

APPLIED CHEMISTRY

Paper Code: BS103/ BS104
Lecture 30



**SCHOOL OF
ENGINEERING AND
TECHNOLOGY**



Corrosion can be defined as degradation or deterioration of a metal by chemical or electrochemical reaction with its environment (gaseous or liquid medium).

Degradation or deterioration means reduction in the useful properties of the material which include:

- Weakening of the material due to loss of cross-sectional area.
- Loss of properties such as malleability, ductility.
- Decaying of surfaces of metals.
- Cracking of a polymer due to sunlight.

The materials affected by corrosion are metals, polymers (plastics or rubbers etc.), ceramics (concrete) etc. But metals, the most useful class of materials corrode most frequently and hence this discussion is mainly devoted to corrosion in metals.

Some of the common examples of corrosion in metals are:

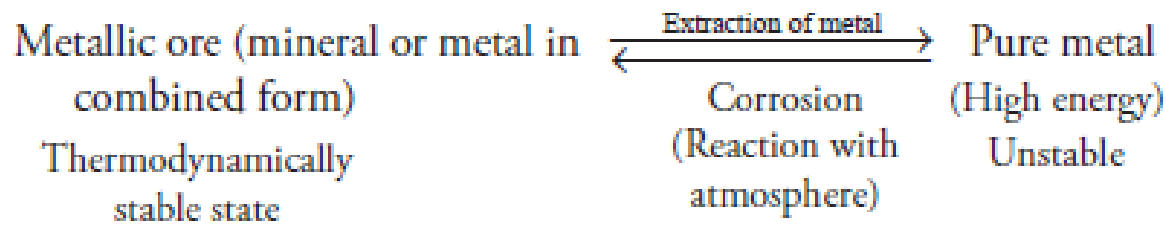
Rusting of Iron: When exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed on the surface.

Formation of green film on the surface of copper: A green layer of basic carbonate consisting of $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ is formed on the surface of copper when exposed to moist air

Tarnishing of silver: When silver is exposed to the atmosphere, a black coating is formed.

• Why does corrosion occur?

- Metals exist in nature in combined forms like oxides, sulphides, sulphates, carbonates, etc. These combined states (ores) are thermodynamically stable states of the metal.
- Energy is supplied to extract such metals from their ores. The extracted metal is at a higher energy level and hence it is in a thermodynamically unstable state.
- Metals try to get back to their stable states by combining with other elements, and in this process, corrosion occurs and oxides, sulphides, chlorides, sulphates, and so forth are formed.



Effects of Corrosion

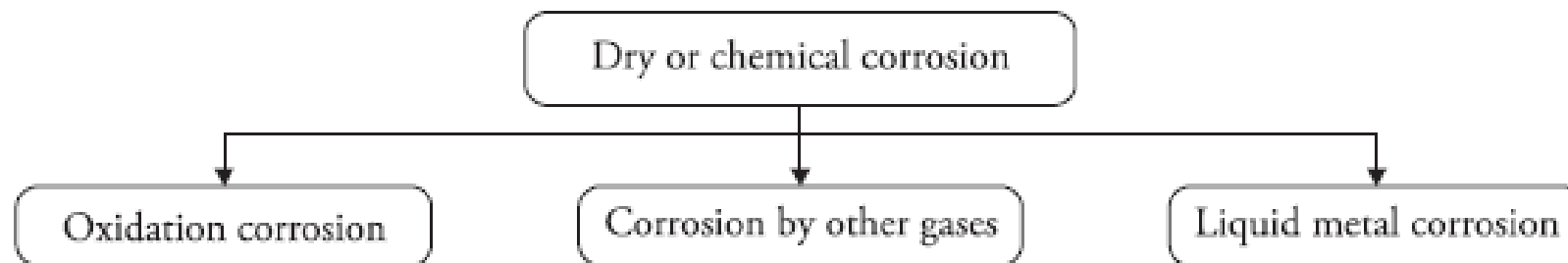
- Corrosion causes severe economic losses and hampers the safety of equipment. It leads to direct economic losses that occur due to money being spent on maintenance and replacement of the corroded parts.
- Metals can become brittle, leading to the failure of machine parts.
- Frequent replacement and maintenance of the corroded parts leads to indirect financial losses, which include production loss during replacement and maintenance.
- Corroded pipes may lead to leakage of inflammable and toxic gases resulting in fire hazards
- It has been estimated that nearly 25% of the annual production of iron is wasted because of corrosion.

Theories/Mechanism of Corrosion

- The two basic theories of corrosion are:
- Dry or chemical corrosion.
- Wet or electrochemical corrosion.

Dry or chemical corrosion

- It occurs because of direct chemical action of the environment on the metal surface in the absence of moisture or a liquid electrolyte.
- It generally occurs at a temperature higher than 100°C when it is not possible to develop a surface water layer.



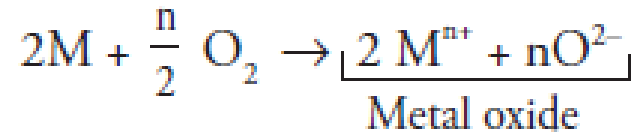
(a) Oxidation corrosion → It is brought about by the direct action of oxygen on the metal surface to form the corresponding oxide at high or low temperature.

→ At low temperature, alkali and alkaline earth metals are oxidized and at high temperatures except Ag, Au and Pt, all other metals are oxidized.

→ It generally takes place in the absence of moisture.

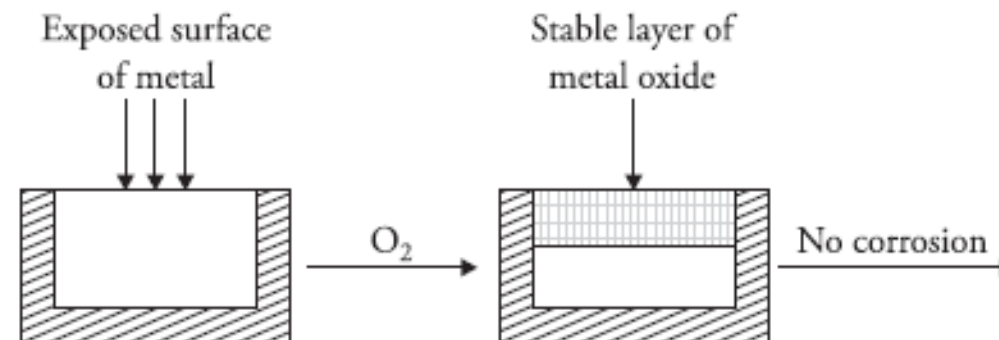
→ Mechanism

- The metal surface reacts directly with oxygen forming an oxide layer.
- This oxide layer acts as a barrier and prevents further oxidation of the metal.
- For further oxidation to take place, either the metal must diffuse outward through the oxide layer or oxygen must diffuse inward. Both the transfers occur, but the outward diffusion of the metal ion is faster as the size of the metal ion is smaller than that of the oxygen atom or the O^{2-} ion.

