CORROSION AND ITS CONTROL

Corrosion can be defined as spontaneous destruction or deterioration of a metal by chemical, electrochemical or biochemical reaction.

Free metals, as such are unstable and whenever favorable situation arises they combine with other elements like oxygen and form the compounds of minimum energy and maximum stability. Hence corrosion can be viewed as the reverse process of extractive metallurgy

Corrosion
METAL ------------------------> METALLIC COMPOUNDS + ENERGY
<-----------------------
Metallurgy

CORROSION CLASSIFICATION:

A) Dry or Chemical Corrosion
B) Wet or Electrochemical Corrosion

A) Dry or Chemical Corrosion: This type of corrosion occurs by direct chemical reactions between the environment and the metals and alloys. Presence of an electrolyte is not at all essential for the corrosion to occur. Therefore this kind of corrosion is also known as dry corrosion.
eg: Direct chemical action of environmental gasses such as oxygen, halogens, hydrogen sulphide,sulphur dioxide, nitrogen or anhydrous inorganic liquid with the metal.

Off all the atmospheric gases, oxygen is one of the important and most reactive element which reacts with almost all types of metals. This type of corrosion is known as oxidation corrosion. The reactions in the oxidation corrosion.

$$2M \longrightarrow 2M^{n+} + ne^-$$

$$nO_2 + 2n^{e-} \longrightarrow 2nO^{2-}$$

$$2M + nO_2 \longrightarrow 2M^{n+} + 2nO^{2-}$$

In general:

Metal + Oxygen-------------> Metal oxide
(Corrosion product)

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

If a stable film is formed, it behaves as protective coating in nature, thereby shielding the metal surface. Consequently, further oxidation of metal is prevented.
Eg: Al, Sn,Pb,Cu and Pt. Unstable metal film decomposes back into the metal and oxygen. Hence oxidation corrosion is not possible in such Cases: Ag, Au, Pt.
Volatile film layer volatilizes as soon as it is formed, thereby accelerating the corrosion. Eg: MoO_3 is highly volatile.

Corrosion by other gases like SO_2 ,Cl_2,CO_2,H_2S etc., depends mainly on the chemical affinity between the metal and the gas involved. Liquid metal corrosion is due to chemical action of flowing liquid metal at high temperature on solid. Such corrosion in devices used for nuclear power.

B) Wet or Electrochemical Corrosion:

Wet corrosion occurs due to the existence of separate anodic and catholic areas, between which current flows through the conducting solution. It involves flow of electron current between the anodic and cathodic areas.

At anode, always there will be oxidation reaction, involving the dissolution of metal as corresponding metallic ions with the liberation of free electrons.

$$M \text{ --------------> } M^{n+} + ne^-$$

On the other hand, the cathodic reaction consumes electrons either by:

i) Hydrogen evolution

ii) Absorption of oxygen depending upon the nature of corrosive environment. Following are the important cathodic reactions:

i) Hydrogen evolution:

$$2H^+_{(aq)} + 2e^- \text{ -------------> } H_2$$

ii) Reduction of oxygen in acid medium:

$$O_2 + 4H^+ + 4e^- \text{ ----------> } 2H_2O\ (l)$$

Iii) Reduction of oxygen in neutral medium:

$$O_{2\ (aq)} + 2H_2O + 4e^- \text{ ---------> } 4OH^-_{(aq)}$$

In addition to the above mentioned cathodic reactions, following reactions may also occur at cathodic region.

iv) Metal ion reduction: $M^{n+} + (n\text{-}1)e^- \text{ -------------------> } M^{(n-1)}$

v) Metal deposition: $M^{n+} + ne^- \text{ -----------------------> } M$

Oxygen reduction is the most common cathode reaction, since any aqueous solution in contact with air contains dissolved oxygen. Hydrogen evolution occurs in acidic media. Metal ion reduction and metal deposition are rare.

From, electrochemical theory, it must be clear that no corrosion take place at the cathodic area, since cathodic reaction does not involve metal dissolution. Corrosion and hence metal dissolution takes place only at anodic area. Cathodic area stimulates corrosion of the anodic part by utilizing the electrons produced at anodic area.

