

CORROSION AND METAL FINISHING

Corrosion is a destructive attack of a metal by its environment either directly or by electrochemical phenomenon. It can also be defined as **“The spontaneous destruction and consequent loss of a metal or alloy due to chemical or electrochemical attack by the environment”**

The most familiar examples are

1. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion. When iron metal is exposed to the corrosive environment, the metal forms a loosely adherent product of hydrated ferric oxide called rust.
2. When Cu is exposed to the corrosive environment it forms an adherent green coloured product of basic cupric carbonate.

Corrosion of metals or alloys occurs in two ways- either by direct chemical attack or electrochemical attack by the corrosive environment.

Direct chemical attack is reaction of metals directly with corrosive medium to form corresponding product in the absence of moisture. This type of corrosion is known as **dry corrosion**.

Most of the metals and alloys undergo corrosion by following electrochemical attack in the presence of moisture or a conducting medium. This type of corrosion is known as **wet corrosion**.

Electrochemical theory of corrosion

Electrochemical theory explains the wet corrosion, i.e. corrosion in presence of moisture. Electrochemical theory tells that corrosion of metals takes place due to the formation of anodic and cathodic regions i.e. small galvanic cells on the same metal surface or when two different metals are in contact with each other in the presence of a conducting medium. At anodic region oxidation takes place and metal dissolves and get converted it to ions, liberating electrons. At the cathode region, reduction takes place. We know that metals cannot be reduced further, metal atoms at the cathode region are unaffected by the cathodic reaction. Only the surrounding atmosphere undergoes reduction by accepting the electrons.

This specify that only anodic region or a metal/alloy acting as anode undergoes corrosion where as cathodic region or metal/alloy acting as cathode remains unaffected.

Corrosion reactions

We know that a metal or region which is more active will undergo corrosion i.e. it will undergo oxidation. Reactions at anode are simple in which metal is converted in to its corresponding ion.

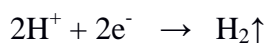


The reactions at cathode are more complicated, (reduction reaction) depends on the nature of the corrosive environment. Common reactions are of two types

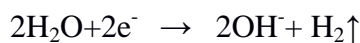
1. Hydrogen liberation type 2. Oxygen absorption type

1. Hydrogen liberation type of reactions takes place only in the absence of dissolved oxygen

a. If the medium is acidic, the reaction is

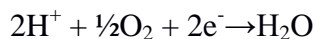


b. If the medium is alkaline / neutral, the reaction is

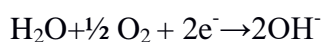


2. Oxygen absorption type of reactions takes place in the presence of dissolved oxygen

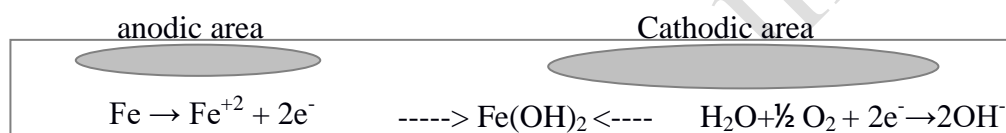
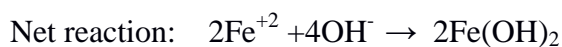
a. If the medium is acidic, the reaction is



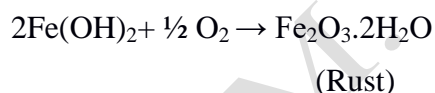
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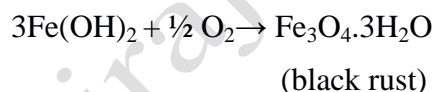
The products formed at anode and cathode diffuses towards each other through conducting medium and form a corrosion product between the anode and cathode.



In the presence of excess of oxygen $\text{Fe}(\text{OH})_2$ is oxidized to rust.



In the limited supply of oxygen $\text{Fe}(\text{OH})_2$ is oxidized to magnetic oxide which is commonly known as black rust.



Factors affecting the rate of corrosion

Ratio of anodic to cathodic areas

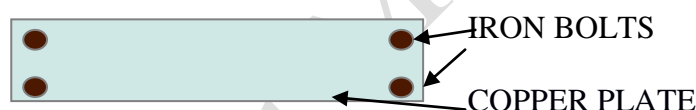
The rate of corrosion is directly proportional to the ratio of area of cathode to the area of anode. i.e.,

Rate of corrosion \propto area of cathode / area of anode

Higher the value of this ratio, greater is the rate of corrosion. When the metal undergoes corrosion liberated electrons from anode are consumed by cathode. When anode is small and cathode is large all the electrons liberated at anode, are rapidly consumed at the cathodic region. Therefore, the rate of anodic reaction is greater and increases the extent of corrosion. If cathode is smaller than anodic region, electrons liberated by anode are not readily consumed by cathodic region so it reduces the corrosion rate.

