

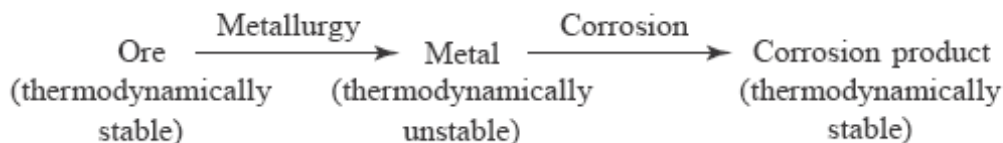
Corrosion and its Control

1. Why metals undergo corrosion? How is corrosion related to metallurgy? Give examples of corrosion of metals?

In nature, metals are not found in free state due to their reactivity. It is the ore from which the metals are extracted by metallurgical process. Metallurgy requires a large amount of heat energy.

2. Why metals are not found in their free state?

The answer to this question is that the metals are thermodynamically unstable in their free state. They are stable in the form of certain compounds. This is given as:



Corrosion is a process of formation of the compound of pure metal by the chemical reaction between metallic surface and its environment. It is an oxidation process. It causes loss of metal. Hence, disintegration of a metal by its surrounding chemicals through a chemical reaction on the surface of the metal is called corrosion.

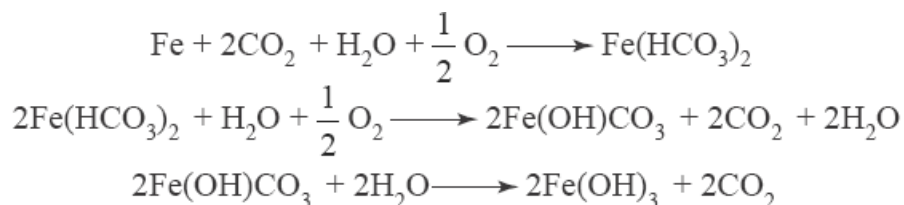
Example: Formation of rust on the surface of iron, formation of green film on the surface of copper. The responsible factors for the corrosion of a metal are the metal itself, the environmental chemicals, temperature and the design.

2. What are different theories of corrosion?

There are three theories of corrosion: (i) acid theory, (ii) dry or chemical corrosion and (iii) galvanic or electrochemical or wet corrosion.

Acid theory of corrosion

This theory suggests that corrosion of a metal (iron) is due to the presence of acids surrounding it. According to this theory, iron is corroded by atmospheric carbon di- oxide, moisture and oxygen. The corrosion products are the mixture of $\text{Fe}(\text{HCO}_3)_2$, $\text{Fe}(\text{OH})\text{CO}_3$ and $\text{Fe}(\text{OH})_3$. The chemical reactions suggested are given below



This theory is supported by the analysis of rust that gives the test for CO_3^{2-} ion. Further, the process of rusting is reduced by the presence of lime and caustic soda (these two can absorb CO_2 , thus reducing corrosion).

2. Explain chemical theory of corrosion?.

According to this theory, corrosion on the surface of a metal is due to direct reaction of atmospheric gases like oxygen, halogens, oxides of sulphur, oxides of nitrogen, hydrogen sulphide and fumes of chemicals with metal. The extent of corrosion of a particular metal depends on the chemical affinity of the metal towards reactive gas. Oxygen is mainly responsible for the corrosion of most metallic substances when compared to other gases and chemicals.

There are three main types of dry corrosion.

- (i) Oxidation corrosion (*Reaction with oxygen*): Some of the metals directly react with oxygen in the absence of moisture. Alkali and alkaline earth metals react with oxygen at room temperature and form corresponding oxides, while some metals react with oxygen at higher temperature. Metals like Ag, Au and Pt are not oxidised as they are noble metals.

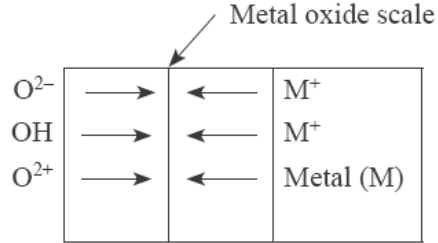
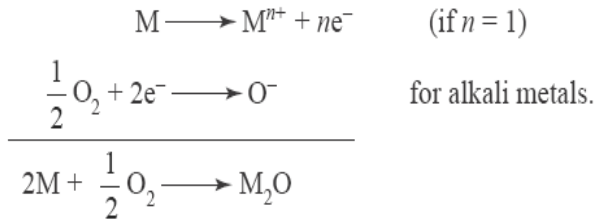


fig. 2.1 O_2 from atmosphere

During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Thus, the layer of metal oxide plays an important role in the process of corrosion. Oxides of Pb, Al and Sn are stable and hence inhibit further corrosion. They form a stable, tightly adhering oxide film.

In case of porous oxide film, atmospheric gases pass through the pores and react with the metal and the process of corrosion continues to occur till the entire metal is converted into oxide. Porous oxide layer is formed by alkali and alkaline earth metals. Molybdenum forms a volatile oxide film of MoO_3 which accelerates corrosion.

Au, Ag, Pt form unstable oxide layer which decomposes soon after the formation, thereby preventing further corrosion.

Pilling Bedworth Rule: If volume of metal oxide on the surface of a metal is more than or equal to the volume of metal, the oxide layer will be protective. For example, for Al_2O_3 , Fe, Ni, Zn, W, Cr. It will be non-protective if volume of oxide is less than volume of metal. (The specific volume ratio of W is 3.6, Cr = 2.0, Ni = 1.6. Hence, the rate of corrosion is very less in tungsten.) It is called Pilling Bedworth rule.

- (ii) Corrosion by other gases such as Cl_2 , SO_2 , H_2S , NO_x : In dry atmosphere, these gases react with metal and form corrosion products which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms AgCl which is a protective layer, while $SnCl_4$ is volatile. In petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.
- (iii) Liquid metal corrosion: In several industries, molten metal passes through metallic pipes and causes corrosion due to dissolution or due to internal penetration. For example, liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

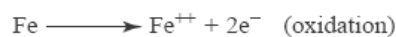
3. Explain Wet or electrochemical theory of corrosion by taking rusting of iron as example?

It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode.

The chemical in the environment and humidity acts as an electrolyte. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode.

To understand the wet theory, let us take the example of corrosion of iron. Oxidation of metal takes place at anode while the reduction process takes place at cathode. By taking rusting of iron as an example, the reaction can be explained as that it may occur in two ways: (i) evolution of hydrogen and (ii) absorption of oxygen.

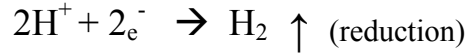
At anode: oxidation occurs.



