

CORROSION AND ITS CONTROL

By

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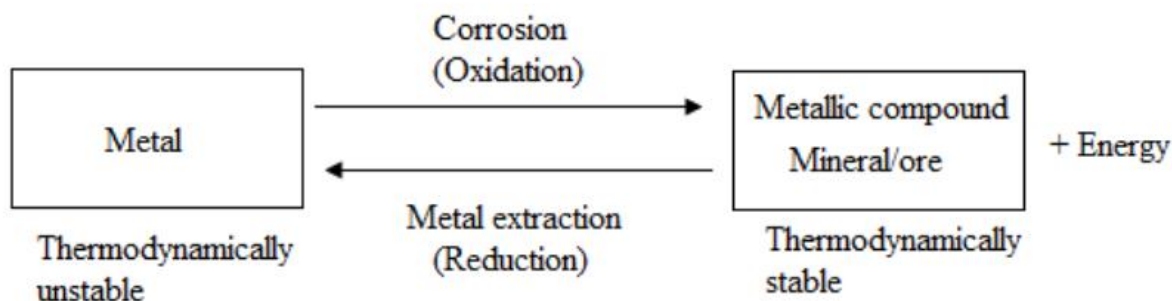
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Corrosion

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium. The process of decay metal by environmental attack is known as corrosion. Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc. eg. Iron undergoes corrosion to form reddish brown colour rust $[\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}]$. Copper undergoes corrosion to form a green film of basic carbonate $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$.

Causes of corrosion

The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy. Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores). When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stable compounds.



Effects of corrosion

1. Wastage of metal in the form of its compounds. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
2. Life span and efficiency of metallic parts of machinery and fabrications is reduced that causes a huge economic loss.

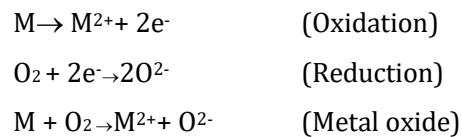
Theories of corrosion

A. Dry corrosion or Chemical corrosion

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2 , halogens, H_2S , SO_2 , NO_2 or anhydrous inorganic liquid with the metal surface. There are three types of chemical Corrosion:

(1) Oxidation corrosion (2) Corrosion due to other gases (3) Liquid metal corrosion

(1) Oxidation Corrosion: This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

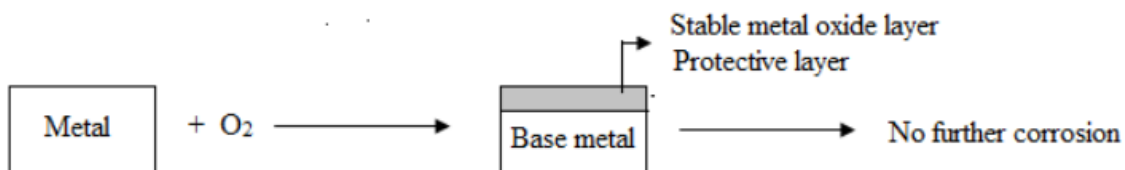


Mechanism:

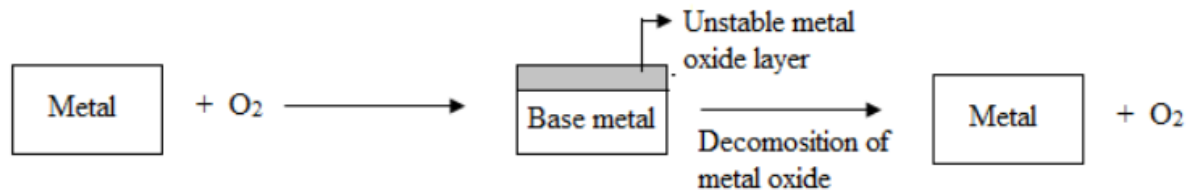
Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

(a) If the metal oxide is stable, it behaves as a protective layer which prevents further corrosion.

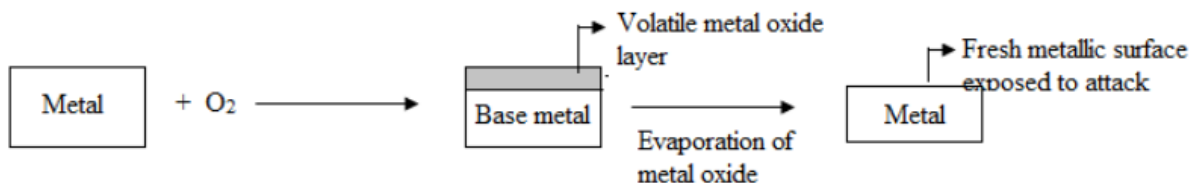
E.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.