Example:

- i. Galvanized iron: Small crack produced on zinc coating will expose the iron material. This exposed iron material will act as cathode and the whole zinc coating will act as anode – Rate of corrosion is slow
- ii. Tinned Iron: Small crack produced on tin coating will expose the iron material. This exposed iron material will act as anode and the whole tin coating will act as cathode – Rate of corrosion is fast
- iii. Copper plate fixed with iron nail. In this case iron acting as anode undergoes rapid corrosion as its area is lesser than copper plate which is acting as cathode.



Polarization of anodic & cathodic regions,

The anodic and cathodic reactions take place simultaneously during corrosion, and causes polarization of the electrodes. The polarization of anode or cathode decreases the corrosion rate considerably. This is because the rate of oxidation of metal decreases i.e. dissolution of metal decreased due to the presence of more concentration of dissolved metal ions near the anodic site. This type of polarization is known as concentration polarization. Sometimes the product formed act as a protective film covering the anodic region, this is known as anodic passivity. Anodic passivity also decreases the rate of corrosion. Cathodic polarization retards the cathodic reactions by hindering the combination of cathode reactant with the electrons or by increasing the cathodic product in the vicinity of cathodic region. The slow rate of one of the anodic and cathodic reaction makes the corrosion reaction slower.

The presence of depolarizers like complexing agents (EDTA) reduces the polarization effect and thereby increases the rate of corrosion. Complexing agents reduce the polarization effect at anode by decreasing the concentration of metal ions in the vicinity of anodic region. Similarly oxidizing agents like oxygen, ferric ions, cupric ions, etc., acts as cathodic depolarizers by rapidly absorbing the electrons from cathodic region

Nature of the metal

The tendency of metal to undergo corrosion depends upon the nature of the metal. The extent of corrosion depends upon the position of the metal in the electrochemical and

galvanic series. The metals with lower electrode potential values are more reactive and more susceptible for corrosion than the metals with higher electrode potential values. The more reactive metals are more susceptible for corrosion, example K Na, Zn, Fe are more prone for corrosion and the noble metals like Gold and Platinum are less susceptible for corrosion. Metals showing passive property like Al, Cr, etc., will have slow corrosion rate.

Nature of the corrosion product

In corrosive atmosphere almost all metals undergo corrosion and form a thin surface film of metal oxide and the nature of the product layer largely decides the rate of corrosion. If product formed is uniform, non porous, continuous and stable layer it will act as a barrier between metal and corrosive atmosphere. This barrier will not allow the corrosive atmosphere to come in contact with fresh metal, which in turn prevents fresh metal from undergoing further corrosion. Best common example for this is aluminium, which undergoes corrosion in aerated atmosphere and forms its oxide layer on the surface, which act as barrier and prevents aluminium from further corrosion. If product formed is non uniform, porous, non continuous and unstable layer it will not act as a barrier between metal and corrosive atmosphere. In this case corrosion takes place continuously. Ex. Iron

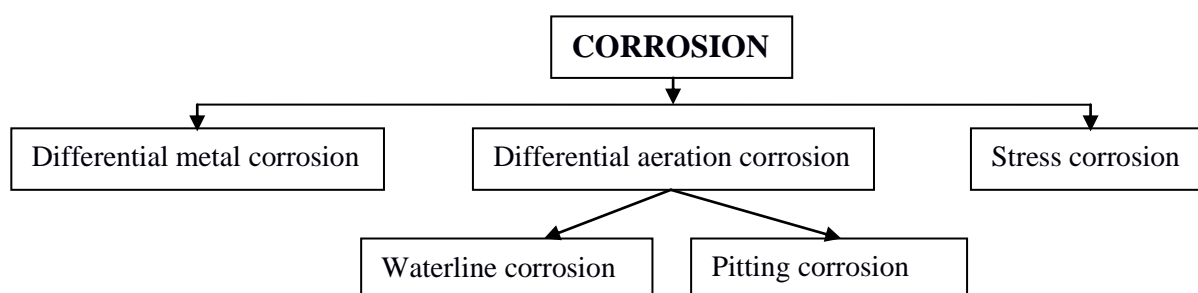
Nature of the medium

pH: In general acidic media (low pH) increases rate of corrosion than basic and neutral medium. The hydrogen ion concentration of the medium plays an important role in rate of corrosion. For example rate of corrosion of Iron in acidic medium is fast compared to basic medium. But some amphoteric metals like Al, Zn, and lead undergo fast corrosion in basic medium. pH of a solution also decides the type of cathodic reactions.

Conductance: Corrosion current depends on the conducting medium to which the metal is associated. As the electrical conductivity of medium increases the rate of corrosion also increases. Higher conducting power of medium facilitates the migration of electrons from anodic region to cathodic region, which increases the corrosion current. Therefore corrosion rate is higher in higher conducting medium like sea water.