Mechanism of rusting: (ELECTROCHEMICAL THEORY OF CORROSION)

Corrosion of iron is known as rusting. Rusting take place when iron is exposed to oxygen in the presence of humidity/moisture. Following reactions are expected to take place during rusting:

At the anodic area $Fe \text{ -------------> } Fe^{2+} + 2e^-$

The liberated electrons flow from anodic to cathodic areas through iron (metallic, electronic conductor) where electrons are taken up by oxygen in presence of moisture.

$$O_2 + H_2O + 2e^- \text{ ----------------->} 2OH^-$$

Fe^{2+} ions and OH^- ions diffuse (electrolytic conductor) and when they meet ferrous hydroxide precipitates.

$$Fe^{2+}_{(a)} + 2OH^- \text{ ------------------>} Fe(OH)_2 .$$

Case (i) In the presence of enough oxygen, ferrous hydroxide is easily oxidized to ferric hydroxide and the product is called yellow rust, which can be represented by the formula $Fe_2O_3.H_2O$.

$$4Fe(OH)_2 + O_2 + 2H_2O \text{ ------------>} 4Fe(OH)_3 \text{ or } 2Fe_2O_3.6H_2O$$

Case (ii) If the supply of oxygen is limited, the corrosion product may be black anhydrous magnetite Fe_3O_4.

Types of corrosion:-

1) Galvanic corrosion:-

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This is because the metal occupying higher position in the e.m.f series due to lower value for its standard electrode potential becomes anodic part of the couple. Other metal occupying the lower position in the emf series due to lower value for its standard electrode potential becomes anodic part of the couple. Other metal occupying the lower position in the emf series due to higher value for its standard electrode potential becomes cathodic part.

Eg: 1.Consider Fe (E^o= -0.44V)   Zn (E^o = -0.76V)
Sn (E^o = -0.14V)   Cu (E^o =+ 0.36V)

In the galvanic couple like Zn/Fe, Fe/Sn, Fe/Cu, Zn/Sn, Zn/Cu; the first metal is anodic with respect to the second metal and hence undergoes corrosion.

2. Steel screws in a brass marine hardware.
3. Lead - antimony solder around the Cu wire.

2) Differential aeration corrosion:

This kind of corrosion is due to the formation of oxygen concentration cell. It occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower concentration of oxygen acts as anodic region. Consequently, the poorly oxygenated region undergoes corrosion.

Differential aeration corrosion is mainly observed in metals partially immersed in a solution below the waterline. If a metal (Zn) is partially immersed in a dilute solution of neutral salt (eg:NaCl) then the parts above the waterline are more strongly aerated and hence become cathodic. On the other hand, parts immersed in water, area in contact with lesser amount of oxygen and thus become anodic.

As a result of this, a difference of potential is created, which causes a flow of current between the two differentially aerated areas of the same metal.

Following reactions take place:

At the anodic area : $Zn \longrightarrow Zn^{+2} + 2e$

At the catholic area: $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$

Differential aeration corrosion may be accelerated in rarer places because oxygen deficient areas serve as anodes. The corrosion rate of such type is accelerated under the accumulation of dirt, sand, scale or other contamination.

3) Water-line Corrosion: - This is also a form of differential aeration corrosion. When unanimated water is kept in an iron tank at a constant level this kind of corrosion is observed.

Surface of water is more aerated and hence more oxygenated. Iron surface in contact with surface of water thus becomes cathodic .Oxygen concentration is low just below the surface of water .Iron surface in contact with water at this part becomes anodic.

Reactions: At the anodic area: $Fe \longrightarrow Fe^{2+} + 2e$

At the cathodic area: $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$

$$Fe + 2OH^- \longrightarrow Fe(OH)_2$$

$$2Fe(OH)_2 + 1/2\ O_2 \longrightarrow Fe_2O_3.2H_2O$$

$$3Fe(OH)_2 + 1/2\ O_2 \longrightarrow Fe_3O_4.3H_2O \text{ (rust)}$$

The rust appears on the inner surface of iron.

Waterline corrosion is quite common in ocean going ships. However ships sunk under water for several years are free from corrosion. This is due to the fact that sunken ship is exposed to almost uniform concentration of air and hence does not undergo differential aeration corrosion.

4. Pitting Corrosion : Pitting corrosion is localized and accelerated corrosion, resulting in the formation of pits or pinholes, around which the metal is relatively unattacked.

