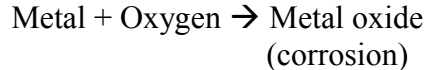


Unit II:
Corrosion & Its Control:

Introduction:

Most of the metals (except noble metals such as Au, Pt and Ag) occur in nature in combined form of their oxides, hydroxides, sulphides, chlorides, carbonates and silicates. This is because of need of stability. But the surfaces of almost all metals begin to decay more or less rapidly, when exposed to gaseous atmosphere, water or any other reactive liquid medium. This phenomenon is called as 'corrosion'.



Corrosion stands for material or metal deterioration or surface damage in an aggressive environment.

Consequences:

- The valuable metallic properties like conductivity, malleability, ductility are lost due to corrosion.
- Corrosion is responsible for the increase of cost production and that of maintenance of machinery. It is estimated that 25% of worlds iron is wasted due to the corrosion.
- The life span of machinery or metal is reduced.
- The metals or machinery appear poor or dull due to corrosion.
- The production rate of a plant will be decreased due to time consumed during replacement of machinery or due to shutdown of plant for repairs.
- Contamination of products is seen in the plants such as food processing plants or pharmaceuticals due to corrosion.
- There will be decrease of safety due to fire hazard or explosion or release of toxic products. This is due to the wear and tear of metals due to corrosion.

Types of corrosion:

1. Dry or Chemical corrosion.
2. Wet or Electrochemical corrosion.

Dry or Chemical Corrosion:

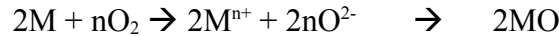
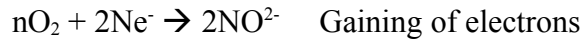
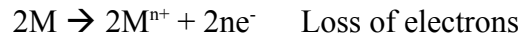
The corrosion that happens due to the direct chemical action of environment or gases or anhydrous inorganic liquids on the surface of metal in the absence of moisture is said to be dry or chemical corrosion. The chemical corrosion is of three types:

- Corrosion by Oxidation.
- Corrosion by gases.
- Liquid – metal Corrosion.

Corrosion by oxidation:

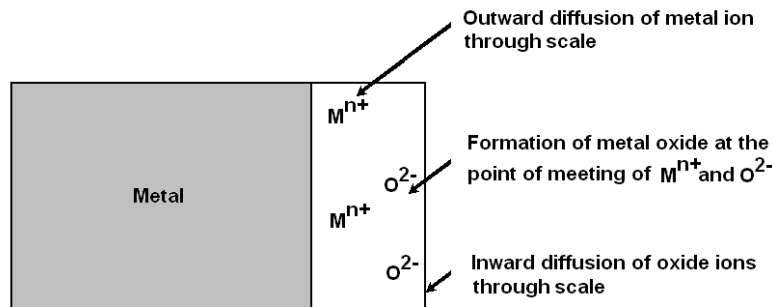
This type of corrosion happens when the oxygen come in contact with the metal surface directly at low or high temperatures. Metals are less prone to oxidation at low temperatures but alkali and alkaline earth metals oxidize rapidly at low temperatures. Where as all the metals oxidize at high temperatures expect the noble metals like Ag, Au and Pt.

Mechanism:



[Metal ion + Oxide ion] \rightarrow Metal oxide

At the surface of the metal, oxidation takes place and resulting metal oxide scale form a barrier which reduce further oxidation. But the oxidation continues, because either the metal ions diffuse outward through the scale to the surface or the oxygen diffuses inwards to the underlying metal. Among both the cases, the metal ion diffusion is more rapid than the oxygen diffusion because the metal ions are appreciably smaller than the oxygen ion.



The oxide film formed at the surface plays an important role in the oxidation. The oxide film formed at the surface decides further action (oxidation) of the metal. The oxide film formed influences further corrosion by the following conditions.

- **Stable:** The corrosion forms stable oxide film which is impervious or tightly adhering as seen in Cu or Al. This impervious coating will prevent further corrosion.
- **Unstable:** Sometimes the oxide film decomposes back to metal and oxygen. In such conditions the corrosion is not possible. This is seen mostly in Ag, Al, and Pt.
- **Volatile:** In some metal surfaces, the oxide film gets volatized as soon as it is formed. This condition exposes the metal surface again and increases corrosion rapidly. Mostly seen in molybdenum.
- **Porous:** At certain times the oxygen passes through pores or cracks of the layer to the underlying metal surface and continues corrosion till the entire metal is converted to metal oxide.

Pilling-Bedworth Rule:

This rule states the extent of protection given by the corrosion layer. 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. It is the ratio of the volume of metal oxide to volume of metal.

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

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which the oxygen can diffuse and increases the corrosion further.

- If the volume of the metal oxide layer is at least as great as the volume of the metal, no corrosion occurs as the oxidation of metal reaches to zero. For example, the specific volume

ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten (W).

- If the volume of metal oxide is less than the volume of the metal, the oxide film will develop cracks and pores. The atmospheric oxygen reaches the metal and increases the corrosion. In this case corrosion is continuous and rapidly increases. For example, Li, Na and K.

Corrosion by other gases:

The gases like SO_2 , CO_2 , Cl_2 , H_2S and F_2 etc., also cause chemical corrosion. This type of corrosion depends mainly on the chemical affinity between the metal and gas involved. The intensity of attack depends on the formation of protective or non-protective films.

1. If the film is protective or non-porous the extent of corrosion decrease. For example when Cl reacts with Ag forms AgCl film which prevents further reaction of Cl with Ag.
2. If the film is non-protective or porous, the metal surface is gradually destroyed, e.g, Formation of volatile SnCl_4 by the attack of chlorine gas on tin.

Liquid-metal Corrosion:

This type of corrosion occurs due to the chemical action of the flowing liquid metal at high temperature on solid metal or alloy. This type of corrosion occurs in food processing plants and nuclear plants. This corrosion is due to the dissolution of solid metal or internal penetration of liquid metal into solid metal.

