CHAPTER 4

CORROSION SCIENCE

Introduction: Definition. Types: Dry corrosion: Mechanism – Pilling – Bedworth rule – Wet corrosion: Mechanism. Types: Galvanic corrosion and differential aeration cell corrosion. Galvanic series and its significance. Factors influencing corrosion. Corrosion prevention: Material selection and design – Cathodic protection. Protective coatings: Paints – Constituents. Mechanism of drying of drying oils.

4.1 INTRODUCTION

Most of the modern day industrial as well as domestic applications involve the use of metals and alloys. A serious problem associated with every use of metal object is corrosion. Corrosion is a general term that refers to the deterioration and ultimate destruction of a metal due to its reaction with the surrounding gaseous or liquid environment. Corrosion occurs with all metals except the noble metals like gold and platinum. Corrosion can also occur in materials other than metals, such as glass, wood, concrete and plastics. In these cases the term degradation is more commonly used than corrosion. The term corrosion is exclusively associated with the surface degradation of metals. The most familiar example of corrosion is rusting of iron and steel. It is the largest problem encountered throughout the world, mainly due to the fact that the iron and steel are the most abundantly used materials. It is estimated that about 20% of iron produced annually are used just to replace the iron objects that have been discarded due to corrosion.
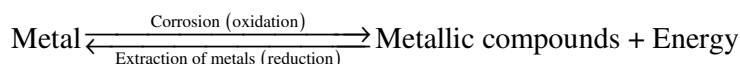
4.2.1 DEFINITION

Corrosion is defined as "the destruction or deterioration or loss of metallic materials through chemical or electrochemical attack by the surrounding environment". The process of corrosion in reality is the transformation of pure metal into its undesired metallic compounds. The life of a metallic object gets shortened by the corrosion process and also loses its useful properties such as malleability, ductility, electrical conductivity and optical reflectability. The familiar examples of corrosion include:

(i)   Rusting of iron – a reddish brown scale formation on iron and steel objects due to the formation of hydrated ferric oxide.
(ii) Green scale formed on copper vessels – it is due to the formation of basic cupric carbonate ($CuCO_3 + Cu(OH)_2$).

4.2.2 CAUSE OF CORROSION

Most of the metals, except noble metals exist in nature in the combined form such as oxides, carbonates, sulphides, chlorides, silicates etc. The metals are generally extracted from the ores by reduction process. During the extraction of metals from their ores a considerable amount of energy is supplied in the form of heat or electrical energy. Hence the pure metals are considered to be in the higher energy state compared to their corresponding ores. They have a natural tendency to revert back to their combined state i.e. lower energy state. Therefore, when metals are put to use in various forms, they combine with the constituents of the environment and get converted into their compounds. Thus corrosion of metals can be considered as the reverse of extraction of metals.

$$\text{Metal} \underset{\text{Extraction of metals (reduction)}}{\overset{\text{Corrosion (oxidation)}}{\rightleftharpoons}} \text{Metallic compounds} + \text{Energy}$$

4.2.3 GRAVITY OF CORROSION

The losses incurred due to corrosion are very high and cannot be estimated by considering only the metal loss. The indirect losses like fabrication cost and cost involved in preventing the corrosion also have to be taken into consideration. The corrosion in metal objects like equipments, instruments, chemical plants, structures etc. may make them inefficient, ineffective, and useless and their unobserved defects due to corrosion may cause their failure. In such cases, the indirect losses may be much higher than the direct losses. It is estimated about two lakh crore worth losses are incurred due to corrosion of steel every year in India. The release of inflammable gases or poisonous gases from the corroded equipments leads to fire accidents or atmospheric pollution.

The secret of effective engineering lies in controlling rather than preventing the corrosion because it is impracticable to eliminate corrosion. This can be successfully done only if we know the mechanism of corrosion and methods of control mechanisms. This chapter highlights some of the important facts about corrosion and its control.

4.3 TYPES OF CORROSION

Corrosion can be broadly classified into two types based on the mechanism of corrosion.
a) Dry or direct chemical corrosion
b) Wet or electrochemical corrosion

4.3.1 DRY OR DIRECT CHEMICAL CORROSION

This type of corrosion mainly occurs through the direct interaction of atmospheric gases such as oxygen, halogens, hydrogen sulphide, sulphur dioxide, oxides of nitrogen or anhydrous liquid with metal surfaces.

When a metal is exposed to a gas, it adsorbs the gas and slowly reacts with it and forms the corrosion product. The corrosion product may be insoluble, soluble or a liquid. In the first case when it is insoluble, a solid film of the corrosion product is usually formed on the surface of the metal which protects the metal from further corrosion. However, if a soluble or a liquid corrosion product is formed, then the metal is exposed to further attack.

There are three main types of chemical corrosion.

1. OXIDATION CORROSION

Oxygen is mainly responsible for the corrosion of most metallic structures as compared to other gases and chemicals. This type of corrosion is brought about by the direct chemical action of oxygen at low or high temperature on metals generally in the absence of moisture. Alkali and alkaline earth metals (e.g., Na, Ca, Mg etc.) suffer extensive oxidation even at low temperatures, where as at high temperatures, practically all metals except Ag, Au and Pt are oxidized.

MECHANISM

When a metal surface is exposed to a gas such as oxygen at room temperature the gas gets adsorbed physically. The gas molecules are attracted to the metal surface by vander Waals forces of attraction. When the temperature is increased, electrons are transferred from the metal to oxygen resulting in the formation of metal ions and oxide ions simultaneously. The metal ions and the oxide ions combine together to form the metal oxide.

$$M \rightarrow M^{2+} + 2e^-$$

$$1/2O_2 + 2e^- \rightarrow O^{2-}$$
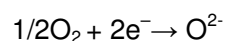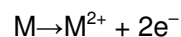
The overall reaction may be represented as,

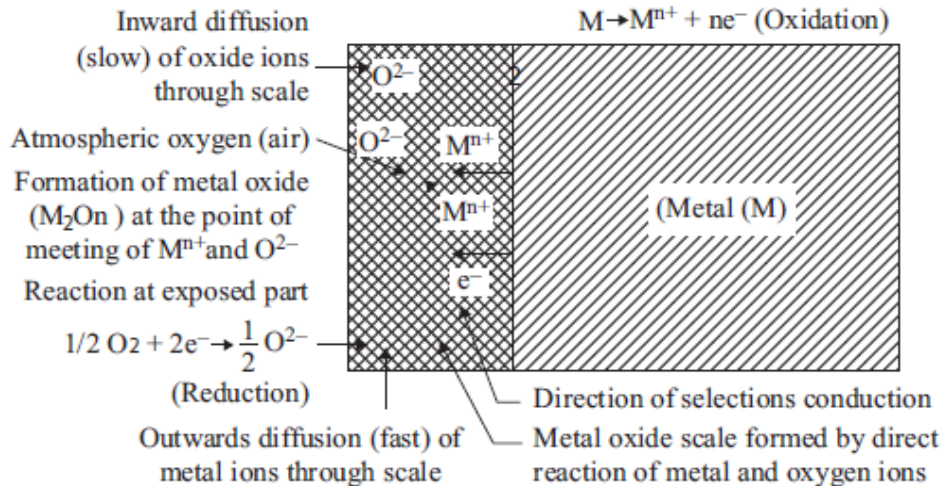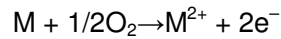$$M + 1/2 O_2 \rightarrow M^{2+} + 2e^-$$
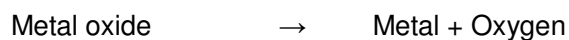

Figure 4.1 Oxidation corrosion

The formation of metal oxide film at the surface actually tends to restrict further oxidation. For oxidation to continue either the metal ions must diffuse outwards through the scale to the surface or the oxide ions must diffuse inwards through the scale to the underlying metal. Both transfers occur (fig. 4.1) but the outward diffusion of metal ions is likely to be more rapid due to the fact that cations are smaller in size compared to the oxide ions.