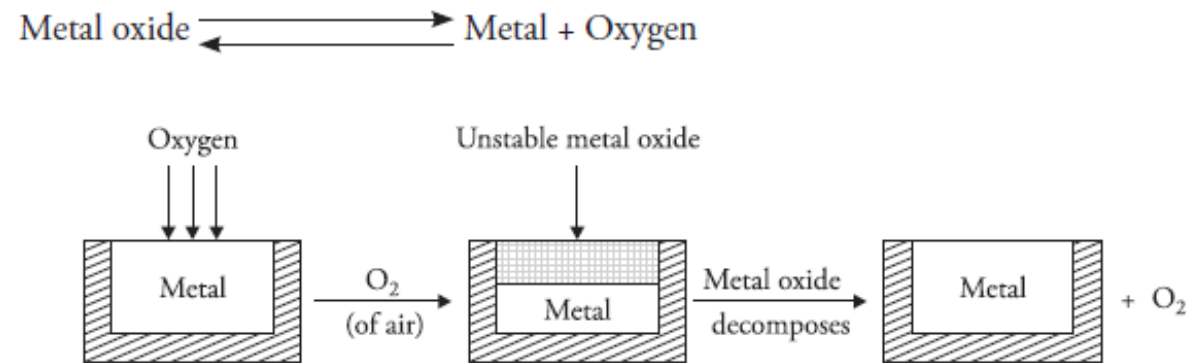


- For corrosion to continue further, the **nature of the oxide film is very important. They are of four types:**

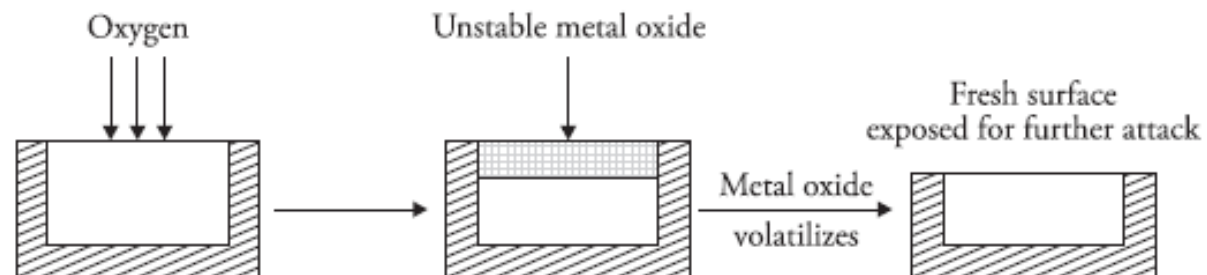
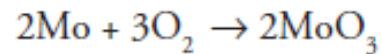
(i) **Stable** It is fine grained, tightly sticking and impervious, for example, Al, Sn, Pb and Cu. It acts as a protective layer and prevents further corrosion.



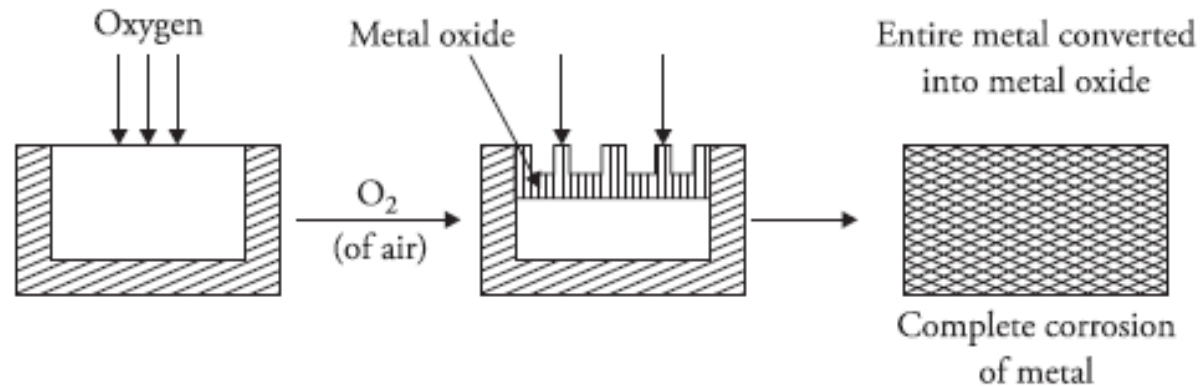
(ii) **Unstable** The oxide formed decomposes back into metal and oxygen, for example, Ag, Pt and Au. As a result, there is **no corrosion**.



(iii) **Volatile** The oxide layer formed volatilizes as soon as it is formed. Fresh metal surface is exposed for further attack. This **causes rapid and continuous corrosion**, for example, molybdenum.



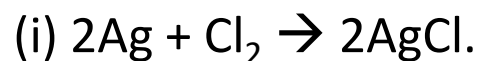
(iv) **Porous** The oxide film is porous, that is, having pores or cracks. Here the O_2 penetrates inside and attacks the underlying metal and hence continuous corrosion occurs, for example, iron and steel.



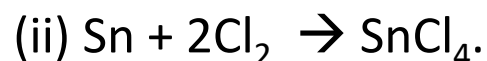
- **Pilling–Bedworth Rule:** → The ratio of the volume of metal oxide to the volume of the underlying metal is called the Pilling– Bedworth ratio or the specific volume ratio.
 - If the volume of the oxide film is *less* than the volume of metal laying underneath then the oxide layer is porous, contains cracks and hence is nonprotective (ratio less than 1). Example: Li, Na, K, Mg, Ca, Sr, etc.
 - If the volume is *equal to or greater than* the volume of the underlying metal, the oxide film is continuous, nonporous and protective, that is, further corrosion does not take place (ratio greater than 1). Eg. Al, Cu
 - This ratio helps to predict the extent of corrosion of a metal. Greater the value of Pilling–Bedworth ratio, lesser is the extent of corrosion

(b) **Corrosion by other gases:** In this, dry gases like H_2 , Cl_2 , F_2 , SO_2 and CO_2 directly attack the metal surface. Rate of corrosion depends upon the chemical affinity between the metal and gas and also on the nature of the film formed.

- For example,



The $AgCl$ film is nonporous and protective (volume of the film > volume of the metal) and thus it protects the metal from further attack.



$SnCl_4$ being volatile, leaving the metal surface exposing and hence, Sn undergoes excessive corrosion.

(c) **Liquid metal corrosion:** → It occurs when an anhydrous liquid attacks the metal surface.

→ When a liquid metal flows over a solid metal at high temperature it weakens the solid metal because of :

- its dissolution in liquid metal.

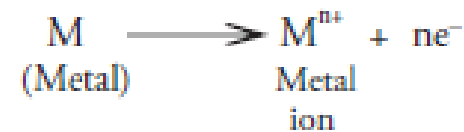
- Penetration of liquid metal into solid metal. For example, sodium metal (coolant) leads to the corrosion of cadmium in a nuclear reactor.

Wet or electrochemical corrosion

- This type of corrosion occurs under wet or moist conditions, and is more common than dry corrosion. It occurs when:
 - (i) A metal is in contact with a conducting liquid or
 - (ii) When metals of different reactivities are in contact with a solution.
- The **following conditions must be fulfilled for the formation of electrochemical cell.**
 - (i) There must be separate anodic and cathodic areas.
 - (ii) There must be electrode potential between the anode and cathode.
 - (iii) There must be a metal path connecting the anode and cathode.
 - (iv) Conducting liquid should be present between the two electrodes.

- The reactions taking place at the anode and cathode in a corrosion cell are as follows:

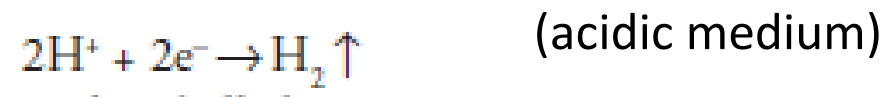
(a) Anodic reactions: Oxidation occurs at the anode; the metal loses electrons and passes them into the solution. Thus, the metal at anode is destroyed by dissolving or by changing into metal ions. *Hence, corrosion always occurs at the anodic areas.*



(b) Cathodic reactions The electrons released at the anodic areas are consumed in the reactions at the cathode. Depending on the nature of the environment, the cathodic reactions are of two types

(i) Evolution of hydrogen This mechanism usually occurs when anodic areas are large and cathodic areas are small and **oxygen is absent**.