Pitting corrosion is characterized by small anodic area and large cathodic area, resulting in accelerated corrosion at the anodic area. It is an autocatalytic process, with the initially formed pit produces conditions which are both stimulating and necessary for the continuing activity of the pit. The important reasons for the pitting corrosion are:

* Surface roughness or non uniform finish.
* Scratches or cut edges.
* Local straining of metal due to non uniform stress.
*Depositions of extraneous matter such as sand, scale, water drop, dust etc.

Whenever dust particles are deposited, owing to the different amount of oxygen in contact, with metal, the small part becomes the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion starts just underneath the impurity.

Pitting is one of the most destructive forms of corrosion of corrosion. It causes equipment to fail because of perforation with only a small percentage weight loss of the entire structure. It is often difficult to detect pits because of their small size, and because the pits are covered with corrosion products. Pitting is dangerous because it is a localized and intense form of corrosion and failure occurs with extreme suddenness.

5) Stress corrosion: - Stress corrosion also known as stress corrosion cracking refers to cracking of metal caused by the combined effect of a tensile stress and

a specific corrosive environment on the metal. Here, the corrosive agents are highly specific and selective.

Eg: 1) Caustic alkalis and strong nitrate solutions on mild steel
2) Traces of ammonia for brass
3) Acid chloride solution for stainless steel.

Materials that are very much susceptible for stress corrosion are the fabricated articles of certain alloys(like high zinc brasses and nickel brasses) due to the presence of stresses caused by heavy working like rolling, drawing, or insufficient annealing.

The metal atoms under stress are always higher energy levels as compared to the one free from stress. The stressed part of the metal therefore becomes more active than the stress free part. As a result, stressed part becomes anode and stress free part becomes cathode and hence stressed part undergoes corrosion.

Eg: 1) Season cracking of brass
2) Caustic embrittlement of steel

Season cracking refers to stress corrosion cracking of Cu alloys (mainly brass), in presence of ammonia. Both Zn and Cu are electrochemically active and they form stable complex ions Cu $(NH_3)_4^{2+}$ and Zn $(NH_3)_4^{2+}$, which results in the dissolution of brass.

Caustic Embitterment: - This is a dangerous form of stress corrosion observed in boiler. Water fed into boilers may contain free alkali. Water softened by lime soda process contains sodium carbonate. Under high temperature and pressure prevailing within boilers sodium carbonate hydrolyses to sodium hydroxide and carbon dioxide.

$Na_2CO_3(aq) + H_2O$ ---------------> $2NaOH + CO_{2(g)}$

Thus water inside the boiler becomes very dilute NaOH solution.

Local stresses exist in metal sheets of boiler under rivets. Minute cracks develop on the metal sheets when the stress is relieved. Dilute NaOH solution flows into these minute hairline cracks. Water evaporates by the heat of the metal, depositing sodium hydroxide within the cracks. Fresh water flows into them and evaporates again depositing more NaOH. Concentration of NaOH increases in these cracks due to the repetition of this process.NaOH concentration cell forms between the stressed and unstressed part of the metal.

Iron (stressed)	/ Concentrated, NaOH	Dilute NaOH	/ Iron (unstressed)
ANODIC		CATHODIC	

Fe^{2+} ions formed at the anode part precipitates as ferrous hydroxide which changes into hydrated ferric oxide and ferroso ferric oxide by the dissolved oxygen, thereby regenerating NaOH

$3Na_2FeO_2 + 4H_2O$ -----------------------------> $6NaOH + Fe_3O_4 + H_2$

$6Na_2FeO_2 + 6H_2O + O_2$ --------------------->$12NaOH + 2Fe_2O_4$

When iron changes to these oxides metallic properties like malleability and ductility are lost. It becomes brittle. The brittleness is caused by caustic alkali. Hence it is called caustic embrittlement.

The minute hairline cracks are caused by local stresses under the rivet heads. The continuation of caustic embrittlement of boiler parts often results in boiler failure.

Prevention: - (i) Na_2SO_4,tannin or lignin is added to water. These substances deposit within the cracks and prevent the accumulation of NaOH.

(ii)Boiler can be constructed by welding the sheets to avoid local stresses.

(iii)Demineralised water does not contain NaOH and Na_2CO_3.Caustic embrittlement is avoided by using demineralised water.

Factors affecting Corrosion Rate These factors can be classified into two types given below:

A) Primary factors.

B) Secondary factors.

