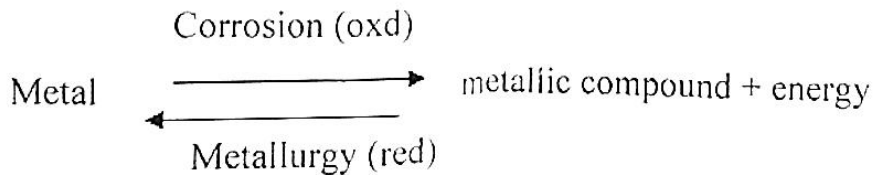


UNIT -II

SCIENCE OF CORROSION

Introduction: Most of the metals (except noble metals like Au, Pt, and Ag) occur in nature in combined form of their oxides, hydroxides, sulphides, chlorides, carbonates and silicates. All these metals have natural tendency to revert back to combined state for stability. The natural combined form of metal is more stable than the other metals. So metals after extraction from its ore tends to revert back to the stable natural combined form when it comes in contact with other elements in the environment. That is why metal after extraction from its ore tends to revert back to the stable natural combined form. So corrosion is reverse process of metallurgy.



The surface of all metals begin to decay when exposed to atmospheric gases, water & other reactive liquid medium as a result they are converted to oxides, hydroxides, carbonates, nitrates, sulphates etc. This natural process is called corrosion.

Definition: - The process of gradual decay or deterioration / eating of metal from its surface by unwanted chemical /electro-chemical attack by its surrounding environment is called corrosion.

Example for corrosion:-

- A reddish brown layer formed on to the surface of Fe
- Green film on surface of copper, etc...

Reason for corrosion:-

- All metals except (Pt, Au, Ag) occurs in a combined state in nature. During extraction of metal from its ore, they are reduced to metallic compound using energy .Hence an isolated metal will be present in its excited unstable state. However, all the metals have natural tendency to go back to their combined state for its stability. As a result metal exposed to environmental factors or chemicals get converted in to its original combined state which is called corrosion.

The corrosion process is a reversible process and is measured in units such as milli inches / year or millimeter/year.

Dis-advantages of corrosion:

- 1.Poor in appearance
- 2.The plant may be shut down due to failure.
- 3.Decrease in production rate and replacement of equipment is time consuming.
- 4.Contamination of product.
- 5.Decreased safety from a fire hazard or explosion or release of toxic product.
- 6.Health hazards from pollution due to corrosion product or due to escaping of chemical from a corroded environment.

TYPES CORROSION:- Based on the process how corrosion occurs, it is classified in to two types.

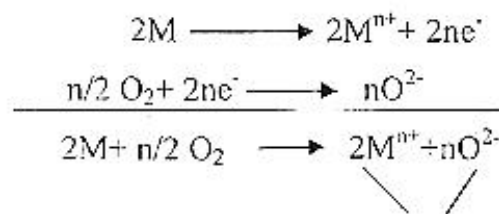
- 1.Chemical/Dry corrosion
- 2.Electrochemical/Wet corrosion

1. Chemical/Dry corrosion:- This occurs mainly due to the direct action of environment or atmospheric gases like O_2 , SO_2 , H_2S , Halogens, Anhydrous in-organic liquids with metal surface that are present in its immediate proximity. It is classified into 3 types based on how corrosion is taking place.

- A. Oxidation corrosion
- B. Corrosion by other gases
- C. Liquid metal corrosion.

A. Oxidation corrosion:- It is brought about by O_2 at low & high temperature on metals, usually in absence of moisture. At ordinary temperature metals are slowly attacked, at low temperature alkali and alkaline earth metals (II group) are rapidly oxidized and at high temperature all metals except Pt, Au, Ag are oxidized.

The reactions that occur during oxidation corrosion are



Metal oxide (M_2O_n)

Mechanism:-

When oxidation takes place at surface of metal, it forms a metal oxide layer on its surface which prevents further oxidation. This layer is called as 'scale'.