At cathode:

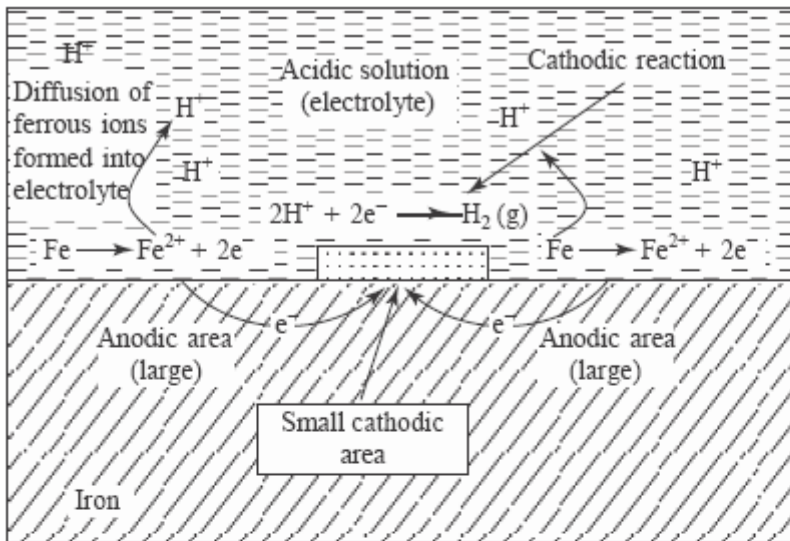
Case I: Evolution of H_2

The hydrogen ions (H^+) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen

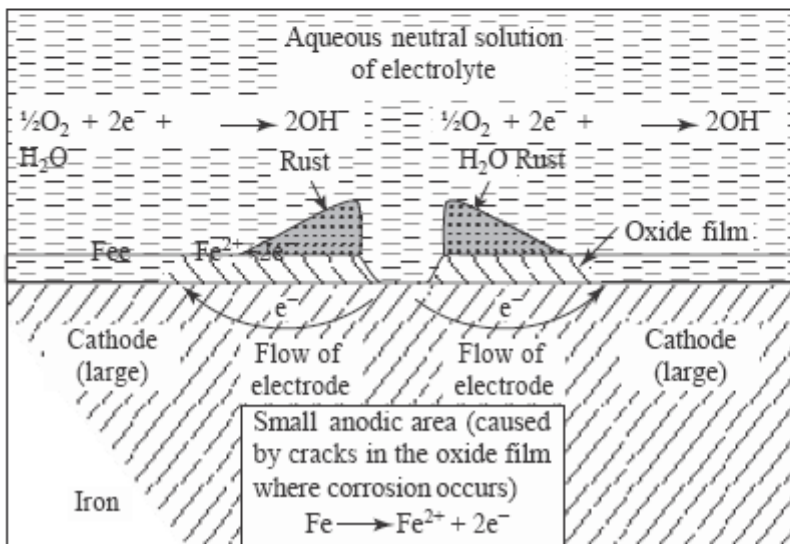


The overall reaction is $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release H_2 gas. All metals above hydrogen in electrochemical series can show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area Fig. (2.2).



(a)

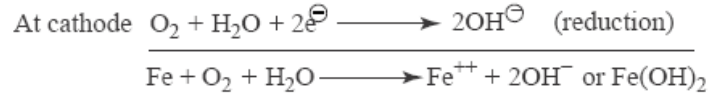


(b)

fig. 2.2 Mechanism of wet corrosion by (a) hydrogen evolution and (b) oxygen absorption

Case II: Absorption of O₂

This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The oxide of iron covers the surface of the iron. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area. The following chemical reactions occur at anode and cathode.



Ferric hydroxide is actually hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which is a yellowish rust. Anhydrous magnetite, Fe_3O_4 [a mixture of $(\text{FeO} + \text{Fe}_2\text{O}_3)$], is also formed, which is brown-black in colour. It is markable that the corrosion occurs at anode but the corrosion product is formed near cathode. It is because of the rapid diffusion of Fe^{++} as compared to OH^- (Fig. 2.1). Hence corrosion occurs at anode, but rust is deposited at or near cathode.

4. What are the differences between dry and wet corrosion

Dry corrosion	Wet or electrochemical corrosion
<ul style="list-style-type: none"> • Corrosion occurs in the absence of moisture. • It involves direct attack of chemicals on the metal surface. • The process is slow. • Corrosion products are produced at the site of corrosion. • The process of corrosion is uniform. 	<ul style="list-style-type: none"> • Corrosion occurs in presence of conducting medium. • It involves formation of electrochemical cells. • It is a rapid process. • Corrosion occurs at anode but rust is deposited at cathode. • It depends on the size of the anodic part of metal.

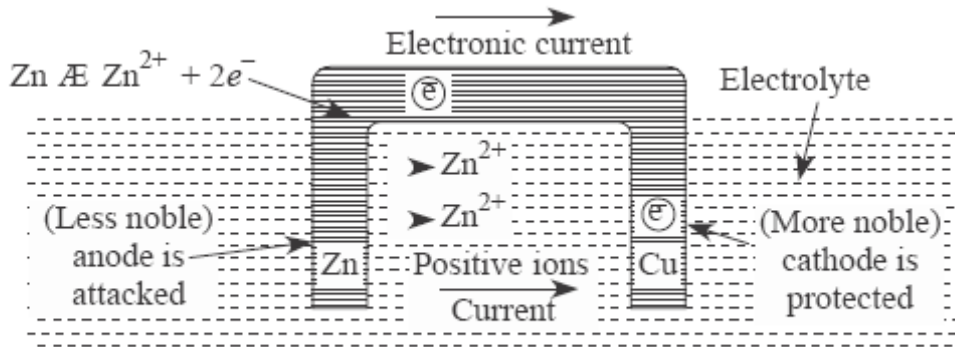
5. Mention different types corrosion ?

There are different types of corrosions based on the reactions and physical states. It has been seen that there are several types of corrosion. They are

- (a) Galvanic Corrosion
- (b) Pitting Corrosion
- (c) Stress Corrosion
- (d) Crevice Corrosion
- (e) Erosion Corrosion
- (f) Soil Corrosion
- (g) Micro-biological Corrosion
- (h) Water-line Corrosion
- (i) Differential aeration Corrosion
- (j) Intergranular corrosion

5. What is galvanic corrosion? How is it prevented? Give examples?

Galvanic corrosion: This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected (Fig. 2.3).



At anode: $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^{-}$ [Oxidation] corrosion

At cathode: $\text{Cu}^{2+} + 2e^{-} \longrightarrow \text{Cu}$ [Reduction] unaffected

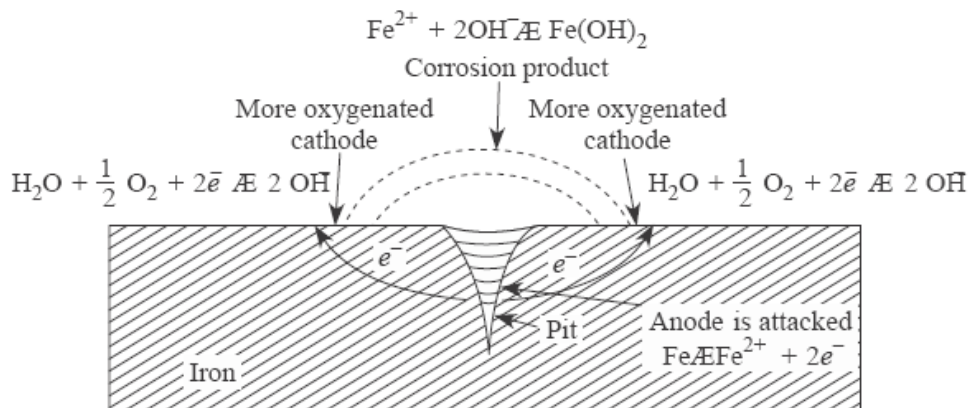
- Galvanic corrosion can be avoided by coupling metals close to the electrochemical series.
- Fixing insulating material between two metals.
- By using larger anodic metal and smaller cathodic metal.

