environments.
- ❖ This type of corrosion involves displacement of hydrogen ions from the acidic solution by metal ions.
- ❖ Therefore all the metals above hydrogen in the electrochemical series have a tendency to dissolve in acidic solution by liberation of hydrogen.



Overall Reaction



Red. \leftrightarrow Ox + e ⁻	E ⁰ [V]
Li \leftrightarrow Li⁺ + e⁻	-3.045
K \leftrightarrow K ⁺ + e ⁻	-2.925
Ca \leftrightarrow Ca ²⁺ + 2e ⁻	-2.866
Na \leftrightarrow Na ⁺ + e ⁻	-2.714
Mg \leftrightarrow Mg ²⁺ + 2e ⁻	-2.363
Al \leftrightarrow Al ³⁺ + 3e ⁻	-1.662
Mn \leftrightarrow Mn ²⁺ + 2e ⁻	-1.180
Zn \leftrightarrow Zn ²⁺ + 2e ⁻	-0.7627
Cr \leftrightarrow Cr ³⁺ + 3e ⁻	-0.744
Cd \leftrightarrow Cd ²⁺ + 2e ⁻	-0.4029
Fe \leftrightarrow Fe ²⁺ + 2e ⁻	-0.4002
Co \leftrightarrow Co ²⁺ + 2e ⁻	-0.277
Ni \leftrightarrow Ni ²⁺ + 2e ⁻	-0.250
Pb \leftrightarrow Pb ²⁺ + 2e ⁻	-0.126
H₂ \leftrightarrow 2H⁺ + 2e⁻	±0.0000
CH ₄ \leftrightarrow C + 4H ⁺ + 4e ⁻	+0.1316
Cu ⁺ \leftrightarrow Cu ²⁺ + e ⁻	+0.153
Cu \leftrightarrow Cu ²⁺ + 2e ⁻	+0.337
2OH ⁻ \leftrightarrow ½ O ₂ + H ₂ O + 2e ⁻	+0.401
I ⁻ \leftrightarrow ½ I ₂ + e ⁻	+0.5355
Fe ²⁺ \leftrightarrow Fe ³⁺ + e ⁻	+0.771
Ag \leftrightarrow Ag⁺ + e⁻	+0.7991
Hg \leftrightarrow Hg ²⁺ + 2e ⁻	+0.854
Hg ₂ ²⁺ \leftrightarrow 2Hg ²⁺ + 2e ⁻	+0.9075
Pd \leftrightarrow Pd ²⁺ + 2e ⁻	+0.987
Br ⁻ \leftrightarrow ½ Br ₂ + e ⁻	+1.0652
Pt \leftrightarrow Pt²⁺ + 2e⁻	~+1.2
Cl ⁻ \leftrightarrow ½ Cl ₂ + e ⁻	+1.3595
Au ⁺ \leftrightarrow Au ³⁺ + 2e ⁻	+1.402
Au \leftrightarrow Au³⁺ + 3e⁻	+1.498
Pb ²⁺ \leftrightarrow Pb ⁴⁺ + 4e ⁻	+1.80
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F ⁻ \leftrightarrow ½ F ₂ + e ⁻	+2.87
HF (aq) \leftrightarrow ½ F₂ + H⁺ + e⁻	+3.06



- Power of reduction increases
- Oxidability increases
- Metals become ignoble

- Metals become noble
- Power of oxidation increase
- Reductibility increases

Absorption of Oxygen type corrosion

- ❖ A common example of this type of corrosion is the rusting of Fe in natural aqueous solution like salt solution.
- ❖ The surface of iron is usually coated with a thin film of oxide but if the film develops cracks, it generates anodic areas on the surface.
- ❖ The metal parts acts as cathodes.



❖ At anodic areas Fe metal dissolves forming Fe^{2+} ions with liberation of free electrons.



❖ These liberated electrons reach the cathodic areas where it react with the dissolved oxygen forming hydroxide ions



❖ The Fe^{2+} ions and OH^{-} ions meet together forming $\text{Fe}(\text{OH})_2$