Electrochemical or Wet corrosion:

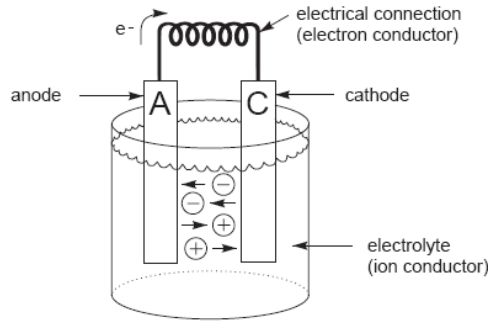
Aqueous corrosion is electrochemical. This is the most common corrosion. This corrosion takes place under wet conditions through the formation of short circuited electrochemical cells. This type of corrosion mostly takes place

- Where a conducting liquid is in contact with metal.
- Two dissimilar metals.
- Alloys are either dipped or immersed partially in solution.
- Cathodic and anodic areas separated by the conducting medium.
- The oxidation of the metal liberating electrons takes place at anodic areas.
- The diffusion of the metallic (M^+) and non metallic (OH^- or O^{2-}) ions towards each other through conducting medium results the formation of corrosion product in between the anodic and cathodic areas.

Mechanism:

Every electrochemical corrosion cell (where the corrosion is normally seen) must have four components.

1. The anode, which is the metal that is corroding.
2. The cathode, which is a metal or other electronic conductor whose surface provides sites for the environment to react.



The components of an electrochemical corrosion cell.

3. The electrolyte (the aqueous environment), in contact with both the anode and the cathode to provide a path for ionic conduction.
4. The electrical connection between the anode and the cathode to allow electrons to flow between them.

Electrochemical corrosion involves flow of electrons between anode and cathode. Corrosion reactions can be separated into anode and cathode half-cell reactions to better understand the process.

Anode Reactions:

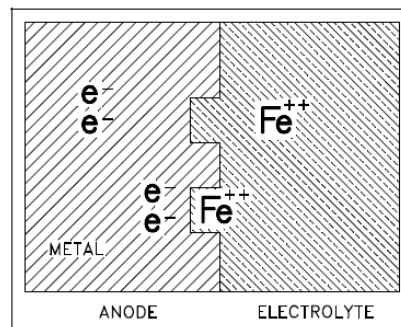
The anode reaction is quite simple—the anode metal M corrodes and goes into solution in the electrolyte as metal ions.



Where n is the number of electrons (e^-) released by the metal.

This is also called as “oxidation,” which means a loss of electrons by the metal atoms. The electrons produced do not flow into the solution but remain behind on the corroding metal, where they migrate through the electronic conductor to the cathode, as indicated in the above figure.

For example, if steel is corroding, the anode reaction is



or if aluminum is corroding the reaction is

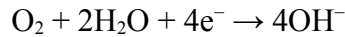


Cathode Reactions:

The cathode reaction consumes the electrons produced at the anode. If it did not, the anode would become so loaded with electrons that all reaction would cease immediately. At the cathode, some reducible species in the electrolyte adsorbs and picks up electrons, although the cathode itself does not react. This is also called as “reduction” because the valence of the reactant is reduced.

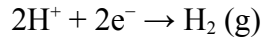
Since it is the corrosive environment that reacts on the cathode, and many different corrosives can attack metals, several cathode reactions are possible.

1. The most common reaction is the one seen in nature and in neutral or basic solutions containing dissolved oxygen:



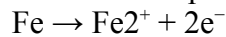
Example: oxygen in the air dissolves in a surface film of water on a metal surface, picks up electrons and forms hydroxide ions which then migrate toward the anode.

2. The next most important reaction is the one in acids.

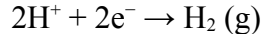


Formation of Rust with evolution of H₂ in Wet corrosion:

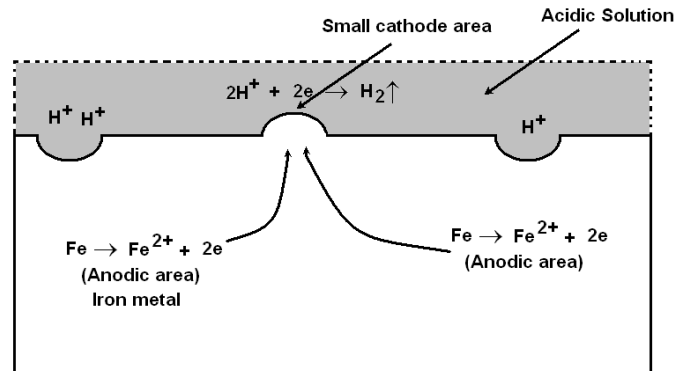
The formation of rust or evolution of hydrogen is seen mostly in acidic environment. At anode the dissolution (oxidation) of iron to ferrous ion takes place liberating electrons.



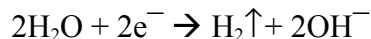
The e⁻ flow from anode to cathode through the metal. At cathode the H⁺ ions of the acidic solution absorb e⁻ forming H₂ bubbles (reduction).



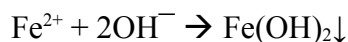
The hydrogen evolution type of corrosion is seen normally where the anodes are usually large and the cathodes are small as shown below.



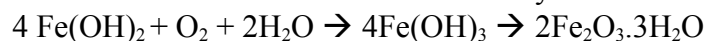
In neutral medium at the cathode formation of OH⁻ takes place along with the liberation of hydrogen.



The Fe²⁺ and OH⁻ diffuse towards each other forming the corrosion product rust in between cathodic and anodic areas.



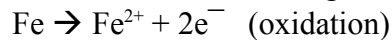
Ferrous Hydroxide



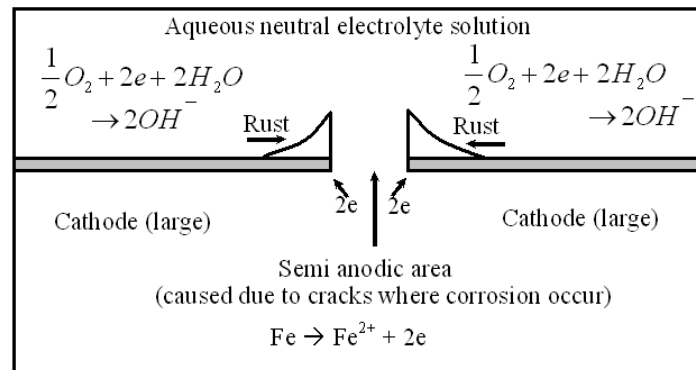
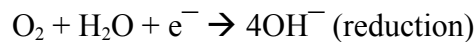
Formation of Rust with evolution of O₂ in wet reaction:

In the presence of neutral or aqueous solution of electrolytes like (NaCl solution) or slightly alkaline solutions, with the dissolved O₂, this type of corrosion occurs. This type of corrosion is normally seen when the iron oxide film develops cracks. The metal exposed at the cracks act as anode and remaining metal acts as cathode, which results in the anodic areas are small and the cathode areas large leading to corrosion.