NATURE OF THE OXIDE

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. This film may be

(i)**Stable** – A stable layer is fine grained structure and can adhere tightly to the parent metal surface. Hence such a layer can cut off penetration of attacking oxygen to the underlying metal. Such a film is protective in nature thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Cr etc. are of stable, hence further oxidation corrosion is prevented.

(ii)**Unstable** – The oxide layer formed decomposes back into the metal and oxygen.

     Metal oxide $\rightarrow$ Metal + Oxygen

Consequently, oxidation corrosion is not possible in such a case. Thus Ag, Au and Pt do not undergo oxidation corrosion.
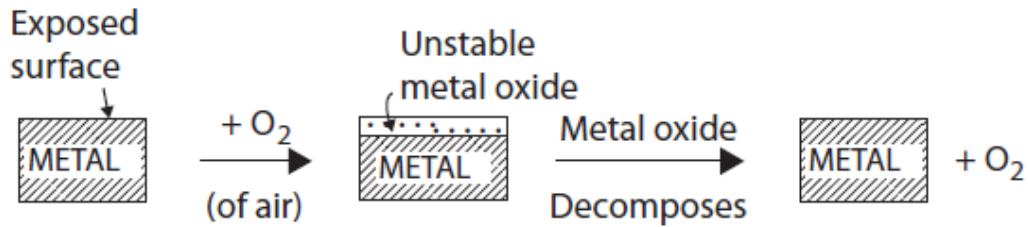
Figure 4.2 Unstable oxide layer

(iii)**Volatile** – The oxide layer volatalizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion. E.g. Molybdenum oxide (MnO_3) is volatile.
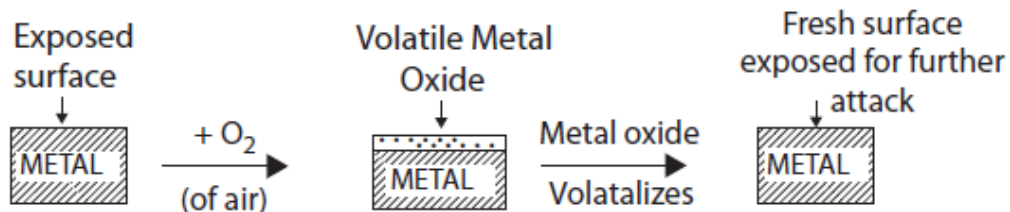

Figure 4.3 Volatile oxide layer

(iv)**Porous** – The oxide film formed has pores or cracks. In this case, the atmospheric oxygen has access to the underlying surface of metal, through the pores or cracks of the layers thereby the corrosion continues unobstructed until the entire metal is completely converted into its oxide. E.g. Li, K, Na, Ca, Mg etc.
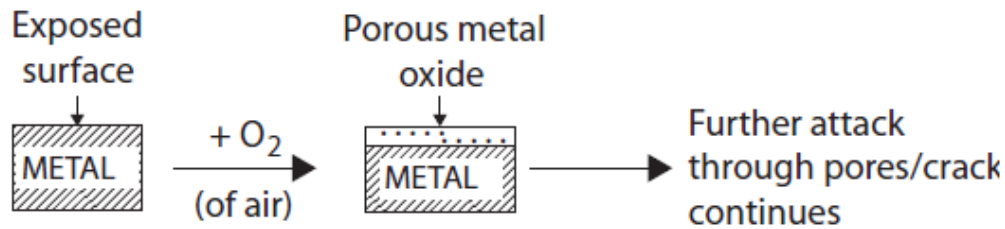

Fig

Figure 4.4 Porous oxide layer

PILLING AND BEDWORTH RULE

The protective and non protective nature of the oxide layer can be predicted on the basis of Pilling – Bedworth rule.

According to this rule an oxide layer 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" and the oxide layer is porous or non – protective "if the volume of the oxide is less than the volume of the metal from which it is formed." For example, heavy metals such as Al, Cr, Pb, Sn etc. form a protective oxide film and prevent further corrosion. Whereas metals like alkali (Li, Na, K etc.) and alkaline earth metals (Be, Ca, Sr etc.) form porous oxide films, which allow further diffusion of oxygen to come in contact with the fresh metal surface and results in severe corrosion.

2. CORROSION BY OTHER GASES

The other gases present in the environment such as chlorine, fluorine, sulphurdioxide, hydrogen sulphide, carbon dioxide etc. are also corrosive. The extent of corrosion of a particular metal depends on the chemical affinity of the metal and the gas involved. The degree of attack depends on the formation of protective or non – protective films on the metal surface.

For example chlorine attacks tin and forms volatile $SnCl_4$ and hence the metal is continuously exposed to the corrosive gas and undergoes rapid corrosion. In contrast a non – porous protective film of $AgCl$ is formed on silver due to attack of chlorine decreases the further corrosion.
Hydrogen sulphide attacks metals forming corresponding metal sulphide and release atomic hydrogen. The hydrogen attacks the metal in two ways.

HYDROGEN EMBRITTLEMENT

At room temperature the atomic hydrogen diffuse readily into the metal and collects at the void spaces, where the atomic hydrogen combines to form hydrogen gas. The accumulation of the gas develops a high pressure causing cracks and blisters in the metal. This condition is known as hydrogen embrittlement.

DECARBURIZATION

At higher temperatures molecular hydrogen undergoes dissociation to yield atomic hydrogen. The active atomic hydrogen attacks the steel and combines with the carbon present in the steel to form methane gas which collects in the voids. As the pressure increases due to the accumulation of the gas, cracks occur in steel, a condition known as decarburization. As a result of decarburization the metal loses some of its strength and ductility.

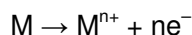$$C + 4H \rightarrow CH_4$$
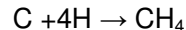
3. LIQUID METAL CORROSION

It is due to the chemical action of flowing liquid metal at high temperature on a solid metal or alloy. This type of corrosion occurs in devices used for nuclear power. The corrosion reaction involves either the dissolution of the solid metal or internal penetration of the liquid metal into the solid metal.
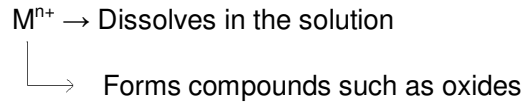
4.3.2 WET OR ELECTROCHEMICAL CORROSION

Most of the corrosion problems are best explained on the basis of electrochemical corrosion. These are often called wet corrosion since aqueous medium or moist air is required for corrosion to take place.

This type of corrosion occurs due to the formation of anodic and cathodic areas on the same metal surface or when two different metals or alloys are in contact with each other in the presence of conducting medium. At the anodic area oxidation reaction takes place and the metal gets converted into its ions, liberating electrons. Consequently, metal undergoes corrosion at the anodic area.

At anodic area,
$$M \rightarrow M^{n+} + ne^-$$

$M^{n+} \rightarrow$ Dissolves in the solution

$\longrightarrow$ Forms compounds such as oxides

On the other hand at the cathodic area, reduction takes place. Since the metal cannot be reduced further some of the constituents present in the corrosion medium take part in the cathodic reaction to form anions like OH^-, O^{2-}. Hence the metal atoms at the cathodic areas are unaffected by the cathodic reaction

The electrons liberated at the anodic area migrate to the cathodic area constituting corrosion current. The metal ions liberated at the anode and some anions (like OH^-, O^{2-}) formed at the cathode diffuse towards each other through the conducting medium and form corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both anodic and cathodic reactions, take place.