Example of galvanic corrosion: 1. Steel screws in brass marine hardware,

- steel pipe connected to copper plumbing,
- steel propeller shaft in bronze bearing,
- zinc coating on mild steel,
- lead-tin solder around copper wires.

6. Write an account on pitting corrosion?

Pitting corrosion: Due to crack on the surface of a metal, local straining of metal, sliding under load, chemical attack, there is formation of a local galvanic cell. The crack portion acts as anode and rest of the metal surface acts as cathode. It is the anodic area which will be corroded and the formation of a pit is observed. This type of corrosion is thus called pitting corrosion (Fig. 2.4). Metals owing to their corrosion resistance to their passive state show pitting and ultimately result in formation of passivity. Presence of external impurities such as sand, dust, scale embedded on the surface of metals lead to pitting. For example, stainless steel and aluminium show pitting in chloride solution.



(c) **Stress corrosion:** In a metallic structure, if there is a portion under stress, it will act as anode and rest part of the structure will act as cathode. It is now a galvanic system and hence anodic part which is small in area will corrode more. Stress corrosions are observed in the following systems:

(i) **Caustic embrittlement** is a type of stress corrosion occurring in steel tank (Boiler) at high temperature and in alkaline medium. Boiler water has Na_2CO_3 ; it will be hydrolysed at high temperature to give NaOH . It flows into hair cracks and crevices. There it reacts with iron and forms Na_2FeO_2 (sodium ferroate) which decomposes to give Fe_3O_4 (ferroferric oxide) and NaOH .

Reaction



NaOH thus formed further reacts with iron to cause corrosion. It is called caustic embrittlement. Addition of Na_2SO_4 to boiler water in addition to tannin and lignin to boiler water prevents caustic cracking. By neutralization of excess of alkali with dilute acid (or) control of pH value caustic embrittlement can be controlled.

(ii) **Season cracking:** It is applied to stress corrosion of copper alloys bronze. Pure copper metal is less sensitive to stress corrosion. However, presence of alloying impurities like P, Zn, Al, etc. results in marked sensitivity for corrosion. Some of the alloys like brass are made of zinc and copper. In the presence of ammonia or amines, zinc and copper undergo inter-granular cracking. These metals form complexes $[\text{Cu}(\text{NH}_3)_4]^{++}$ $[\text{Zn}(\text{NH}_3)_4]^{++}$ which appear as corrosion products. Stress corrosion may be reduced:

1. By applying protective coatings
2. Using corrosion inhibitors
3. By stress relief heat treatments

d) **Crevice corrosion:** If surface of painted metal is scratched, it will undergo corrosion. The scratched portion acts as small anode and the rest part will act as cathode forming a local cell. Crevice corrosion is formed near joints, rivets and bolts. Changes in the concentration of oxygen/acidic medium causes crevice corrosion.

(e) **Erosion corrosion:** Due to mechanical wear and tear, corrosion occurs on the surface of a metal and is called erosion corrosion.

(f) **Soil corrosion:** Underground pipes, cables, etc. corrode due to soil corrosion.

It is caused due to moisture, pH of soil and micro-organisms. The differential aeration is also the cause of corrosion.

(g) **Microbiological corrosion:** Some types of bacteria consume oxygen and cause differential aeration type of system which results in corrosion. The corrosion occurs at the portion poor in oxygen concentration. Ex: The bacillus, algae diatoms

(h) **Waterline corrosion:** It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode (fig 2.5).

Reactions:

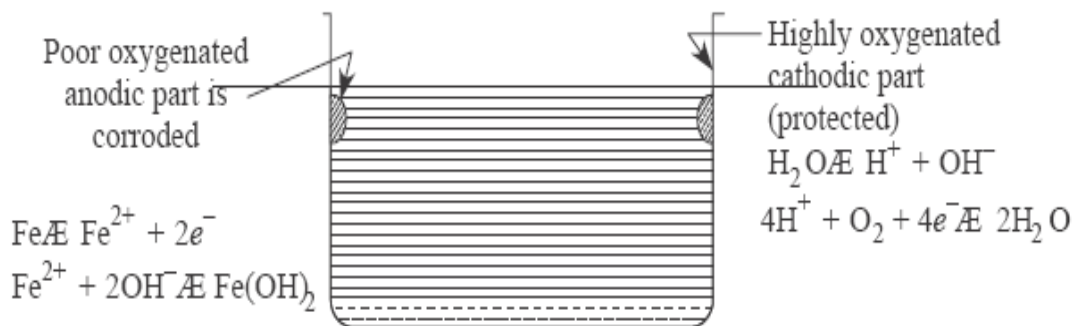
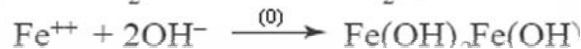
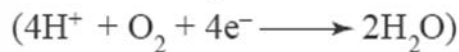
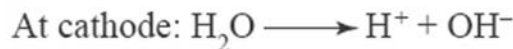
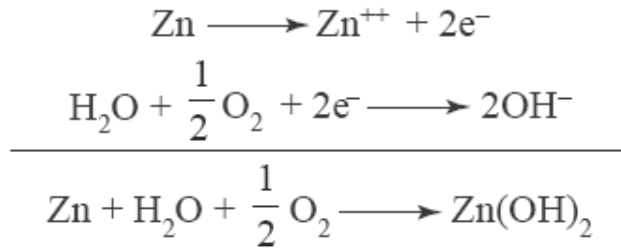


fig. 2.5 Waterline corrosion occurs just underneath the meniscus and the water level

- (i) *Differential aeration corrosion*: If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cathode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:



Zn(OH)₂ appears as corrosion products (fig 2.6)

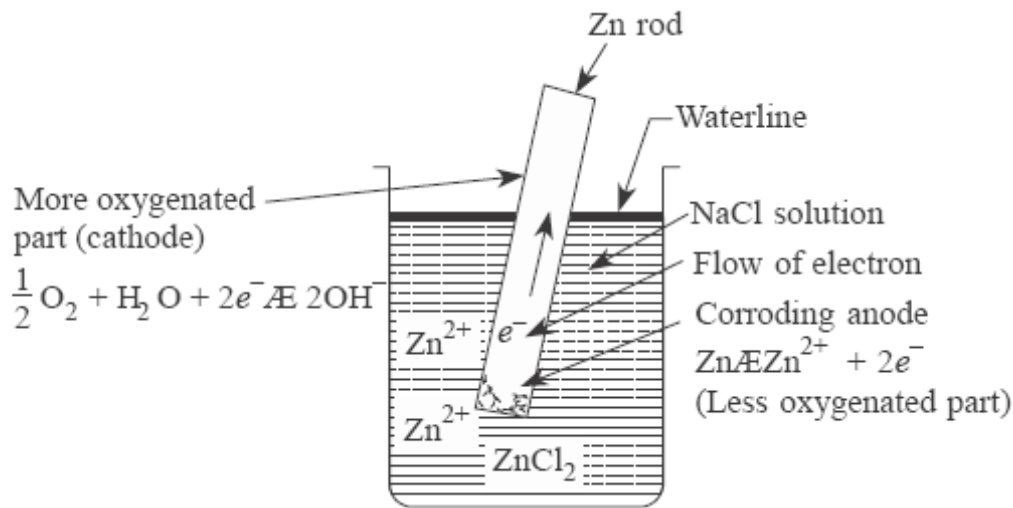


Fig. 2.6 Mechanism of differential aeration attack caused by partial immersion of a metal

- (j) *Inter-granular corrosion*: This corrosion is observed in case of alloys. The corrosion product is observed at the boundaries of grains. Externally, it is not seen. There is a sudden failure of material due to this Corrosion. For example, during the welding of stainless steel (an alloy of Fe, C, Cr), chromium carbide is precipitated at the grain boundaries and the region adjacent to grain boundaries becomes depleted of chromium composition and is made anodic with respect to solid solution within the grains richer in chromium. Rapid quenching after heat treatment of a metal is the remedy of inter-granular corrosion (Fig. 2.7).