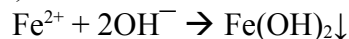
The rusting of iron at such circumstances can be explained as follows.
At anodic areas the metal oxidises as ferrous ions liberating electrons.



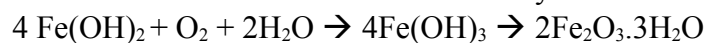
The electrons travel through the metal and reach the cathode areas where they are accepted by water generating OH⁻ ions.



The combination of Fe²⁺ and OH⁻ occurs at cathode resulting in rust, since the mobility of Fe²⁺ is greater than OH⁻ (Fe²⁺ being smaller).



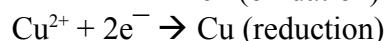
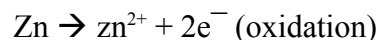
Ferrous Hydroxide

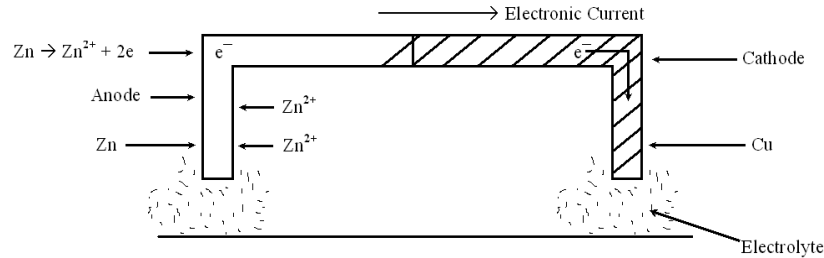


GALVANIC CORROSION:

Galvanic corrosion is either a chemical or an electrochemical corrosion. When two dissimilar metals are connected and jointly exposed to the corrosive atmosphere, the metal possessing higher oxidation potential or higher in the electrochemical series becomes anodic and undergoes corrosion.

For example, when zinc and copper are connected & exposed to corrosive environment, zinc being higher oxidative agent, acts as anode and get oxidized where as copper acts as cathode and get reduced.





From the above reactions & figure it is evident that the corrosion occurs to the metal which is anodic while the cathodic metal is protective.

Note:
 Electrochemical series: when the metals are arranged in the order of increasing reduction potentials or decreasing oxidation potentials which are determined with respect to one molar solution of their ions and measured on the hydrogen scale, a list is resulted called electrochemical series. The higher a metal in the series, the greater will be oxidation tendency and acts as noble anodes.
 Series: Li, K, Ca, Na, Mg, **Zn**, Fe, Cd, Pb, Pt/H⁺, **Cu**, Ag, Cl, Au

Galvanic Series:

This is the list of metals which gives the information to find the more corrosive metal among the metals used for making a structure.

Though electrochemical series gives the information regarding chemical reactivity of metals, it does not give the sufficient information in predicting the corrosion behaviour under a particular set of environmental conditions. Several side reactions taking place during corrosion will influence the corrosion. Hence, oxidation potentials of various metals and alloys commonly used are measured by using standard calomel electrode as the reference electrode and immersing the metals and alloys in sea water. When the oxidation potentials measured are arranged in the decreasing order of activity, a list will be generated called galvanic series. This series gives more practical information about the corrosive tendency of metals and alloys.

When more than two metals are used in a structure, it is easy to find the more corrosive metal with galvanic series. For example in an equipment using zinc in contact with iron parts, zinc will be corroded because zinc will be in the high order and is more anodic to iron. When iron is in contact with copper, iron will undergo corrosion because iron is anodic to copper.

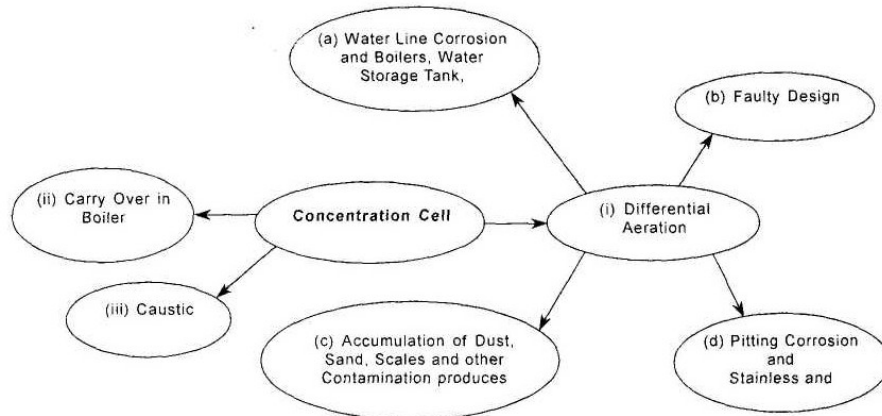
Galvanic series

Mg, Mn, Zn, Al, Low C, Cast Fe, Stainless Steel (active), Lead tin alloys, Pb, Tin, Brass, Cu,
 <----- Anodic

Bronze, Cu – Ni, inconel, Ag, Stainless Steel (passive), Monel, Graphite, Titanium, Gold, Pt
 -----> Cathodic

Concentration Cell Corrosion:

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



The concentration cell corrosion may be due to:

1. difference in the concentration of the metal ions or
2. difference in the exposure to air/oxygen (differential aeration corrosion)
3. difference in the temperature or
4. inadequate agitation or
5. different diffusions of metal.

When a metal is exposed to different air concentrations or concentrations anodic and well oxygenated part of the metal becomes cathodic. A difference of potential is created, which causes the flow of electrons (current) between the two differently aerated parts of the same metal.