MECHANISM OF WET OR ELECTROCHEMICAL CORROSION

Electrochemical corrosion involves flow of electron – current between the anodic and cathodic areas. Anodic reaction is a simple oxidation reaction in which metal atoms are converted into their ions liberating electrons.

At the anodic area: $M \rightarrow M^{n+} + ne^-$
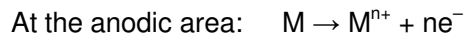
For example when iron undergoes corrosion,

$$Fe \rightarrow Fe^{2+} + 2e^-$$
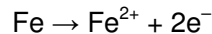
On the other hand the cathodic reaction consumes electrons with either by (a) evolution of hydrogen or (b) absorption of oxygen depending on the nature of the corrosive environment. Correspondingly the corrosion types are known as hydrogen type corrosion and oxygen type corrosion.

(a) Evolution of hydrogen

This type of corrosion occurs in acidic medium and in the absence of oxygen. For example in the case of iron metal, the anodic reaction is dissolution of iron as ferrous iron with the liberation of electrons.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad \text{(oxidation)}$$
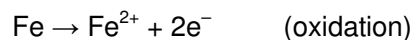
These electrons flow through the metal from anode to cathode, where H+ ions (of acidic solution) are reduced to form H_2 gas.

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \qquad \text{(reduction)}$$
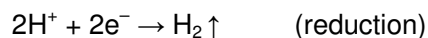
The overall reaction is,

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$$
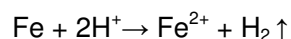
Figure 4.5 Mechanism of wet corrosion by hydrogen evolution

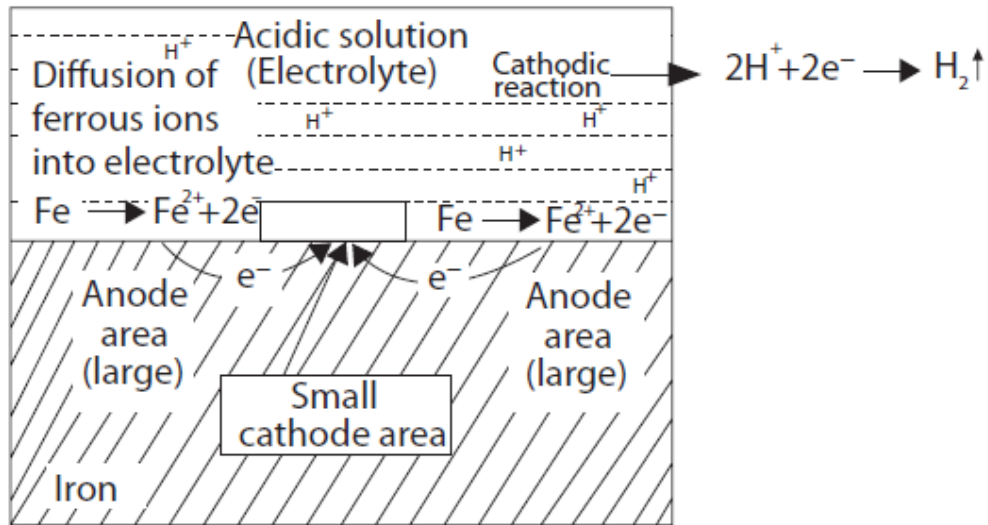This type of corrosion is generally considered as the displacement of hydrogen ions from the acidic solution by the metal ions. The metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen. In this type of corrosion anodes have large areas whereas cathodes are small areas.

(b) Absorption of oxygen

This type of corrosion occurs in neutral or alkaline medium and in the presence of oxygen. Hydrogen ion concentration is very low in neutral or alkaline solution, thus evolution of hydrogen gas is not favorable. In such cases, reduction of oxygen to hydroxyl ion occurs.

The surface of iron is usually coated with a thin film of iron oxide. The small cracks in the oxide film create small anodic areas while the rest of the part acts as a cathode.
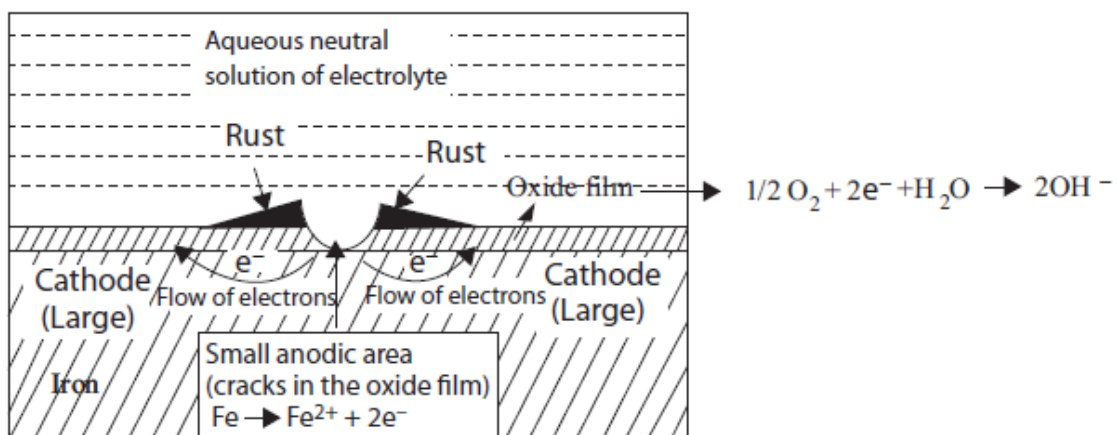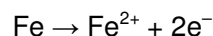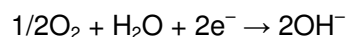

**Figure 4.6** Mechanism of wet corrosion by oxygen absorption

At the anodic areas the metal (iron) dissolves as ferrous ions with the liberation of electrons.

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The liberated electrons flow from anode to cathode through iron metal, where electrons are intercepted by the dissolved oxygen as,

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

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

$$Fe^{2+} + OH^- \rightarrow Fe(OH)_2$$
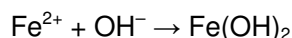
Since smaller Fe^{2+} ions diffuse more rapidly than OH^- ions, their combination occurs more commonly near the cathodic area. The corrosion occurs near the anodic area and the corrosion product deposits near the cathodic area.

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3$$
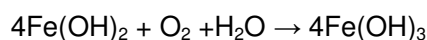
This product is called yellow rust and it is chemically $Fe_2O_3.H_2O$.

If the supply of oxygen is limited the corrosion product may be black anhydrous magnetite, Fe_3O_4. Generally, presence of oxygen greatly accelerates both corrosion and rust formation.