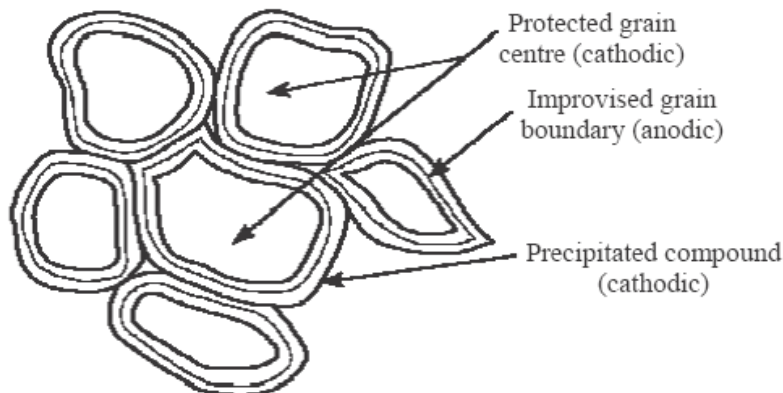
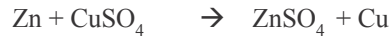


Fig 2.7 Inter granular corrosion

GALVANIC SERIES

Electrochemical reactions are predicted by electrochemical series. A metal having higher position can replace (reduce) other metals that have lower position in the series. For example,



that is, $\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$

Or in other words, zinc will corrode faster than copper.

Some exceptions have been observed in this generalisation. For example, Ti is less reactive than Ag.

Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e. sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble nature.

More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni–Mo–Fe alloys) Brasses, Cu, Ni, Cr–steel alloy,
Ag, Ti, Au, Pt towards noble nature.

Comparison between Galvanic Series Vs Electrochemical Series:

Galvanic Series	Electrochemical Series
1. It predicts the corrosive tendencies of metal alloys	It predicts the relative displacement tendencies
2. Calomel electrode is used as a reference electrode	Standard hydrogen electrode is used as reference electrode
3. Positioning of metal or alloy may change	Position of metal is fixed. That cannot be changed
4. The metals and alloys are immersed in the sea water for study	concentration of salts of the same metal that was being used
5. Electrode potentials are measured for both metals and alloys.	Electrode potentials measured only for metals and non-metals

FACTORS INFLUENCING CORROSION

Since corrosion is a process of destruction of metal surface by its environment, the two factors that govern the corrosion process are:

(i) Metallic and (ii) Environmental.

- (i) **Nature of metal:** Different properties of a metal are responsible for corrosion. These properties are given here.
- (a) *Position of metal in galvanic series:* It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it. Also, more difference in the position of galvanic series will cause faster corrosion at anodic metal.
- (b) *Hydrogen over voltage:* In case of zinc metal placed in a normal solution of H_2SO_4 , reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high hydrogen over voltage of zinc (0.76 V). The addition of few drops of CuSO_4 accelerates corrosion due to reduction of hydrogen over voltage (0.34 V). Further, faster corrosion is observed in the presence of PtCl_4 (hydrogen over voltage = 0.2 V). The reduction in over voltage of corroding metal or alloy accelerates the rate of corrosion. Hence hydrogen over voltage governs the process of corrosion.

- (c) *Purity of metal*: Pure metal resists corrosion, while impurities in a metal form a local galvanic cell (metal as anode and impurity as cathode) and result in the corrosion of metal. Rate of corrosion increases due to more exposure of impurities. For alloys the system is a homogeneous solid solution, hence no local action and no corrosion.
- (d) *Relative areas of anode and cathode*: Smaller the area of anode compared to cathode will lead to faster corrosion of anode. It is because the corrosion current at anode and at cathode will be same. But for small anodic area the current density will be large at anode and larger cathodic area will demand more electron which will be fulfilled by fast reaction at anode (oxidation), i.e. rapid corrosion.
- (e) *Physical state of the metal*: Small granular metal will corrode faster than the larger one. Also the type of structure formed by a metal will have effect on the corrosion rate. A bent metal (stress) is rapidly corroded due to stress.
- (f) *Nature of oxide film*: An oxide film is formed by the reaction between metal and oxygen. If this oxide film is porous and oxygen can be diffused through it, more corrosion is expected (already shown in dry or chemical corrosion). Also, if volume of metal oxide is more than the volume of metal (The specific volume ratios of Ni, Cl, W are 1.6, 2.0 and 3.6) least corrosion or no further corrosion occurs.
- (g) *Volatility and solubility of corrosion product*: In both the cases, the corrosion will be faster. MnO_3 , SnCl_4 are volatile, so faster is corrosion of Sn in chlorine atmosphere. In case of soluble corrosion product, it will be enhanced by water and metal surface will be exposed for further corrosion.

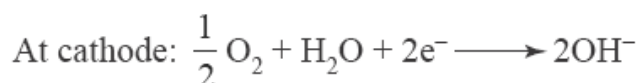
(ii) Effect of environment

The role of environment in the corrosion of a metal is very important. Environmental parameters like temperature, humidity, pH, etc. play important role. The effect is discussed here.

- (a) *Temperature*: The rate of diffusion increases by rise in temperature, hence the rate of corrosion is also increased. At higher temperature, passive metals also become active and undergo corrosion. But higher temperature reduces the concentration of oxygen and hence corrosion is reduced (in case of water where oxygen is dissolved).
- (b) *Humidity*: In humidity, gases like CO_2 , SO_2 , NO_x are dissolved which form electrolytes. It will cause galvanic corrosion. Some oxides are water soluble, humidity washes away the corrosion products and metal surface is further corroded. Other soluble corrosion products can also be washed away by humidity, causing further corrosion.
- (c) *Impurity of atmosphere*: Pollutants like H_2S , SO_2 , CO_2 and acid vapours cause more pollution where they dissolve. In sea water (salty in nature which acts as an electrolyte) corrosion rate increases. Some suspended particles are dissolved in humidity and form electrolyte which helps in corrosion.
- (d) *pH value*: pH value means concentration of H^+ (acidic nature). In acidic medium (pH less than 7), corrosion is faster. Also, in basic medium $\text{pH} > 7$, some metals such as Pb, Zn, Al, etc. form complexes and hence they corrode. *Pourbiac relation* between pH of medium and potential of metal deals with the corrosion process and it gives idea how to reduce corrosion.

Example: Zn corrodes minimum at pH 11, but at higher pH (more than 11) it corrodes faster. At pH 5.5, Al corrodes minimum.