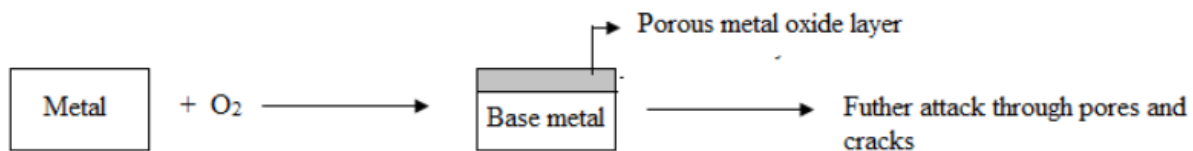
(b) If the metal oxide is unstable, the oxide layer formed decomposes back into metal and oxygen. So, oxidation corrosion is not possible. E.g., Ag, Au and Pt do not undergo oxidation corrosion.



(c) If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).



(d) If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrodes the underlying metal surface. This causes continuous corrosion till conversion of metal into its oxide is completed. Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

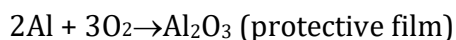


(2) Corrosion due to other gases:

This type of corrosion is due to gases like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc.

In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling-Bedworth rule. According to this rule;

- (i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous, does not allow the penetration of corrosive gases thus, protective.



- (ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal, thus, non-protective.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale.



(3.) Liquid metal corrosion:

This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal. Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

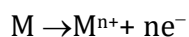
B. Wet corrosion or electrochemical corrosion.

This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism:

Electrochemical corrosion involves flow of electrons between anode and cathode.

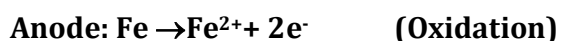
The anodic reaction involves dissolution of metal liberating free electrons.



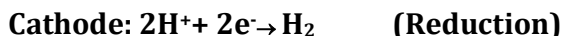
The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

i. Hydrogen Evolution Theory

This type of corrosion occurs in acidic medium. e.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



The electrons released flow through the metal from anode to cathode, whereas H^+ ions of acidic solution are eliminated as hydrogen gas.

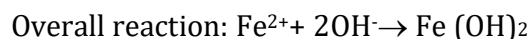
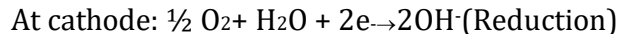
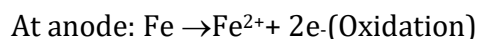


This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

ii. Oxygen Absorption Theory

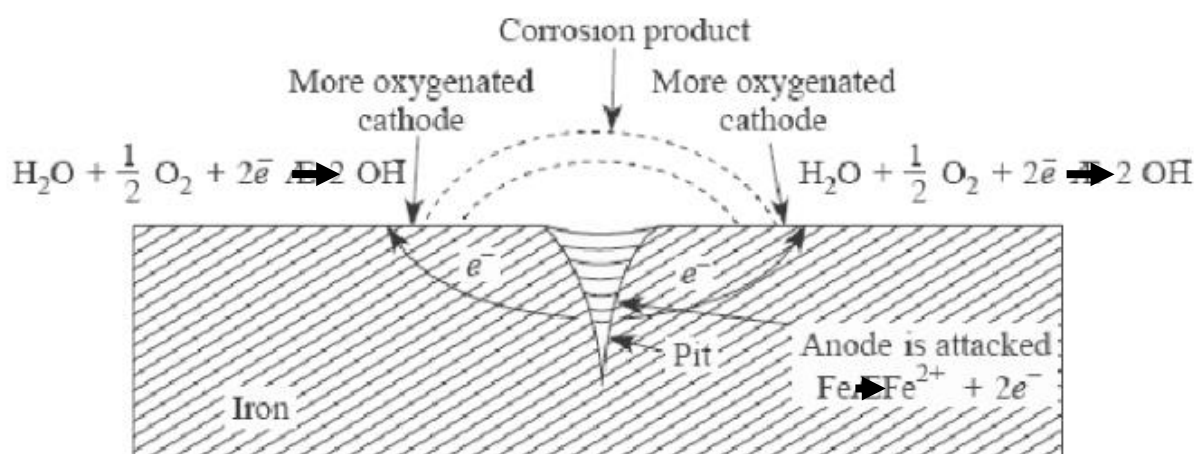
For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen,

Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface and surrounding becomes cathode. It shows that anodes are small areas, while the surrounding environment forms large cathodes. The released electrons flow from anode to cathode through iron metal.