A) Primary factors: Factors related to the corroding metals are known as primary factors.

!.Relative electrode potentials of metals: Magnitude of corrosion cell potential is one of the major factors which decides the corrosion rate. The larger the potential difference between the anodic region and cathodic region of the corrosion cell, higher is the corrosion rate. When two different metals with large difference in their electrode potential are in contact with each other, the more reactive metals undergoes corrosion. When potential difference is more, higher corrosion current is produced., and the free energy decrease accompanying the process is higher and corrosion rate is also higher.

2. Nature of metal: In general the metals with lower electrode potential values are more e reactive than the metals with higher electrode potential values. However, there are few exceptions for this general trend, as some metals show the property of passivity. Passivated metals resists corrosion. Metal like Al,Ti and Cr exhibit this property. Passivation of these metals is due to formation of a thin adherent oxide film, as a result of initial corrosion. This oxide film is uniform, insoluble in the medium, non porous and self healing under certain conditions.

3. Relative Cathodic and Anodic area: The rate of corrosion is greatly influenced by the relative areas of anode and cathode. If a metal has a small anodic area and large cathodic area, then the corrosion is more intense and faster is the corrosion rate at the anodic region.

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When the anode is smaller and cathode region is large all the electrons liberated at the anode are rapidly consumed at the cathode region. This makes the anodic reactions to take place at its maximum rate thus increasing the corrosion rate.

If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.

4. Hydrogen Over voltage: The difference between the observed potential at which reduction of H^+ ions to H_2 gas occurs at a cathode and the theoretical potential at which it should have occurred is known as hydrogen overvlotage. Magnitude of hydrogen over voltage depends upon the nature of the metal used as cathode. Increased hydrogen over voltage at a cathode reduces corrosion rate, when the reduction of H^+ ions is the cathodic process.

B) Secondary factors: Factors related to the environment are known as secondary factors:

1. Concentration and nature of electrolytes: Conductance of an electrolyte medium depends upon its ionic concentration. Corrosion current, I = V/R becomes large at small R. Resistance is low and conductance is high at high ionic concentrations. Hence rapid corrosion rate is observed at high ionic concentration. Conductivity of deionised water is 1-10 milli mhos per meter. Conductivities of tap water and sea water are 10-20 milli mhos per meter and 5.3 mho per meter respectively. Therefore corrosion rate in sea water is nearly 500 times as fast as that in tap water and 5000 times as fast as that in demineralised water, based on their conductivity.

Nature of electrolyte is another factor. Some electrolyte cause polarisation and bring down the corrosion rate. The phosphate ions form an insoluble, protective phosphate film of metal ions on the surface of a metal and reduce its corrosion rate. The chloride ions penetrate the protective oxide film of a metal increasing the ionic conductance of the film. Protective action of this film decreases as a result of this and corrosion rate gets enhanced.

2. pH of the medium: In general lower the pH of the corrosion medium, higher is the corrosion rate. However some metals like Al, Zn etc., undergoes fast corrosion in highly alkaline solution. The corrosion rate increases slowly and gradually with decreasing pH and becomes rapid at pH less than 4.

3. Temperature: The rate of a chemical reaction in general, increases with rise in temperature. The rate of corrosion increases as the temperature increases. Increase in temperature increases the conductance of the corrosion medium, which also contributes to the increase in corrosion rate. In the case of corrosion resistant passive metals the rise in temperature decreases the passive range and thereby increases the corrosion rate.

4. Polarization: Displacement of electrode potential resulting from a net current is called polarization. During the process of corrosion, the polarization of anode or cathode decreases the corrosion rate substantially. Because of anodic polarization, the rate of dissolution of metal as metal ions is decreased. This is generally the result of an increase in the concentration of ions of the dissolved metals in the vicinity of the electrode, or due to the formation of a protective film covering the anode.

Cathode polarization retards the cathodic reaction. This can be due to hindering the combination of cathode reactant with electron. For the corrosion to continue both anodic and cathodic reactions should take place simultaneously. The slow rate of one of the reactions makes the corrosion reaction slower.

Corrosion current I = V/R, Polarization increases R and hence decreases I. Therefore rate of corrosion decreases with increasing polarization. Conditions leading to the development of polarization in corrosion cells reduce the corrosion rate and depolarization increases the corrosion rate.