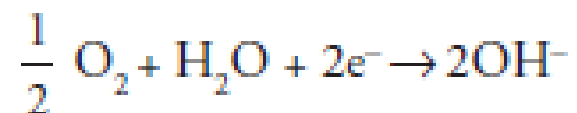
When the **environment is acidic**, H^+ ions of the acid take up electrons and hydrogen gas is evolved.





Neutral or alkaline medium

- (ii) **Absorption of oxygen:** This mechanism occurs when:
 → Anodic areas are small and cathodic areas are large.
 → **Oxygen is present** and the environment is neutral or alkaline.



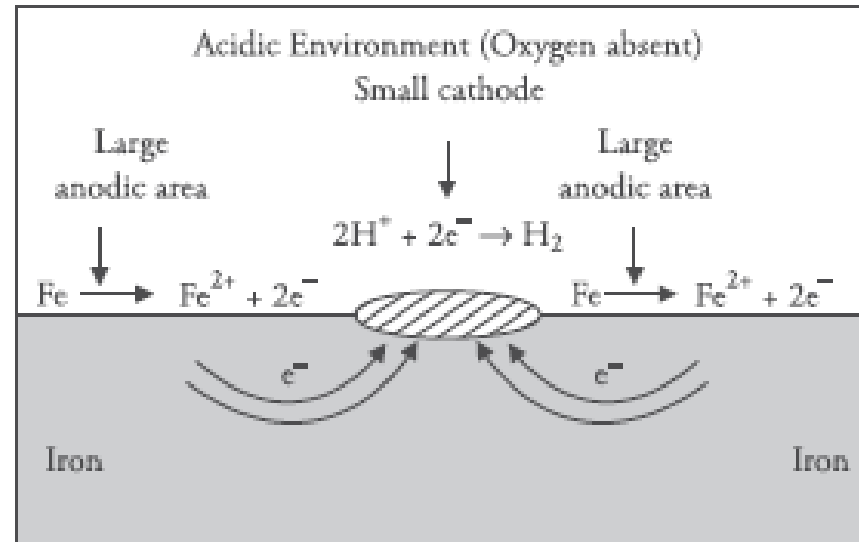
→ MECHANISM FOR RUSTING OF IRON

A) In the absence of oxygen

→ Acidic medium



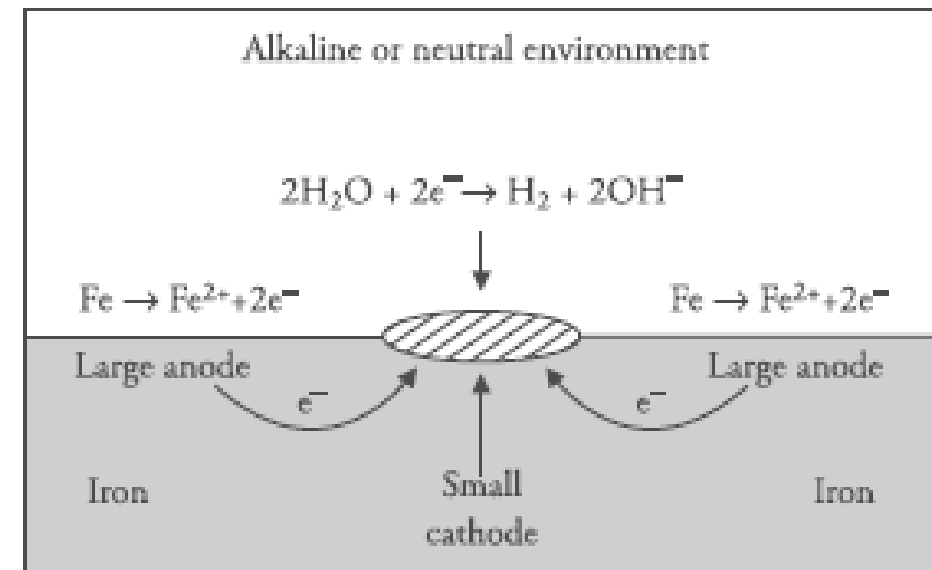
The Fe^{2+} ions react with the anion of the acid to form the corrosion product.



→ In neutral or alkaline medium, the following reactions occur

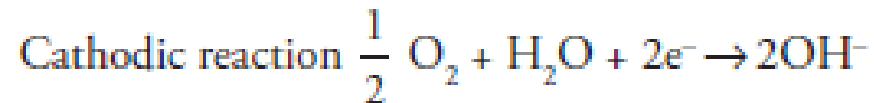


The Fe^{2+} formed at the anode and OH^- formed at the cathode diffuse towards each other and meet to form $\text{Fe}(\text{OH})_2$



(B) In presence of oxygen

- neutral aqueous solution
- Anodic areas are small and cathodic areas are large.



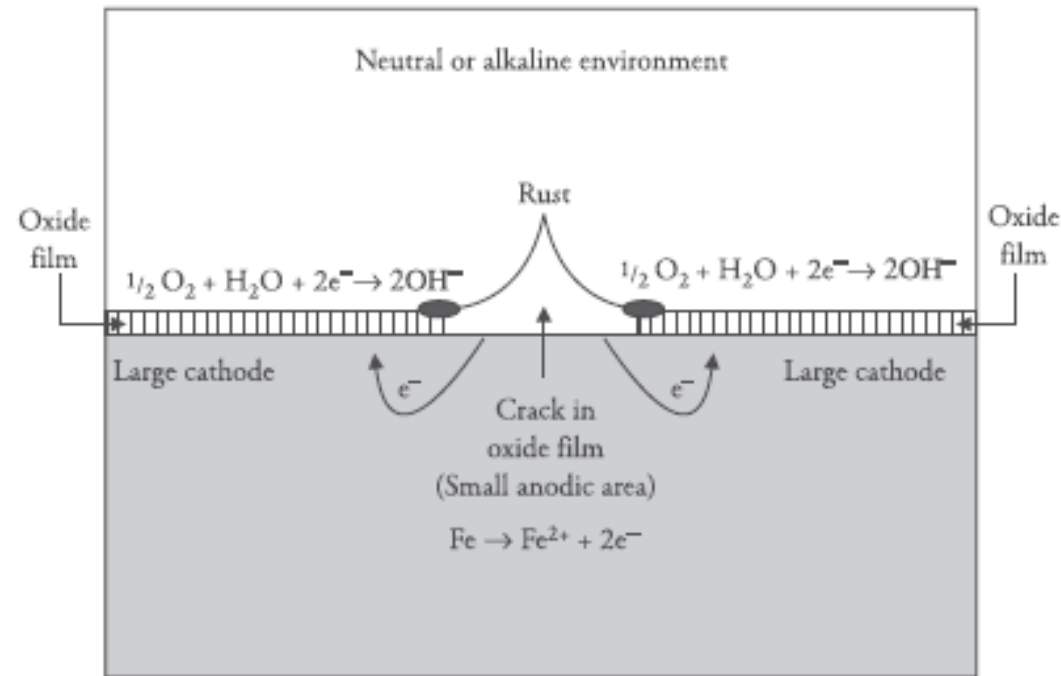
- The Fe^{2+} ions (at anode) and OH^{-} ions (at cathode) diffuse, and when they meet, ferrous hydroxide is precipitated.



