

CORROSION AND ITS CONTROL

Introduction:

Definition: Any process of deterioration and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment starting at its surface is called as corrosion. Thus corrosion is a process reverse of extraction of metals.

Fundamental reason of corrosion:



Most of the metals exist in nature are in combined state such as oxides, Carbonates, Sulphites, Chloride, Silicates etc. These can be reduced to the pure metallic state (high energy states) hence, when extraction process occurs ores can be reduced to metallic state.

These extracted pure metals can be regarded as higher energy state than their corresponding ores and thus they have natural tendency to come back to combined states (low energy state) hence, when metal comes in contact with environment, its surface begins to decay more or less rapidly.

Electrochemical corrosion (Wet corrosion):

If metal is partially dipped in a salt solution, then a chemical potential/potential difference is developed between the rod surfaces and the solution, this potential difference depends upon concentration of solution, nature of metal and temperature.

If two such electrodes are electrically connected to complete the circuit, then it forms a galvanic cell which conducts an electric current. This phenomenon of electric current is strongly associated with electrochemical corrosion.

Thus, electrochemical corrosion occurs when-

- a) Conducting liquid is in contact with metal
- b) Two dissimilar metals are dipped in a solution

Due to this, separate the anodic and cathodic areas in which current flow through the conducting solution.

At anode, oxidation reaction takes place by loss of electron. Thus there is a tendency at anode to destroy the metal by forming metallic ions therefore corrosion always occurs at the anodic area.

At anode following reaction takes place,



On the other hand, at cathode reduction reaction takes place (gain of electrons), the dissolved constituents in the electrolyte gain this electron and form ions such as OH^- , O^{2-} etc.

Rate of electrochemical corrosion:

Rate of electrochemical corrosion depends upon the nature of corrosion product.

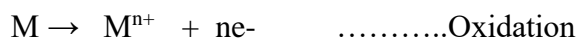
- a) If the corrosion product dissolves into the solution or evolves as a gas, then corrosion reaction goes on changing.
- b) If the corrosion product is insoluble compound, then it forms or covers the metal surface.

Therefore, decrease the rate of corrosion.

Mechanism:

Corrosion of metal in an aqueous solution is an electrochemical phenomenon in which current flows between anode and cathode areas. The reaction occurring at anode involves liberation of free electrons forming metallic ions with dissolution of metal.

Thus, at anode following reaction takes place,



At cathode, it consumes these electrons either by evolution of hydrogen or by absorption of O_2 depending upon the nature of corrosion product.



A) Evolution of Hydrogen: The evolution of H_2 takes place in the acidic solution like industrial waste, non-oxidizing acid (HCL) etc.

Let us consider the iron metal:

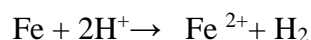
1. At anode, dissolution of iron takes place by forming ferrous ion with liberation of electrons.



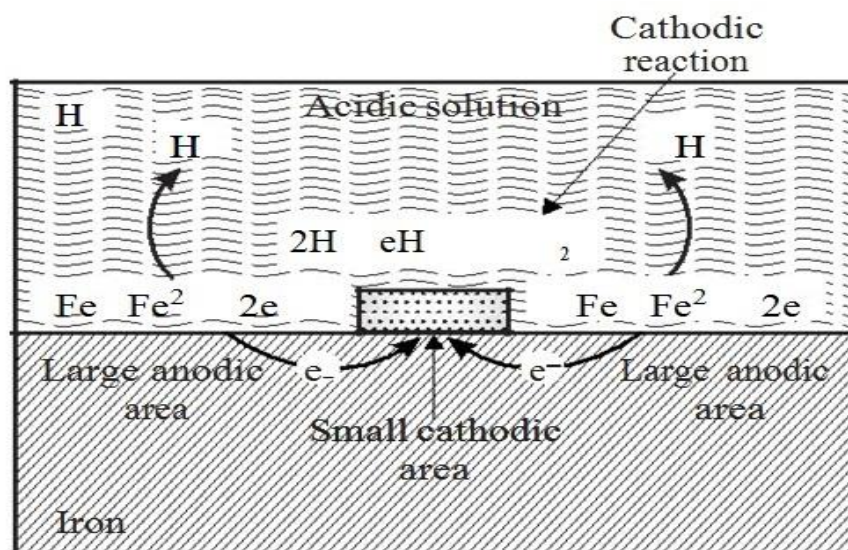
2. These liberated electron flow through the metal from anode to cathode, at cathode ,H⁺ ions in the acidic solution are liberated as hydrogen gas.