Temperature: In general, the velocity of a chemical reaction increases with increase in temperature. Similarly rate of corrosion (redox reaction) also increases with increase in temperature. Increase in temperature increases the conductance of the corrosion medium which facilitated higher corrosion rate. Even Passive metal become active at high temperature and increases the rate of corrosion with increasing temperature. Ex. Caustic embrittlement in high pressure boilers. In hydrogen liberation reaction at cathode the rate of diffusion of H^+ towards cathode increases with increase in temperature and enhances the rate of corrosion. In oxygen absorption reaction the solubility of the dissolved gases decreases with increase in temperature, the rate of corrosion also decreases.

Types of corrosion



Differential metal corrosion

When two different metals are in direct contact with one another and are exposed to a corrosive conducting medium, the more active metal behaves as anode and suffers from corrosion, whereas the less active metal becomes cathode and protected from corrosion. The potential difference between the two metals facilitates the corrosion reaction. This type of corrosion is also known as galvanic corrosion.

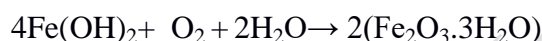
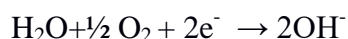
Following reaction takes place during galvanic corrosion

At anode oxidation takes place:



The reduction at cathode depends on the nature of the corrosive environment mainly it follows hydrogen evolution or oxygen absorption reaction.

Reduction Reaction:



Examples:

1. When Zn and Cu metals are electrically connected and exposed to an electrolyte, Zn (more active) forms anode and suffers from corrosion whereas Cu (less reactive) forms cathode and protected from corrosion.
2. Steel screws in a brass marine hardware
3. Steel pipe connected to copper plumbing
4. Lead antimony solder around copper wire

Differential aeration corrosion

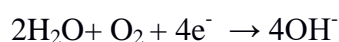
This type of corrosion is due to the formation of differential aeration cell or oxygen concentration cell. When a metal surface is exposed to differential air or oxygen concentrations it forms differential aeration cell (oxygen concentration cell). The more oxygenated region of the metal behaves as cathode and less oxygenated region becomes anode. That means less oxygenated or less aerated region undergoes corrosion.

Reactions are as follows

At less oxygenated region oxidation takes place:



At more oxygenated region reduction takes place



Examples:

1. Partially buried pipeline in soil or water
2. Window rods inside the frame suffer from corrosion
3. Metal under dirt, dust, scale or water undergoes corrosion

4. Part of the nail inside the wall

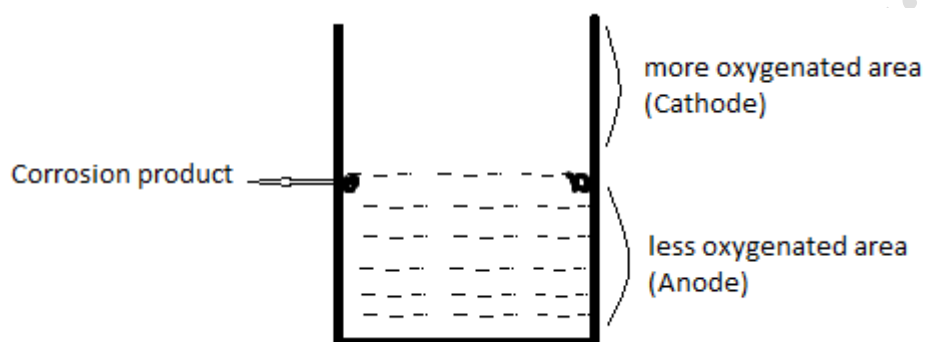
5. Paper pin inside the paper

Two common cases of differential aeration corrosion are

a. Water line corrosion

Water line corrosion occurs in which a part of the metal is partially dipped in water. Consider a steel tank containing water. The maximum corrosion takes place along a line just beneath the level of water meniscus. The part of the metal below the water line is exposed to dissolved oxygen (less oxygen concentration) acts as anode and undergoes corrosion whereas the part which is above the water line is exposed to atmospheric oxygen (more oxygen concentration) acts as cathode, which remains completely unaffected by corrosion.

Ex. Partially filled metal water tank

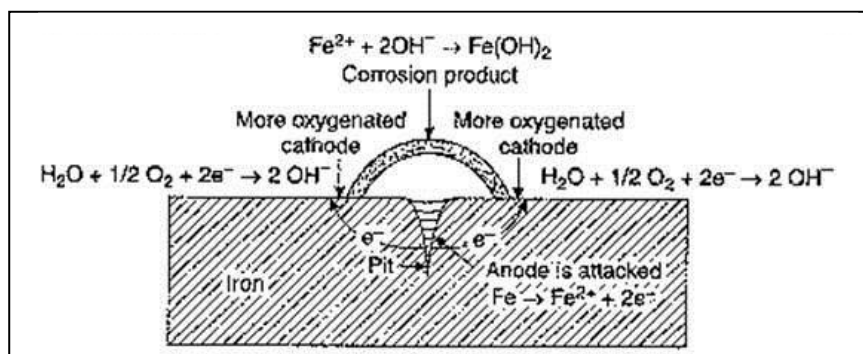


Other examples of waterline corrosion are corrosion of ship hull, partially immersed metallic pipe.

b. Pitting corrosion is a localized accelerated attack in which only small areas of the metal surface are attacked while the remainder is largely unaffected. This localized attack results in small pin holes (pits). The pits may initiate and propagate to a certain depth resulting in the formation of cavities and becomes inactive. This is also a type of differential aeration corrosion.