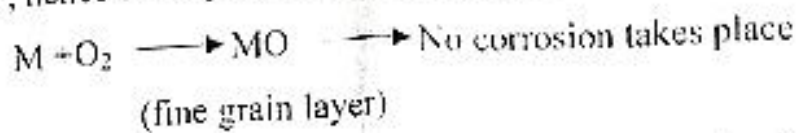
If oxidation continues, either metal diffuse out wards through scale or oxygen diffuses in wards through scale.

Both cases can take place but the outward diffusion of metal is predominant than inward diffusion of O_2 , since the size of metal is smaller than O_2 ion and is having much higher mobility.

Types of scales: The following types of metal oxide layers (scales) are formed by corrosion

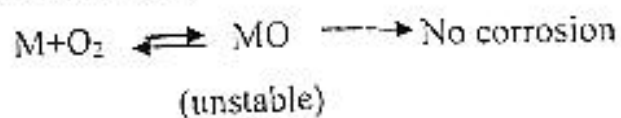
1. Stable
2. Unstable
3. Volatile
4. Porous

1. Stable:- It is a fine grained layer in texture and it tightly adheres to metal surface, hence this layer don't permit further corrosion.



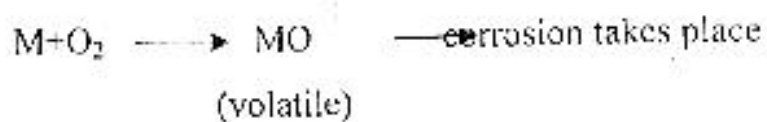
Examples of metals that form stable scales are-- Al, Cu, Pt etc.

2. Unstable:- The metal oxide film immediately decomposes to metal & O₂ as soon as it is formed, hence further oxidation doesn't take place.



Examples of metals that form stable scales are -- Pt, Au, Ag

3. Volatile:- This type of metal oxide layer get continuously evaporated and hence fresh metal surface again get exposed for further corrosion leading to rapid corrosion of the metal. This type is seen in Mb (molybdenum)



4. Porous:- The metal oxide layer that is formed contains pores or cracks on its surface and through this pores atmospheric O₂ passes up to the metal surface, hence corrosion continues till the entire metal is converted to metal oxide.



| S.No | Type of metal oxide | Example | Corrosion |
|------|---------------------|--------------------------------|--------------------|
| 1. | Stable | Cu, Al | Doesn't take place |
| 2. | unstable | Pt, Au, Ag | Doesn't take place |
| 3. | volatile | Mb | Takes place |
| 4. | porous | alkali & alkaline earth metals | Takes place |

Pilling – Bedworth Rule:

The rule states that 'an oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed'.

This is expressed in terms of **specific ratio**.

$$\text{Specific ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous. So oxygen can diffuse and further corrosion takes place.

Ex: 1. Oxides formed by Alkali and Alkaline earth metals have less volume than the volume of metal, so they form porous scales and have high corrosion.

1. Metals like 'Al' form oxides whose volume is greater than the volume of metals, so they form non-porous scales and have low corrosion.

B. Corrosion By Other Gases ($\text{SO}_2, \text{H}_2\text{S}, \text{CO}_2, \text{F}_2, \text{Cl}_2$) :-

This type of corrosion mainly depends on chemical affinity between metal & the gas involved.

The intensity of attack depends on formation of protective or non protective films on metal surface.

If the film is protective or non porous, the volume of metal oxide layer is greater than that of metal. So further corrosion of metal doesn't take place.

Eg: Formation of AgCl film by the attack of chlorine on Ag:
The intensity of corrosion decreases due to formation AgCl non porous film on its surface which is tightly adherent on Ag.

If the film is non- protective or porous, the volume of metal oxide layer is lesser than that of metal so further corrosion takes place.

Eg: SnCl_4 formed by attack of Cl_2 on Sn (tin) which volatiles immediately there by leaving fresh metal surface for further corrosion.

C. Liquid metal corrosion:-

This is due to chemical action of flowing liquid metal at high temperature on solid metal or alloy.