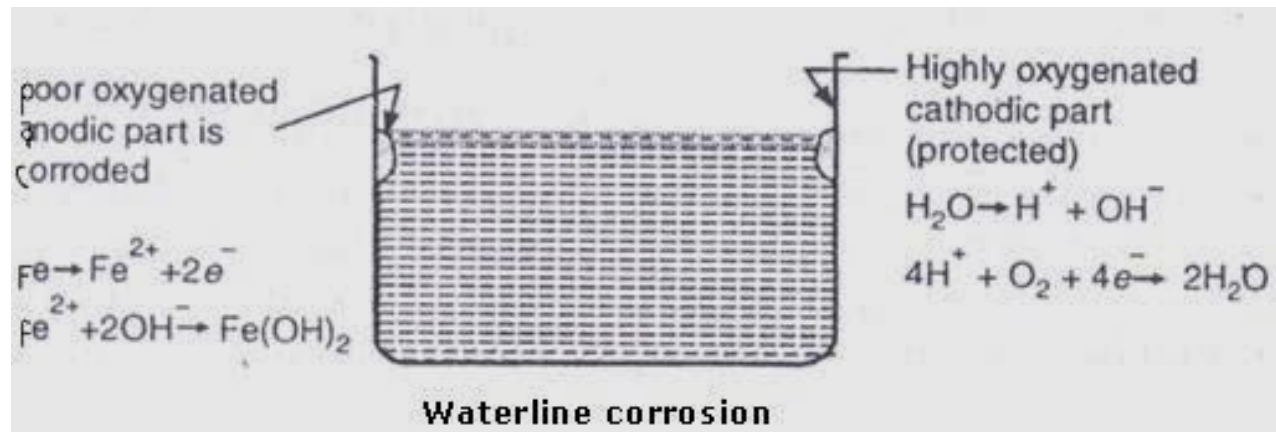


❖ When the supply of oxygen is enough, ferrous hydroxide converts to ferric hydroxide called as yellow rust .



Waterline Corrosion

- ❖ If water is stored in a steel tank, it is observed that maximum corrosion takes place along a line just below the water meniscus.
- ❖ This is because the area above the water line is highly oxygenated and acts as cathode and is not affected by corrosion.
- ❖ Whereas the area below the water level are poorly oxygenated and act as anodic. Therefore the anodic part (below waterline) gets corroded whereas the cathodic part remains unaffected by corrosion.

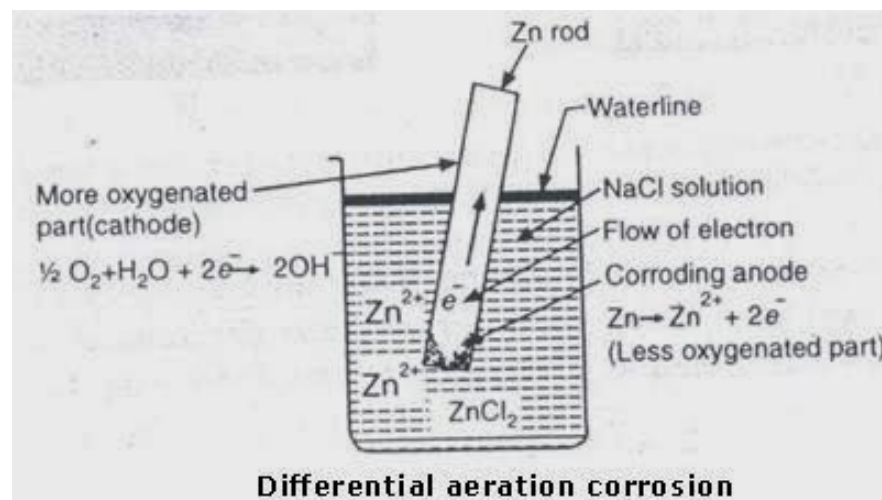


e.g. Corrosion of water filled steel containers occurs below the waterline.

The reason for this is electrochemical corrosion. The areas above water line are highly oxygenated and act as cathodic whereas the area below the water level are poorly oxygenated and act as anodic. Therefore the anodic part (below waterline) gets corroded whereas the cathodic part remains unaffected by corrosion.

Concentration cell Corrosion

- ❖ This type of corrosion involves electrochemical attack on metal surface where a metal is exposed to an electrolyte.
- ❖ **Differential aeration corrosion** is a type of concentration cell corrosion and it takes place when one part of metal is exposed to a different air concentration than other part.
- ❖ This leads to a potential difference between differently aerated areas. The area poorly oxygenated become anodic.
- ❖ Therefore a differential aeration of metals causes a flow of current called as differential current.



e.g. iron nail under drops of salt solution

This happens because of differential aeration. Those areas of nail covered with salt solution get poor access to air and become anodic with respect to other areas freely exposed to air and . Because of electrochemical corrosion, the areas under the drop of salt solution undergo corrosion while the other parts remain unaffected

Passivity

Definition:

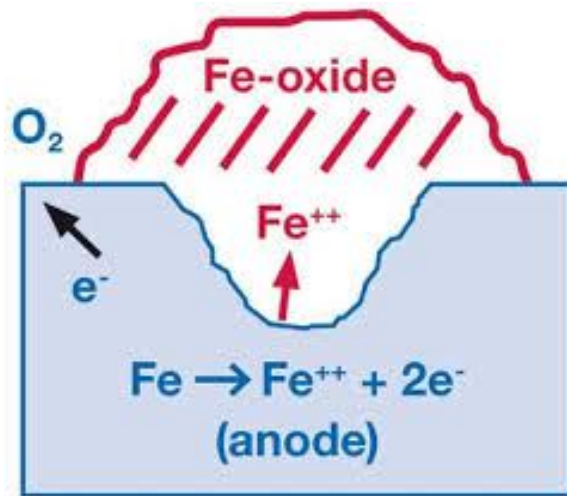
“ It is the phenomenon in which a metal or alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series”.