- (e) *Nature of ions present*: Cu^{++} ions present in the vicinity of Fe, accelerate corrosion, while silicates present in the vicinity resist corrosion.
- (f) *Conductance effect*: Due to presence of salts and water in earth, it is of conducting nature. More conductance leads to more stray current and hence fast corrosion. Dry sandy soil is less conducting and hence less corrosion, while mineralised clay soil is more conducting hence more corrosion occurs.
- (g) *Oxygen concentration and oxygen concentration cell*: Oxygen is one of the important element responsible for corrosion. It forms oxides and hydroxides (in presence of H_2O) on the surface of metal as corrosion product. Oxygen concentration cell is formed on the surface of metal due to difference in oxygen concentration (iron rod half dipped in water corrodes due to this effect). Dipped portion will be anode and outer portion will be cathode.



- (h) *Polarisation of electrodes*: More the polarisation at electrodes, less current will be passed and hence less corrosion.
- (i) *Flow of process stream*: Low flow velocity will reduce corrosion of non-passive metals, while for passive metals it may or may not be true.

MEASUREMENT OF CORROSION

The process of corrosion is a slow chemical reaction. During the corrosion process, there is loss of weight of the metal. The loss in mg/dm^2 per day or inches per year measures the extent of corrosion.

$$\text{Rate of corrosion (R)} = \frac{kw}{atd}$$

w = loss of weight of metal in milligrams

a = area of metal surface in sq. cm

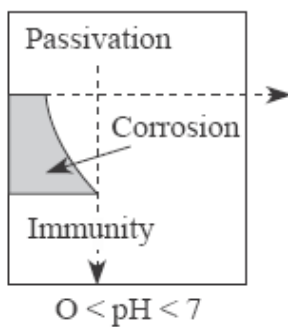
t = exposure time for corrosion in 100th part of an hour or a day

d = density in g/cm^2

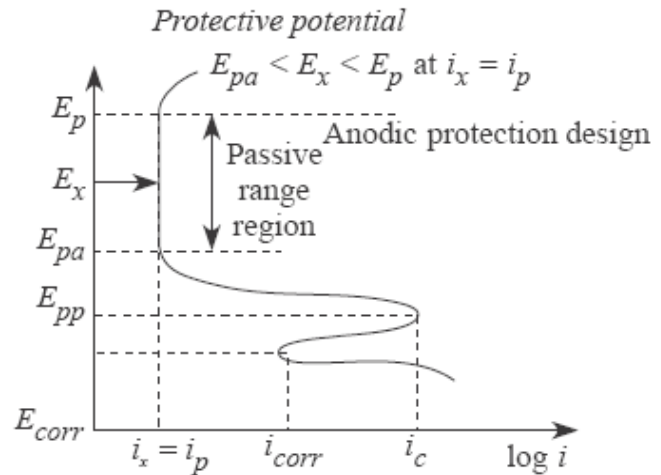
k = constant of proportionality

The condition is that the surface of the metal must be uniform.

Pourbiax diagram



(a) Schematic Pourbiax diagram



(b) Active-passive curve indicating passive region for anodic protection

There are several units for the measurement of the rate of corrosion (R), i.e. $\text{mg}/\text{dm}^2/\text{day}$, $\text{oz}/\text{ft}^2/\text{day}$, inch/year or millimetre/year

A cleaned metal is taken, weighed and exposed for corrosion. Time taken in the process is recorded and then the piece of the metal is taken out; corrosion product is removed and is weighed again. The loss in the weight of the metal is noted which helps to calculate corrosion rate.

EFFECT OF CORROSION

Consequences of corrosion cause a great loss of economy and life. The following harmful effects are specific.

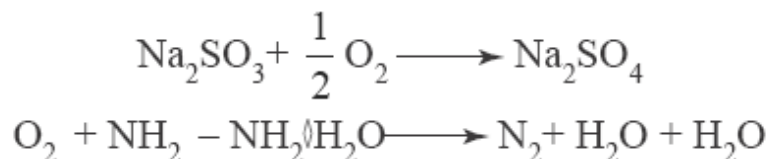
1. Corrosion reduces the thickness of the metal resulting in loss of mechanical strength and failure of the structure.
2. Corrosion causes structural failure as it is hazardous (e.g. car and aircraft).
3. Because of the deterioration of appearance, the cost of the machine is reduced.
4. Efficiency of the machine is reduced due to corrosion.
5. Because of corrosion, pipes are blocked and pumps are difficult to operate.

6. Because of corrosion, boilers are damaged.
7. Buildings and other historic monuments are damaged due to corrosion (e.g. Taj Mahal).
8. Valuable metallic properties such as conductivity, malleability, ductility, etc. are lost due to corrosion.

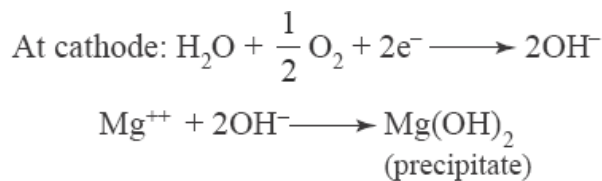
PROTECTION FROM CORROSION

Due to corrosion, there is a great loss of material and money. Therefore, it is essential to protect metals from corrosion. Since, there are two components involved in corrosion—the metal and environment—both are considered in corrosion protection. Following methods have been adopted for the protection of metal from corrosion.

- (i) Proper designing of an object helps in prevention of corrosion.
- (ii) Contact of two dissimilar metals must be avoided. If it is unavoidable, anodic area should be very large compared to cathodic area.
- (iii) Two different metals used in the structure should be such that they are occupying near positions in galvanic series.
- (iv) Putting an insulator between two metals resists corrosion.
- (v) As far as possible, metal used in a structure should be extremely pure. Small amount of impurity causes corrosion.
- (vi) While using an alloy, it should be completely homogeneous.
- (vii) Design or fabricate equipment or metal parts in such a manner that they have minimised sharp edges and corners and also avoid, as far as possible, the crevices in joints, etc.
- (viii) The modification of environment also helps in protection from corrosion. It includes:
 - (a) De-aeration removes oxygen by adjusting temperature and mechanical ageing.
 - (b) Deactivation involves addition of chemicals such as Na_2SO_3 , $\text{NH}_2 - \text{NH}_2/\text{H}_2\text{O}$ which absorb oxygen.



- (c) Dehumidification of environment is done by adding alumina or silica gel. These chemicals absorb humidity from metallic surface.
In humidity, gases such as CO_2 , H_2S , SO_2 and HCl give acidic medium responsible for corrosion. They are neutralised by NH_3 or NaOH or lime.
- (ix) There are some chemicals which reduce the rate of corrosion. These chemicals are called *corrosion inhibitors*. They are of two types, *anodic* and *cathodic*. Phosphate, chromate, tungstate protect anode. They form sparingly soluble products which are adsorbed on the surface of metal and hence check corrosion. Cathodic protection is done by organic amines, mercaptans, thiourea and substituted urea. The above chemicals retard reduction reaction taking place at cathode.
Also, by the use of salts of Mg, Zn or Ni, the insoluble hydroxides of Mg, Zn, Ni are deposited preventing corrosion.



Methods of application of metal coatings: Metallic dipping causes a coat of metal over the base metal. It is of two types, anodic coating and cathodic coating.