Galvanic Series: In the electrochemical series a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For eg: Li corrodes faster than Mg, Zn corrodes faster than Fe and so on. However, some exceptions to this generalization are known. In Zn-Al couple, Zn (below Al in the electrochemical series) is corroded; while Al acts cathodic is protected. These observations, exactly opposite to that predicted by the e.m.f series are due to the fact that metals like Al and Ti develop strongly adhere ring oxide layers on their surfaces.

Protection against Corrosion:-

Corrosion of metals occurs when they come in electrical contact with a corrosive environment. Therefore metallic corrosion can be prevented by either changing the metal or altering the environment or by separating the metal from the environment. In addition, corrosion can also be prevented by changing electrode potential of the metal. The most effective and economic method; however is to deal with the corrosion problem at the design stage itself.

Various methods available for corrosion prevention are listed below:

*Selection of material & design improvement

*Change of metal

*Change of environment

*Use of coatings for separating metal from environment

1) **Design and Selection of materials:-**

Selection of materials: Planning of corrosion prevention starts always with selection of proper metals and alloys. Therefore one has to take into account the following measures while selecting construction metals.

a) Noble metals such as Pt,Au,Pd etc do not undergo corrosion. But one cannot use noble metals because of its prohibitive price. Pure metals show greater resistance to corrosion than impure one.

b) Suitable alloying of metals always improves its corrosion resistivity.

c) Avoid residual stress in fabricated articles by proper heat treatment (annealing)

d) The use of two dissimilar metals having large difference in their electrode potentials should be avoided. Under unavoidable circumstances, the metals chosen should be very close in the electrochemical series.

Design: - A good design minimizes corrosion in metallic structures or equipments. A large number of corrosion failures are due to improper design and failure to use available knowledge. Some of the more important general rules for design which should be observed are described below:

1) Simplify forms: - structures having simpler forms can be protected easily and efficiently. A complicated shape having more angles, corners, edges and internal surfaces will have a larger surface area exposed to the corrosive environment and will be difficult to protect by painting or other surface treatment

2) Avoid Crevices: Crevices allow moisture and dirt to be trapped which result in increased corrosion. If crevices are either present in a structural or cannot be avoided they should be filled by welding or by using filler.

3) Avoid residual moisture: - The design should be such as to protect the structure from retained or residual moisture. In order to avoid residual moisture, ventilation is usually as important as drainage. Condensation should be reduced by free circulation of air.

4) Avoid sharp corners and sharp bends: - These are the potential corrosion sites and these must be replaced by round corners. Sharp corners result in thin coating at corners and are not protected effectively rounding the corners resulting in an even coating. Sharp bends and other areas were the fluid direction is changed rapidly can promote corrosion and should therefore be avoided.

5) Avoid Galvanic corrosion: - To avoid the possibility of galvanic corrosion different metals and alloys should not be joined and particularly when they are situated far from each other in the galvanic series. When this is unavoidable galvanic corrosion can be prevented by using an insulating material which does not absorb moisture, use paint or exclude oxygen from the environment.

6) Avoid mechanical stresses:-Mechanical stresses either residual or applied should be minimized when the component is to be exposed to a corrosive environment so as to avoid the risk of stress corrosion.

2)**Cathodic protection:-**

Corrosion of a structure can be controlled if it can be changed into the cathodic part of a corrosion cell. This is called cathodic protection.

Ship's steel hulls, offshore drilling platforms, oil and gas under sea pipelines, containers used to store water and other liquids are protected by this method.

Cathodic protection is done by two different methods.

a) Sacrificial anode method b) Impressed current method

a) **Sacrificial anode method: -** A more reactive metal is kept in contact with the metal structure to be protected by this method. The reactive metal becomes anodic part and the structure becomes cathodic part of the corrosion cell. The anode is sacrificed to protect the structure. Hence this method is called sacrificial anode method.

Usually Zn and Al are used as sacrificial anodes to protect iron and steel in sea water environment. Mg is used in soil. pure water and estuary water environment. These metals are more reactive metals than iron and hence they become anodic part in contact with iron. The sacrificial anode must be used in proper quantities. The method is effective only when proper quantities of sacrificial anodes are used and when they are kept in proper places .Number and spacing of anodes depends upon the system to be protected.