COMPARISON BETWEEN CHEMICAL AND ELECTROCHEMICAL CORROSION

S. No	Chemical corrosion	Electrochemical Corrosion
1.	It occurs in the dry state	It takes place in the presence of moisture or electrolyte
2.	It is due to direct chemical attack of the metal by the environment.	It is due to the formation of large number of small galvanic cells.
3.	Follows adsorption mechanism	Follows electrochemical reaction mechanism
4.	Even a homogeneous metal surface will be corroded	Surface heterogeneity or bimetallic contact is necessary for this type of corrosion
5.	Corrosion products accumulate in the same place where corrosion occurs. So the corrosion is often self controlled	Corrosion occurs at the anode and the product settles near the cathode. So the Corrosion is not self controlled.
6.	Uniform corrosion occurs.	Pitting corrosion is likely to occur when the anode is small in area
7.	Examples Rusting of iron in dry state, reaction of dry HCl gas on Fe and tarnishing of Ag in air containing H_2S	Examples Rusting of iron in moist atmosphere and dezincification of brass

TYPES OF ELECTROCHEMICAL CORROSION

4.3.3. GALVANIC CORROSION

Galvanic corrosion (also called "dissimilar metal corrosion") occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte. In a galvanic couple, the more active metal (called the anode) corrodes at a faster rate and the more noble metal (called the cathode) corrodes at a slower rate. For galvanic corrosion to occur, three conditions must be present. They are

1. Electrochemically dissimilar metals must be present

2. The metals must be in electrical contact, and

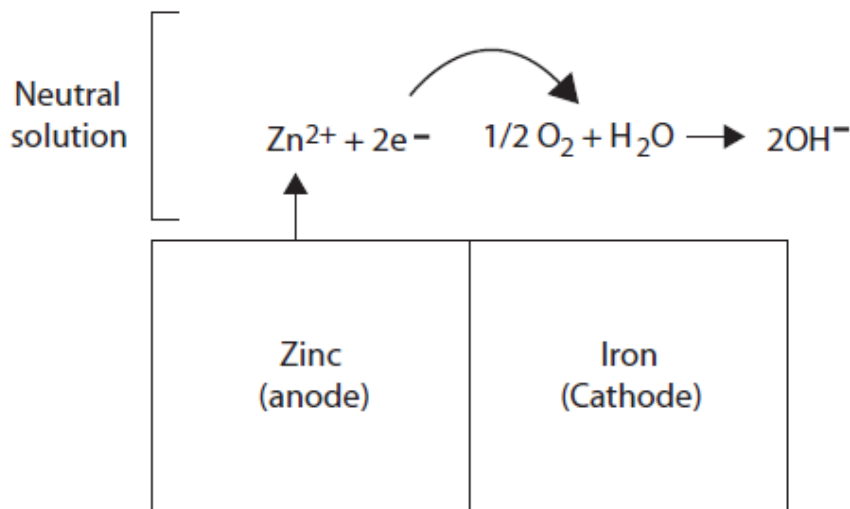3. The metals must be exposed to an electrolyte

Neutral solution

$$Zn^{2+} + 2e^- \quad 1/2\,O_2 + H_2O \longrightarrow 2OH^-$$

Zinc (anode)   Iron (Cathode)

Figure 4.7 Galvanic corrosion

Figure 4.7 represents Zn-Fe bimetallic couple. Of the two metals, zinc (more active) dissolves at a faster rate compared to iron (less active). Here zinc act as the anode and undergo corrosion, whereas, iron act as cathode and is protected from corrosion. Similarly, a bimetallic couple can be set up with iron and copper in which, iron (more active) undergo corrosion at a faster rate whereas Cu (less active) is protected from corrosion.

Factors such as relative size of anode, types of metal and operating conditions (temperature, humidity, salinity, etc) affect galvanic corrosion. The surface area ratio of the anode and cathode directly affects the corrosion rates of the materials. Galvanic corrosion is often utilized in sacrificial anodes.

4.3.4 DIFFERENTIAL AERATION CORROSION OR CONCENTRATION CELL CORROSION

Corrosion of metals arising as a result of the formation of an oxygen concentration cell due to the uneven supply of air on the metal surface is known as differential aeration corrosion. It occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as

cathodic region and part of the metal exposed to lower oxygen concentration acts as anodic region. Consequently, poorly oxygenated region of the metal undergo corrosion.
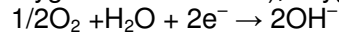
At the anode (less oxygen concentration), metal undergoes corrosion.

$$M \rightarrow M^{n+} + ne^-$$
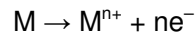
At the cathode (more oxygen concentration), oxygen is reduced.
$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

There are different types of differential aeration corrosion. Some examples are pitting corrosion, pipeline corrosion, corrosion in wire fence and water line corrosion.

4.3.5 PITTING CORROSION

Pitting corrosion is a localized corrosion that occurs on a metal surface. The pits are often found underneath surface deposits caused by corrosion product accumulation. Pitting is considered to be more dangerous than uniform corrosion damage as it is more difficult to detect, predict and design against. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system.
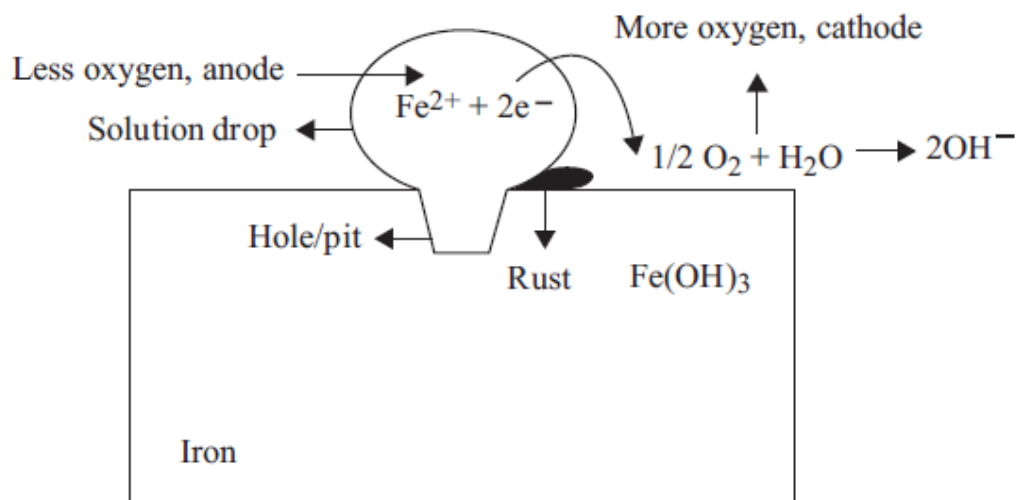
Figure 4.8 Pitting corrosion

Pitting corrosion can be explained from the figure shown above.

When a drop of water or NaCl solution is placed on a metal surface, the area below the drop of water, which does not have much access to oxygen, becomes anodic with respect to the other areas, which are freely exposed to air.

The area exposed to air demand more electrons for reduction from the smaller area covered by the drop of solution. Therefore, more and more material is removed from the smaller anodic area, which results in the formation of a hole or a pit. Pit formed is now more away from the atmosphere which act as better anode and corrosion proceeds at a very fast rate.

At anode the metal (iron) undergoes oxidation:

$$Fe \rightarrow Fe^{2+} + 2e^-$$
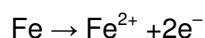
At cathode, oxygen undergoes reduction:

$$1/2 O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
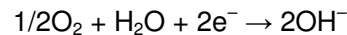
Pitting is initiated by,

1. Localized chemical or mechanical damage to the protective oxide film

2. Localized damage to, or poor application of, a protective coating

3. Presence of non-uniformities in the metal structure of the component, e.g. nonmetallic inclusions.

Stainless steels are sensitive to pitting corrosion, but other metals, such as passive iron, chromium, cobalt, aluminium, copper and their alloys are prone to this form of damage.

4.3.6 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Micribiologically influenced corrosion, also called bacterial corrosion, bio-corrosion, microbiologically-induced corrosion or microbial corrosion is caused by specific genera of bacteria which feed on nutrients and other elements found in waters and soils. Sea water is a primary source of sulphate reducing bacteria (SRB). The biological activities modify the local environment and render it more corrosive to the metals. For example, iron-oxidizing bacteria can perforate a 5mm thick stainless steel tank in just over a month.

MIC is not caused by a single microbe, but is attributed to many different microbes. These are often categorized by common characteristics such as by-products (i.e., sludge producing) or compounds they affect (i.e., sulfur oxidising). In a general sense, they fall into one of the two groups based upon their oxygen requirements; on being aerobic (requires oxygen) such as sulfur oxidizing bacteria, and the other being anaerobic, (requires little or no oxygen), such as sulfate reducing bacteria. MIC can cause various forms of localized corrosions such as pitting corrosion, de-alloying, stress corrosion, cracking and hydrogen embrittlement etc. The wide variety of bacteria associated with MIC can cause problems in almost any type of residential, commercial or industrial setting.