This type of corrosion is seen in devices used for nuclear plant.

The corrosion reaction is carried out either by dissolution of solid metal or by liquid metal or internal penetration of liquid metal into solid metal. Both reactions lead to weakening of solid metal.

Eg: Na metal causes corrosion of Cd in nuclear reactor.

2. Electrochemical / wet corrosion:- This type of corrosion takes place when a conducting liquid is in contact with a metal or two dissimilar metals are either dipped or immersed partially in a solution.

Usually it takes place in liquid medium.

The electrochemical corrosion involves the following--

1. Existence of separate anodic or cathodic parts between which current flows through conducting medium.

2. **At anode:** Oxidation takes place at anodic part and releases electrons, forms metallic ions. Hence corrosion always occurs at anode.



3. **At cathode:** Reduction reaction takes place at anode, so the released electrons from anode are accepted by non metals and forms non-metallic ions such as OH^{-} & O^{2-}

4. The metallic & non-metallic ions diffuse towards each other through conducting medium & form corrosion product.

Mechanism:-

Electrochemical corrosion involves flow of electrons between anode & cathode.

The anodic reaction involves dissolution of metal as metal ion with liberation of electrons.



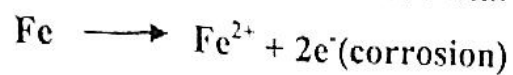
On the other hand cathodic reactions consume electrons in two ways depending on nature of corroding environment. They are

a) Evolution of hydrogen

b) Absorption of O₂

a) Evolution of H₂:- This type of corrosion takes place generally in acidic medium.

For example if Fe metal is in contact with acidic medium, anodic reaction is dissolution of Fe as ferrous with liberation of electron.



The reduced electrons from anode flow through metal to cathode where H⁺ ions are reduced to H₂.



The overall reaction is $\text{Fe} + 2\text{H}^{+} \longrightarrow \text{Fe}^{2+} + \text{H}_2$

This type of corrosion causes displacement of H⁺ ions by metal ion.

All the metals above hydrogen in electro chemical series have a tendency to get dissolved in acidic solution with simultaneously liberation of H₂ gas.

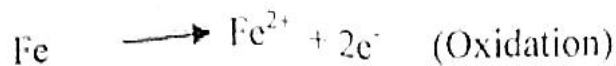
b) Absorption of O₂:-

When metals are in contact with slightly alkaline or neutral solution (water) with some amount of dissolved O₂, this type of corrosion takes place.

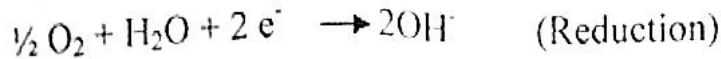
Ex: Rusting of iron in neutral aqueous electrolyte solution in presence of atmospheric O₂.

The surface of Fe is usually coated with thin film of FeO. However the oxide film develops cracks, which behave as anodic area & remaining metal part acts a cathode. It shows that anodes are of small area while rest of metallic part forms large area of cathode.

At anode:- Fe dissolves in aqueous solution forms Fe²⁺ with release of electrons.



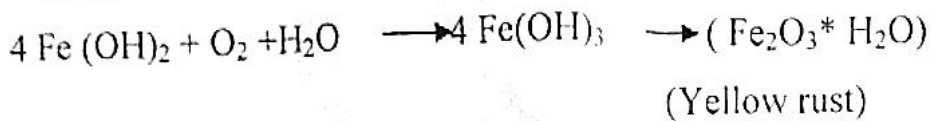
- **At cathode:-** The liberated e^- flows from anode to cathode through Fe metal, these electrons are accepted by dissolved O_2 to form OH^- ions.



- The Fe^{2+} at anode & 2OH^- at cathode react to produce $\text{Fe}(\text{OH})_2$ precipitate



- If O_2 is available in excess, $\text{Fe}(\text{OH})_2$ is easily oxidized to $\text{Fe}(\text{OH})_3$



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

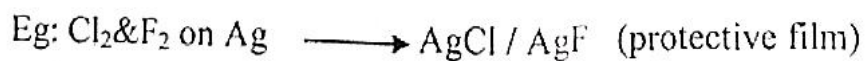
THEORIES OF CORROSION :-

The following theories explain about tendency & process of corrosion.