Cause:

- ❖ Formation of a highly protective, invisible thin film on the surface metal or alloy.
- ❖ The film is insoluble, non porous and self healing (i.e. when broken it will repair itself) in nature.
- ❖ Example of passive metals are: Ti, Al, Cr

Pitting Corrosion

- ❖ “It is localized attack on a metal by its surrounding results in the formation of cavities around which metal is relatively un attacked”.
- ❖ It results in the formation of small holes, or pits in the metals.
- ❖ It is due to the breaking of the protective film at specific points.
- ❖ This leads to formation small anodic and large cathodic areas.



Galvanic Series

- ❖ In electrochemical series metals are arranged downwards based on their electrode reduction potential in an increasing manner.
- ❖ A metal high in the series is more anodic and undergoes corrosion faster than metal lying below in the series.
- ❖ e.g. Li corrodes faster than Mg, Zn corrodes faster than Fe. , Fe corrodes faster than Sn and so on..
- ❖ But there are some exceptions! For example , Ti which is above Ag, is less reactive than Ag also Zn which is below Al in the series, it is Zn which acts as anode when Zn-Al are combined.
- ❖ A more practical series has been designed which exactly accounts for the corrosion of metals known as galvanic series.

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Active or
Anodic



Noble or
Cathodic

1. Mg
2. Mg alloys
3. Zn
4. Al
5. Cd
6. Al alloy
7. Mild steel
8. Cast iron
9. High Ni cast iron
10. Pb-Sn solder
11. Pb
12. Sn
13. Inconel
14. Ni-Mo-Fe alloys
15. Barss
16. Monel
17. silver solder
18. Cu
19. Ni
20. Ag
21. Ti
22. Graphite
23. Au
24. Pt

Factors influencing rate of corrosion

1. Nature of Metal

- ❖ Position in the galvanic series: when two metals or alloys are in contact in presence of an electrolyte, the more active metal (higher in series) suffers corrosion.
- ❖ The extent or severity of corrosion depends on the difference in their position. Greater the difference faster the corrosion.
- ❖ Relative size of the Anodic and Cathodic parts: The corrosion of the anodic part is directly proportional to the ratio of areas of cathodic part and anodic parts. Corrosion is rapid and severe if anodic area is small.
- ❖ Purity of the metal: Impurities will cause formation of different small sized electrochemical cells and lead to corrosion.

Physical state of the metal: the rate of corrosion depends on the physical state of the metal such as its grain size, crystal orientation, stress etc. The smaller the grain size of the metal. Faster will be corrosion.

Nature of surface film : Ratio of the volume of the metal oxide to metal. Greater the ratio lesser is the corrosion.

Passive character of the metal: Metals such as Ti, Al, Cr, Mg, Ni and Co are passive and hence exhibit higher corrosion resistance than expected from their position in galvanic series.

Solubility and Volatility of corrosion products: higher the solubility and volatility of the corrosion product higher is the rate of corrosion as the underlying area are exposed rapidly.

Nature of corroding environment:

- ❖ Temperature : higher the temperature higher the diffusion rate and hence corrosion is faster.
- ❖ Humidity of air: there exists a critical humidity above which the atmospheric corrosion rate of a metal increases sharply. Humidity provides moisture or water which can be absorbed by the thin film and form electrochemical cell leading to enhanced corrosion.
- ❖ Presence of impurities in atmosphere: Atmosphere containing corrosive gases like CO_2 , H_2S , SO_2 , or acidic fumes of HCl , H_2SO_4 can attack the metal surface and enhance its conductivity.
- ❖ Presence of suspended impurities in atmosphere: if the suspended impurities or particles are chemically active or they absorb moisture, they can act as strong electrolytes causing enhancement in corrosion rate.
- ❖ Influence of pH: Generally acidic pH leads to more faster corrosion than alkaline or neutral medium.

- ❖ Nature of ions present:
- ❖ Conductance of corroding medium
- ❖ Formation of oxygen concentration cell
- ❖ Flow velocity of process stream

Corrosion Control

1. Proper designing: Minimise the conditions which can lead to corrosion.
 - a. Avoid contact between dissimilar metals in presence of a corroding solution.
 - b. If at all two dissimilar metals are brought together the anodic metal should have large area.
 - c. Choose the metals such that they are close to each other in the electrochemical series.
 - d. Use of an insulating cover between these metals.
 - e. Painting the anodic metal.
2. Use pure metal:

Cathodic Protection

It is the protection of parent metal from corrosion by connecting it with a more active metal (more anodic metal) like Mg, Al etc. The connected active metal undergoes corrosion thereby protecting the parent metal from corrosion.

Anodic Protection.

Anodic protection (AP) is a technique to control the corrosion of a metal surface by making it the anode of an electrochemical cell and controlling the electrode potential in a zone where the metal is passive.

- ❖ In other words, a metal has higher oxidation potential than the base metal is plated. Thus it serves as anode with respect to the base metal.
- ❖ e.g. Al, Zn, Cd are anodic with respect to steel.
- ❖ If any scratch is developed on zinc coated steel, a galvanic cell is formed between zinc & exposed iron.
- ❖ Zinc being anodic to steel, it gets dissolved while steel or iron gets protected. Thus iron is protected by sacrificial zinc.