3. Overall reaction may be given as



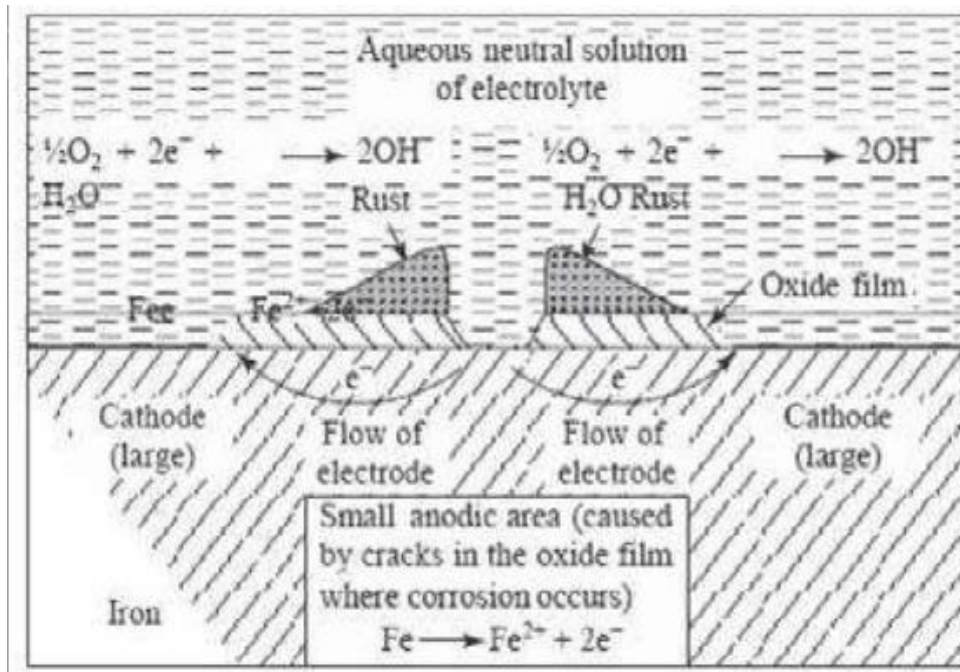
In this type of corrosion, anodes are very large areas while cathodes are very small areas. Thus in hydrogen evolution mechanism, the displacement of hydrogen ions from acidic solution by metal ions.



Generally, all metals above hydrogen in the electrochemical series are a tendency to dissolve in acidic medium with the evolution of hydrogen.

B) Absorption of Oxygen: In this process, corrosion of metal occurs in the presence of aqueous neutral solution of electrolyte (NaCl).

Let us consider the iron metal on the surface of iron, thin oxide film is obtained, however if this oxide film develops some cracks, then it forms anode areas on the surface. While remaining part of the metal acts as cathode, thus it is clear that anode areas are very small while cathode areas are very large.



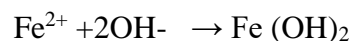
1. At anode, iron dissolves as ferrous ion with liberation of free electrons.



2. The liberated free electrons flow through the metal from anode to cathode and combines with dissolved O_2 .



3. The Fe^{2+} ions at the anode and OH^- ions at the cathode combines and ferrous hydroxide are precipitate.



4. If enough oxygen is present, then ferrous hydroxide undergoes further oxidation and ferric hydroxide is obtained.



If O_2 concentration is low, then black anhydrous compound is obtained.