Advantages: *No external power supply is necessary.
*Can be used in remote and difficult to reach areas.
*Low installation cost.
*Minimum maintenance cost.

b) **Impressed Current method** In this method the metallic structure is made cathode with the use of impressed current by connecting the negative terminal of the external source to the metallic structure to be protected. and positive to an inert anode. The anode may be made up of steel, graphite and platinum group metals. The anode may be consumed very slowly or may not be consumed at all. depending on the anode material. The anode is surrounded by back film consisting of coke breeze, gypsum to improve electrical contact between the anode and the environment if it is a poor ionic conductor. (Eg: soil)

Advantages:

* Applicable to large objects.
* Uncoated parts can be protected.

Limitations:

* Larger installation cost.
* Higher maintenance cost.

3) Surface Coating: A protective coating on the metals and alloys isolates them from electrolyte medium without which corrosion cells do not work. This prevents corrosion.
Metallic Coating: Coating of a metal on a substrate metal requiring protection against corrosion is metallic coating. There are two types of metallic coating:
i) Anodic metal Coating: Mg (E^o = -1.55V), Al (E^o =-1.28V) and Zn (E^o = -O.76V) and anodic with Fe (E^o = -0.44) Hence coating of these metals on iron and steel are known as anodic metal coatings. These coating are applied by different techniques like hot dipping, metal spraying , vapour deposition.

Galvanization: Giving a Zn metal coating on iron and mild steel is known as galvanization.

When the coating covers the entire surface of the substrate metal, the coating isolates it from the environment and protects it against corrosion. When the coating breaks or cracks zinc acts as anode and the substrate iron and mild steel acts as cathode. Thus zinc becomes sacrificial anode and provides protection to iron and mild steel sheets, pipes, wires are usually galvanized.

Galvanization is done by hot dipping processes. Melting point of Zn is 419^{o}C. Zn is melted and kept at 425-430^{o}C. Ammonium chloride flux is spread over it to prevent its oxidation by air. Iron and mild steel objects are degreased. pickled and cleaned. They are then dipped in molten Zn. Excess liquid Zn is squeezed out and the objects with Zn coating are cooled.
ii) Cathodic metal coating: Ni(E^o=-0.23V), Sn (E^o =- 0.14V), Cu (E^o= +0.34V) are

cathodic with Fe(E^o= -0.44) Hence coating of these metals on iron and steel are known as cathodic metal coatings. They are applied using the same technique used to apply anodic metal coating.

Tinning: - Giving a coating of tin on iron and mild steel is called tinning. Tinning protects the article until the coating covers the surface completely, by isolating it from the environment. When the coating cracks or breaks intense or pitting corrosion of the articles at the exposed region occurs, because tin is cathodic with iron and small anodic regions are in contact with large cathodic area.

Galvanized sheets cannot be used to prepare tins or cans for storing food materials, because zinc salts are toxic. Tin salts are nontoxic. Therefore tinned iron and mild steel sheets are used to prepare tins, cans and containers for storing food materials.

Tinning is done by hot dipping. Melting point of Sn is 232^oC. Tin is melted and kept at 250^oC. It is covered with $ZnCl_2$ and NH_4Cl flux to protect liquid tin from oxidation by air. Steel sheet is degreased , pickled and cleaned. It is dipped in molten tin and the passed through rollers kept in palm oil to squeeze out excess tin from it. Sheet is cooled, rolled and stored.

4**. Corrosion Inhibitors:** corrosion stops when anodic reaction or catholic reactions is stopped. This is achieved using corrosion inhibitors. An inhibitor is a substance added to the electrolyte medium to stop anode reaction, or cathodic reactions. Accordingly there are two types of inhibitors:

(a) Anodic Inhibitors

(b) Cathodic Inhibitors

a) **Anodic Inhibitors:** Substances used to stop anodic reaction are called anodic inhibitors. They form insoluble compounds with the metal ions formed at the anodic part due to its initial corrosion. These insoluble compounds form a protective film on the anode surface. This film isolates the anode from the electrolyte medium and stops its corrosion. The anions such as chromate,tungstate,molybdate,phosphate etc. are used to arrest anodic process.

Anodic inhibitors are found to be effective provided they are added above their critical concentrations. If the added inhibitor is insufficient, it cannot plug all the anodic sites. This leads to severe pitting corrosion.

b)**Cathodic Inhibitors:** Substances used to stop cathodic reaction are called cathodic inhibitors. They form a protective film on cathodic surface and isolate it from the electrolyte medium.Cathodic reaction stops as a result of this.