This type of localized corrosion is usually created by dirt deposits, corrosion products, cracks in paint or protective coatings, etc. the metal below the deposit is less oxygenated acts as anode and undergoes corrosion. Small anodic and large cathodic area increases the corrosion rate. Anode area is covered by the corrosion product making it less aerated, which also accelerate the corrosion reaction. The shape of the pit is often responsible for its continued accelerated growth. Initially formed pits produce conditions which stimulate the autocatalytic process.

Pitting is very destructive and frequently ruins the metallic instruments, tubes, pipes etc.



Stress corrosion

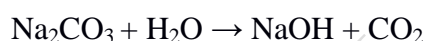
It is a highly localized attack on the metal because most of its surface is virtually un-attacked while cracks progress towards stress. This corrosion occurs only in the presence of specific corrosive environment and the presence of tensile stress on the metal.

Stress can be internal stress developed during fabrication of the article or during etching, drawing, servicing, bending, welding, etc or stress can also be external stress acting during service conditions like heavy load on material. The metal atoms under stress will always at higher energy level compared to unstressed atoms. Therefore, stressed atoms are more active and acts as anode. This corrosion involves an attack along the narrow paths forming local anodic areas with respect to more cathodic area of the metal surface. The crack grows and propagates perpendicular to the operating stress, and failure occurs after progressing a finite distance.

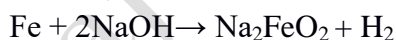
Example: Season cracking of brass in presence of ammonia, Caustic embrittlement of boiler in presence of chloride ions and caustics.

Caustic embrittlement

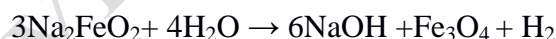
It is an example for stress corrosion. The boiler feed water usually contains a certain amount of sodium carbonate. In high pressure boilers, the sodium carbonate undergoes hydrolysis to give sodium hydroxide (Caustic soda) and carbon dioxide, and makes boiler water alkaline.



This very dilute alkaline water flows into the minute hairline cracks and crevices by capillary action. The water evaporates and increases the concentration of the alkali. This concentrated alkali reacts with iron forming sodium ferroate (Na_2FeO_2) in crevices, cracks and the metal under stress..



The sodium ferroate decomposes into magnetite and alkali is regenerated in the process as per the following reactions



This type of stress corrosion in boilers in the presence of alkaline medium, called caustic embrittlement. This can be prevented by the addition of the substances such as sodium sulphate, tannin, etc., which blocks the cracks and crevices, thereby prevents the penetration of alkali.