MIC operates as an individual nodule covering a pit. The development of this process occurs in three phases, which are:

1. Attachment of microbes

2. Growth of nodule and initial pit

3. Mature pit and nodule.

Once MIC is established in a system it is quite difficult to eliminate. There are several ways to test MIC and one of the most nondestructive methods is to simply determine the types and quantities of microbes present in a system.

Many industries such as chemical processing industries, nuclear power generation, onshore and offshore oil and gas industries and underground pipeline industries are affected by MIC.

Mechanism

Under favourable conditions, bacteria such as SRB reduce inorganic sulphates to sulphides. When these compounds come into contact with iron (buried pipelines and pipe from deep water wells) in the presence of moisture, it gets converted to rust and FeS.

$$Na_2S + 4H_2O + 2Fe \rightarrow Fe(OH)_2 + FeS + 2NaOH$$

Prevention

MIC can be prevented through a number of methods:
1. Regular mechanical cleaning

2. Chemical treatment with biocides to control the population of bacteria

3. Complete drainage and dry-storage

4.4 FACTORS INFLUENCING THE RATE OF CHEMICAL AND ELECTROCHEMICAL CORROSION

The type, speed, cause and seriousness of corrosion depends upon the following factors that can be classified based on the

1. Nature of the metal and

2. Nature of the environment

4.4.1 NATURE OF THE METALS

a) Electrode potential or position in EMF series

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum, silver. Metals with lower electrode potentials, readily undergo corrosion e.g. metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g., the potential difference between iron and copper is0.78V which is more than that between iron and tin (0.3V). Therefore, iron corrodes faster when in contact with copper that with tin. On this account, the use of dissimilar metals should be avoided wherever possible.

b) Hydrogen overvoltage

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since, at lower hydrogen over voltage, liberation of hydrogen gas is easy, cathodic reaction occurs at a very fast rate. This in turn, makes the anodic reaction(corrosion) also to proceed at a faster rate. Thus, higher the over voltage lesser is the corrosion.

c) **Ratio of cathodic to anodic region**

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio inreases corrosion rate further increases. This is because at anode electrons are liberated and are consumed at cathodic region. If the cathodic region is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to an increase in the overall rate of corrosion.

d) Nature of the corrosion product

The corrosion product (like metal oxide) formed act as protective film, if it is stable, insoluble, and nonporous. If it acts as protective film it prevents further corrosion by acting as a barrier between the metal surface and the corrosion medium. On the other hand, if the corrosion product is unstable, porous, and soluble it further enhances the corrosion.

e) Purity of metals

Hundred percentage pure metals will not undergo any type of corrosion. Presence of impurity creates heterogeneity in the metal resulting in the formation of large number of distinct galvanic cells at different parts of the metal leading to corrosion of the metal. Higher the percentage of impurity higher will be the rate of corrosion.

4.4.2. NATURE OF THE ENVIRONMENT

a) Temperature

Rate of corrosion increases with the increase in temperature. This is due to the increase in the conductance of the medium with increase in temperature and hence an increase in the diffusion rate. Consequently, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

b) Humidity

Rate of corrosion will be high when the relative humidity of the environment is high. Presence of moisture enhances electrochemical type of corrosion.

c) Suspended solids
Solid pollutants in the environment such as NaCl, dirt, dust, charcoal increases the rate of corrosion.

d) Impurities in the environment
Gaseous impurities such as SO_2, CO_2, H_2S which makes the environment acidic increases the rate of corrosion of metals.

e) pH of the corrosive environment
Rate of corrosion is higher in acidic pH than in the neutral or alkaline pHs. In the case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion, whereas, at low pH severe corrosion takes place. For metals like aluminium, corrosion rate is high even at high pH values.

4.5 GALVANIC SERIES

In the electrochemical series, a metal which is present above is more active than the metal which is present below. Though this series gives useful information about the chemical reactivity of metals, it does not provide any information in predicting the corrosion of metals.

For example, in Zn – Al couple, zinc which is below aluminium in the electrochemical series is corroded while aluminium is protected from corrosion. In view of this, the electrode potential of various metals and their alloys was measured using Calomel electrode as the reference electrode and immersing the metal or alloy in sea water.

The galvanic series is 'the arrangement of all the metals and alloys in the decreasing order of their activity'.

Active (or Anodic) ↑ ↓ Noble (or cathodic)	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. Iconel 14. Ni – Mo – Fe alloys 15. Brasses 16. Monel metal (7% Ni, 30% Cu. Rest Fe) 17. Silver solder 18. Cu 19. Ni 20. Chromium stainless steel 21. 18 – 8 stainless steel 22. 18 – 8 Mo stainless steel 23. Ag 24. Ti 25. Graphite 26. Au 27. Pt

SIGNIFICANCE OF GALVANIC SERIES

Because of the limitations of the Emf Series for predicting galvanic relations, and also because alloys are not included, the *Galvanic Series* has been developed.

1. The potentials that determine the position of a metal in the Galvanic Series may include steady - state values in addition to truly reversible values; hence, alloys and passive metals are included.

2. Some metals occupy two positions in the Galvanic Series, depending on whether they are active or passive, whereas in the Emf Series only the active positions are possible.

3. Although only one Emf Series exists, there can be several Galvanic Series with various environments and differences in tendency to form surface films. In general, therefore, a specific Galvanic Series exists for each environment, and the relative positions of metals in such Series may vary from one environment to another.

4. When two dissimilar metals are coupled together the corrosion depends not only on how far apart they are in the Galvanic Series (potential difference), but also on their relative areas and the extent to which they are polarized.

5. The potential difference of the polarized electrodes and the conductivity of the corrosive environment determine how much current flows between them.

4.6 CORROSION PREVENTION

Corrosion can be controlled in so many ways. The basic methods of protection of a metal from corrosion are

    (i) Material selection and design

    (ii) Cathodic protection

    (iii) Use of inhibitors

4.6.1. MATERIAL SELECTION AND DESIGN

Corrosion in metals can be prevented right from the initial step of making equipments like choosing the appropriate metal which does not undergo corrosion and framing a suitable structure for the equipment.

Material Selection

The first and the foremost method of controlling corrosion is the selection of right type of material. The material selection should be made not only on its cost and structure but also on its chemical properties and its environment.

1. Noble metals are more immune to corrosion. But they cannot be used for general purpose since they are costly.

2. The next choice is the selection of pure metal. Impurities in a metal cause heterogeneity which increases the rate corrosion. Even the presence of minute amount of impurities may cause severe corrosion. For example minute quantities of Fe in Mg or Pb in Zn leads to extensive corrosion.

3. Alloying improves corrosion resistance e.g. Presence of Chromium in stainless steel. It produces an exceptionally coherent oxide film which is self healing and protects steel from corrosion.

4. Heat treatment like annealing helps to reduce internal stresses and reduces corrosion.

5. If an active metal is selected, it should be insulated from more cathodic metal.

Designing

The equipment should be designed in such a way that even if corrosion occurs it should be uniform and should not be intense and localized. The following conditions may be followed during designing of the equipments to reduce the rate of corrosion.

1. Two dissimilar metals should not be in contact with each other. Otherwise the more active metal gets corroded and the less active metal is protected from corrosion.

2. If the contact between two dissimilar metals is unavoidable, then the metals should be selected in such a way that their oxidation potentials are as near as possible i.e. they should be as close as possible to each other in the electrochemical series.

3. If the contact between two dissimilar metals is unavoidable, then the anodic area should be very large when compared to the cathodic area.