- $\text{Fe}(\text{OH})_2$ is not stable, and in the presence of oxygen and moisture, it oxidizes as follows:



- $\text{Fe}(\text{OH})_3$ corresponds to rust, which is hydrated iron(III) oxide of variable composition $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. The degree of hydration of iron (III) oxide affects the color of rust that may vary from black (Fe_3O_4) anhydrous magnetite to yellow reddish brown ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$).



- The corrosion product is formed closer to the cathode. This is because the smaller Fe^{2+} ions produced at anode diffuse rapidly toward cathode as compared with the diffusion of larger OH^- ions toward the anode.

S.No	Chemical corrosion	Electrochemical corrosion
1	It takes place in dry conditions	Presence of aqueous solution or electrolyte is a must
2	It takes place by direct chemical attack of the environment on the metal	It takes place indirectly by the formation of electrochemical cells
3	It can take place on a homogenous and heterogeneous surface	It takes place on heterogeneous metal surfaces only
4	Corrosion product deposits at the same spot where corrosion has occurred	Corrosion occurs at the anode but the corrosion product deposits near the cathode
5	Corrosion occurs uniformly	Nonuniform corrosion takes place

THANK YOU



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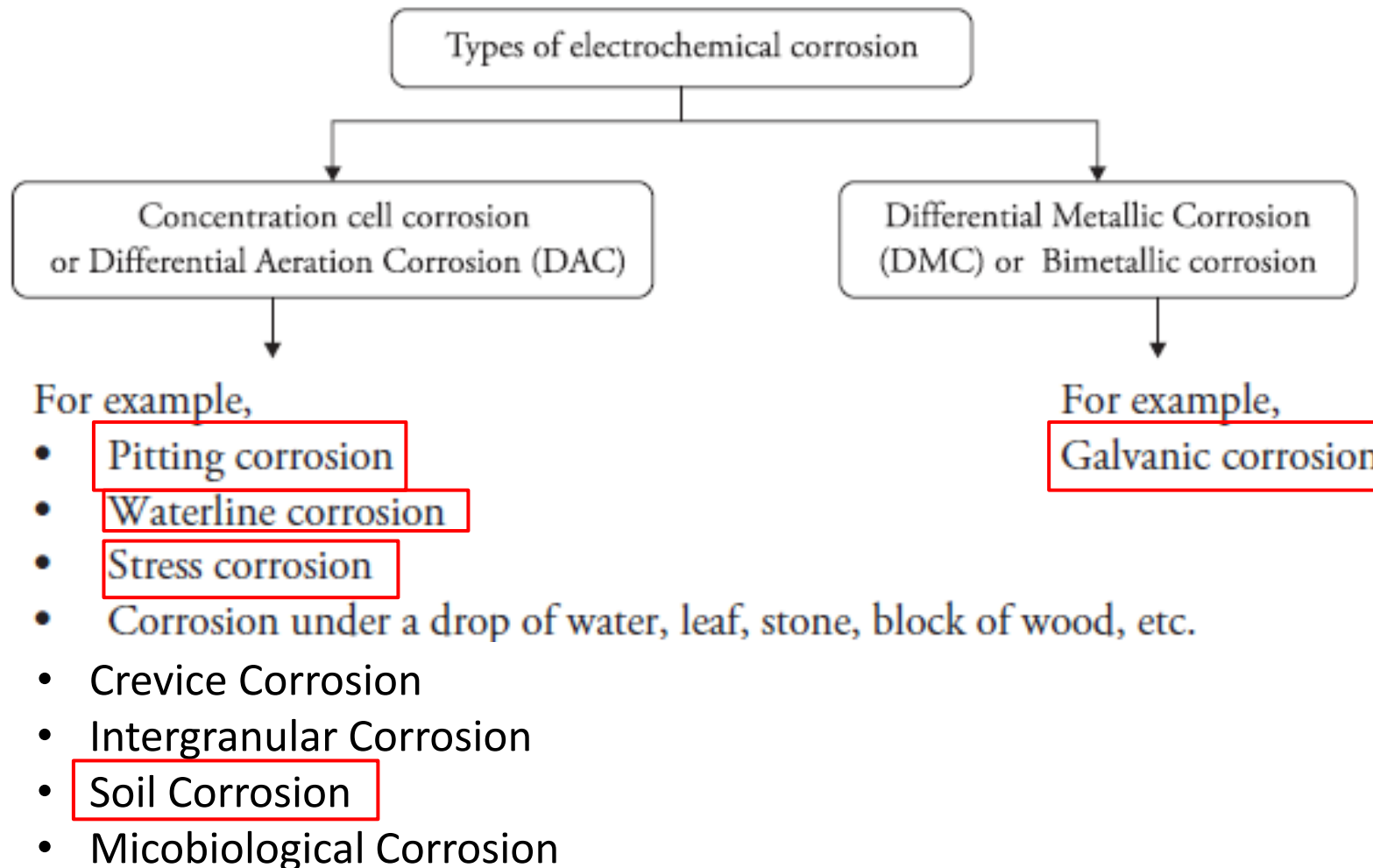
Lecture 31



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Types of corrosion



1. Galvanic Corrosion

➤ It occurs when two dissimilar metals (for example, Zn and Cu) are electrically connected and exposed to an electrolyte and then the metal higher in the electrochemical series undergoes corrosion.

➤ **Mechanism: In a Zn – Cu couple**

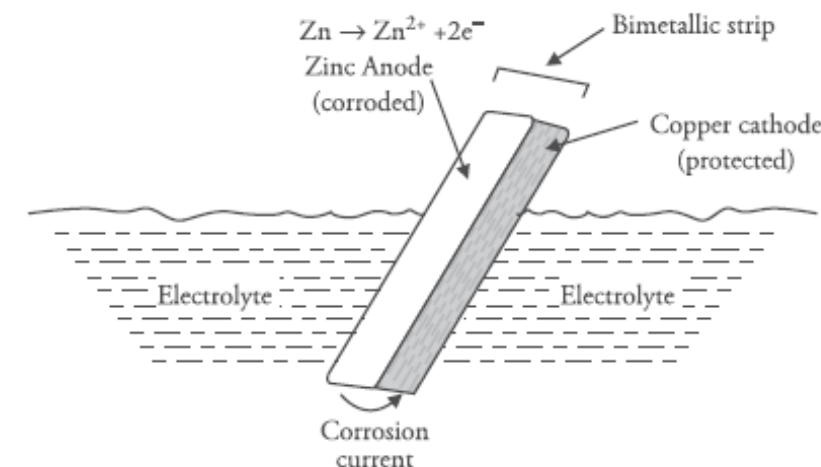
At anode $\rightarrow \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

The reaction at the cathode depends upon the environment.

Acidic environment $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$ (evolution of hydrogen)

Alkaline or neutral environment $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (absorption of oxygen)

Zn^{2+} and 2OH^- ions interact to form $\text{Zn}(\text{OH})_2$. Hence, Zn dissolves and Cu is protected.



2. Concentration cell corrosion → Concentration cell corrosion takes place when different areas of a metal surface are in contact with an electrolyte of different concentration or varying aeration.

→ The difference in electrolyte/air concentration may be because of local temperature differences or inadequate stirring or slow diffusion of metal ions.

Differential aeration corrosion (DAC) → This is the most common type of concentration cell corrosion. It occurs when one part of the metal is exposed to a different air concentration than the other. There will be a difference of potential between differently aerated areas.