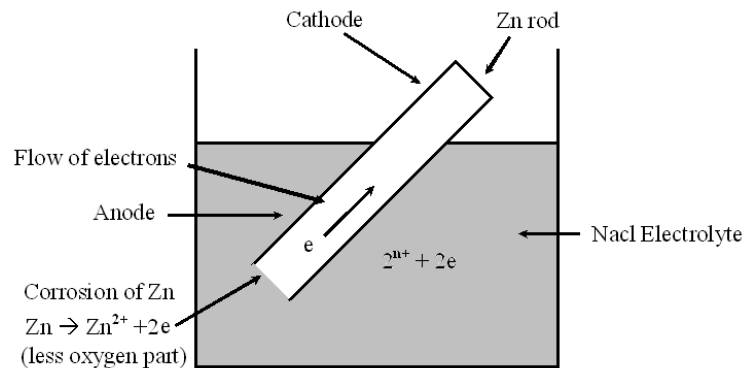
The general ways of production of oxygen deficient areas on metal surface can be as followed.

Differential aeration corrosion:

The different ways of creating differential aeration on the metal surface is listed as followed.

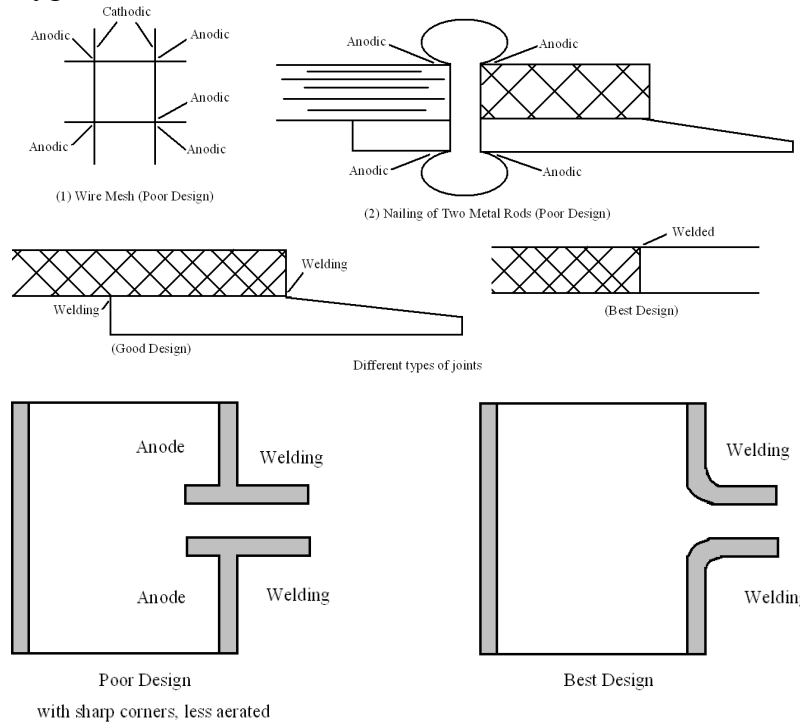
- Partial immersion of metal in a solution:

If the electrode is partially immersed in a diluted neutral electrolyte solution, the part above and adjacent to the water line are well aerated and hence becomes cathodic. Whereas parts immersed show a poor oxygenated and become anodic. So a difference in potential is created which causes flow of current between the two differential aerated areas of the same metal. By this the metal will dissolve at the anode and oxygen will take up electrons at the cathodic area to form hydroxyl ions.

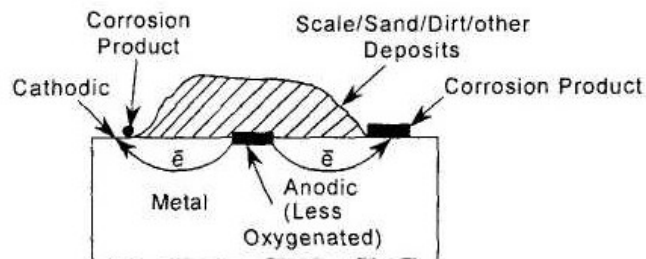


- Faulty design of the equipment:

An anodic area can be created due to difference in the aeration of metal parts due to faulty design. In such a situation the metal part less exposed to oxygen will become anode and that exposed more to oxygen becomes cathode and corrosion is seen as shown below.

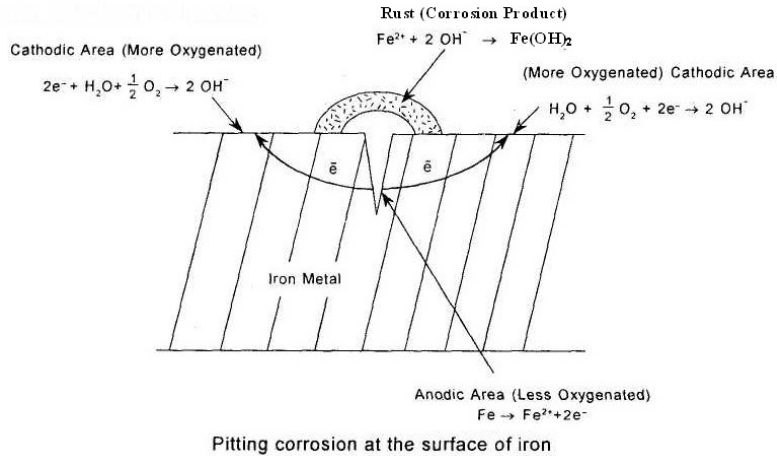


- Accumulation of dirt, sand, scale and other contaminations:
When the dirt, sand, scale and other contaminations are deposited on the metal surface, the metal under the deposit is exposed to less oxygen supply and becomes anodic and the remaining part becomes cathodic resulting to corrosion as shown below.



Pitting corrosion:

A cavity, pinholes, pits and cracks of the protective film developed on the metal surface creates the formation of small anodic areas in the less oxygenated parts and large cathodic areas in well oxygenated parts. The flow of electrons from anodic part to the cathodic part takes place and the ions move through medium (atmospheric moisture). The corrosion product is formed between cathodic and anodic areas.



Cracking of protective film may be due to

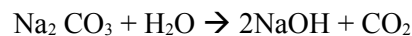
1. Surface roughness or non uniform stresses.
2. Scratches or cut edges.
3. Local strain of metal.
4. Alternating stresses
5. Sliding under load.
6. Impingement attack (caused by the turbulent flow of a solution over metal).
7. Chemical attack.