Dry corrosion or Direct chemical corrosion:

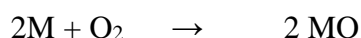
This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O₂, CO₂, H₂S, Cl₂, and Br₂, SO₂ etc. with metal or alloy surfaces.

The extent of corrosion depends on;

- (a) Chemical affinity between metal and corrosive environment.
- (b) The ability of metal to form a protective film.

Thus, the surfaces of metals are directly attacked by the atmospheric gases and get coated with corresponding compounds like Oxides, Sulphides, Chlorides, Carbonates etc. Such type of corrosion is called as direct chemical corrosion or Dry corrosion.

Generally Dry corrosion occurs due to oxygen. It has been found that oxygen present in the medium directly attacked the metal surface at low or high temperature in the absence of moisture. It is represented by this equation



When oxidation starts, a thin oxide film is formed on the surface of the metal. The nature of oxide film plays an important role in oxidation process. This film decides the prevention or continuation of corrosion.

The oxide film so produced can be classified into three categories:

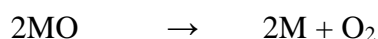
A) Stable Film:

1) Alkali and alkaline earth metals on oxidation produce oxide film of smaller volume than the respective metals from which they were formed. This results in the formation of porous film through which oxygen can diffuse to bring the further attack of the metal.

2) On the other hand, heavy metals like Al, Cr, Pb, Cu etc. form oxide film of greater volume than the metal from which they were formed. This non porous stable film prevents the diffusion of oxygen and hence the rate of further attack decreases.

B) Unstable Oxide film :

When oxide film formed is unstable then it decomposes back into the metal and oxygen.



Therefore oxidation process or corrosion is not possible in case of noble metals like Ag, Au, Pt etc.

C) Volatile Oxide Film :

When the oxide film formed is volatile , it vaporizes as soon as it is formed. Therefore, the underlying metal surface is exposed for further attack of oxygen and thus causes continuous and excessive corrosion.

e.g. Molybdenum oxide (MoO_3) is volatile.

• FACTORS AFFECTING THE RATE OF CORROSION :

The rate extent of corrosion depends upon the following factors

- 1) Nature of the metal
- 2) Nature of the corroding environment

1) Nature of the metal:

a) Position in galvanic series:

When two metals or alloys are electrically connected and exposed to an electrolyte, then metal which is higher in electrochemical series suffers from corrosion. The rate of corrosion depends upon relative difference in their electrochemical positions, Greater is the difference, and faster is the rate of corrosion.

b) Relative areas of anodic and cathodic parts:

When two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the ratios of areas of anodic and cathodic parts. The rate of corrosion is more rapid, if the anodic area is smaller because the current density at the smaller anodic area is much higher thus rapid destruction of anodic metal takes place .

c) Purity of Metal:

Impurities in a metal cause heterogeneity and form small electrochemical cell with rest of the metal. Thus anodic part gets corroded.

E.g. Zn metal containing impurity such as Pb or Fe. Zn undergoes corrosion around the impurity this is due to formation of local electrochemical cells. The rate and extent of corrosion depends upon the percentage of the impurities.

d) Solubility of corrosion product:

In electrochemical corrosion, if the corrosion product is soluble in the corroding medium the rate of corrosion increases. On the other hand, if the corrosion product is insoluble then it covers the metal surface and thus the rate of corrosion decreases.

2) Nature of the corroding environment:

a) Temperature:

As temp. increases the rate of corrosion as well as diffusion increases. But the rate of solubility of oxygen decreases. Thus corrosion generally increases with rise in environmental temperature.

b) Presence of impurities in atmosphere:

Atmospheric air contains some corrosive gases such as CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 etc. In the presence of these gases, acidity of the liquid occurs adjacent to the metal surfaces. This increases its electrical conductivity thereby increase the corrosion current following in the local electrochemical cells on the exposed metal surface.

c) Presence of suspended particles in atmosphere:

Atmospheric condition is influenced by the presence of solid particles in air.