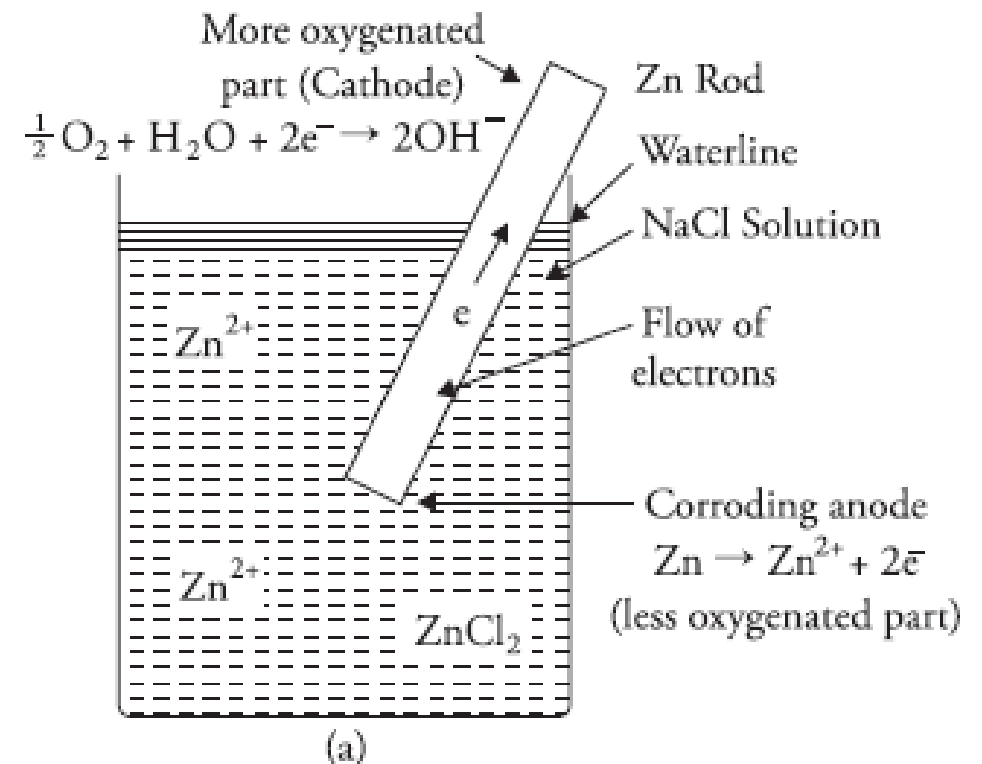
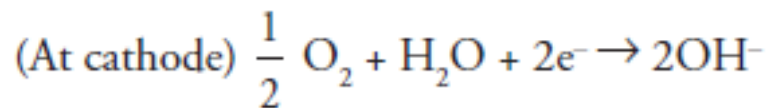
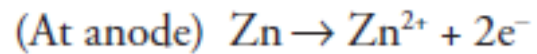
→ Experimental observations have shown that:

- Poorly oxygenated areas become anodic and
 - Highly oxygenated areas become cathodic.
 - Corrosion occurs at the anode
-
- Some common examples of differential aeration corrosion are cited below

(a) Waterline corrosion → Example 1: If a Zn metal is partially immersed in a neutral solution (say NaCl) and the solution is not stirred, the parts above and close to the waterline are well aerated and act as cathode.

→ Areas deep inside the solution are anodic, as the concentration of oxygen is less.

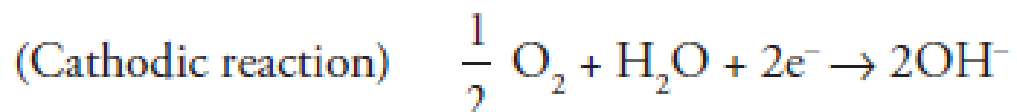
→ Thus, a potential develops that causes a flow of current between two areas of the same metal. Zn dissolves at the anodic area



- **Example 2:** → Rusting along a line just beneath the level of water stored in an iron tank. This is also waterline corrosion and is because of differential aeration.

→ The area just above the waterline is well aerated and acts as cathode, whereas the areas below the waterline are poorly aerated/oxygenated and hence become anodic and get corroded.

→ The reactions at anodic and cathodic areas are:



→ The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and when they meet ferrous hydroxide is precipitated



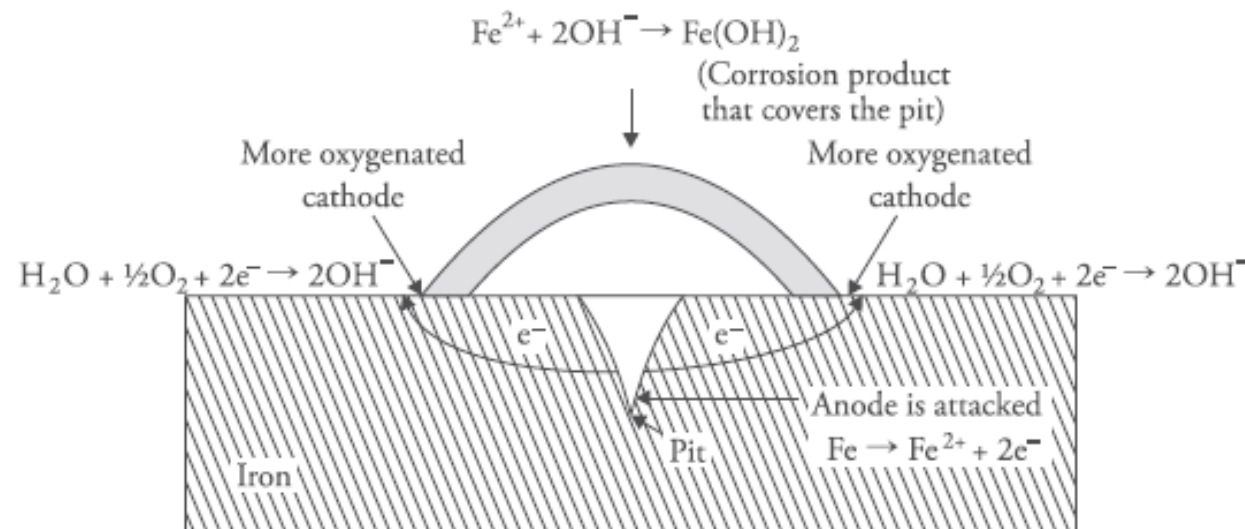
b) Pitting corrosion → It is also an example of differential aeration corrosion.

→ It is a localized type of corrosion and occurs in areas of pits, cavities and pinholes that penetrate deeply within the metals.

→ The pit is oxygen deficient and acts as anode, whereas the plane surface is oxygen-rich and acts as cathode. As the area of anode is small the rate of corrosion will be high.

→ Anodic metal dissolves and the pit gradually deepens resulting in the weakening of the metal in these areas.

→ Pitting of metal generally occurs because of breakdown or cracking in the protective film on the metal surface at specific points. It may be due to scratches, surface roughness, chemical attack, stresses and strains, etc.