1. Direct chemical attack
2. Acid theory
3. Electro chemical theory

1. Direct chemical attack:-

- This theory explains about dry or chemical corrosion.
- The corrosion takes place by direct chemical attack.
- The film of a corrosive product normally formed on surface of metal, protects the metal, so further corrosion doesn't take place.

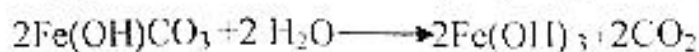
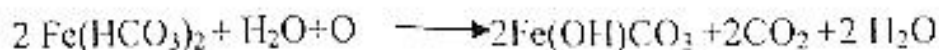
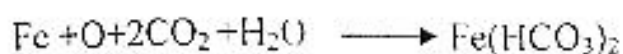


- If corrosion product is soluble, then metal is exposed to further corrosion, then metals are attacked by atmospheric O_2 to produce metal oxide at their respective temperatures.
- The intensity of corrosion depends on the nature of oxide deposit.
- If the formed metal oxide is non-porous, then the metal surface becomes protective and if it is porous, then O_2 diffuses inside the metal & thus further corrosion takes place.

Ex: Al and Cr forms extremely protective oxide layers and hence these metals are normally used for alloy formation with metals that undergo easy corrosion.

2. Acid theory:--

- This theory states that presence of acid is essential for corrosion.
- Rusting of Fe is well explained by this theory.
- Fe reacts with O_2 , CO_2 and moisture present in atmosphere and results in formation of a soluble Ferrous carbonate, which is further oxidized to basic ferric carbonate and finally ferric hydroxide is formed.



3. Electro chemical theory:-

- This theory explains about electro chemical corrosion.
- The modern electro chemical theory is based on Nernst theory. This states that all metals have tendency to pass into solution when immersed in its own salt solution (Zn – metal – immersed in $ZnSO_4$ salt). This tendency is called as electrode potential.
- If a metal having higher electrode potential comes in contact with a metal having lower electrode potential, a galvanic cell set up occurs and metal at higher electrode potential becomes anode and goes in to solution.
- If the solution is acidic then, H_2 gas evolves at cathode while anodic metal dissolves in it.
- The greater the difference in potential b/n anode & cathode , the greater will be corrosion and also if the anode area is smaller than cathodic area , then more severe corrosion takes place.

Galvanic series:-

- Electrochemical series gives useful information regarding chemical reactivity of metals, however this series doesn't give sufficient information about corrosion behavior of metal in a particular set environmental conditions.

- Passivation makes effective electrode potential of some metals more passive and makes them act like cathode and exhibits noble behavior. This behavior is exactly opposite to electro chemical series.
- So a more practical series have been prepared by studying the corrosion of metals and alloys in common electrolyte called sea water using calomel electrode as reference electrode.
- Then the metals electrode potentials are arranged in increasing order towards down. This series is called **galvanic series**.
- A metal present high in series is more anodic & undergoes corrosion faster than metal below.
- This series gives real and useful information about corrosion behavior of metals and alloys in a given environment.
- Galvanic series predicts the tendency of both metals and non- metals in actual environment where as electrochemical series predicts the displacement of metals and non-metals in electrolyte.

| | | | | |
|----|-------------------|---------------------|----|-----------------------|
| 1 | Mg | Anodic (active) | 14 | Brass |
| 2 | Mg alloy | | 15 | Monel |
| 3 | Zn | | 16 | Silver |
| 4 | Al | | 17 | Cu |
| 5 | Al alloy | | 18 | Ni |
| 6 | Fe | | 19 | Stainless steel |
| 7 | Mild steel | | 20 | 18-08 Stainless steel |
| 8 | High Ni cast iron | | 21 | 18-08 MO steel |
| 9 | Pb- Sn solder | | 22 | Ag |
| 10 | Pb | | 23 | Ti |
| 11 | Sn | | 24 | Graphite |
| 12 | Inconel | | 25 | Au |

| | | | | |
|----|--------------------|--------------------------|----|----|
| 13 | Ni - mo - Fe alloy | Cathodic (stable/ noble) | 26 | Pt |
|----|--------------------|--------------------------|----|----|