Corrosion control

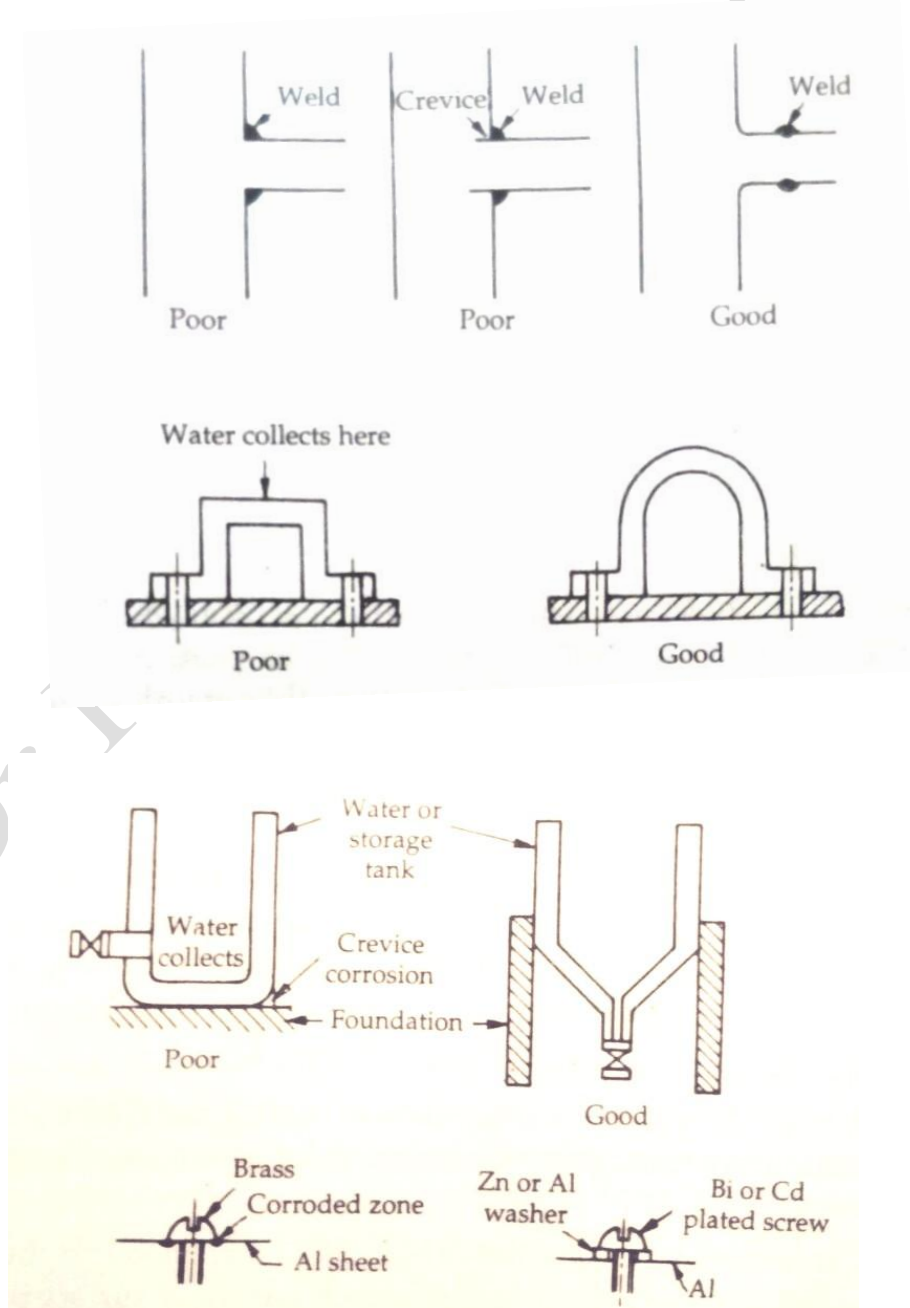
Design and selection of materials:

No material is resistant to all corrosive environments but materials selection is critical to preventing many types of failures.

Appropriate system design is also important for effective corrosion control, and includes the consideration of many factors, such as

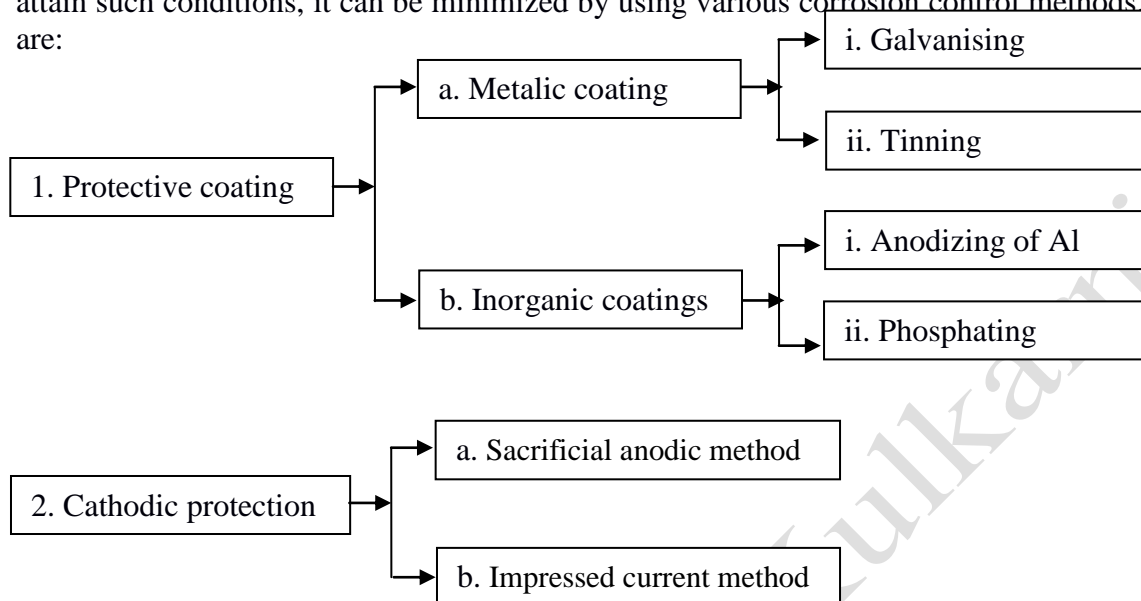
1. Selection of the proper material should be made not only on its cost and structure but also on its chemical properties and its environment.
2. If active metal is used then it should be insulated from cathodic materials.