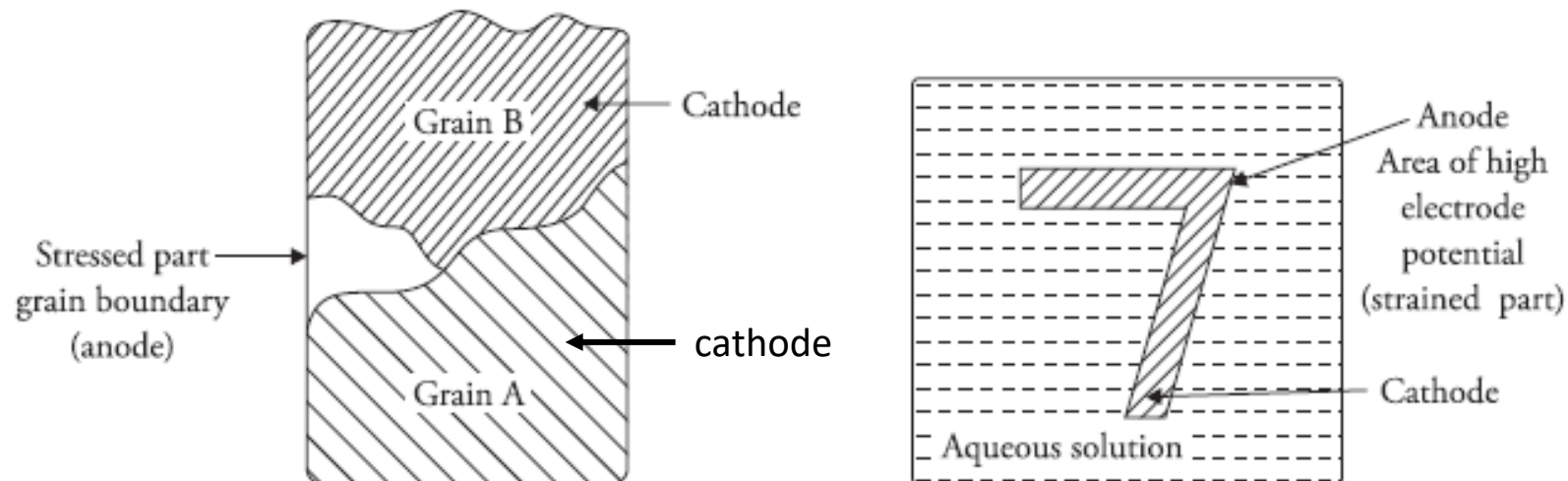


c) Stress corrosion (season cracking) → It occurs because of the combined effect of Static tensile stress and Corrosive environment near the metal.

→ The metals develop internal stress during manufacture process like fabrication, heat treatment, rolling, insufficient annealing, etc.

→ Thermodynamically, areas under stress are at higher energy level. Therefore, they have high electrode potential and act as anode. The stress-free areas are at lower electrode potential and act as cathode.

→ The anodic area becomes highly reactive and is attacked even by a mild corrosive environment, resulting in the formation of a crack.



- Examples of stress corrosion are as follows:

(i) **Season cracking in brass** → It is a term that applies specifically to stress corrosion in brass (copper alloy).

→ Pure copper is immune to stress corrosion but the presence of alloying agents like Zn, Al, P and Sb makes it prone to stress corrosion.

→ Brass undergoes intergranular cracking in an atmosphere having traces of NH_3 .

→ Both copper and zinc present in brass can react with NH_3 forming $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$, respectively, causing Brass to dissolve, and initiating a fissure formation that later forms a crack in the presence of high tensile stress.

→ This can be avoided by avoiding contamination of air with NH_3 .

(ii) **Caustic embrittlement** → It is corrosion in boilers due to excess NaOH . Inside the boiler the riveted areas, and areas of bends and joints are under great stress and hence undergo corrosion. The mechanism has already been discussed in Unit 2

d) Soil corrosion → It is also called underground corrosion. **There are various factors responsible for the corrosiveness of the soil. Some of them are:**

- Acidity of soil (soils containing organic acids derived from humus are quite corrosive to steel, zinc, lead and copper).
- Moisture of the soil
- Electrical conductivity
- Electrolytes (dissolved salts)
- Degree of aeration (porosity)
- Presence of bacteria and microorganisms.

→ **Underground structures like water mains, cables, etc. passing from one soil to the other suffer from corrosion because of differential aeration in different parts of the soil.**

→ The presence of electrolytes enhances the rate of corrosion.

→ Certain types of bacteria that oxidize organic matter and produce gases also cause soil corrosion. Soil corrosion is purely electrochemical in nature.

→ **Soil corrosion can be prevented by organic and inorganic coatings, metallic coatings, soil alteration by surrounding the metal structure by limestone chips and by the use of various cathodic protection methods.**

Passivity

inertness , non
reactive

- It is defined as the phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series.
- In an electrochemical series, the metals are arranged from top to bottom in the order of their increasing reduction potentials (or decreasing reactivities). The metal placed higher in the series is more reactive than the one placed below it.
- In a Zn–Al couple, Zn which is below Al in the electrochemical series, is corroded/more reactive. Similarly, there are some Ti, which is above Ag in the electrochemical series, is less reactive than Ag. This is because Ti and Al develop strongly adhering oxide layers on their surface, thereby making their effective electrode potential more positive (or less negative). These metals are said to be rendered passive.
- Passivity is because of the development of a highly protective, very thin (0.004-mm-thick) invisible oxide film on the surface of the metal. The film so formed makes the metal behave as a noble metal. The presence of ample excess oxygen on the metal surface favours passivation.
- Passivity has been used to protect metals from corrosion. Passive oxide films are artificially produced on metals and alloys by treatment with strong oxidizing agents and hence the metals are protected from being corroded.

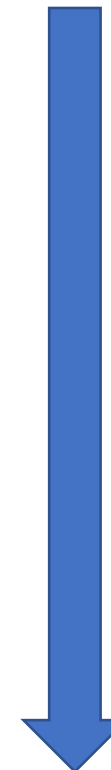
Electrochemical Series

Metal reducing activity increasing



Element	Electrode reaction	$E^\circ(V)$
Li	$\text{Li} + e^- \rightarrow \text{Li}$	-3.045
K	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.925
Cs	$\text{Cs}^+ + e^- \rightarrow \text{Cs}$	-2.923
Ba	$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.906
Ca	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.866
Na	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.363
Al	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.662
H ₂	$\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.829
Zn	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763
Fe	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440
Cd	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403
Pb	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.310
Co	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.280
Ni	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
Sn	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.136
Pb	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
Fe	$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$	-0.036
H ₂	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{SHE})$	0
Cu	$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	+0.153
S	$\text{S}_4\text{O}_6^{2-} + 2e^- \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+0.170
Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.337
I ₂	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.534
Fe	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.77
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	+0.854
Br ₂	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+1.066
O ₂	$\text{O}_2 + 4\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$	+1.230
Cr	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.330
Cl ₂	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.359
Au	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.498
Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.510
F ₂	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+2.870

Metal oxidising activity increasing



Galvanic Series

- Owing to passivation the effective electrode potential of some metals changes they become less reactive. Their behavior becomes opposite to that predicted by the electrochemical series. Hence, a more reliable series for predicting the corrosion in different environments is the *galvanic series*.

Active (or anodic)	1. Mg
	2. Mg alloys
	3. Zn
	4. Al
	5. Cd
	6. Al alloys
	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. Brasses
	16. Monel(Ni=7; Cu =30; Fe=rest)
	17. Silver solder
	18. Cu
	19. Ni
	20. Cr stainless steel
	21. 18-8 stainless steel
	22. 18-8 Mo stainless steel
	23. Ag
	24. Ti
	25. Graphite
	26. Au
	27. Pt
Noble (or cathodic)	

Examples of passivity:

1. Metals like Cr, Al, Ni, Ti and a wide variety of stainless steel alloys containing Cr show outstanding corrosion resistance in oxidizing environment. These metals and alloys form insoluble oxide films on their surface in the presence of oxygen and are rendered passive.
2. Iron is readily attacked by dilute HNO_3 but in concentrated acid it forms a very thin protective film and becomes passive or inactive.
3. Al becomes passive in concentrated HNO_3 due to the formation of thin protective oxide film.