If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

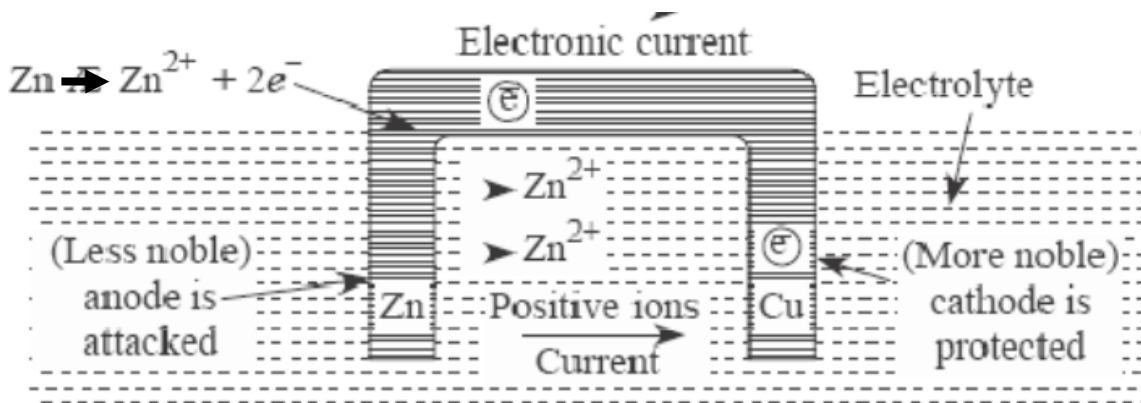
$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ leads to the formation of **Rust** $Fe_2O_3 \cdot 3H_2O$ (Red-Brown).



Types of corrosion

1. Galvanic Corrosion

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series (low reduction potential) undergoes corrosion and the metal lower in electrochemical series (high reduction potential) is protected. This type of corrosion is called Galvanic corrosion. e.g. When Zn and Cu are connected and exposed to corroding environment, Zinc (higher in electrochemical series) forms the anode; undergoes oxidation and gets corroded. Cu (lower in electrochemical series) acts as cathode; undergoes reduction and protected.



2. Concentration cell corrosion

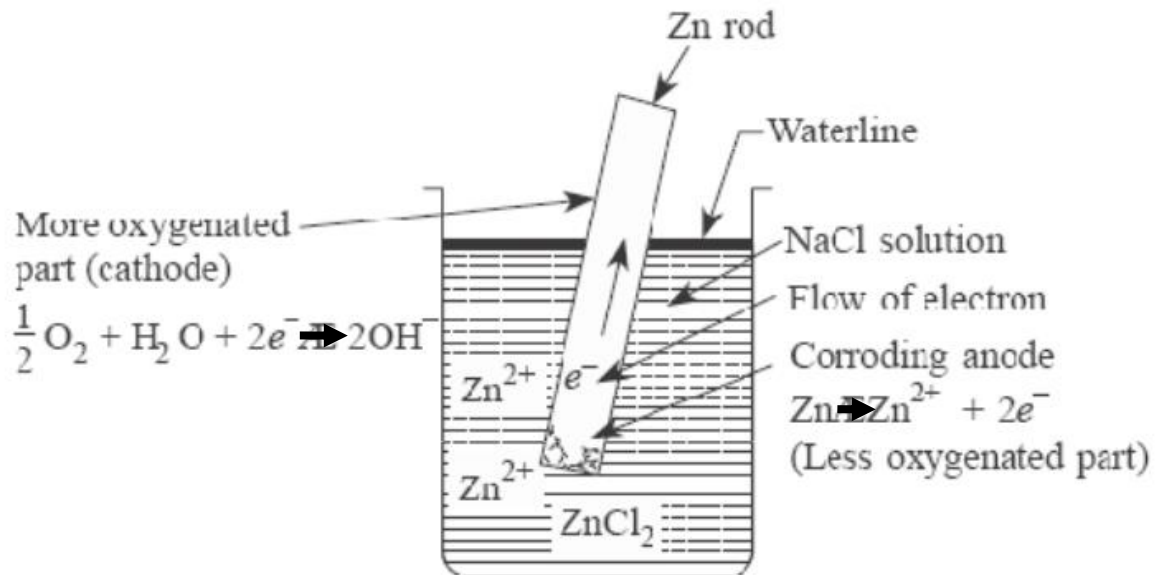
This type of corrosion occurs due to electrochemical attack of the metal surface exposed to electrolyte of varying concentrations or varying aeration. This type of corrosion is due to

- i) Difference in concentration of metal ions.
- ii) Difference in the exposure to air/oxygen (Differential aeration corrosion)
- (iii) Difference in temperature.