- i) If these particles are chemically active in nature, then they absorb moisture and acts as strong electrolytes and thus increases the rate of corrosion.
- ii) If these particles are chemically inactive in nature, then they absorb both Sulphur gases and moisture and slowly enhance the rate of corrosion.

d) Effect of pH :

Generally acidic media are more corrosive than alkaline or neutral media. The corrosion of iron in oxygen free water is slow. However the corresponding corrosion rate in the presence of oxygen is much higher.

Zn suffers minimum corrosion at $\text{pH} = 11$, Al has minimum corrosion rate around $\text{pH} = 5.5$. While Tin corrodes rapidly at pH greater than 8.5.

TYPES OF CORROSION :

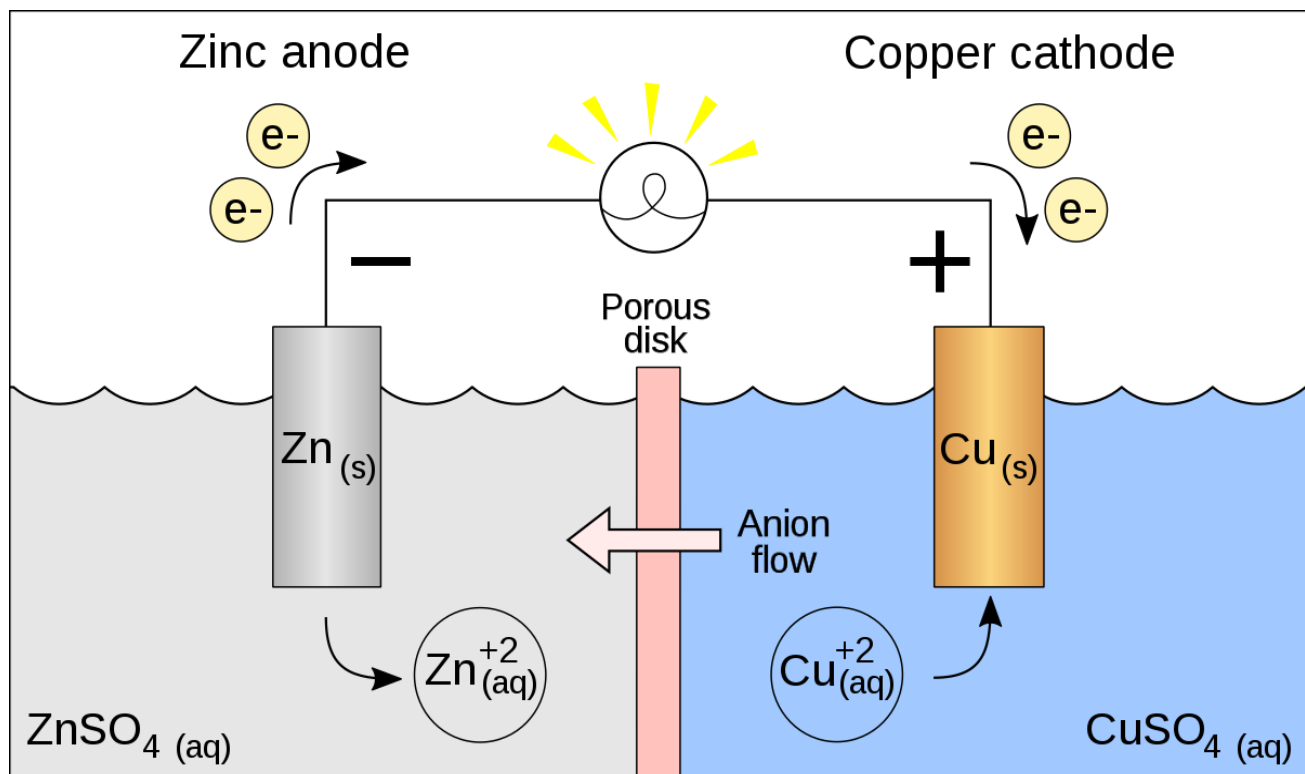
1) Galvanic Corrosion :