- Eg: Zn corrodes faster than Fe & Cu corrodes faster than Ag, Fe corrodes faster than Sn.
- However some exceptions to this generalization are known.
- Eg: Ti is less reactive than Ag.
- In Zn - Al couple, Zn is less corroded, while Al acts as cathode and is protected.
- These experiments clearly prove that metals like Ti & Al develop strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more +ve.

Galvanic corrosion or Bimetallic corrosion: -

- When two dissimilar metals are electrically connected & exposed to electrolyte, metal higher in electrochemical series undergoes corrosion. This is called galvanic corrosion.

Eg: Zn - Cu galvanic cell:- Here Zn acts as anode where oxidation takes place, corrosion occurs & Cu act as cathode & is protected.

Mechanism:-

- In acidic solution, corrosion occurs by evolution of H_2 , while in neutral & slightly alkaline solution absorption of O_2 occur.
- The e^- flow from anodic metal to cathodic metal.

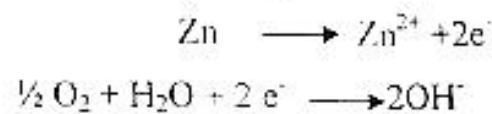


- This means corrosion occurs at anodic metal, while cathodic part is protected from attack eg: Steel pipe connected to copper plumbing.

Concentration Cell Corrosion / Differential Aeration Corrosion:-

- This type of corrosion is due to electrochemical attack on metal surface exposed to an electrolyte of varying concentrations or of varying aeration.

- The most common type of concentration cell corrosion is differential aeration corrosion.
 - This occurs when one part of metal is exposed to different air concentration from other part.
 - This causes a difference in potentials between differently aerated areas.
 - Poorly oxygenated metallic part becomes anodic & undergoes oxidation where as well oxygenated part acts as cathode.
 - Eg: When Zn metal is partially immersed in dilute neutral NaCl solution, the part above & closely adjacent to water line are well aerated. Hence become cathodic. On the other hand, part that is immersed to greater depth show a smaller oxygen concentration, thus become anodic. So a difference of potential is created which causes flow of current between two differentially aerated areas of same metal.
- Zn can dissolve at anode & releases electrons which are accepted by O₂ at cathodic area to form hydroxyl ions.



FACTORS INFLUENCING CORROSION:- The intensity and rate of corrosion depends on two types of factors

1. Nature of metal
2. Nature of environment

I. Nature of metal :- Many factors influence corrosion of metal that depend on its nature. They are--

- i. Position of in galvanic series
- ii. Over voltage
- iii. Relative areas of cathode & anode
- iv. Purity of metal
- v. Physical state of metal
- vi. Nature of surface film.
- vii. Passivity of metal.
- viii. Solubility of corrosion product

ix. Volatility of corrosion product

1. **Position in galvanic series:-** When two metals or alloys are in contact with conducting medium the more active metal suffers corrosion. The intensity of corrosion depends on difference in their position, the faster will be corrosion of anodic metal /alloy.

2. **Over voltage:-** It is defined as difference of potential b/n practical & theoretical decomposition potentials for same solution.

Eg: Electrolysis of H_2SO_4 with Pt electrode, its practical potential is about 1.70 v where as its theoretical potential is 1.229v. The diff is 0.471v which is over voltage of H_2SO_4 . Reduction in over voltage of corroding metal or alloy accelerate corrosion rate.

3. **Relative areas of anode & cathode:-** Small anodic & large cathodic area causes severe corrosion when two dissimilar metals or alloys are in contact the corrosion of anode part is directly proportional to ratio of areas of cathodic & anodic part.

