

Q3. What is electrochemical corrosion and how does it take place? Describe the mechanism.

Mechanism of wet or electrochemical corrosion:-

In wet corrosion the anodic reaction involves- the dissolution of metal as corresponding metal ions with the liberation of free electrons:



Whereas the cathodic reaction consumes e^{-} s either by a) evolution of hydrogen b) or by absorption of oxygen depending on the nature of the corrosive environment.

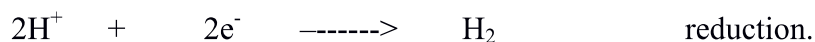
Q4. Define metallic corrosion. Explain the electrochemical theory of corrosion by Hydrogen evolution and oxygen absorption.

Evolution of hydrogen: occurs

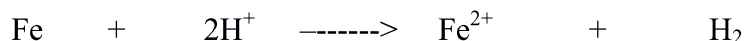
- In acidic environments.
- For eg in the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of e^{-} s.



- These electrons flow through the metal from anode to cathode (acidic region) where H^{+} ions are eliminated as H_2 gas.



- The overall reaction is



- This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.
- In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

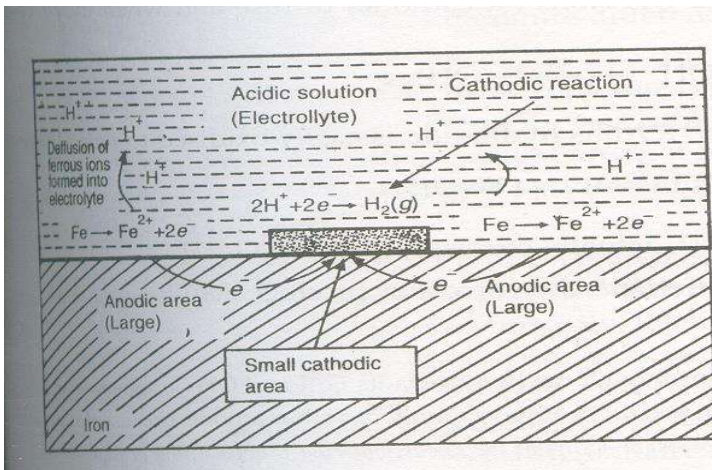


Fig. 5. Mechanism of wet corrosion by hydrogen evolution.

Q5. Explain the corrosion of iron by dilute mineral acids.

Absorption of oxygen type corrosion: Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.

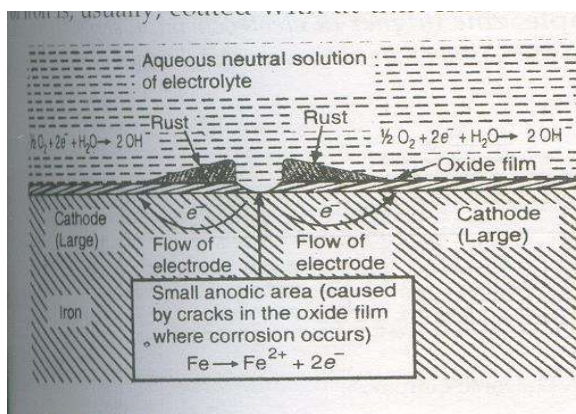


Fig. 6. Mechanism of wet corrosion by oxygen absorption.

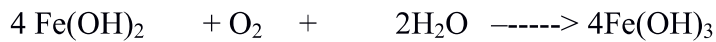
- The surface of iron will be usually coated with a thin film of iron oxide. However if this oxide film develops some cracks, anodic areas are created on the surface.
 - While pure metal parts act as cathode.
 - Thus anodic areas are very small surface parts.
 - The rest of the surface of the metal forms cathodes.
 - Thus at the anodic part iron metal dissolves as Fe^{+2} ions with the liberation of e^- s.
- $$\text{Fe} \longrightarrow \text{Fe}^{+2} + 2\text{e}^-$$
- The liberated e^- s flow from anodic to cathodic areas through iron metal during which they interact with dissolved oxygen and moisture.



- The Fe^{+2} ions and OH^- ions diffuse and form ferrous hydroxide precipitate when they meet with each other



- If enough O_2 is present Fe(OH)_2 is easily oxidized to Fe(OH)_3 (ferric hydroxide)



The product called yellow rust actually corresponds to $\text{Fe(OH)}_3 \cdot \text{H}_2\text{O}$.