4. Moisture should be removed whenever possible. If moisture or electrolytic solution is present, suitable inhibitors should be added.

5. When two dissimilar metals have to be in contact, then they should be separated by a suitable insulating material.

6. A proper design should not contain crevices between two adjacent parts since this causes differential aeration corrosion.
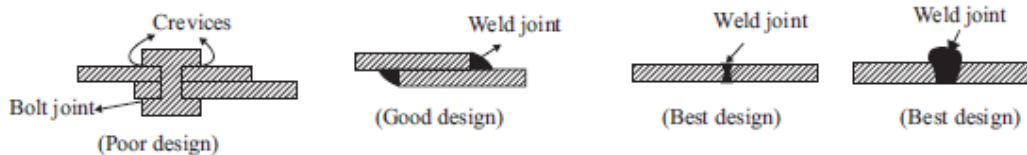

Figure 4.9 Designs with and without crevices

7. A proper design should allow the adequate cleaning of the critical parts. For example, if sharp corners or recesses are present, there may be accumulation of dirt or impurities which causes heterogeneity. Hence a proper design should have smooth joints and bents to avoid the accumulation of impurities.
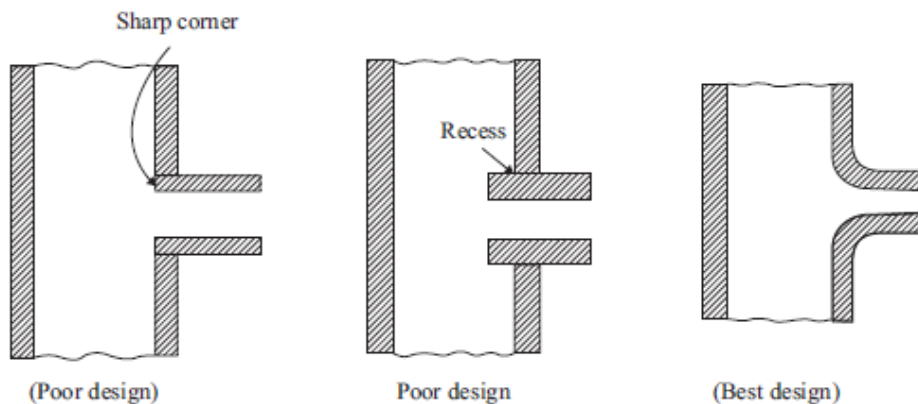

Figure 4.10 Designing of materials with smooth joint and bends

Whenever possible, the equipment should be supported on legs to allow free circulation of air.
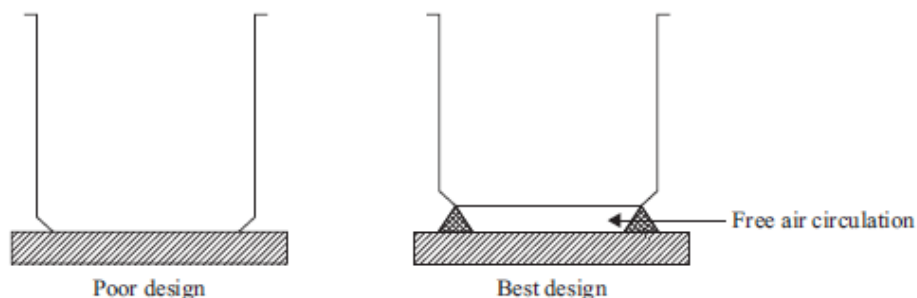
Figure 4.11 Design having free circulation of air

4.6.2. CATHODIC PROTECTION

When two dissimilar metals are coupled together, the more active metal acts as anode and undergoes corrosion. The less active metal acts as cathode and is protected from corrosion. Hence, anode always undergoes corrosion. Cathodic protection is forcing a metal to act as cathode so that corrosion does not occur in this base metal. There are two ways by which cathodic protection is carried out.

1. Sacrificial anodic protection

2. Impressed current cathodic protection

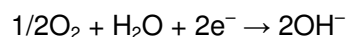### SACRIFICIAL ANODIC PROTECTION

Sacrificial anodic protection involves the protection of a metal at the expense of some other more active metal. The more active metal acts as sacrificial anode and protects the less active metal. This method is generally used for the protection of underground cables or pipes.

In this method, a plate or block of a reactive metal is buried beside the iron pipe or tank which is to be protected from corrosion and both are connected by a wire. Since the more reactive metal has a greater tendency to get oxidized, it undergoes oxidation in preference to iron. The more active metal thus acts as anode and is called 'sacrificial anode'. Metals commonly used as sacrificial anodes are magnesium, zinc, aluminium and their alloys.

Magnesium has the most negative potential and is widely used in high resistivity electrolytes such as soil. Zinc is used as anode in good electrolytes like sea water.

$$Mg \rightarrow Mg^{2+} + 2e^-$$

The electrons migrate to the iron object which starts acting as cathode. At iron cathode, electrons reduce oxygen into OH^- ions.

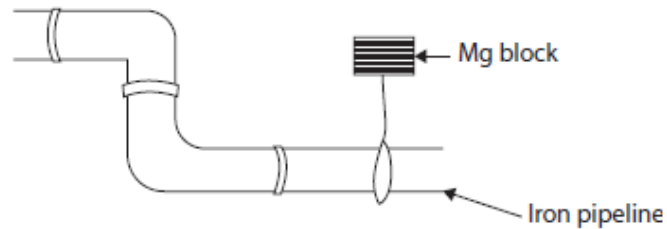$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

Figure 4.12 Sacrificial anodic protection

The anode gradually disappears due to oxidation. The iron object remains protected as long as the sacrificial anode is present. The corroded anode block is replaced by a fresh one, when corroded completely. Important applications of sacrificial anodic method are protection of buried pipeline, underground cables, marine structures, ship hulls etc.

IMPRESSED CURRENT CATHODIC PROTECTION

Whenever there is corrosion, because of the redox reaction (oxidation of anode and reduction at the cathode), a current is produced which is called corrosion current. In this method, an impressed current is applies in the opposite direction to convert the anode to cathode and to nullify the corrosion current.

The metal structure to be protected is connected to the negative terminal of a DC source like a battery or a rectifier. The positive terminal of the DC source is connected to an inert anode. The inert anodes used for this purpose are graphite, high silica iron, platinised titanium etc. The anode is usually buried in a backfill composed of a mixture of gypsum, bentonite and sodium sulphate. This increases the electrical contact with the surrounding soil.
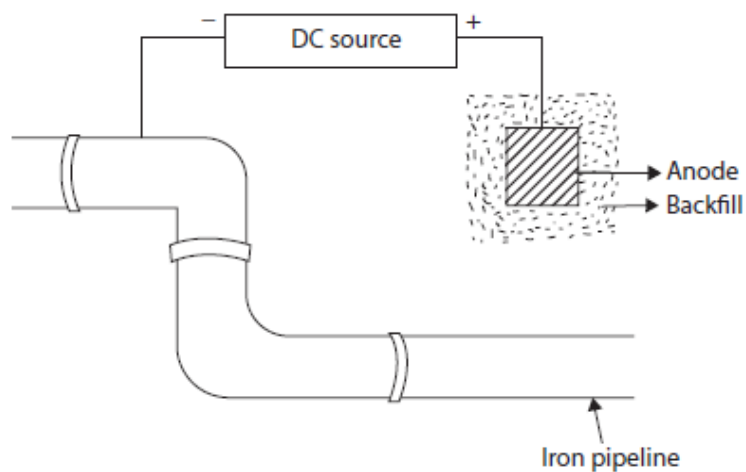

Figure 4.13 Impressed current method

This method is useful for the protection of large underground structures like water tanks, buried oil or water pipes, transmission line towers, marine pipes etc. However, this method involves large installation and maintenance cost.