Differential aeration corrosion is the most common type of concentration cell corrosion. When a metal is exposed to different air concentrations, it has been found to be poorly oxygenated of the metal becomes anodic and well oxygenated part becomes cathodic. The potential difference is created which causes the flow of electrons from anode (metallic part immersed in NaCl solution) to cathode (exposed to atmosphere).

eg. Zn rod immersed deep in NaCl solution: **Anode**

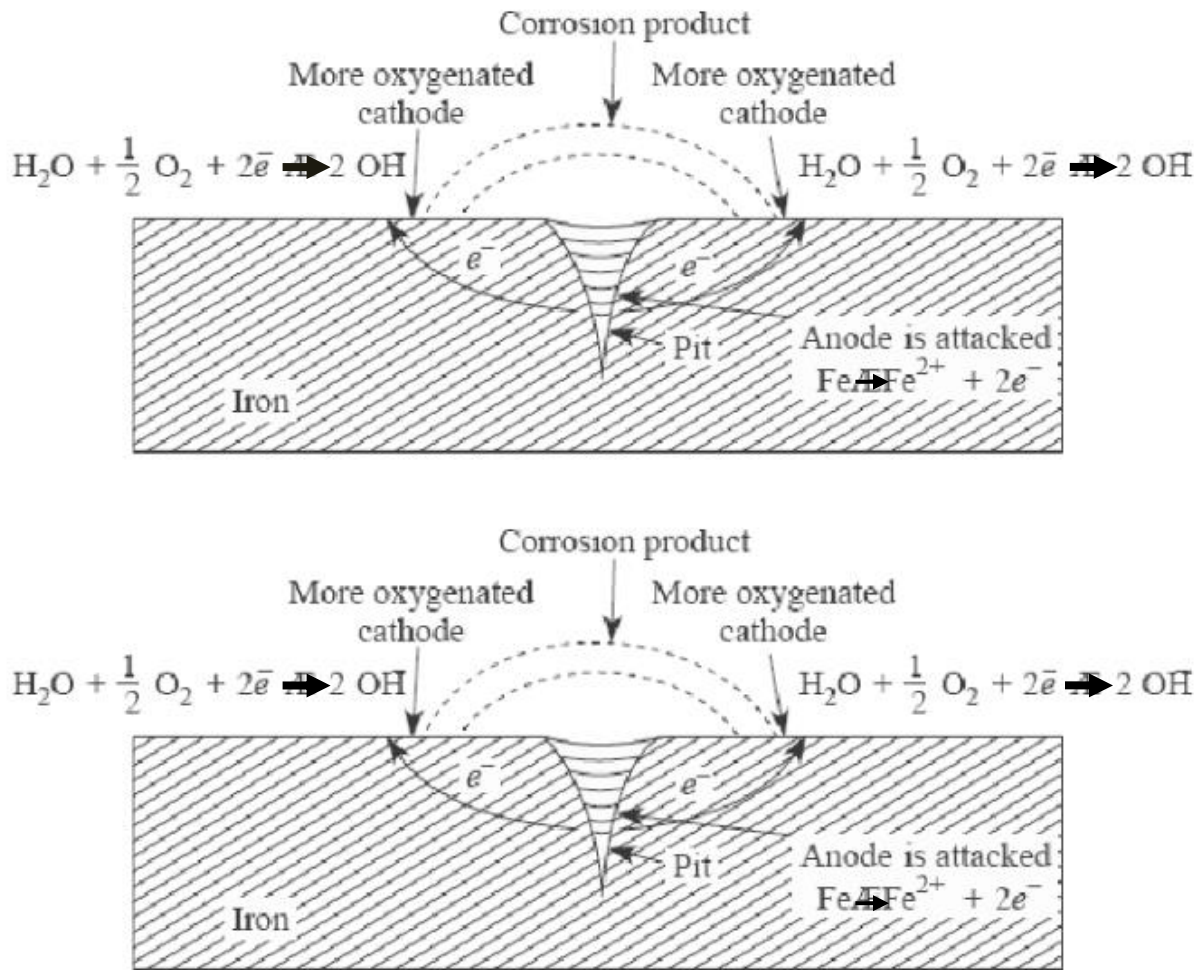
Zn rod above NaCl solution: **Cathode**



3. Pitting corrosion

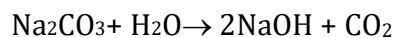
A cavity, pinholes and cracks on the protective film developed on the metal surface creates the formation of small anodic areas in the less oxygenated parts and large cathodic areas in well oxygenated parts. The flow of electrons is from anode to cathode and ions move through atmospheric moisture medium.