- If the supply of O_2 is limited, the corrosion product may be even black anhydrous magnetite Fe_3O_4 .

Q6. Explain the factors which influence the rate of corrosion?

Factors influencing corrosion:

- Nature of metals
- Nature of the corroding environment.

Nature of metals:

1) **Position in galvanic series:**-The metal higher in series is more active and suffers corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

2) **Over voltage:** - when a metal, which occupies a high position in galvanic series (say Zinc), is placed in H_2SO_4 , it undergoes corrosion forming a film and hydrogen gas.

The initial rate of reaction is quite slow, because of high over voltage (0.70 V) of the zinc metal, which reduces the effective electrode potential to a small value. However, if few drops of copper sulphate (CuSO_4) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal forming minute cathodes, where the hydrogen over voltage is only 0.33 V, thus, reduction in over voltage of the corroding metal/ alloy accelerates the corrosion rate.

Zn has over hydrogen voltage due to which the rate of corrosion of Zn is very slow (Zn rod dipped in ZnSO_4). But when CuSO_4 solution is added to H_2SO_4 Cu gets deposited on Zn rod and acts as small cathode. For Cu higher over hydrogen voltage value is less. Hence rate of corrosion of Zn in presence of Cu becomes more. Thus metals for which over voltages are more get corrode slowly, whereas those which have higher over voltages, the rate of corrosion is high.

Ex: corrosion of Zn rod dipped in H_2SO_4 is very slow. When small amount of CuSO_4 solution is added to H_2SO_4 , Cu gets deposited on the Zn rod and acts as cathode and the rate of corrosion of Zn increases.

(Over voltage of Zn metal is 0.73)

- 3) **Purity of metal:** - Impurity of a metal generally causes heterogeneity and form minute electrochemical cells and the anodic part gets corroded. For eg: Zn metal containing impurity such as Pb (or) Fe undergoes corrosion .

The rate and extent of corrosion increases with extent of impurities.

- 4) **Nature of the surface film:** - when metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For eg: the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Consequently the rate of oxidation corrosion is least for (w) tungsten.

5) **Nature of the corrosion product:-** a) Solubility of corrosion products : If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed e.g: PbSO_4 formation in case of Pb in H_2SO_4 .

b) Volatility of corrosion products : - If the corrosion product is volatile , it evaporates as soon as it is formed, there by leaving the underlying metal surface exposed for further attack.

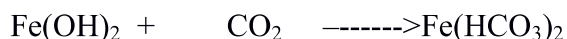
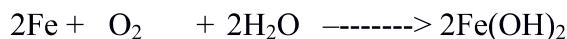
This causes rapid and continuous corrosion.

For eg: Mo forms MoO_3 volatile oxide.

Nature of the corroding environment:-

- i) **Temperature:** With increase of temperature, the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosion medium increases.
- ii) **Humidity:** The higher the humidity of the atmosphere the greater is rate and extent of corrosion because the moisture acts as medium for O_2 in air and behaves as an electrolyte.

For eg: atmospheric corrosion of iron is slow in dry air compared to moist air. Iron combines with O_2 and water to form ferrous hydroxide which combines with atmospheric CO_2 to form ferrous bicarbonate.

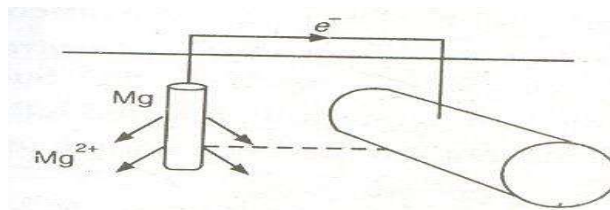


- iii) **Effect of pH:** - Generally acidic media are more corrosive than alkaline and neutral media. Hence metals may be virtually classified according to pH range in which they will be affected (or) resistant. However atmospheric metals like Al, Pb etc. are corroded in alkaline medium and the corrosion rate of iron in O_2 free water is slow, until the pH is below Zn is rapidly corroded in weakly acidic solutions.