Carry over in boiler causing corrosion to turbine plates:

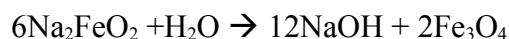
The boiler water concentrated with dissolved salts is carried along the steam or in the form of droplets of water and deposits on the metal (Ex: turbine plates). The metal under the drop becomes anodic due to high concentration of the dissolved salts and starts corroding while the remaining large areas of the turbine plates become cathodic. The flow of electrons takes place through the metal and the ions pass through the medium. Thus the electrochemical corrosion due to concentration cell occurs to the metal.

Corrosion due to caustic embrittlement:

Boiler feed water contains certain amount of sodium carbonate which decomposes to sodium hydroxide under the high pressure of the boilers, which deposits in the hair cracks, pits etc. of the boiler plate creating a concentration cell. The metal deposited with NaOH becomes anodic while the metal surround the drop becomes cathodic.



The concentrated alkali in the anodic area dissolves the metal as sodium ferrite (Na_2FeO_2), which decomposes a short distance away from the point of formation as magnetite and sodium hydroxide thereby enhancing corrosion.



The concentration cell formed can be represented as



FACTORS INFLUENCING CORROSION

The rate of extent of corrosion depends on the following factors

1. Nature of metal
2. Nature of corroding atmosphere

Nature of the metal:

1. **Position in the galvanic series:** When two metals or alloys are in electrical contact, in presence of an electrolyte, the metal with higher oxidation potential suffers corrosion. The metal higher in the electrochemical series becomes anodic. The extent of corrosion is determined by the difference in the position of the metals. The greater is difference, the faster and higher is the corrosion.
2. **Over voltage:** When metal say zinc is placed in 1N H_2SO_4 , it undergoes corrosion forming a film and evolving hydrogen gas, the initial rate of corrosion is slow because of the high over voltage i.e. 0.70 volts of the zinc metal which reduces the effective electrode potential to a small value. If a few drops of $CuSO_4$ are added, some copper gets deposited on the zinc metal, forming minute cathodes where hydrogen over voltage reduces to 0.33 volts. The reduction in over voltage of corroding metal/ alloy accelerates the corrosion rate.
3. **Relative areas of the anodic and cathodic parts:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. i.e, the corrosion is more rapid, severe and highly localised if the anodic area is small. For example, a small pipe made of steel fitted in a large copper tank.
 1. The reasons rapid corrosion due to smaller anodic areas is the current density at a smaller anodic area is much greater and
 2. The larger cathodic area demands more electrons, which should be met by smaller anodic areas only by undergoing corrosion rapidly.
4. **Purity of metal:** Heterogeneity is produced if impurities are present in a metal, which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded. As the extent of exposure and impurities increase, the extent of corrosion increases with the increasing exposure and impurities. For example zinc metal containing impurity such as Pb or Fe undergoes corrosion due to the formation of local electrochemical cells.
5. **Nature of surface film:** In aerated atmosphere, practically all metals produce a thin surface film of metal oxide. The ratio of the volumes of the metal oxide formed to the metal is called "specific volume ratio". If the specific volume ratio is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface. For example, the specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. The rate of corrosion for tungsten (W) is least even at elevated temperatures.
6. **Physical state of metal:** The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion. The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility. The areas under stress become anodic and corrosion takes place in these areas.
7. **Passive character of metal:** Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series. This is because the metal forms very thin, highly protective corrosion film, by reacting with atmospheric oxygen. If the film is broken, it compensates the film by re exposure to oxidising conditions. Thus

they produce "self healing film". This property is called passive character of metal. For example the corrosion resistance of "stainless steel" is due to passivating character of chromium present in it.

8. **Volatility of corrosion products:** If the corrosion produced volatilizes as soon as it is formed, the metal surface is exposed for further attack. This creates rapid and excessive corrosion. For example the corrosion product of molybdenum as molybdenum oxide (MoO_3) is volatile.
9. **Solubility of corrosion product:** If the oxide film formed as corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate. The corrosion product acts as a physical barrier between the metal and environment.
For example PbSO_4 film formed by Pb on sulphuric acid medium.

Nature of corroding environment:

1. **Temperature:** The rate of corrosion reaction and diffusion rate increases with increase in temperature, causing the increase in rate of corrosion.
2. **Humidity of air:** The humidity of air is a deciding factor for rate of corrosion. The relative humidity above which, the rate of corrosion increases sharply is called "critical humidity". The value of critical humidity depends on the physical characteristics of the metal and the nature of corroding atmosphere. The reasons for increase of corrosion with humidity are
 1. The moisture or vapours present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical cell.
 2. The oxide film formed has the tendency to absorb moisture, which creates other electrochemical cell corrosion.

The rain water not only supplies necessary moisture for electrochemical attack but also wash away a good part of oxide film the metal surface, leading to enhanced atmospheric attack, unless the oxide film is exceptionally adherent.

3. **Presence of impurities in atmosphere:** Atmosphere is contaminated in the vicinity of industrial areas with
 1. Gases like CO_2 , SO_2 , H_2S etc., and fumes of H_2SO_4 , HCl etc.
 2. Suspended particles of chemically active/inactive by nature like NaCl , $(\text{NH}_4)_2\text{SO}_4$ and charcoal.

The gases and acidity of the atmosphere increases the electrical conductivity, thereby increases corrosion. In marine atmosphere the presence of sodium and other chlorides lead to increased conductivity thereby increased corrosion.

The suspended particles absorb moisture and act as strong electrolytes increasing the rate of corrosion. These suspended impurities also absorb both gases and moisture and slowly enhance the rate of corrosion.

4. **Nature of ions present in the medium:** The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which "inhibit"

further corrosion. On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal, thereby exposing the metal surface for fresh corrosion attack. Presence of traces of copper in marine waters enhances the corrosion of the iron pipes or steel body of the ships.