4. Caustic embrittlement

Boiler feed water contains certain amount of Na_2CO_3 which decomposes to NaOH under the high pressure of the boilers.



NaOH gets deposited in the cracks/pits of the boiler plate creating a concentration cell. The metal deposited with NaOH becomes anodic while the metal surround the drop becomes cathodic. Iron metal of metal react with NaOH at high temperature to form sodium ferroate causing damage to boiler, such corrosion is called as Caustic embrittlement.

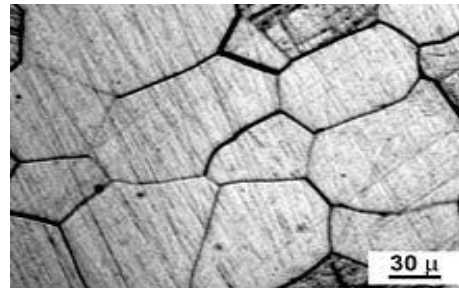
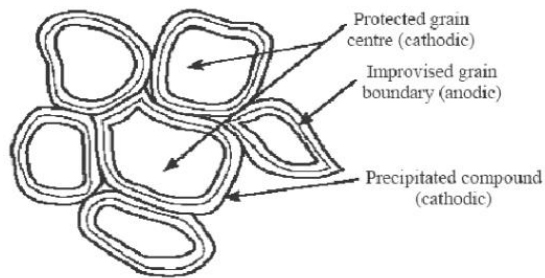
5. Underground corrosion (Soil corrosion)

Underground corrosion is due to the corrosiveness of the soil. As the acidity of the soil increases, the rate of corrosion increases.



6. Inter granular corrosion

This corrosion occurs along grain boundaries. The grain boundary where the metal is sensitive undergoes corrosive attack. The grain boundary contains a material which shows more anodic potential. The metal at the grain boundary decays as it becomes anodic and the centre of the grain becomes cathodic which is protected. Due to formation of many tiny cells in metallic structure intergranular corrosion takes place.



7. Stress corrosion

Stress corrosion is due to the combined effect of the tensile stresses and the corrosive environment of the metal. The tensile stress is usually observed in fabricated articles like alloys of Zn and Ni. Under applied stress metal undergoes cracking due to inter-granular corrosion, called as stress corrosion cracking.



8. Erosion corrosion

Erosion Corrosion results by the combined effect of the abrading action of vapours, gases and liquids and the mechanical rubbing action of solids over the surface of metals. This type of corrosion is caused by the breakdown of a protective film at the spot of abrasion. Abrading action removes protective films from localized spots on the metal surface, thereby resulting in the formation of differential cell at such areas and localized corrosion at anodic points of the cells. Erosion corrosion is most common in agitators, piping, condensers, tubes and vessels in which steams of liquids or gases emerge from an opening and strike the side walls with high velocities.



Crevice Corrosion

The corrosion, occurring at the joint of two metallic surfaces, where a narrow opening is created. The narrow slit acts as an anode where corrosion takes place. Such type of corrosion is called as crevice corrosion.



Factors effecting corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

A. Factors due to nature of metal

1. Purity of the metal: Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

2. Electrode potentials: Metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. The metals with lower reduction potentials readily undergo corrosion. (eg. Zn, Mg, Al etc.).

3. Position of metal in Galvanic series: Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected. When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion. The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

Eg. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

4. Relative areas of anodic and cathodic cells: The relative areas of corrosion is influenced by cathodic to anodic cells. If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the electrons are liberated at anode which is consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.

5. Hydrogen over voltage: When a cathode reaction is hydrogen evolution type, the metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

6. Physical state of metal: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

7. Nature of surface film: If the corrosion product formed is more stable, insoluble and non-porous, it acts as protective layer and prevents further corrosion (Eg. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

8. Proper Designing

- a. Free from sharp corners and edges.
- b. Smooth flow of liquid from the container.
- c. Minimizing of bimetallic corrosion by joining compatible materials without the risk of galvanic corrosion.
- d. Complete internal and external coating of the containers, if cost effective.
- e. Weld rather than rivet tanks and other containers.
- f. Metallic structures should be supported on legs.