CORROSION CONTROL

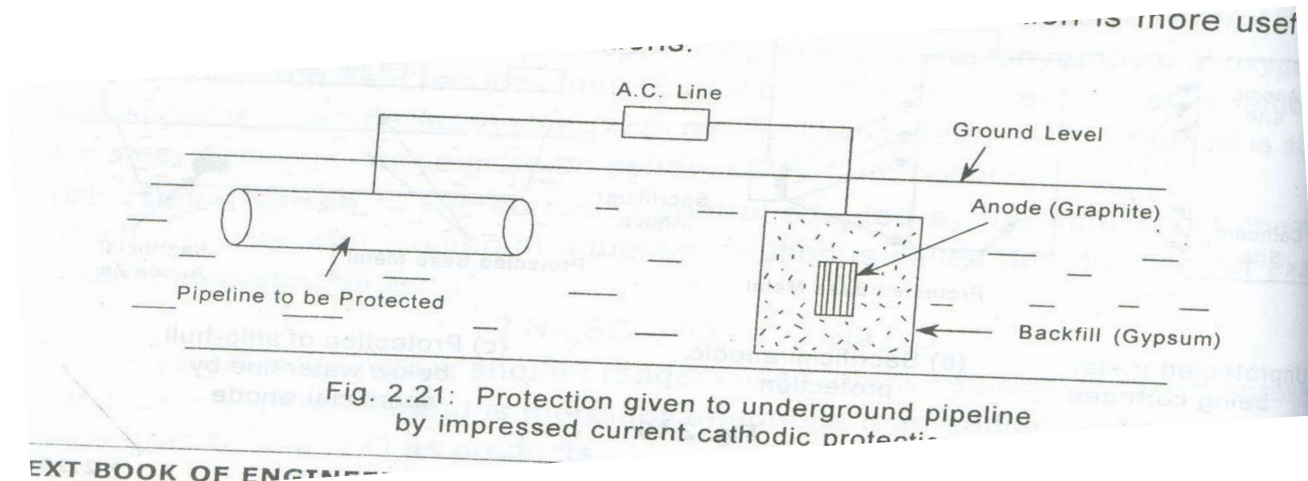
Q7. What is sacrificial anode? Mention its role in control.

- 1) **Cathodic protection** : The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur. There are two types of cathodic protection.
- i) **Sacrificial anodic protection method**: - In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal itself gets corroded slowly. While the parent structure which is cathodic is protected. The more active metal so employed is called "sacrificial anode" whenever the sacrificial anode is consumed completely. It is replaced by a fresh one. Metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc.



Q8. What is the principle of cathodic protection? Explain impressed current method of protection. (Or) How are metals protected by impressed current method?

Impressed current – cathodic protection: - In this method an impressed current is applied in opposite direction to nullify the corrosion current and current the corroding metal from anode to cathode. Usually the impressed current is derived from a direct current source (like battery or rectifier on ac line) with an insoluble anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient d.c is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected.



The anode is buried in a backfill such as coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.

Applications:- This type of protection is used in buried structures such as tanks and pipelines, transmission line towers, marine piers, laid up ships etc.,

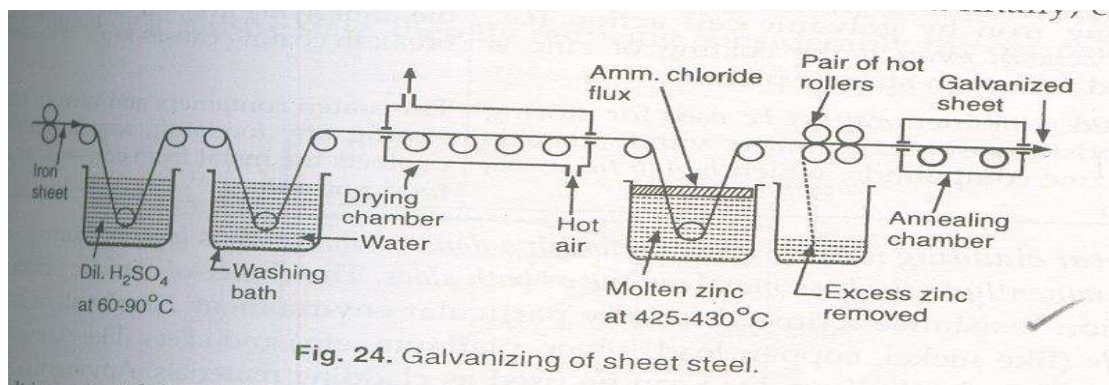
Advantages:- They can be automatically controlled which reduce maintenance and operational costs.

Q9. What are metallic coatings? Explain the galvanization process? Or Explain the process of hot dipping to prevent from corrosion?