Factors Influencing Corrosion

1. Nature of the metal

- Corrosion rate depends on the properties of the metal:

(i) **Position in the galvanic series** When two metals or alloys are in contact in the presence of an electrolyte, the metal that is higher in the galvanic series undergoes corrosion. Greater the difference in the position of the two metals greater is the corrosion of the anodic metal.

(ii) **Purity of the metal** Pure metals are less prone to corrosion. Impurities in a metal cause 'heterogeneity' and forms minute/tiny electrochemical cells, where the anodic part gets corroded.

% Aluminium	99.998	99.97	99.2
Relative corrosion rate	1	1000	30,000

(iii) **Physical state of the metal** Rate of corrosion is greatly influenced by the physical state of the metal like particle size, orientation of grains, localised stresses, smooth or rough surface, etc. Smaller the grain size greater will be the corrosion; similarly, areas under stress, even in a pure metal, are likely to be anodic and corrosion takes place at these areas.

(iv) **Nature of surface film** In the presence of air, all metals are covered with a thin film of metal oxide. The ratio of the volume of metal oxide to that of the metal is called “*specific volume ratio*.” If the specific volume ratio of the metal is greater than one the metal will be protected from corrosion, and if the specific volume ratio is less than unity the film will be unstable and the underlying metal will be corroded (**Pilling–Bedworth rule**).

(v) **Relative areas of anodic and cathodic parts** Rate of corrosion is high if anodic areas are small and cathodic areas are large. This is because the current density at smaller anodic areas is much greater. Moreover, if the cathodic areas are large, then it will demand more electrons, which will be met by the brisk and rapid corrosion of the anodic area.

(vi) **Solubility of corrosion products** Corrosion is faster if the corrosion product is soluble in the corroding medium. If the corrosion product is insoluble in the corroding medium, or it reacts with the corroding medium to form insoluble product; the product acts as a physical barrier and suppresses further corrosion.

(vii) **Volatility of the corrosion product** If the corrosion product is volatile, it leaves the surface as soon as it is formed, leaving the underlying metal surface exposed for further attack. This causes rapid, continuous and excessive corrosion. MoO_3 is the volatile corrosion product formed on the oxidation of Mo.

2. Nature of the corroding environment

- Environmental factors have a vital role in deciding the rate of corrosion. The major environmental factors that affect corrosion are as follows:

(i) **Temperature** As the rate of all chemical reactions increases with the rise in temperature, rate of corrosion also increases as temperature rises. This is because of the faster diffusion of O_2 into pits and crevices.

(ii) **Humidity** Corrosion increases with the increase in humidity of the atmosphere. This is due to the fact that moisture acts as a solvent for O_2 , H_2S , SO_2 , $NaCl$, and so on to furnish the electrolyte for setting up a corrosion cell.

- Examples: → Atmospheric corrosion of Fe is slow in dry air compared with moist air. Steel parts left in desert areas remain bright and tarnish free for very long periods of time.

(iii) **Presence of impurities in atmosphere** Gases like H_2S , SO_2 and CO_2 increase acidity of the liquid closer to the metal surface and hence increases the rate of corrosion. Salts like $NaCl$ present in marine environment increase the conductivity of the electrolyte, thus speeding up the corrosion process.

(iv) **Effect of pH** Generally, acidic media ($pH < 7$) are more corrosive than alkaline or neutral media. However, amphoteric metals like Al, Zn, Pb form complexes in alkaline medium.

(v) Nature of ions present

- Presence of ions like silicate ions in the medium leads to the formation of insoluble products (like silica gel), which inhibit further corrosion.
- Chloride ions present in the medium destroy the protective and passive film, thereby exposing the fresh metal surface for further corrosion.

(vi) **Conductance of the corroding medium** Conductance of the corroding medium has a vital role in corrosion. Dry sandy soils have lower conductance compared with clay or mineralized soils. Hence, metallic structures buried under clay or mineralized soils undergo corrosion faster than under dry sandy soils.

(vii) **Formation of oxygen concentration cell** Owing to differential aeration “oxygen concentration cell” is set up and the anodic parts having less oxygen concentration suffers corrosion.

Protection against Corrosion

1. Protection by proper designing Corrosion can be prevented by using proper design.

Important design principles are as follows:

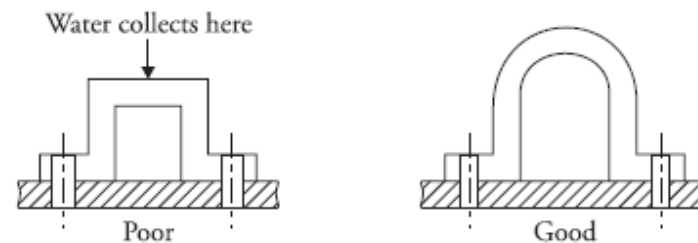
(i) **Avoid direct contact of two dissimilar metals in a corroding medium.** If it cannot be avoided then use an insulating fitting between them.

(ii) **When two dissimilar metals in direct contact are to be used then**

- They should be as close as possible in the galvanic series.
- The anodic material should have a large area and the area of cathodic material should be as small as possible.
- The screws, bolts, nuts and welds should be of less reactive metals so that they can act as cathode with small area.

Example: copper rivets are used to fasten steel sheets and not vice versa because copper is nobler than steel and hence acts as a cathode. Owing to the small area of the cathode, the cathodic reaction is limited and corrosion of anodic steel proceeds slowly.

(iii) As moisture has an important role in corrosion, the design should be such that moisture retention is as low as possible.



2. Material selection

(i) **Using pure metals** → Impurities in metals cause heterogeneity that leads to corrosion.

→ Pure metal is less prone to corrosion. However, pure metals are expensive and are usually weak and do not possess the required strength.

(ii) **Using metal alloys** → The metals can be made corrosion-resistant by alloying them with suitable alloying elements.

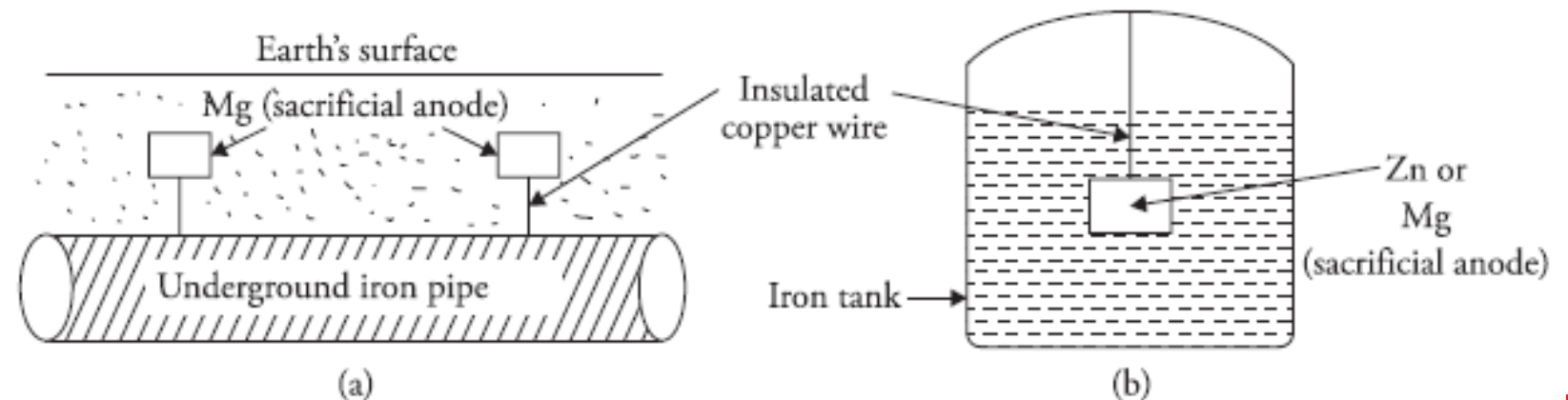
→ For example, chromium is used as alloying metal for iron and steel as it produces an exceptionally coherent oxide film, which protects the steel from further corrosion.