B. Factors due to nature corrosive environment

- 1. Temperature:** The rate of corrosion reactions increases with increase in temperature.
- 2. Humidity in air:** The moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.
- 3. Presence of impurities:** Atmosphere is contaminated with gases like CO_2 , SO_2 , H_2S ; fumes of H_2SO_4 , HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.
- 4. pH value:** pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.
- 5. 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.

Corrosion control methods

1. By corrosion inhibitors:

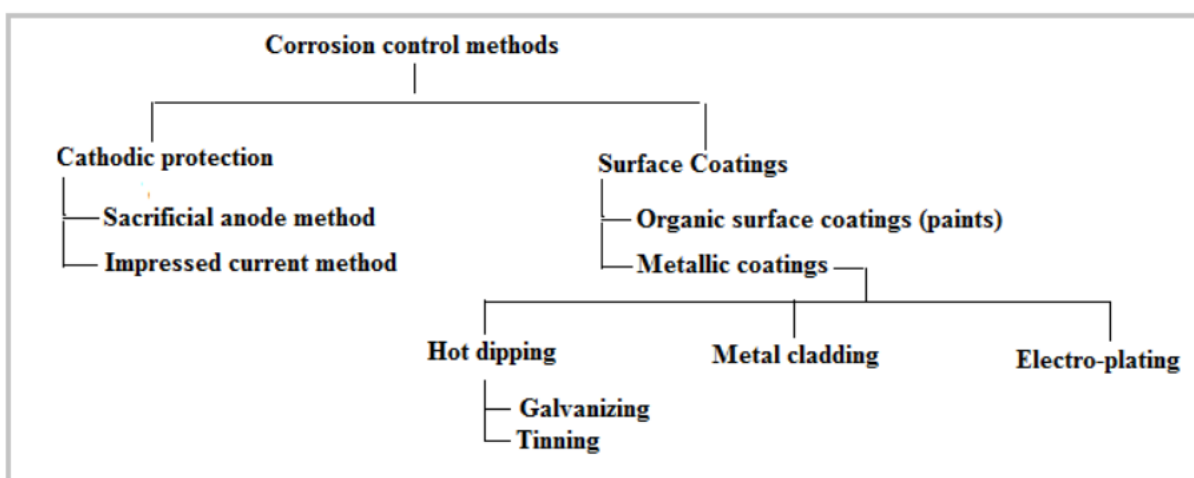
Corrosion Inhibitors: These are the chemical substances (may be organic/inorganic) when added in small quantities to the corrosive environment, forms a protective layer around anodic or cathodic regions by dissolving in the environment and effectively decreases the corrosion rate.

Types of Corrosion inhibitors

- a. Anodic inhibitors:
- b. cathodic inhibitors

Anodic Inhibitors: Anions such as tungstates, phosphates, chromates, ions of transitional metals with high oxygen content, are used as anodic inhibitors. They form a sparingly soluble corrosion product with a newly formed metal ion. It is adsorbed on the surface of anode forming a protective film and reduces the rate of corrosion.

Cathodic Inhibitors: They are used in acidic solutions, alkaline / neutral solution. Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Other cathodic inhibitors, ions such as calcium, zinc or magnesium, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization Caused by oxygen.



2. Cathodic protection

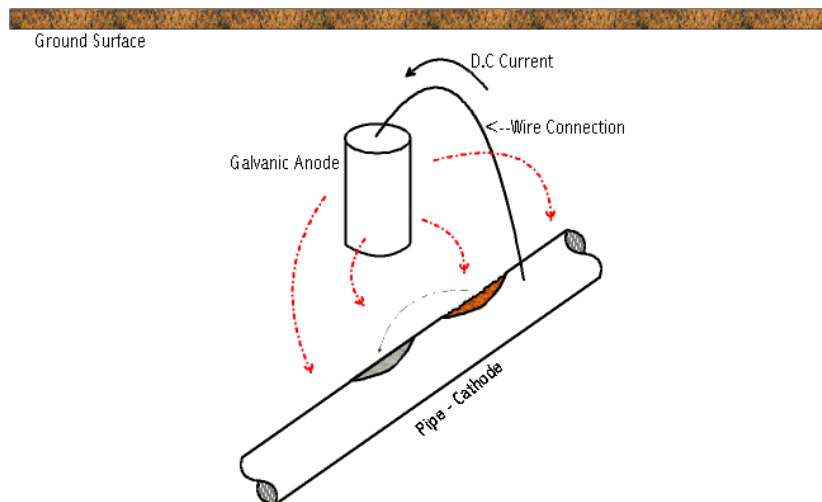
The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection. There are two types of cathodic protection