There are two major reactions taking place on cathodic surface depending on the nature of corrosive environment. They are:

1) Hydrogen evolution type

2) Oxygen absorption type

1) Hydrogen evolution:- $2H^+ + 2e$ -------->H_2 (acid medium)

The evolution of hydrogen gas over the cathode can be prevented either by retarding the diffusion of H^+ ions to the cathode or by increasing the hydrogen over voltage. The diffusion of H^+ to the cathode is retarded by the addition of certain organic compounds which contain N or S. Urea, thiourea, mercaptans and heterocyclic compounds are widely used as cathodic inhibitors. Such substances when added to corroding environment are adsorbed on the cathodic sites forming a protective film that suppresses cathodic reaction. Even the use of insufficient concentration of these substances does not have any adverse effect.

The evolution of H_2 at the cathode can also be prevented by increasing over voltage of hydrogen. This is achieved by the addition of oxides of Arsenic, Antimony or salts like sodium meta arsenite .They deposit as adherent metallic film on the cathode areas and thereby prevents the evolution of H_2, since hydrogen over voltage for those metals is quite high.

2) Oxygen absorption type:- $O_2 + 2H_2O + 4e^-$ ------------------> $4OH^-$(in neutral or slightly alkaline medium)

This cathodic reaction can be easily stifled either by removing the oxygen from the corrosive media or by decreasing the diffusion rate of oxygen to cathode. Reducing agents such as N_2H_4,Na_2SO_3 etc remove oxygen from the corroding environment by combining with it.

$N_2H_4 + O_2$ ------------------------------> $N_2 + 2H_2O$.

Decreasing the diffusion rate of oxygen is achieved by adding salts such as $ZnSO_4$,$MgSO_4$,$NiSO_4$ recto the aqueous environment. They undergo hydrolysis and form a deposit of their insoluble hydroxide on the cathodic sites.

$Zn^{2}+ + 2OH^-$ --------------> $Zn(OH)_2$.

The protective film being impermeable to oxygen prevents its further diffusion to cathodic sites. The action of an inhibitor depends on the nature of the metal to be protected as well as corrosive environment. It is therefore necessary to choose an appropriate inhibitor for a particular system.

5)**Anodic protection:-** This method is based upon the ability of a metal or an alloy to undergo passivation in the surrounding environment. Certain metals and alloys lose chemical reactivity under certain environmental conditions .This is a phenomena of complex nature and it occurs under specific conditions. This phenomenon is called passivity of metals.Eg:Al,Ti.Cr.Ni.Mo and alloys containing major amount of these metals. When a passivating metal is immersed in an electrolyte with increasing oxidising power behaves as shown in the following graph.

The curve is obtained by a applying a known potential to a metal specimen and measuring the current changes. As the potential is increased, initially current also increases (AB) indicating the dissolution of the metal. This trend continues until the current reaches a critical value and passivation due to the development of an oxide layer sets in. This potential is called passivating potential (E_p).

Above Ep the current flow decreases and reaches a minimum value called the passivating current, I passive. The decrease in current is due to the formation of a passive film on the metal. If the potential is further increased the metal remains unattacked upto a particular potential is reached (CD).In this range corrosion rate of the metal is very small. The potential range in which the anodic protection can be achieved is called passive region. The optimum potential for anodic protection is midway in the passive region since it permits slight variations in the controlled potential without affecting corrosion rate. Beyond the point D any further increase in potential tends to increase the current due to the dissolution of metal. It is called transpassive region.

The anodic protection to a structure is applied by using a device called potentiostat. It is an electronic device that maintains a constant potential with respect to a reference. The anodic protection of steel tank containing sulphuric acid is shown in the following figure.

Potentiostat has three terminals. One connected to the storage tank, other to an auxiliary cathode and third to a reference electrode (Calomel).In operation the potentiostat maintains a constant potential between the tank and the reference electrode, corresponding to the passive range.

Advantages:- *Its applicability in extremely corrosive environment
*Low current demand.

Limitations:- *Anodic protection is restricted to the metals that show active-passive behaviour.
*Its initial installation cost is high.
*Cannot reduce the corrosion rate to zero unlike cathodic protection.
*This needs continuous supply of electric current.