4.6.3. CORROSION INHIBITORS

Corrosion inhibitors are 'chemical substances which when added in small quantities to the aqueous or gaseous corrosion environment, retard or slow down the corrosion processes resulting in the reduction of overall corrosion rate'. Corrosion inhibitors are broadly classified two types.

1. Immersion inhibitors

2. Atmospheric inhibitors

IMMERSION INHIBITORS

They are used in solutions to achieve inhibition. There are two types of immersion inhibitors.

(1) Anodic inhibitors

(2) Cathodic inhibitors
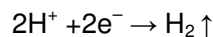
ANODIC INHIBITORS

Examples of anodic inhibitors are alkalis, chromates, phosphates, molybdates etc. The basic reaction at the anodic area is oxidation i.e. formation of metal ions.

$$M \rightarrow M^{n+} + 2e^-$$

When the anodic inhibitors are added to the corrosive environment, they react with the metal ions from the anodic area and form a sparingly soluble salt which gets adsorbed at the surface of the anodic area. This forms a protective film or barrier on the anode, which prevents the oxidation of the metals. This reduces the rate of corrosion.

CATHODIC INHIBITORS

(a) In acidic medium, the basic cathodic reaction is evolution of hydrogen gas.

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$

Rate of corrosion may be reduced either by slowing down the diffusion of hydrogen ions through the cathode or by increasing the hydrogen over voltage. The diffusion of hydrogen ions can be reduced by adding organic inhibitors like amines, pyridine, mercaptans, substituted urea and thiourea, quinoline etc. These positively charged cationic groups attach themselves to the cathodic areas through the nitrogen and provide inhibition. The efficiency of inhibition depends upon the size and the number of alkyl groups. For example, primary amyl amine ($C_5H_{11}NH_2$) has been found to be a more effective inhibitor than primary ethyl amine ($C_2H_5NH_2$).

The hydrogen over voltage can be increased by adding antimony oxide, arsenic oxide or sodium meta arsenite. These substances deposit an adherent film of metallic antimony or arsenic at the cathodic areas, thereby considerably increasing the hydrogen over voltage.

(b) In neutral aqueous medium, the cathodic reaction is,

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
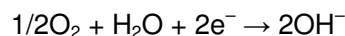
The formation of OH^- ions is only due to the presence of oxygen. Hence, corrosion can be controlled either by removing oxygen from the environment or by preventing the diffusion of

oxygen to the cathodic area. Oxygen can be removed from the solution by adding substances like sodium sulphide, sodium sulphate or hyrdazene. The diffusion of oxygen towards the cathodic area is prevented by adding inhibitors like magnesium, zinc or nickel salts which react with the hydroxyl ions at the cathode to form insoluble hydroxides which deposit on the cathode. These deposits are impermeable barriers and hence retard the diffusion of oxygen at the cathode.

VAPOUR PHASE INHIBITORS

These are organic inhibitors which readily vapourise and form a protective layer of the inhibitor on the metal surface. These are conveniently used to avoid corrosion in enclosed spaces and also during storage, packing, shipping etc. Cyclohexylamine carbonate, benzoate, Dicyclohexylamine nitrite most widely used vapour phase inhibitors.

4.7 PROTECTIVE COATINGS

Due to modern technology there is an increase in stress on the metals. The use of metals increases and also the stress on the metals. Stress leads to corrosion and this can be prevented by many methods which are discussed in the previous sections. Some of the methods are costly. New alloys with improved properties can prevent corrosion. But even alloys undergo stress corrosion. Hence protective coatings plays an important role in preventing corrosion.

Protective coating is coating a metal to be prevented from corrosion with another metal or an inorganic material or an organic material. This coating forms a physical barrier between the surface of the metal and the environment thereby protecting the metal from corrosion.

Organic coating is one of the important protective coatings. Examples of organic coating are paints, varnishes and lacquers.

Paints

Paint is a viscous, opaque solution consisting of one or more pigments in a medium or vehicle. Vehicle (drying oil) is a non-volatile film forming material dissolved in a suitable volatile solvent called thinner.

Ingredients of a paint

A paint essentially consists of the following ingredients.
(i) Pigment, (ii) Vehicle or drying oil, (iii) Thinner, (iv) Drier,   (v) Filler or extender, (vi) Plasticiser and (vii) Antiskinning agent.

1. Pigments

They are finely ground colouring matters.

Functions : To give colour and opacity to the paint.

Examples: Black   -   Lamp black
                  Blue   -   Prussian blue
                  Brown -   Burnt umber

           Green -   Chrome green
           Red   -   Red lead
           Yellow -   Chrome yellow
           White -   Zinc oxide

2. Vehicle or Drying oil

The vehicle is a non-volatile liquid and film forming material which holds all the ingredients of a paint together.

Functions: (i) To spread the paint evenly on the surface. (ii) To provide a binder for the ingredients of a paint so that they may stick or adhere to the surface.

Examples: Linseed oil, Tung oil.

3. Thinner

It is a highly volatile solvent.

Functions :
   (i) To make the paint thin so that it can be easily applied on the surface.
   (iii) To dissolve the vehicle.
   (iv) (iii) To suspend the pigments.

Examples: Turpentine, Toluol, Xylol, Kerosene, etc.

4. Driers

These are the substances used to accelerate the process of drying.

Functions: To accelerate the drying of drying oil through oxidation, polymerization and condensation.

Examples: Litharge, Red lead, (Resinates and linoleates of Co, Mn and Pb).

5. Extenders or Fillers

Functions: (i) To bring down the cost of paint. (ii) To improve the durability of paint. (iii) To prevent shrinkage and cracking.

Examples : Barytes ($BaSO_4$), Gypsum, China clay.

6. Plasticisers

Sometimes they are added to paint to provide elasticity to the film and to minimize its crack.

Examples : Triphenyl phosphate, Tributyl phthalate.

7. Antiskinning Agents

They are added to the paint in order to prevent gelling and skinning of the finished product.

Examples : Poly hydroxy phenol.

Pigment Volume Concentration (P.V.C.)

Pigment Volume Concentration (P.V.C.) is an important property of paint. The higher the volume of P.V.C., the lower will be durability, adhesion, consistency and glossy of the paint.

The following equation is used to calculate the P.V.C.

$$P.V.C. = \frac{V_1}{V_1 + V_2}$$

Where V_1 = Volume of pigment in paint

   V_2 = Volume of non-volatile vehicle in the paint.

Characteristics of a good paint

(i)   It should have a good spreading power. (Maximum area of the surface should be covered by minimum quantity of the paint).

(ii)   It should form durable, tough and resistant to wear film on drying.

(iii)   Colour of paint should not fade or change.
(iv)   It should not crack on drying.
(v)   It should dry quickly.
(vi)   It should give a smooth and pleasing appearance.

Mechanism of Drying of Drying Oils

Drying oils are glyceryl esters of high molecular weight fatty acids. They are the main film forming agent of a paint. They are the binder of all other ingredients of paint. Examples are Linseed oil, Tung oil, etc.