5. **Conductance of the corroding medium:** For the corrosion of underground or submerged structures the conductance of the corroding medium plays an important role. The conductance of dry sandy soils is lower than the conductance of clayey and mineralised soils. Hence the rate of corrosion is more in clayey and mineralized soils, causing severe damage to metallic structures buried.
6. **Amount of oxygen in atmosphere:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.
 anodic reaction for iron : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$
 cathodic reaction : $2 \text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$
 corrosion product : $2 \text{Fe}^{2+} + 4 \text{OH}^{-} \rightarrow \text{Fe}(\text{OH})_2$
 $\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$
 rust
7. **Velocity of ions which flow in the medium:** As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.
8. **pH value of the medium:** pH value of the medium has greater effect on corrosion. When pH value is lowered, the corrosion is increased.

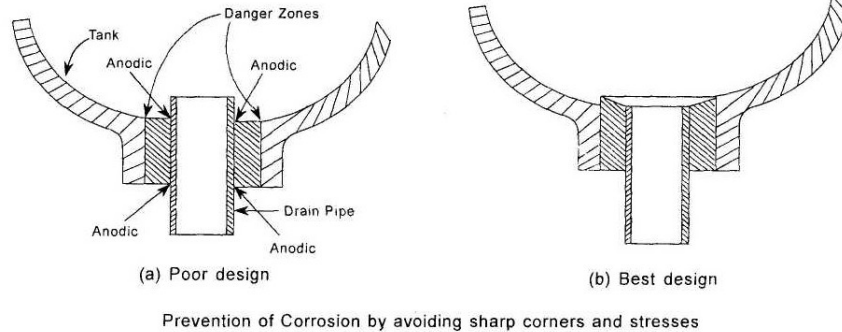
CORROSION CONTROL METHODS

As we have discussed the disadvantages and different mechanisms of corrosion so far, it is essential to know the different corrosion control methods. The following are the important control methods of corrosion.

1. Proper designing
2. Using pure metal
3. Using metal alloys
4. Modifying the environment
5. Use of inhibitors
6. Cathodic protection
7. Application of protection coatings.

Proper designing: The design of the metal under corroding atmosphere must be such that it is uniform and does not produce intense and localised corrosion, important principles of proper designing are:

1. Avoid the contact of two dissimilar metals in the presence of corroding solution.



Use of Pure Metal:

The impurities in metal producing which decreases corrosion resistance by producing electrochemical cells. Thus corrosion resistance of a metal is increased by increasing the purity of metal. The pure metals provide adherent and impermeable protective metal oxide film on surface of metals when exposed to environment. In presence of alkaline environment both the metal oxide film and metal are attacked. Due to the following reasons it is not possible to produce high chemically pure metal.

1. Cost of production is high.
2. Very pure metal possesses inadequate mechanical properties like softness and low strength.
3. Only electrochemical corrosion can be avoided in pure metals not direct chemical attack.

Corrosion in alloys can be avoided by alloying the metals completely in a homogenous state. Chromium is best suitable metal for iron or steel, because it forms a uniform, resistant film which is self-healing.

Thus steel containing 13 to 25% chromium are called “ferrite stainless steels” are used in turbine brackets, heat resisting parts, cutlery, surgical instruments, springs etc.

Modifying the environment:

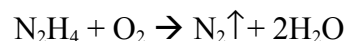
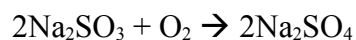
The corrosive nature of the environment can be reduced by

1. The removal of harmful constituents.
2. The addition of specific substances, which neutralise the effect of corrosive constituents of the environment.

Some of the adopted methods of corrosion control are:

Deaeration: In oxygen concentration type of corrosion removal of oxygen from aqueous environment reduces corrosion. The dissolved oxygen is removed by adjustments of temperature along with mechanical agitation. This method is adopted for steel pipelines carrying steam condensates from boilers.

Deactivation: It is the process of adding certain chemicals like sodium sulphate, hydrazine etc. to remove oxygen from aqueous solutions.



Dehumidification:

The process of reduction of moisture content of air to such an extent that the amount of water condensed on metal is too small to cause corrosion. For example by keeping alumina and silica gel in closed atmosphere like air conditioning rooms absorb moisture preferably on their surfaces and reduces the corrosion.

Alkaline neutralisation:

The corrosion process in presence of acidic atmosphere can be prevented by neutralising the acidic character of the corrosive environment. The presence of gases like H₂S, HCl, CO₂, SO₂ etc, enhance the acidic nature of the environment, thereby enhancing the rate of corrosion. Some examples of alkaline neutralisers are NH₃, NaOH, lime, naphthlenic soaps etc., which are injected either in vapour or liquid form to the corroding system or its parts.

This method is used in controlling the corrosion of refinery equipments.

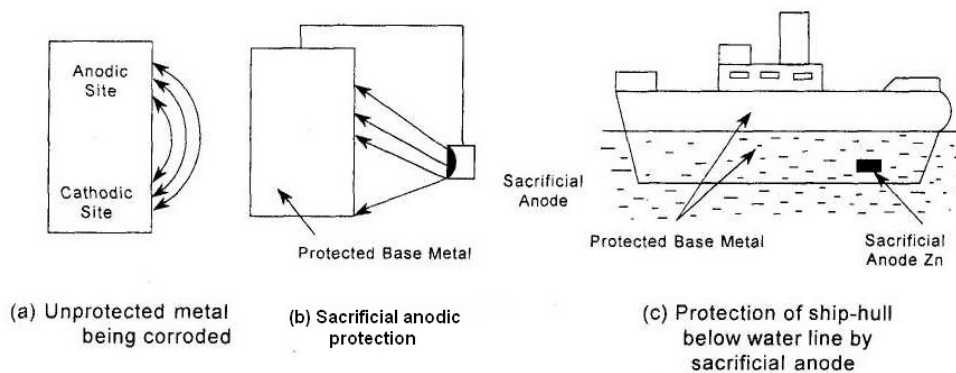
CATHODIC PROTECTION

The method of protection given to a metal by forcibly making it to behave like a cathode is called cathodic protection. There are two types of cathodic protection.