3. Suitable insulators should be used between two dissimilar metals.
4. If two metals have to be in contact, they should be selected such a way that their electrode potentials are nearer as possible.
5. Wherever possible exclude moisture if not use corrosion inhibitors.
6. Adjust the pH of solution such a way that material should be least reactive in that pH.
7. Suitable protective coating can be applied to minimize the corrosion
8. The equipment must be designed with minimum localized stresses, sharp bends, lap joints, etc.
9. Use noble metals which are less reactive and least subjected to corrosion.
10. As far as possible, metal used in a structure should be extremely pure. Small amount of impurity causes corrosion.
11. While using an alloy, it should be completely homogeneous.



Corrosion control methods

Corrosion can be completely avoided only under ideal conditions. Since it is impossible to attain such conditions, it can be minimized by using various corrosion control methods. They are:



Protective Coating:

Corrosion is prevented by the application of protective coating on the surface of metal, thereby the metal surface is isolated from the corrosive environment. The coatings being chemically inert to the environment under specific conditions of temperature and pressure, forms a physical barrier between the coated surface and its environment. Coatings are not only prevents corrosion but also decorates the surface of the metal.

- **Metallic coatings**

Coating or depositing a metal layer on base metal is known as metallic coating. Metal coatings can be applied on the base metal by hot dipping process, electro-deposition, flame spraying, diffusion coating, cladding, vapor deposition etc., This method is used for producing a coating of low melting metals such as Zn, Al, Sn etc., on iron / steel metals which have relatively high melting point. Metal coating is classified in to two – anodic coating and cathodic coating.

Anodic coating which is produced by coating more active metal than the base metal. If any crack or pit is formed on the coated metal, it will act as anode and base metal as cathode and hence base metal will not corrode. Coating of zinc over iron is anodic coating is also known as galvanizing. Zinc is more active than iron, which sacrifices itself to protect iron. Anodic coating of iron is done by Al and Cd also. Since Zn is toxic, galvanized utensils are not used for cooking or food storing.

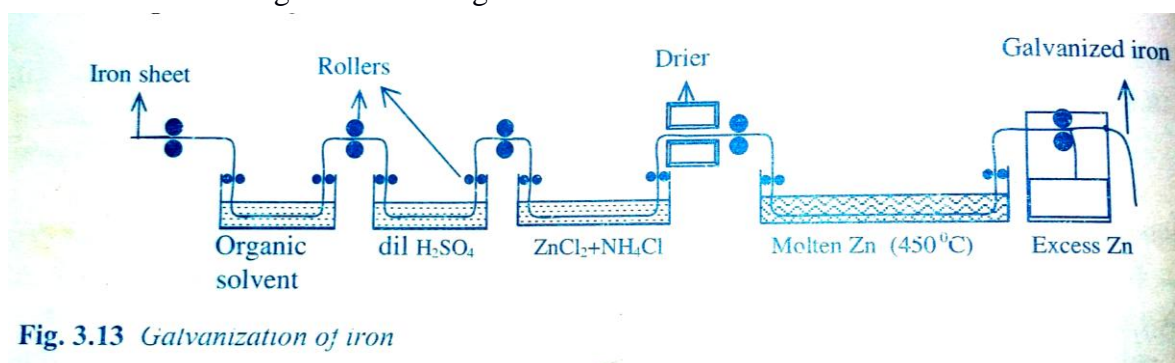


Fig. 3.13 Galvanization of iron

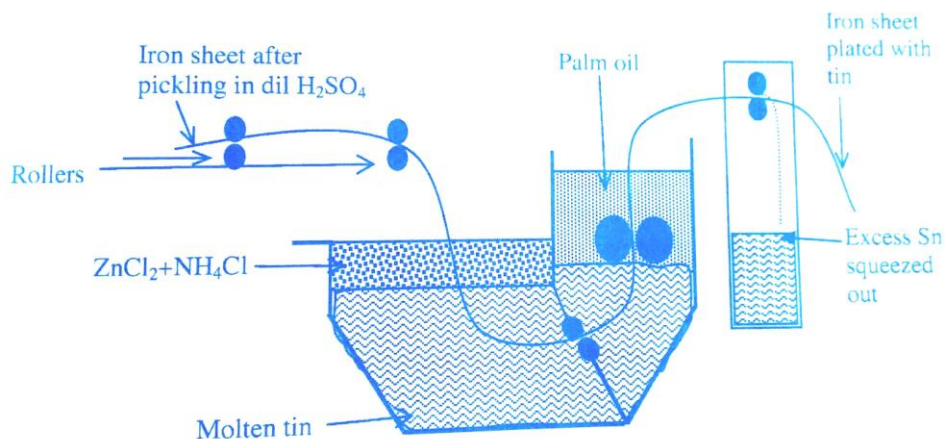
Steps involved in galvanizing are:

- **Degreasing:** The base metal is washed with organic solvents to remove oil/grease,
- **Pickling:** The base metal is washed with dilute sulphuric acid to remove scale/rust
- **Washing:** Then it is washed with water and dried, before coating.
- **Flux Treatment:** The base metal is treated with NH_4Cl and ZnCl_2 flux. This is done to prevent the oxidation of coating metal Zn and also to get adherent coating.
- **Hot Dipping process:** The base metal is then dipped in a molten bath of Zn ($\sim 450^\circ\text{C}$)
- **Stripping:** The excess of coated metal is stripped off using a pair of hot rollers and cooled gradually.