- (a) **Anodic coating** is done by a metal which is situated prior to the base metal in electrochemical series. Coating of zinc over iron is anodic coating and this process has its special name galvanisation. Zinc occupies a position before iron. In this process base metal is immersed in molten coating metal. The base metal should be very clean. Anodic coating of iron is done by Al and Cd also. If any crack or pit is formed on the coated metal, Zn will act as anode and Fe as cathode and hence Fe will not corrode (Fig. 2.8). Since Zn is toxic, galvanised utensils are not used for cooking or food storing. Zinc coating protects iron sacrificially.

Galvanised iron is used for buckets, tubes, wires, roof sheets etc.

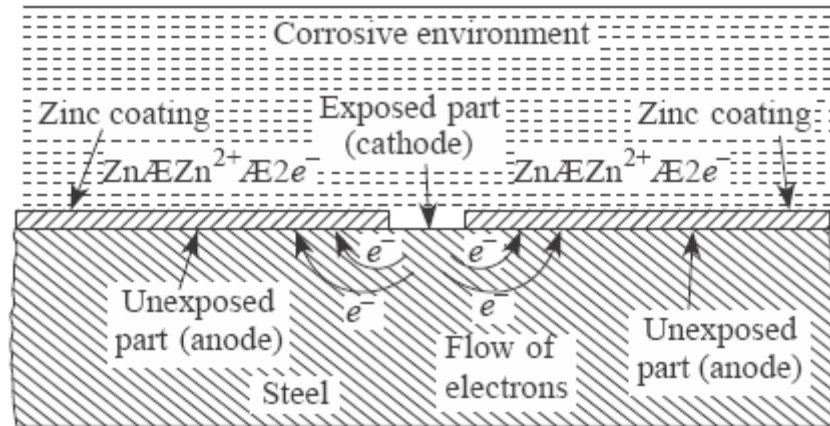


Fig 2.8 Functioning of anodic coating. In galvanised steel, Zn serves as anode; while iron of steel serves as the cathode. Therefore, the iron is protected, even if it is exposed, when a part of the zinc coating is scrapped off

- b) **Cathodic coating** of a base metal (say iron) is done by another metal which occupies a position below it in electrochemical series but it will be higher corrosion resistant. Coating of Sn over iron (tinning) is an example of cathodic protection. Cathodic protection of iron is successful only when there is no pit or crack formation on the surface of metal. Coating of tin is called tinning. Tin-coated iron is used for cooking as well as storage purposes.

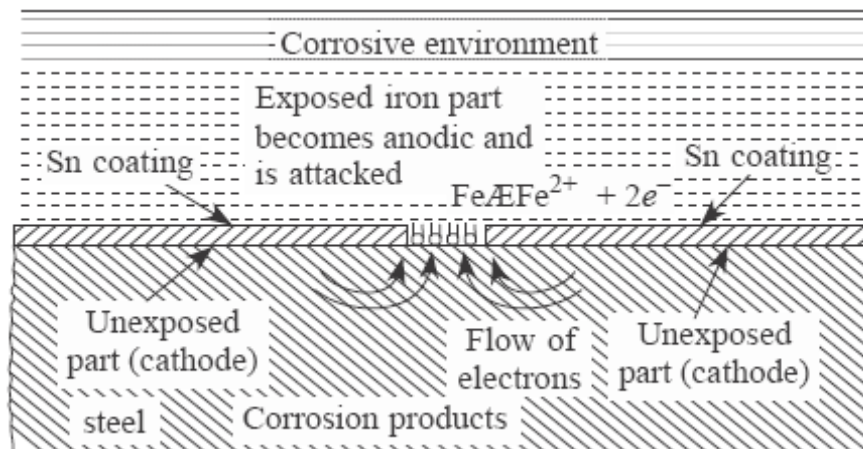


Fig 2.9 Tin-plated steel. Tin protects the iron, when the coating is continuous. When the coating is broken, the iron of the steel becomes the anode and is subjected to accelerated local corrosion.

9. What are the differences between galvanizing & tinning?

Galvanizing	Tinning
1. Galvanizing is the process of covering iron or steel with thin layer of Zn	1. In tinning, steel is covered with a thin coat of tin to prevent corrosion
2. Zinc protects iron sacrificially	2. Due to noble nature tin protects base metal
3. Zinc protects iron even when coating of zinc is punctured	3. If the coating is punctured intense corrosion of steel occurs.
4. Since zinc is toxic galvanized utensils are not used for storing food	4. Since tin is non-toxic tinned containers can be used even for storing food.

8. What is metal cladding? Give an example?

- (xi) **Metal cladding** is a process of sandwiching a metal between two corrosion resistant metals. Ni, Pb, Cu, Al, Ag, Pt are used as cladding metals over a base metal. For example, aluminium acts as cladding metal for duralumin (Fig. 2.10).

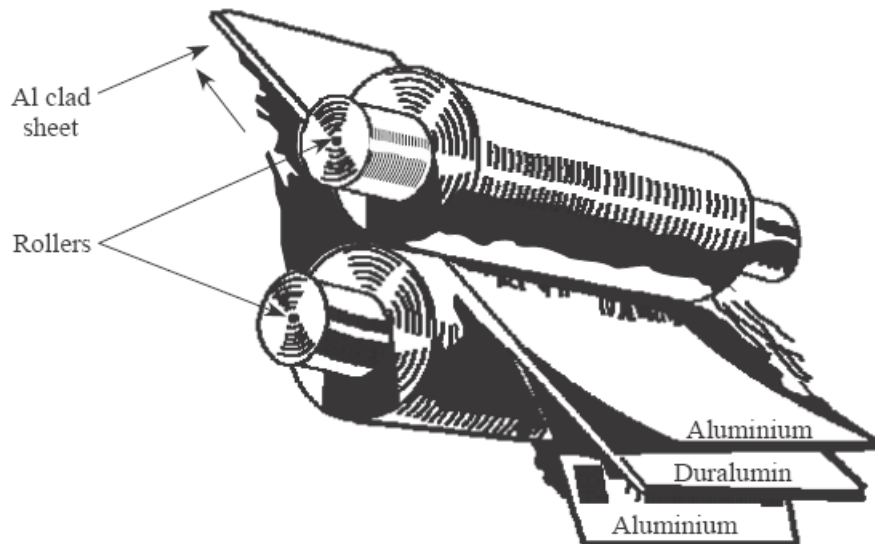


Fig. 2.10 The cladding of duralumin

- (xii) **Metal spraying:** Molten metal is sprayed on the cleaned surface of a metal for its protection from corrosion. It is helpful to protect towers and bridges.
- (xiii) **Pack cementation:** Heating a base metal with another powdered metal is done. The powdered metal forms a coat on the base metal, and hence protects it from corrosion. Sherardising and colourising are two important pack cementation processes in which Zn and Al powders are heated, respectively. This type of coating is also known as diffusion coating. The third one is chromising in which the chromium powder and alumina are heated with Fe.
- (xiv) **Electroplating:** It is an electrochemical process in which a base metal is coated by Zn, Ag, Cr, Au, Sn, etc. to protect it from corrosion and also to make it shining and decorative. The base metal is made cathode, dipped in a suitable electrolyte, and the metal to be deposited is made the anode.
- Anodised coating is done for non-ferrous metals, such as Zn, Mg and Al. (xv) In organic coatings, paints, varnishes, enamels, lacquers and emulsion paints are included. They not only protect from corrosion but also give a good look to the metal. Organic coats must have chemical inertness, good surface adhesiveness and non-effectiveness towards inorganic chemicals and water.