(a) Sacrificial anode method (b) Impressed current method.

a. Sacrificial anode method

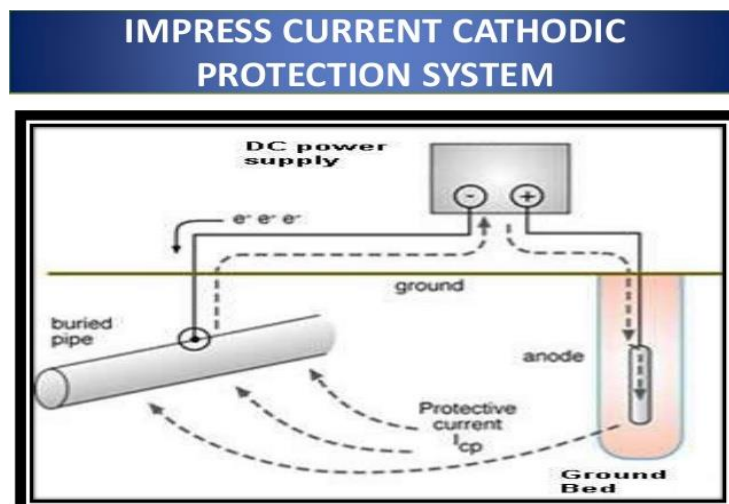
In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal. The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded

sacrificial anode is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series. Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected. Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



b. Impressed current cathodic method

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. The impressed current is slightly higher than the corrosion current. 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 impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



3. Surface coatings

The application of surface coating is the common method to protect the surface of the metal from the corroding environment. The coating acts as a physical barrier between metal and the environment. These surface coatings exhibit chemical inertness to corrosive environment, adhesive properties and impermeable.

a. Organic surface coatings

Organic surface coatings are applied over the metallic surfaces to prevent from the corrosion.

Properties of Organic surface coatings.

1. **Chemical inertness to the corrosive environment**
2. **Good surface adhesion**
3. **Impermeability to water, gases and salts**

Eg. Paints Paint is a mechanical dispersion mixture of several constituents in a vehicle oil or drying oil. The following are the constituents of paints and their functions.

1. Pigment: It is a major constituent of the paint. Provides desired colour to the paint

It protects the paint by reflecting harmful U.V radiation. Gives strength and increases weather resistance of the film. White- white lead, ZnO Red- Red lead, Ferric oxide

2. Vehicle oil/ Drying oil: It forms the film forming constituent of the paint.

It acts as medium for the dispersion of various

constituents. It gives durability , adhesion and water proofness to the paint. Sunflower oil, Mustard oil, Soyabean oil.

3. Thinners: Reduces the viscosity and increases the elasticity of the paint film. Enhances the dissolving the additives in vehicle medium. Turpentine, Kerosene, Naphtha.

4. Driers: Driers are oxygen carrying catalysts. They accelerate the drying of the paint film through oxidation, polymerization and condensation. Tungstates and nahthalates of Pb, Zn and Co.

5. Extenders/ Fillers Low refractive indices materials: They reduce the cost and cracking nature of the paint film. BaSO₄, gypsum, talc, china clay.

6. Plasticizers: They provide elasticity to the film and minimize cracking. Tributylphosphate, triphenylphosphate

7. Anti skinning agents: They prevent the gelling nature of the paint film. Polyhydroxy phenols

b. Metallic coatings

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

1. Anodic coating:

The metal used for the surface coating is more anodic than the base metal which is to be protected. For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially. The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected. Galvanization is a form of anodic coating.

2. Cathodic coating:

Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature. Cathodic coating protect the base metal only when the coating is uniform and free from pores. The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings