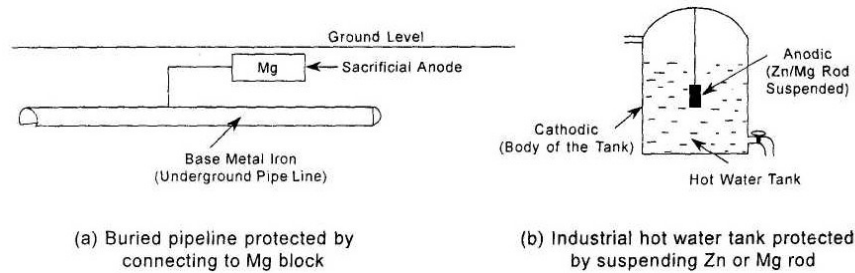
1. Sacrificial anodic protection
2. Impressed current cathodic protection

Sacrificial anodic protection: In this method of protection, the metallic structure to be protected called "base metal" is connected to more anodic metal through a wire. The anodic metal undergoes corrosion slowly, while the base metal is protected. The corroded sacrificial anode block is replaced by a fresh one. The commonly used anodic metals are magnesium, zinc and aluminium and their alloys. The important applications of sacrificial anodic protection are given below (a) and (b).

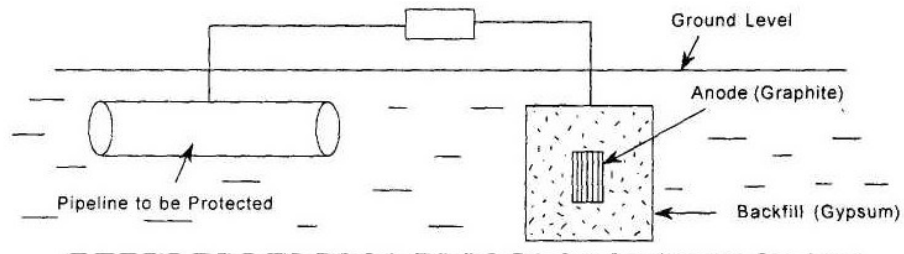
1. To protect marine structures and ship-hulls, which are made of steel are connected to a sacrificial anode, which undergoes corrosion leaving the base metal protected, (c).



2. Protection of buried pipelines, underground cables, water tanks, piers etc. are also protected by sacrificial anode method. By referring to electrochemical series, a small piece of the metal, anodic base metal is attached to the metal. The anodic metal undergoes corrosion and it is replaced from time to time [(a) and (b)].



(b) Impressed current cathodic protection: In this method an impressed current little more than corrosion current is applied in the opposite direction to nullify the corrosion current producing a reverse cell reaction. Thus the anodic corroding metal becomes cathodic and protected from corrosion. The impressed current is taken from a battery or rectified on A.C. line. The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum. Usually a sufficient D.C. current is passed on to the insoluble anode kept in a 'back fill' composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.



This type of impressed current cathodic protection is given to (1) open water box coolers (2) water tanks (3) buried water or oil pipeline (4) condensers (5) transmission line towers (6) marine pipes (7) this type of protection is more useful for large structures for long term operations.

Disadvantages of cathodic protection:

1. The cathodic protection may be efficient in protecting a pipeline, yet may increase the corrosion of the adjacent pipelines or metal structure because of stray currents.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e., the use of much higher potential than the open circuit voltage for the metal/metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H_2 or formation and accumulation of OH^- will take place.

In spite of these disadvantages, cathodic protection has been widely used with success, when suitable precautions are taken.

CORROSION INHIBITORS

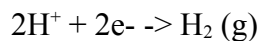
A substance which when added in small quantities to the aqueous corrosive environment, effectively decrease the corrosion of a metal is called corrosion inhibitor.

Inhibitors are two types

- (a) Anodic inhibitors and
- (b) Cathodic inhibitors.

1. **Anodic inhibitors:** These inhibitors avoid the corrosion reaction occurring at the anode by forming sparingly soluble compound with the newly produced metal ion and absorbed on the surface forming a protective film on the surface of the metal, reducing the corrosion. If certain areas are left unprotected severe corrosion occurs to the metal. Some common anodic corrosion inhibitors are chromates, phosphates, tungstates and other ions of transition metals with high oxygen content.

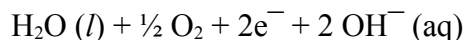
2. **Cathodic inhibitors:** In acidic environment, the corrosion reaction takes place with evolution of hydrogen.



Corrosion may be reduced by

- (1) Slowing down the diffusion of hydrated H^+ ions to the cathode or
- (2) By increasing the over voltage of hydrogen evolution.

The diffusion of H^+ is decreased by the addition of organic inhibitors like amines, mercaptans, heterocyclic nitrogen compounds, substituted ureas and thioureas which are capable of being adsorbed on the metal surface. Antimony and arsenic oxides are used as inhibitors because they produce adherent film of metallic arsenic or antimony at the cathodic area, considerably increasing the hydrogen over voltage. The cathodic reaction in neutral medium is



Hence the corrosion can be controlled by

- 1. Eliminating oxygen from the corrosion medium by the addition of $\text{Na}_2 \text{SO}_3$.
- 2. Retarding the diffusion to the cathodic area by the inhibitors like Mg, Zn or Ni salts to the environments, which react with hydroxy ions forming the corresponding insoluble hydroxides which form impermeable self barrier between the metal and the corrosion environment.

SURFACE COATINGS - METHODS OF APPLICATION ON METALS

The oldest and common method of protection of a metal from its surroundings is applying a protective coating on the surface of the metal. The coated surface isolates the metal from its corroding environment. The coating should have the following properties:

- 1. The coating applied must be chemically inert to the environment under particular conditions of temperature and pressure.

2. Coatings must prevent the penetration of the environment to the material, which they protect.

The different types of protection coatings and their methods of application are discussed below, along with the preparation of metal surface for the application of protective coating.

Methods of cleansing the metal surface before applying the surface coatings:

Before applying any protective coating, the metal surface must be thoroughly cleaned to remove dirt, old protective coatings like paints, greases, corrosion products etc.

The following are some of the methods adopted for metal cleansing.

1. Solvent cleaning: This method is used to remove oils, greases, buffing compounds, and fatty substances. This method involves the cleaning of metal surface by the applying organic solvents like naphtha, chlorinated hydrocarbons like carbon tetrachloride, toluene, xylene or acetone. This treatment is specially adopted for electroplating where the metal surface requires wetting.