- (xvi) Water-repellent paints are organosilicon compounds, which on hydrolysis give a permanent coat that can work for 4–6 years as corrosion resistant.
- (xvii) **Cathodic protection or Electrochemical method:** The principle involved in this method is that the metal is forced to behave like cathode, thereby preventing corrosion. For protecting corrosion–electrochemically, there are two methods for the protection from corrosion.

9. Give an account on sacrificial anodic protection.

1. *Sacrificial anodic protection:* Underground steel pipes are protected from corrosion by this method. A magnesium rod is fixed near the metal under protection and both are connected with a conducting wire. Magnesium is more positive than iron and, hence, in electrochemical cell it acts as anode and the iron acts as cathode. According to the principle of galvanic cell, it is anode that undergoes oxidation, and, hence, corrosion occurs at anode saving cathode (iron) from corrosion. Thus, magnesium sacrifices itself for saving the iron (Fig. 2.11)

10. What do you mean by impressed current?

2. *Impressed current cathodic protection:* The object to be protected is made cathode and it is connected to the negative terminal of a DC (direct current) source. The positive terminal of the source is connected to the other electrode made of graphite or platinum, lead or nickel. The impressed current opposes the galvanic current (corrosion current) and, hence, protection from corrosion takes place (Fig. 2.12).

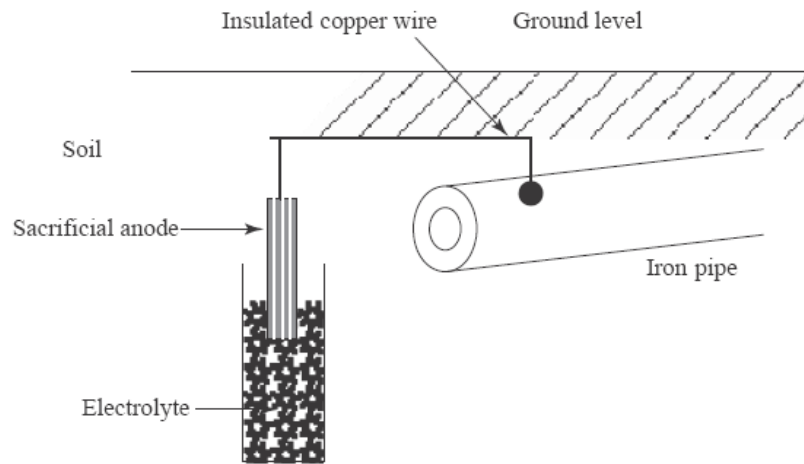


Fig. 2.11 Sacrificial anodic protection

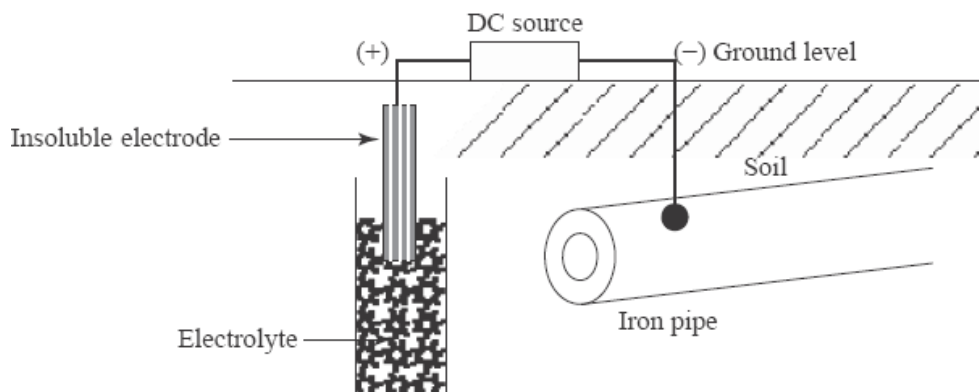


Fig. 2.12 Impressed current cathodic protection

Recent developments have given paints that automatically fill the gap if scratches are there and, thus, protect the metal from corrosion

What is passivity? Explain.

The process in which a metal exhibits higher corrosion resistance is called passivity. When a very thin, invisible and highly protective film is formed on the surface of a metal or an alloy, it is called passivity. This film is insoluble and non-passive. A metal is passive in a certain environment if its corrosion rate is very low. By the change of the environment, the passivity of a metal may change and may become active towards corrosion. The formation of a passive film on the metal surface is determined by the Pourbaix diagram, which depends on the electrode potential and pH of the medium. Low carbon steel does not corrode in conc. HNO_3 due to protection effect of passive film. However, in dil. HN_3 does not form a stable passive film and therefore dissolves steel. Passive film is formed on the surface of aluminium, Cr, Si, Ti in air, water and dilute acids. There is a good corrosion and oxidation resistance of stainless oxide passive layer.

A damage of passive film may cause intensive localised corrosion (pitting corrosion). Passive oxide layers are dissolved in electrolytes containing SO^{-2} and chloride. Phosphate and chromate ions stabilise passive films, promoting the regain of its defects.

PAINTS

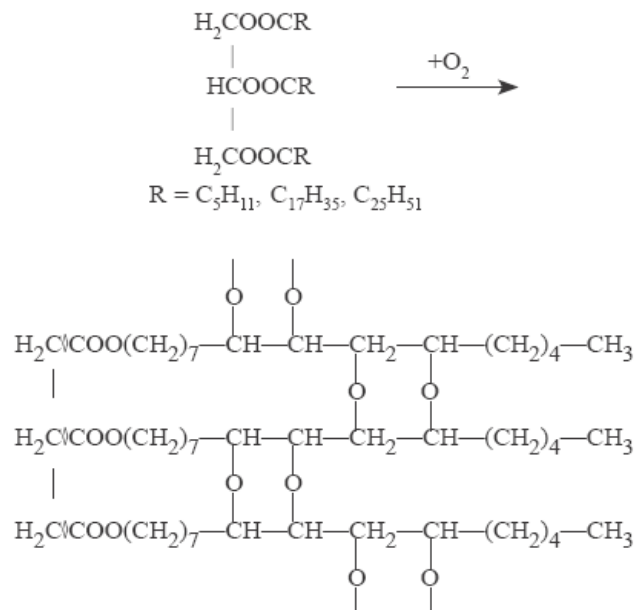
A paint is a mechanical dispersion of one or more pigments in medium (liquid, non-volatile) drying oil and thinner. When a metallic surface is painted, the thinner evaporates while the drying oil forms a dry pigmented film after oxidising itself. A paint has following qualities: (i) it should be spread easily on the surface, (ii) it should form a tough, uniform and adherent film, (iii) the coating of paint should not crack after drying, (iv) it should have high covering power, (v) it should neither be oxidised nor reduced in environment and (vi) the colour due to paint should be shining and stable.

Constituents of a paint: There are three constituents of a paint, viz. pigment, dry- ing oil or vehicle and thinner.

- (a) *Pigment* is a solid substance which is of different colours depending upon the composition, e.g. zinc oxide, white lead, lithophone, titanium oxide (all are white in colour). Red lead, ferric oxide, chrome red are of red colour. Chromium oxide is green, while carbon black is black. Pigments provide (i) strength to paint (ii) protection to the film by reflecting harmful ultraviolet light (iii) resistance against abrasion/wear (iv) impermeability to moisture and (v) Easthetic appeal to the paint film.