Metallic coatings:

Anodic coatings (galvanization):

Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. For carrying out galvanizing firstly the iron or steel article such as sheet, pipe or wire is cleaned by pickling with dil H_2SO_4 solution for 15-20 mts at $60-90^\circ C$. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface. The article is washed well and then dried. It is then dipped in bath of molten zinc maintained at $425-430^\circ C$. The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath. It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness then it is annealed and finally collected slowly.



Uses: - Roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. which are made of iron are protected from atmospheric corrosion by galvanizing them. But galvanized utensils cannot be used for preparing and storing food stuffs, especially acidic ores since zinc gets dissolved in all acids forming highly toxic compounds.

Q10. Write a brief note on cementation.

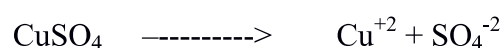
Cementation (sheradising):

Developed by sherad cowpercoles in 1980. It is the process of cementation ,using zinc powder as coating material. The iron article to be coated is cleaned by acid pickling process and rotated for 2 to 3 hours in a drum containing zinc dust at 350-370⁰C. During this process zinc diffuses into iron forming Fe-Zn alloy at the junction of base metal and coating metal and a thin layer of zinc is deposited on the surface of iron. Sheradising is used for coating small steel articles like bolts, screws, nuts and valves etc. The advantage of sheradizing is that the metal coating is uniform and there is no change in the dimension of article.

Q11. What are metallic coatings? Describe the electroplating method with the help of neat diagram.

Electroplating Is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

Theory of electroplating:- suppose the anode is made up of coating metal (M) itself, during electrolysis the concentration of the electrolytic bath remains unaltered since the metal ions deposited from the bath are replenished continuously by the reaction of the free anions of the electrolyte with the anode metal. Thus for e.g. if CuSO₄ solution is used as an electrolyte it ionizes as



On passing current Cu^{+2} ions go to the cathode (the article to be plated) and get deposited there.

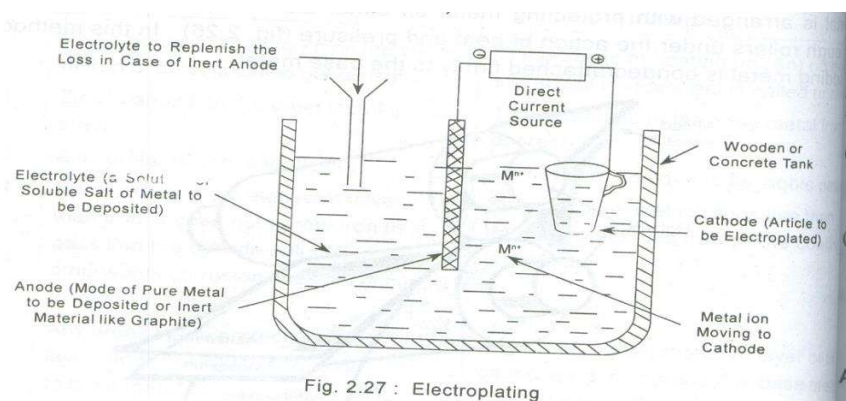


The free sulphate ions migrate to the Cu anode and dissolve an equivalent amount of the Cu to form CuSO_4



The CuSO_4 thus formed dissolves in the electrolyte thus there is continuous replenishment of electrolytic salt during electrolysis.

Procedure:- The article to be electroplated is first treated with organic solvent like tetrachloro ethylene to remove oil, grease etc. then it is treated with dil HCl or H_2SO_4 to remove surface scales, oxides etc. For Ni and Cu HCl is used while for Cr plating H_2SO_4 is used. The cleared article is then made as cathode of an electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity like graphite. The electrolyte is a solution of a soluble salt of the coating metal. When direct current is passed coating metal ions migrate to the cathode and get deposited there. Thus a thin layer of coating metal is obtained on the article made as cathode. For brighter and smooth deposits, favorable conditions such as low temp, medium current density and low metal ion concentrations are used.



Organic coatings:-

Organic coatings are inert organic barriers like paints, varnishes, lacquers and enamels applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. A good organic coating should possess the following qualities.

- i) Should be chemically inert to the corrosive environment.
- ii) Should have good surface adhesion.
- iii) Should be impermeable to water, salts and gases.
- iv) Should possess good spreading capability.