Uses: Galvanizing is applied to nails, bolts, pipes, roofing sheets etc.

If any crack is produced on the galvanized sheets, Zn undergoes severe corrosion by protecting the base metal.

Cathodic coating: Coating a base metal with cathodic metal is known as cathodic coating. Copper, nickel, tin and silver metals are commonly used as cathodic coatings on steel. Coating of tin over iron is cathodic coating which is also known as tinning. Cathodic protection of iron is successful only when there is no pit or crack formation on the surface of metal. When crack is formed on coating, an intense localized corrosion occurs due to setting up of small anodic and large cathodic area galvanic cell.



Steps involved in tinning are:

- **Degreasing:** The base metal is washed with organic solvents to remove oil/grease,
- **Pickling:** The base metal is washed with dilute sulphuric acid to remove scale/rust
- **Washing:** Then it is washed with water and dried, before coating.
- **Flux Treatment:** The base metal is treated with ZnCl_2 flux. This is done to prevent the oxidation of coating metal Sn and also to get adherent coating.
- **Hot Dipping process:** The base metal is then dipped in a molten bath of Sn ($\sim 250^\circ\text{C}$)

- The excess of coated metal is removed by passing through a pair of hot rollers immersed in palm oil and cooled gradually. The palm oil prevents the oxidation of tin coated surface.

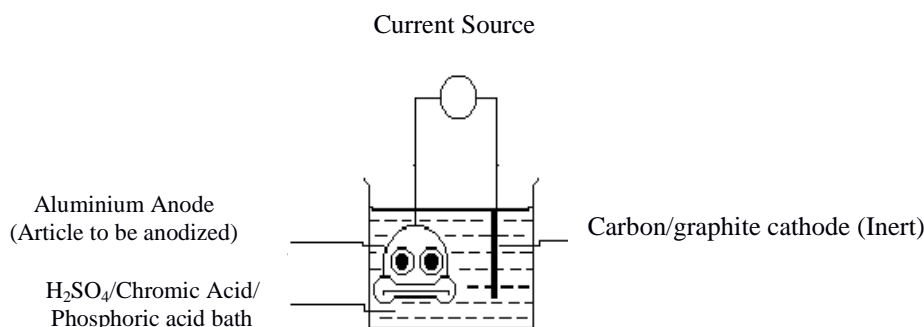
Inorganic coatings (Chemical conversion coatings)

These coatings are produced at the surface of the metal by chemical / electrochemical reactions. This coating is a chemical conversion process in the sense that, coatings are integral part of the metal itself. Inorganic coating is process of conversion of atoms of the base metals to its compounds and which is generally produced by chemical dip, spraying or by electrolytic methods. These coatings are applied on the article for decorative effect and to increase the corrosion resistance of the base metal. This coating serves as an excellent base coating for paints, enamels and also acts as an excellent insulator.

Examples:

- **Anodizing of Al**

Anodizing is a process of artificially converting protective passive oxide film on the surface of metal by electrochemical oxidation. Anodized coatings are generally produced on non-ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process. The base metal is made as anode. It is carried out to produce a porous/nonporous coating.



The electrolysis is conducted in an acid bath, at moderate temperature 30-40°C, using moderate current densities, in which the base metal is made as anode. The commonly used baths are H₂SO₄ / Chromic acid / Phosphoric acid / oxalic acid. Lead is generally used as cathode.

Steps involved in anodizing of Al are,

- **Anodizing:** Aluminum is immersed in a tank containing an electrolyte having around 15% sulfuric acid concentration having temperature about 40°C. Electric current is passed through the electrolyte and the aluminum is made the anode in this electrolytic cell; the lead is the cathode. Voltage applied across the anode and cathode causes negatively charged anions to migrate to the anode where the oxygen in the anions combines with the aluminum to form aluminum oxide (Al₂O₃).

Reaction at anode,



At Cathode,



- Coloring: Anodic films are initially porous and non-continuous which is well suited to a variety of coloring methods including dyeing, both organic and inorganic dyestuffs, and electrolytic coloring processes.
- Sealing: These pores are sealed by exposing the metal to boiling water. In this process the metal oxide layer changes into its metal oxide mono hydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

Uses: Anodized articles are used as Tiffin carriers, soapboxes, household utensils, window frames, etc.