Eg: A small steel pipe fitted in a large copper tank.

4. **Purity of metal:-** Impurities in metal cause heterogeneity and form tiny electrochemical cells(at exposed parts) & anodic part gets corroded.

Eg: Zn metal containing impurities Pb / Fe undergoes corrosion due to formation of local electrochemical cells.

-The rate & extent of corrosion increases with increase in exposure and extent of impurities.

- The intensity of corrosion is less when its purity is high.

5. **Physical state of metal:-** The rate of corrosion is influenced by physical state of metal such as grain size, orientation of crystals, stress etc.

-If grain size is smaller, its solubility is more and hence greater will be its corrosion.

-Moreover areas under stress, even in pure metal tend to be anodic and corrosion takes place at these areas.

6. **Nature of surface film:-** In aerated atmosphere practically all metals get covered with a thin surface film of metal oxide.

-The ratio of volume of metal oxide to metal is called specific volume ratio.

-Greater the specific volume ratio (SVR), lesser is oxidation corrosion rate

For eg: The S.V.R of Ni, Cr, W are 1.6, 2.0, & 3.6 respectively.

The rate of corrosion of tungsten is least even at elevated temperature.

7. **Passivity of metal**:- Passivity is a phenomenon in which metal/ alloy exhibits a much greater corrosion resistance the resulting film is highly protective but very thin & quite invisible film on surface of metal / alloy, which makes it more noble.

-Metal like Ti, Al, Cr, Mg, Ni & Co are passive and they exhibit much higher corrosion resistance than expected from their positions in galvanic series.

Passivity of metal decrease corrosion rate.

Eg: Corrosion resistance of stainless steel is due to passive character of Cr present in steel.

8. **Solubility of corrosion product**:- In electrochemical corrosion if corrosion product is soluble in corroding medium, then corrosion proceeds at faster rate. If corrosion product is insoluble in medium or it forms another insoluble product which create physical barrier there by corrosion is suppressed.

Eg: corrosion of Pb in H_2SO_4 decreases due to formation of insoluble $PbSO_4$.

9. **Volatility of corrosion product**:- If corrosion product has volatile nature, underlined metal is exposed further and causes severe corrosion.

Eg: MoO_3 is volatile.

II. NATURE OF THE CORRODING ENVIRONMENT:- The following environmental factors influence intensity of corrosion.

1. Temperature.
2. Humidity of air.
3. Presence of impurities.
4. Presence of suspended particles in atmosphere.
5. Influence of p^H .
6. Nature of ions.
7. Conductance of conducting medium.
8. Formation of O_2 conc cell.

1. **Temperature**:- With rise in temp. of environment, the reaction rate and also diffusion rate increases there by generally corrosion rate also increase.

2. **Humidity of air**:- It is the deciding factor in atmospheric corrosion.

- Critical Humidity is defined as relative humidity above which the atmospheric corrosion rate of metal increases sharply.
- The value of critical humidity depends on physical characters of metal & corrosion product.
- In Humid environment the rate of corrosion is higher due to gases & vapors present in atmosphere furnish (give) water to form electrolyte, essential for setting up an electrochemical corrosion cell.
- More over the oxide film on metal surface has a property to absorb the moisture, then corrosion rate enhanced.
- The nature of moisture sources also play important role.
Eg: Rain water apart from supplying moisture for electrochemical attack, may also wash away a good part of oxide film from metal surface (unless the oxide film is exceptionally adherent).

3. Presence of impurities in atmosphere:-

- Presence of corrosive gases like SO_2 , CO_2 , H_2S , O_2 etc in atmosphere increases acidity and increase electrical conductivity which causes severe corrosion.
- In marine atmosphere presence of Na & other chlorides leads to increase in conductivity there by corrosion increases.

4. Presence of suspended particles in atmosphere:-

- The suspended particles in atmosphere may be are of two types.
- i) **Chemically active:-** If suspended particles are active (NaCl , $(\text{NH}_4)_2\text{SO}_4$) they absorb moisture & act as strong electrolytes , thereby causing enhance corrosion .
- ii) **Chemically in-active:-** If suspended particles are chemically inactive, in nature (charcoal) they absorb both sulphur gas & moisture & slowly enhance corrosion rate.