2. Alkali cleaning: The metal surface is cleaned with alkali cleansing agents like trisodium phosphate, along with soaps and wetting agents like caustic soda. This method removes old paint coating from metal surfaces. Alkali treatment is followed by thorough rinsing with water and then immersion in 0.1% chromic acid, to remove the last traces of alkalis. A more effective cleaning with alkali is made by the application electric current, by making the metal to be coated as cathode. This removes effectively the grease or oily substances attached to the metal surface.

3. Mechanical cleaning: This method removes loose rust, scales, dirt etc. from the metal surface. Cleaning of the metal surface is done by using bristle brushes and metal brushes to remove the loosely adhering impurities. Different methods adopted for cleaning are:

1. Sand paper is used to remove strongly adhering scales and rust.
2. Detergents like soap are adopted for cleaning the metal surface. This method is followed by steam or hot water treatment.
3. **Flame cleaning:** This method involves heating the metal surface with a hot flame to remove and loosely adhering scales, followed by wire brushing.
4. **Sand blasting:** This method is used to remove the oxide scales, particularly when a slightly roughen surface is desired to be removed. For sand blasting the samples of sand of different grain size were blasted on the metal surface with a pressure of 25 to 100 atmospheres. This blast impact removes the scales on the metal surface also hardens the metal surface and the protective coating is more durable.

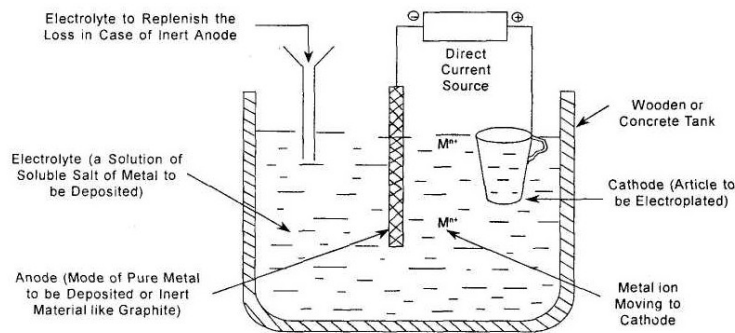
Usually this method is adopted for cleaning large surface areas like large steel structures etc.

The only disadvantage of this method is that the workers are affected by the disease 'Silicosis'.

Electroplating or electrode position: The process of depositing the coating metal on the surface of base metal/non metal by electrolysis is called electroplating.

The base metals are inferior or anodic to the coating metal (or alloy) and electrolyte is the solution containing the metal ions to be deposited on the base metal. The base metal is made cathode and the coating metal is made anode or an inert material of good electrical conductivity is also used as an anode. A direct current (D.C.) is passed through the electrolytic solution. If anode is made of graphite, the electrolytic salt is added continuously to maintain the proper coating metal ion concentration in the electrolyte bath.

The article to be electroplated is subjected to solvent cleaning by trichlorethylene to remove oil, greases etc. Then it is subjected to acid pickling with dil. HCl or dil. H_2SO_4 to remove any scales, oxides etc. The cleaned article is made cathode of the electrolytic cell and the anode can be made of the pure coating metal or graphite. The electrodes were dipped in the salt solution of the coating metal, which acts as an electrolyte. When direct current is passed, the coating metal ions migrate to the cathode and deposit on the base metal article in the form of a thin layer. For brighter and smooth deposits, conditions like low temperatures, medium current density, low metal ion concentration are used.



For example for electroplating of nickel on iron article, the following are maintained

- | | | |
|----|----------------------------|--|
| 1. | Electrolytic bath solution | Nickel sulphate, nickel chloride and boric acid. |
| 2. | pH maintained | 4 (by boric acid buffer) |
| 3. | Temperature maintained | 40 - 70° C |
| 4. | Current density | 20 - 30 mA/cm ² |
| 5. | Additives added | Saccharin or coumarin or acetylene derivatives |
| 6. | Anode | Nickel pellets (99% pure) taken in a titanium mesh basket. |
| 7. | Cathode | Base metal article. |

Applications: Electroplating is a most important and frequently used technique in industries to produce metallic coatings. Both metals and non metals can be electroplated. In metals the electroplating increase resistance to corrosion, chemical attack, hardness, wear resistance and surface properties. In non metals electroplating increases strength and decorates the surface of non metals like plastics, wood, glass etc.

Electroplating of Nickel:

Nickel plating gives hard, adherent and good wear resistance surface. General nickel plating is used as an undercoat for articles which are finally to be chromium plated.

Requirement for electroplating:

1. Electrolytic bath: It consists of nickel sulphate (250g/L), nickel chloride (450g/L) and boric acid (30g/L).
2. pH: Maintained at 4.0 by boric acid buffer.
3. Operating temperature: 40 – 70°C.
4. Current density: 20 – 30mA/cm².
5. Additive agent Saccharin/coumarin derivatives.
6. Cathode: Metal articles to be plated.
7. Anode: Nickel pallets/pieces taken in a titanium mesh basket.
8. Current efficiency: 95%.

Electroplating of Chromium:

Chromium plating is a porous and non-adherent in which it requires that the article is first given under coat of copper or Nickel. Chromium electroplating is carried out in acidic medium by insoluble anode.

1. Plating bath: Chromic acid(H₂CrO₄) and H₂SO₄ is 100:1 by volume.
2. Operating temp: 40 – 50°C.
3. Catalyst: SO₄²⁻ ion (Cr(IV) converts to Cr(III)) by complex anodic reaction is presence of SO₄²⁻
4. Current density: 100 – 200 mA/cm².
5. Anode: Lead and antimony alloy is used for getting insoluble anodes.
6. Cathode: Article to be plated and pretreated with organic solvents to remove oils and greases.
7. Current efficiency: 10 – 20%.

Electroless plating:

Electroless plating is also a widely used technique to protect the base metal from the corrosion. It is also called displacement plating or Immersion coating/plating. It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms a thin uniform deposit on the base metal article. The better example for electroless plating is nickel plating.

The base metal to be protected from corrosion, is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5 – 5.0 and maintain bath temperature of about 100°C. The hypophosphate reduces nickel ion to metal nickel and finally converts into nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface forming a strong adherent non-porous coating with high corrosion resistance.