- **Phosphating**

Phosphate coating is a process of converting the surface atoms of the base metal into their phosphates by chemical or electrochemical reaction between base metal and certain metal phosphates in aqueous solution of phosphoric acid. Phosphate coatings are a surface conversion coating that is formed generally on iron, steel and zinc metal substrate.

Phosphating reaction is slow; hence it is enhanced by using accelerators such as nitrate, nitrite, chlorate and hydrogen peroxide. These coatings are applied by immersion or spraying or brushing techniques. Phosphate coating is given as undercoat for paints and enamels.

Steps involved in Phosphating of iron are

- The metal to be coated is dipped in a solution containing mixture of phosphoric acid, metal phosphates such as Fe / Mn / Zn phosphates.
- Accelerators such as nitrate, nitrite, chlorate and hydrogen peroxide, etc are added
- Required pH of the bath is maintained by using buffers
- Temperature is maintained about 35°C .
- The metal ions dissolve and react with phosphate ions forming metal phosphate and the metal phosphates deposits on the surface of base metal.

Uses: - Phosphate coated metal widely used in automobile industry, bolts, nuts, and refrigerators, washing machining, cars bodies etc.

Cathodic Protection:

Cathodic protection is a method in which the base metal to be protected from corrosion is made to act as cathode and no part of it is allowed to act as anode.

We all know that corrosion of the metal takes place at the anode not at the cathode. Therefore corrosion of the metal can be prevented by converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites. Cathodic protection systems protect a wide range of metallic structures in various environments. Common applications are of cathodic protections are steel water pipelines and storage tanks, steel piers piles, ship and boat hulls, offshore oil platforms and onshore oil well casings and metal reinforcement bars in concrete buildings etc.

Cathodic protection may be achieved in either of two ways.

1. Sacrificial anodic protection
2. Impressed current cathodic

Sacrificial anodic protection:

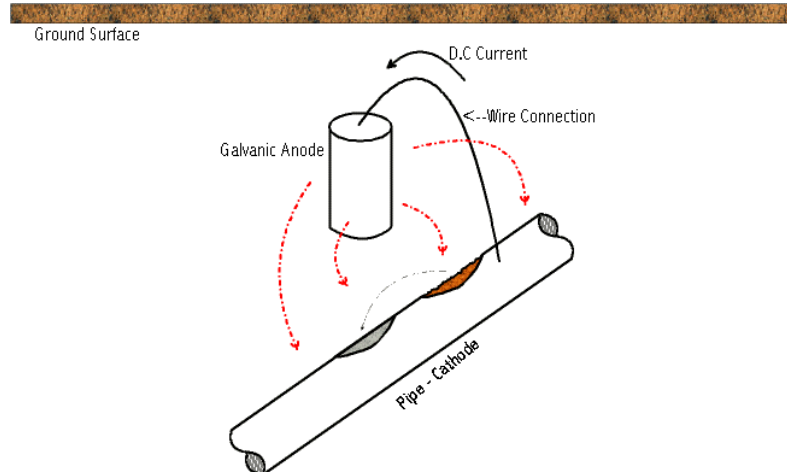


Figure: The steel pipe is connected to a more active Mg block.

In this method the more active metals like Zn, Mg, and Al etc are attached to base metal. The anodic metals being more reactive undergo corrosion but base metal remains unaffected. The more active metal so employed is called sacrificial anode and the method is called sacrificial anode method. The sacrificial anodes have to be replaced from time to time after complete corrosion.

Examples: The method is used for protecting buried pipeline, ship hulls, industrial water tank steel rods in RCC columns.

Impressed current cathodic protection:

The metallic structure to be protected is made as cathode by impressing the current from external source. The direct current is applied in the opposite direction larger than the corrosion current.

The arrangement for protecting a buried steel tank is illustrated in the figure given below. The steel tank receives current larger than the corrosion current from a DC power source via an auxiliary inert electrode buried in the ground. The tank becomes the cathode and the auxiliary electrode acts as anode. The auxiliary electrodes used are generally inert metals like Graphite. The structure being cathode will not undergo corrosion and graphite being inert it will remain unchanged. The anode used is a noble metal or an electrochemically inert material, the surrounding environment will be oxidized.

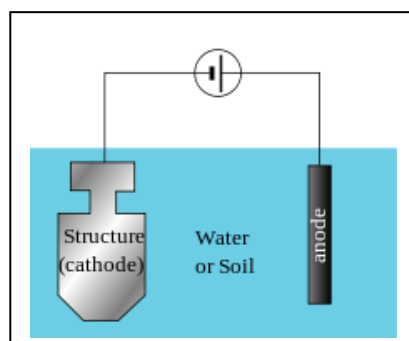


Figure: Impressed current method.