A good pigment should be (i) opaque, (ii) chemically inert, (iii) non-toxic so that there is no bad effect on the health of painter as well as inhabitant (iv) cheap and (v) freely mixable with film forming constituent oils.

- (b) *Drying oil* is also called vehicle. It is a film-forming constituent. They are glycerides of higher fatty acids (saturated or unsaturated), e.g.



Drying oil may be vegetable oil. Drying oil absorbs oxygen and forms peroxides, hydroperoxides, etc. and forms tough, coherent, insoluble and highly cross-linked structure on the surface. They provide toughness, durability, adhesion and water proofness to the film. When paint is applied in the form of a film, the drying oil absorbs oxygen from air and forms peroxides and hydroperoxides at double bonds. These peroxides isomerise, polymerise condense to form tough, elastic, insoluble, infusible polymer film.

- (c) *Thinner* is a highly volatile liquid, it reduces viscosity of the paint and increases its elasticity. It increases the penetration power of drying oil. The common thinner is turpentine oil. Other thinners are benzene, mineral spirit, xylol, kerosene, etc. Some other constituents of paint are—*driers* (oxygen carrier catalyst) helpful in drying, e.g. tungstate, linoleates of Co, Mn, Pb and Zn, turpentine, mineral spirit, naphtha, methylated naphthalene etc.
- (d) *Extenders* or *fillers* which reduce the cost and increase durability, e.g. barytes (BaSO_4), talc, asbestos, gypsum (CaSO_4) etc. They serve to fill voids in the film and act as carries for pigment colour.
- (e) *Plasticisers* are used to increase elasticity and to minimise cracking, e.g. dibutyl phosphate, tri-cresyl phosphate, dibutyl tartarate etc.
- (f) *Anti-skinning* agents prevent skinning and gelling of paint film, e.g. polyhydroxyphenols.

THEORETICAL QUESTIONS

1. What is corrosion? Why do metals corrode?
2. Why most of the metals are found in the ore form and not in the pure form? Explain.
3. Describe the electrochemical theory of corrosion.
4. Show the reactions involved in the hydrogen evolution and oxygen absorption types of corrosion.
5. Describe the factors on which corrosion depends.
6. Discuss various methods of protection corrosion.
7. Discuss the wet theory of corrosion.
8. Explain the rusting of iron with the help of electrochemical theory of corrosion.
9. Explain two methods to prevent from corrosion.
10. Define passivity with an example.
11. Explain the acid theory of corrosion.
12. Why rusting of iron is fast in saline water than in ordinary water?
13. What is differential aeration corrosion?
14. What is meant by passivity?
15. What is cementation?
16. Give the functions of pigments?
17. What is electrochemical series?
18. Explain sacrificial anodic and impressed current cathodic protection?
19. Give the characteristic features of paints and their functions?
20. Differentiate anodic and cathodic protection methods?
21. Differentiate galvanizing and tinning?
22. Rusting of iron is quicker in saline water than in ordinary water. Why?
23. What is cathodic protection?
24. State the two conditions for wet corrosion?

MULTIPLE CHOICE QUESTIONS

1. Corrosion is a process of

(a) reduction	(b) oxidation
(c) ozonolysis	(d) electrolysis

2. In the wet theory of corrosion
 - (a) dry cell is formed
 - (b) galvanic cell is formed
 - (c) concentration cell is formed
 - (d) none
3. Which one of the following causes corrosion of iron? (a) oxygen (b) hydrogen
 - (c) strong base
 - (d) moisture and oxygen
4. The method in which the base metal is heated with another powdered metal to prevent corrosion is known as
 - (a) electroplating
 - (b) metal spraying
 - (c) pack cementation
 - (d) metal cladding
5. The method to prevent corrosion of iron by zinc coating is called
 - (a) galvanisation
 - (b) electrolysis
 - (c) cathode protection
 - (d) anode protection
6. The rusting of iron is catalysed by
 - (a) Zn
 - (b) Fe
 - (c) Al
 - (d) H_2O (H)
7. A process in which metal is protected from corrosion by dipping it in molten zinc is known as
 - (a) tinning
 - (b) galvanisation
 - (c) cladding
 - (d) electroplating
8. During wet corrosion
 - (a) the anodic part undergoes reduction
 - (b) the cathodic part undergoes oxidation
 - (c) the anodic part undergoes corrosion
 - (d) none
9. The chemical composition of rust is
 - (a) $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
 - (b) $\text{Fe}_3\text{O}_4 \cdot x\text{H}_2\text{O}$
 - (c) $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
 - (d) $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$
10. When the ratio of anodic to cathodic area decreases, the rate of corrosion
 - (a) decreases
 - (b) increases
 - (c) has no effect
11. Pitting corrosion is due to
 - (a) breaking of the oxide layer of the metal
 - (b) acidity
 - (c) stress in the metal
 - (d) All the above
12. One of the acids that causes passivity in iron is
 - (a) concentrated sulfuric acid
 - (b) concentrated nitric acid
 - (c) concentrated hydrochloric acid
 - (d) oxalic acid
13. In sacrificial anodic protection
 - (a) an artificial cathode is connected to the metal to be protected
 - (b) an anodic metal is coated on the surface of the metal to be protected
 - (c) protection of the metal given by galvanising the metal
 - (d) an artificial weak anode is connected to the metal to be protected
14. Generally machine parts to be protected are
 - (a) curved shape
 - (b) polished surfaces
 - (c) different metal parts having nearly the same electrode potential are joined
 - (d) all are applicable

15. One of the common sacrificial anodic metal is
(a) zinc (b) magnesium
(c) copper (d) titanium
16. In impressed current cathodic protection method
(a) negative charge of the battery is connected to the metal to be protected by making the metal positive
(b) the negative charge of the battery is connected to graphite anode
(c) +ve charge of the battery is connected to graphite anode
(d) none of the above
17. When a buried pipeline is protected from corrosion by connecting to Mg block. It is called as
(a) sacrificial anodic protection
(b) sacrificial cathodic protection
(c) impressed current cathodic protection
(d) any of these
18. White lead in paint acts as
(a) thinner (b) pigment
(c) drier (d) drying oil
19. Non-volatile film forming constituents of a paint is called
(a) drier (b) pigment
(c) drying oil (d) thinner
20. Food stuff containers should not be
(a) galvanized (b) tinned
(c) electroplated (d) clad
21. The metal at the top of electrochemical series is
(a) most stable (b) more noble
(c) less active (d) more active
22. Atmospheric corrosion is detected by
(a) presence of SO_2 (b) presence of O_2
(c) Humidity of air (d) frequency of rain fall
23. Oxygen carrier catalyst in the paint is
(a) drier (b) pigment
(c) thinner (d) drying oil
24. Anodic coating protects underlying metal
(a) due to higher oxidation potential
(b) due to noble character
(c) due to higher reduction potential
(d) due to low reduction potential

Answers

1. (b) 2. (b) 3. (d) 4. (c) 5. (a) 6. (d) 7. (b) 8. (c) 9. (c)
10. (b) 11. (a) 12. (b) 13. (d) 14. (d) 15. (b) 16. (a) 17. (a) 18. (b)
19. (c) 20. (a) 21. (d) 22. (c) 23. (a) 24. (a)