The mechanism of drying of drying oils involve oxidation followed by polymerization and condensation. The structural arrangements required for drying of drying oils are

(i)   Conjugated oil structure (Example: Tung oil)
   $- CH = CH - CH = CH - CH = CH -$

(ii)   Non-conjugated oil structure (Example: Linseed oil)
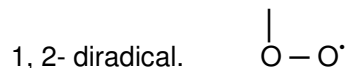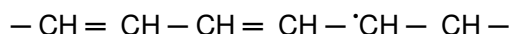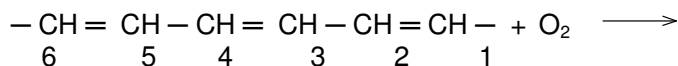 $- CH = CH - CH_2 - CH = CH -$

Time required for drying of oils at 25^{0}C under standard conditions

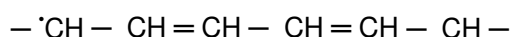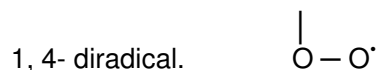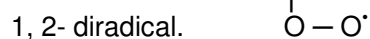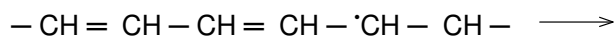| Linseed oil (Non-conjugated)	120 Hrs (Without drier)	3 Hrs. (With drier)
Tung oil (Conjugated)	8 – 72 Hrs. (Without drier)	1 ½ Hrs. (With drier)

Mechanism of drying of conjugated oils

Conjugated oils contain higher proportion of fatty acids with triple unsaturation. They have more positions (double bonds) for oxidation (O_2 attack).
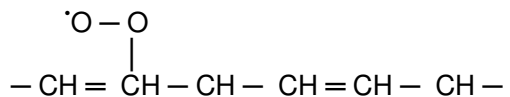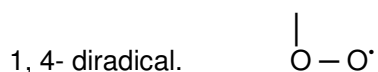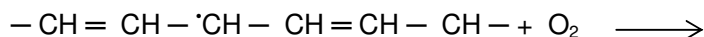
   The absorption of O_2 at the site of the double bond gives 1, 2- diradical.

$$-CH = CH - CH = CH - CH = CH - \ + O_2 \longrightarrow$$
$$6 \quad\;\; 5 \quad\;\; 4 \quad\;\; 3 \quad\;\; 2 \quad\;\; 1$$

$$-CH = CH - CH = CH - \overset{\bullet}{C}H - CH -$$

1, 2- diradical. $\quad\quad \overset{|}{O} - O^{\bullet}$

Rearrangement of double bonds in the above diradical can give 1, 4 and 1, 6- diradicals.

$$-CH = CH - CH = CH - \overset{\bullet}{C}H - CH - \longrightarrow$$

1, 2- diradical. $\quad\quad \overset{|}{O} - O^{\bullet}$

$$-CH = CH - \overset{\bullet}{C}H - CH = CH - CH - \ \text{and}$$

1, 4- diradical. $\quad\quad \overset{|}{O} - O^{\bullet}$

$$-\overset{\bullet}{C}H - CH = CH - CH = CH - CH -$$

1, 6- diradical. $\quad\quad \overset{|}{O} - O^{\bullet}$
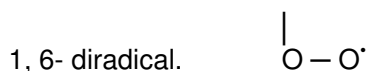
Oxygen attack at the radical site gives peroxide radical.

$$-CH = CH - \overset{\bullet}{C}H - CH = CH - CH - + \ O_2 \longrightarrow$$

1, 4- diradical. $\quad\quad \overset{|}{O} - O^{\bullet}$

$$\overset{\overset{\bullet}{O} - O}{\underset{|}{}}$$
$$-CH = CH - CH - CH = CH - CH -$$

peroxide radical $\quad\quad \overset{|}{O} - O^{\bullet}$

The peroxide radicals produce polyperoxides by polymerization, which is a durable, hard, and adherent film.

Peroxide radicals $\xrightarrow{\text{Polymerization}}$ Polyperoxide (durable, adherent film).

### Mechanism of drying of non-conjugated oils

The reaction between oxygen and non-conjugated oils takes place without loss of unsaturation. That is the methylene group present between the two double bonds is prone to direct oxidation and this reaction produces hydroperoxides.

$$- CH= CH - CH_2 - CH = CH - \ + O_2 \longrightarrow$$

$$- CH = CH - CH - CH = CH -$$
$$| $$
$$O–O–H$$

Hydroperoxide - ROOH
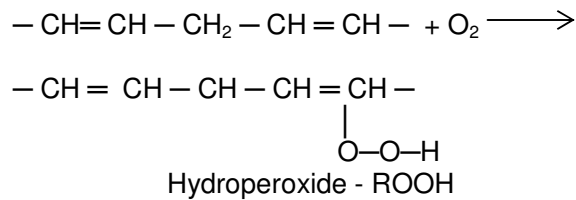
This hydroperoxide decomposes to give free radicals under the influence of heat and light.

$$ROOH \longrightarrow RO^{\bullet} + \ ^{\bullet}OH$$
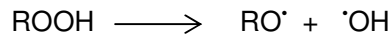
The new free radical may rearrange to give a conjugated system of double bonds.

$$RO^{\bullet} + \ - CH= CH - CH_2 - CH = CH - \longrightarrow$$

$$ROH + - CH= CH - \ ^{\bullet}CH - CH = CH -$$
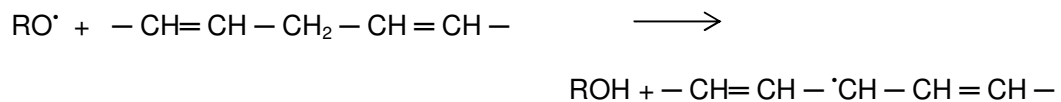
Reaction between oxygen and these conjugated systems gives peroxide radicals, and then polyperoxide, a durable, adherent film.

PART – A QUESTION

1. Define corrosion.
2. State the Pilling – Bedworth rule.
3. What is dry corrosion?
4. Fe corrodes faster than Al even though Fe is placed below Al in the electrochemical series. Why?
5. What is electrochemical corrosion?
6. Mention the conditions at which electrochemical corrosion occurs.
7. Mention the catodic reactions taking place in electrochemical corrosion.
8. Define galvanic corrosion.
9. A steel screw in brass marine hardware corrodes. Give reason.
10. What is meant by differential aeration corrosion?
11. Define pitting corrosion.
12. Define microbial corrosion.
13. Iron corrodes under a drop of water or salt solution. Explain.
14. What is meant by galvanic series?
15. Distinguish between chemical corrosion and electrochemical corrosion.
16. Distinguish between electrochemical series and galvanic series.
17. A small steel tap fitted in a large copper tank undergoes severe corrosion. Justify.
18. What is meant by cathodic protection?
19. Define sacrificial anodic protection.
20. Define impressed current cathodic protection.
21. What are corrosion inhibitors?

22. What are vapour phase inhibitors? Give an example.

23. What are protective coatings?

24. What are paints?

25. What are the various ingredients present in paints?

26. What are the functions of thinner in paint? Give examples?

27. Write a note on vehicle.

28. Give two examples of fillers in paint.

29. Mention the functions of fillers.

30. Define pigment volume concentration.

31. Write the characteristics of a good paint.

PART – B QUESTION

1. Compare the galvanic series with the electrochemical series.

2. Explain the mechanism of oxidation corrosion.

3. Explain the mechanism of electrochemical corrosion.

4. Distinguish between chemical corrosion and electrochemical corrosion.

5. Discuss the factors influencing the rate of corrosion by the nature of the metal.

6. Discuss the factors influencing the rate of corrosion by the nature of the environment.

7. Write a short note on galvanic corrosion and microbial corrosion.

8. Write a note on corrosion control by material selection and design.

9. Describe the cathodic protection method of corrosion control.

10. What are corrosion inhibitors? Explain the various inhibitors.

11. Write a short note on differential aeration corrosion.

12. What are electrochemical cells? How are they represented?

13. What is Pilling Bedworth rule? Discuss the role of nature of oxides formed in oxidation corrosion.

14. Explain the sacrificial anodic protection method of corrosion control.

15. What is galvanic series? Explain its significance.

16. Explain in detail the various constituents present in paint.

17. Explain the mechanism of drying of drying oils in paints.

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