1. Hot dipping

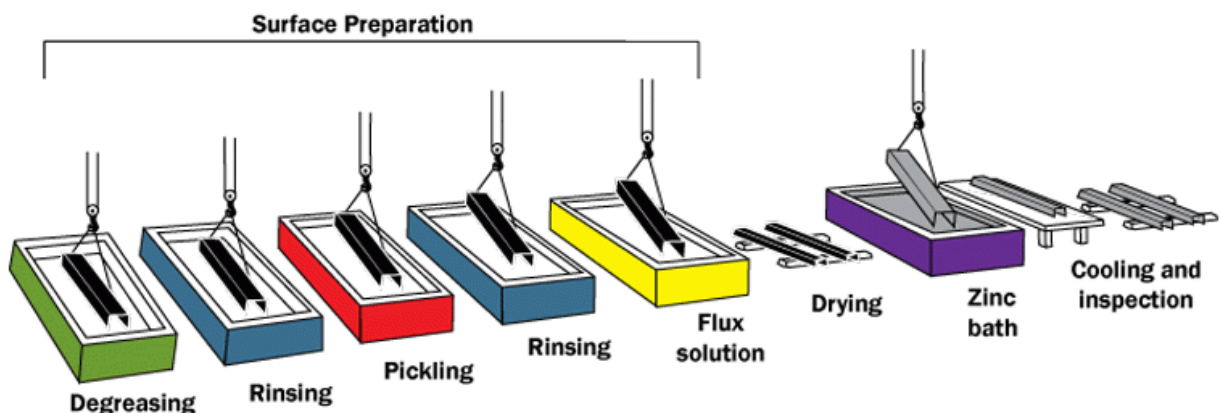
Hot dipping process is applicable to the metals having higher melting point than the coating metal. It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal. e. g. Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are (a) Galvanizing and (b) Tinning.

a. Galvanizing

Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. It is the sacrificial anodic protection offered by the zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried. Then after dipped in the bath containing molten zinc which is at 425-450°C. To prevent it from oxide formation, the surface

of bath is covered with an ammonium chloride flux. When the iron sheet is taken out it is coated with a thin layer of zinc. To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450°C followed by cooling. Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

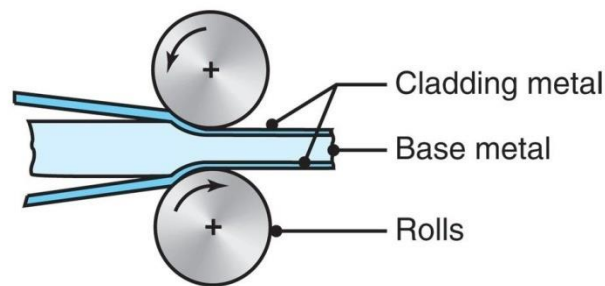


b. Tinning

The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning. Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present. A cleaned iron sheet is passed through a bath ZnCl_2 molten flux followed by molten tin and finally through a suitable vegetable oil. The ZnCl_2 flux helps the molten metal to adhere to the base metal.

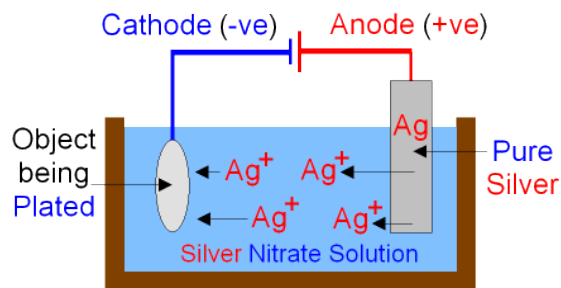
2. Metal cladding

The surface of the base metal to be protected is sandwiched between two thin layers of coat metal and pressed between rollers. Coating of a thin homogeneous layer of a coating metal on a base metal such that it strongly binds permanently either on one side or on both sides under heat and pressure. The finished product may be welded at the edges. The coat metal has to be anodic to the base metal and only plain surfaces can be cladded. This method is used for coating Al, Cr, Ni, Duralumin, etc. All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt and alloys like steel/nickel alloys can be used as cladding materials. Duralumin is very light metal alloys used in aircrafts industry which is cladded with aluminum to get Alclad.



3. Electroplating

Electroplating is the process of coating metals and protect them from corrosion, wear and chemical attack. Electroplating is the method of electro-deposition of metal by means of electrolysis over surface of metals and alloys. The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode. The two electrodes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal. When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer. Low temperature, medium current density, low metal ion concentration conditions are maintained for better electroplating.



Anodizing

Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. Anodizing is a method of increasing the corrosion resistance of a metal part by forming a layer of oxide on its surface.

The process is called *anodizing* because the part to be treated forms the anode electrode of an electrolytic cell. Anodizing increases resistance to corrosion and wear, and provides better adhesion for paint primers and glues than bare metal does. Anodizing changes the microscopic texture of the surface and the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance. Anodized aluminum surfaces, for example, are harder than aluminum. The process of creating this protective oxide coating is achieved electrolytically.

The metal part to be treated (generally aluminum) is first submerged in an electrolytic solution bath along with a cathode. When a current is passed through the acid solution hydrogen is released from the cathode and oxygen forms on the surface of an anode. This results in a metal oxide film growing on the surface of the part being treated.