5. Influence of pH:-

- Generally acidic media ($\text{pH} < 7$) are more corrosive than alkaline & neutral media.

-The metals are readily attacked by acid, so corrosion of metal can be reduced by increase of pH of attacking environment.

Eg: Zn rapidly corrodes in weak acidic solution and suffers minimum corrosion at pH-11.

6. Nature of ions present:-

-Some ions increase corrosion while others decrease it.

-The presence of anions like silicate in medium leads to formation of insoluble reaction products (silica gel), which inhibit further corrosion.

-On other hand Cl^- ions destroy protective & passive surface film, hence metal surface is exposed for fresh corrosion.

-Presence of NH_4 salts increase corrosion of Fe.

-The presence of even traces of Cu in mine water accelerates corrosion of Fe pipes, used for carrying such water.

7. Conductance of conducting medium:-

-Conductance of conducting media is important in case of underground & submerged structures.

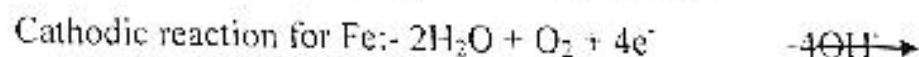
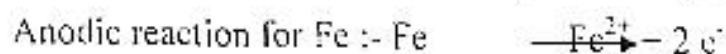
-Conductance of dry sandy soil is lower than those of mineralized/ clayey soils.

-Stray currents (from power breakages) will cause more damage to metallic structures buried under clay & mineralized soil than those under dry sandy soils.

8. Formation of O_2 concentration cell:-

-As percentage of O_2 increases, the rate of corrosion also increases due to formation of O_2 conc. Cell.

-The decay of metal occurs at anodic part & cathodic part is protected.



-Thus formation of concentration cell promotes corrosion, but it occurs where O_2 conc. is lower.

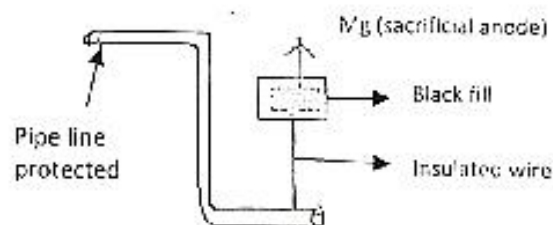
Control of corrosion (protection against corrosion):-

Cathodic protection:-

- In this method of protection, a metal that acts as anode is forced to behave like cathode there by its corrosion doesn't occur.
- This is done by two methods
 1. Sacrificial anodic protection
 2. Impressed current cathodic protection

1. Sacrificial anodic protection: -

- In this method of protection, metallic structure to be protected is called base metal.
- Using more active metal called sacrificial anode, base metal is protected by connecting it to sacrificial anode through a wire.
- Hence all corrosion is concentrated at sacrificial anode while base metal is protected.
- Corroded sacrificial anode block is replaced by fresh one.
- The commonly used anodic metals are Mg, Zn, Al and their alloys. Zn is used as sacrificial anode in good electrolytes as sea water. Mg is used in high resistive electrolytes due to its more -ve potential & it can provide highest current output.



2. Impressed current cathode protection :-

- In this method all impressed current is applied in opposite direction to corrosion current to nullify & convert corroding metal from anode to cathode.
- Once the metal becomes cathode it is protected from corrosion.
- The impressed current is taken from battery or rectified AC line.
- The anode may be either an inert material or insoluble material such as graphite, Pt, stainless steel, high silica iron, scrap Fe etc.

- Usually sufficient DC current is passed on to insoluble anode kept in back fill composed of coke /gypsum. So as to increase electrical contact with surrounding soil.
- This protection technique is: Anode / Cathode buried structures like water tanks, water pipelines, transmission line towers, marine pipes , laid up ships etc.