3. Cathodic Protection or Electrochemical Protection

- The principle involved is that the metal to be protected is made to behave like a cathode.
- Alloys/metals like steel, brass, copper and lead can be protected in all types of soils and almost all sorts of aqueous media by cathodic protection method.
- This technique is also employed to prevent pitting corrosion in stainless steel or aluminium and can also be used to prevent stress corrosion cracking in brass, mild steel, stainless steel, magnesium and aluminium. This can be done in two ways:
 - (i) Sacrificial Anode Cathodic Protection Method (SACP)
 - (ii) Impressed current cathodic protection (ICCP)

(i) Sacrificial Anode Cathodic Protection Method (SACP)

- In this method, the metal structure to be protected is connected to a more reactive metal.
- **Example:** → If an iron structure is to be protected it is connected to a more reactive metal like Zn or Mg. The more reactive metal behaves as an anode and the iron structure becomes cathodic.
- Thus, the iron structure is protected and the anode undergoes corrosion. After sometime, the anode is corroded completely and is replaced with a fresh anode. This anode (Zn or Mg), which is sacrificed to protect the base metal is called the *sacrificial anode* and the method is called *sacrificial anode cathodic protection method*.
- This type of protection method is used in industry to protect buried pipelines, underground cables, ship hulls and even in railway tracks.



4. **Galvanising** → The process of coating iron and steel articles with a thin coat of zinc to prevent them from rusting is called galvanisation.

Process

- Article to be coated is first cleaned with dilute H_2SO_4 solution (7–8%) for about 15–20 minutes at 60–90°C. This process is called *pickling*. Pickling removes dust, rust, scale, oxide layer and other impurities.
- Article is then treated with 5% HF to dissolve sand particles on the surface of the article. Any other superficial oxide if present is cleaned by passing the article through a 5–20% solution of zinc ammonium chloride.
- The article is then washed, dried and dipped in a bath of molten zinc, maintained at 425–430 °C.
- The surface of the bath is covered with a flux of ammonium chloride to prevent the formation of oxide.
- The article coated with zinc layer is then taken out and passed through rollers to remove excess zinc and produce thin film of uniform thickness. It is then annealed at a temperature of 650 °C and then cooled.
- Uses: For coating iron sheets, wires, pipes, bolts, screws, buckets, etc, it may be noted here that zinc gets dissolved in dilute acids to form toxic compounds. Hence, galvanized utensils cannot be used for storing food articles.

5. **Tinning:** It is the process of coating iron or steel articles with tin.

Process

- The iron or steel article is cleaned by pickling with dilute H_2SO_4 solution (5–8%) to remove impurities like dust, rust, scale or any oxide film.
- It is then passed into a zinc chloride flux that helps the molten metal to stick to the metal sheet.
- The sheet passes through a tank containing molten tin and finally through a series of rollers immersed in baths containing palm oil. The palm oil protects the tin-coated surface against oxidation
- Rollers help to remove excess tin and produce a thin film of uniform thickness.

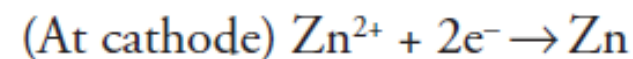
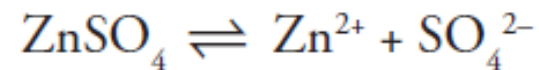
→ **Uses:** Because of the nontoxic nature of tin, tinning is widely used for coating steel, copper and brass sheets used for manufacturing containers for storing food articles. Tinned copper sheets are used for making utensils.

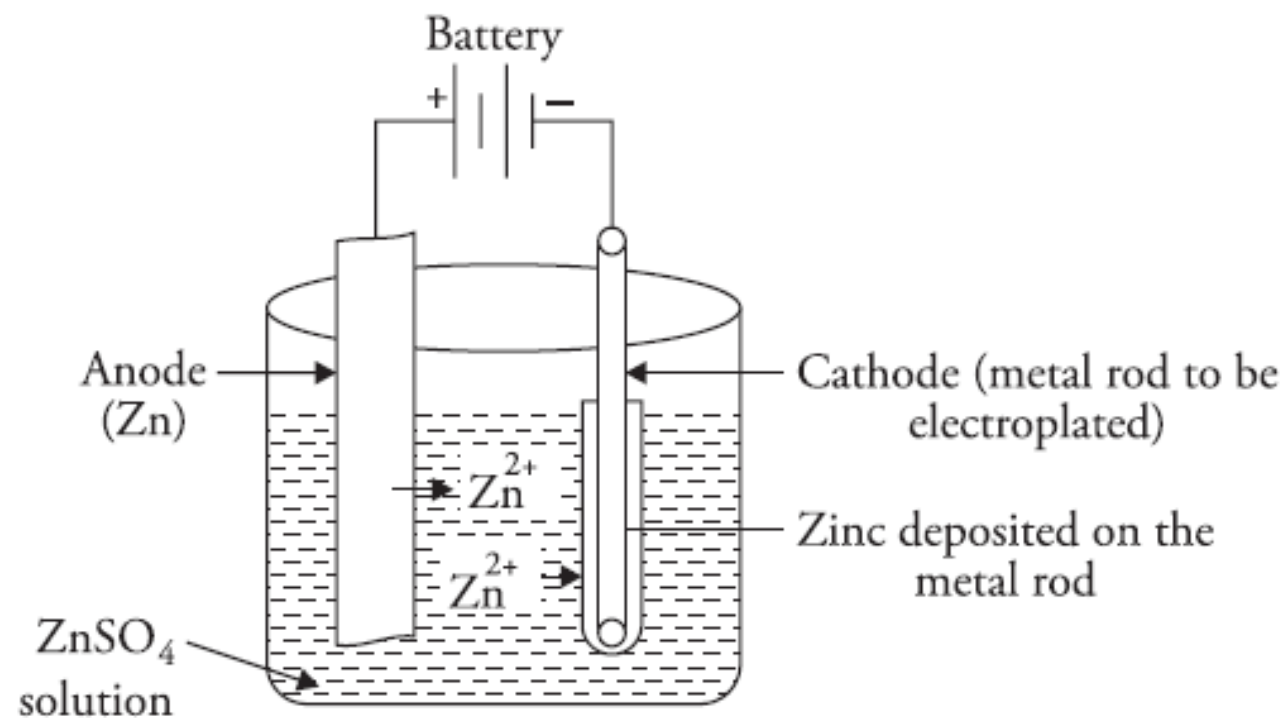
6. Electroplating

- It is the process of deposition of a metal on a metal, nonmetal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.
- The base metal to be coated or electroplated is made the cathode.
- The anode consists of the metal to be deposited and then immersed in the electrolyte containing the ions of the anode material.

Example:

- If zinc is to be deposited on iron then the cathode is made of iron and the anode is made up of zinc.
- The electrolytic solution is ZnSO_4 , which ionizes to form Zn^{2+} ions and SO_4^{2-} ions. The zinc ions migrate to the cathode and get deposited at the cathode and the SO_4^{2-} ions migrate to the anode and combines with zinc metal of the anode to form zinc sulphate.





THANK YOU