When there is two dissimilar metals e.g. Zn and Cu are electrically connected and exposed to an electrolytes the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called as galvanic corrosion. In the above example, Zn is higher in electrochemical series and thus forms the anode and gets dissolved in solution. Whereas, Cu which lower in electrochemical series and thus acts as cathode. The nature of corrosive environment decides the type of cathodic reaction.

In acidic solution, the corrosion occurs by H_2 evolution, oxygen absorption mechanism occurs. The electronic current flow from Zn metal to Cu metal. Thus it is clear that, corrosion occurs at the anodic metal while the cathodic area is protected from attack

e.g. 1) Lead –Antimony solder around the Cu wire.

2) Steel pipe connected to Cu plumbing.



2) Microbiological Corrosion :

Corrosion occurs by the metabolic activity of various micro-organisms is called as microbiological corrosion. The micro-organisms are formed in an environment with or without oxygen and thus they are classified as aerobic and anaerobic micro-organisms.



I) Sulphate reducing bacterias :

Sulphate reducing bacterias are responsible for anaerobic corrosion of iron and steel. Because they can grow only under anaerobic conditions. They require in addition to O_2 , adequate amount of sulphates for nourishment. Other optimum conditions for their growth are temp, which is around 25 deg. C to 30 deg. C and pH from 5 to 9. The main corrosion product is black iron sulphide and ferrous hydroxide.

II) Sulphate bacterias:

Sulphur bacterias are mostly aerobic in nature. Such bacterias oxidize Sulphur and produce sulphuric acid which attacks the metal surface. Sulphur bacterias are grow in acid conditions.

III) Iron and Manganese micro-organisms: These are aerobic micro-organisms they take iron and manganese ions and digest in the presence of O_2 and thus insoluble hydrates of iron and MnO_2 are

formed. These bacteria grow in running water at temperature from 5°C to 40°C and pH between 4 to 10.

IV) Film forming Micro-organisms:-

These include bacteria, fungus, algae etc. Film forming micro-organisms film onto the metal surface. Such films are capable of maintaining concentration gradient of dissolved salts, acid and gases onto the metal surfaces and thus local biological concentration cells are formed and consequently corrosion occurs.

METHODS TO MINIMISE THE RATE OF CORROSION :

Only under ideal service conditions corrosion can be stopped completely. However ideal condition means uniform composition without heterogeneity and absolute uniform environment are impossible to attain. Thus it is possible only to minimize the rate corrosion considerably.

Since types of corrosion are so numerous and the conditions under which corrosion occurs are so different that diverse methods are used control corrosion. The choice of the method depends upon the environmental conditions to which metal is exposed. Some of corrosion control methods describe as following:

1) Proper Designing :

A proper selection of metallic material for any particular environment and proper design is the best way of controlling corrosion. The design of the material should be such that corrosion even if it occurs, which is uniform does not result intense and localized corrosion. Important design principles are:

- a) Avoid the contacts of dissimilar metals in the presence of a corroding solution. If this principle is not taken into the consideration then corrosion occurs on the more active metal while less active metal remains protected.
- b) If two dissimilar metals in contact but they should be as close as possible to each other in the electrochemical series.
- c) Whenever the direct joining of dissimilar metal is unavoidable, then insulating fitting may be applied between them to avoid metal-metal electrical contact.

- d) The anodic metal should not be painted or coated, when in contact with a dissimilar cathodic metal, because any break or crack in the coating lead to rapid destruction.

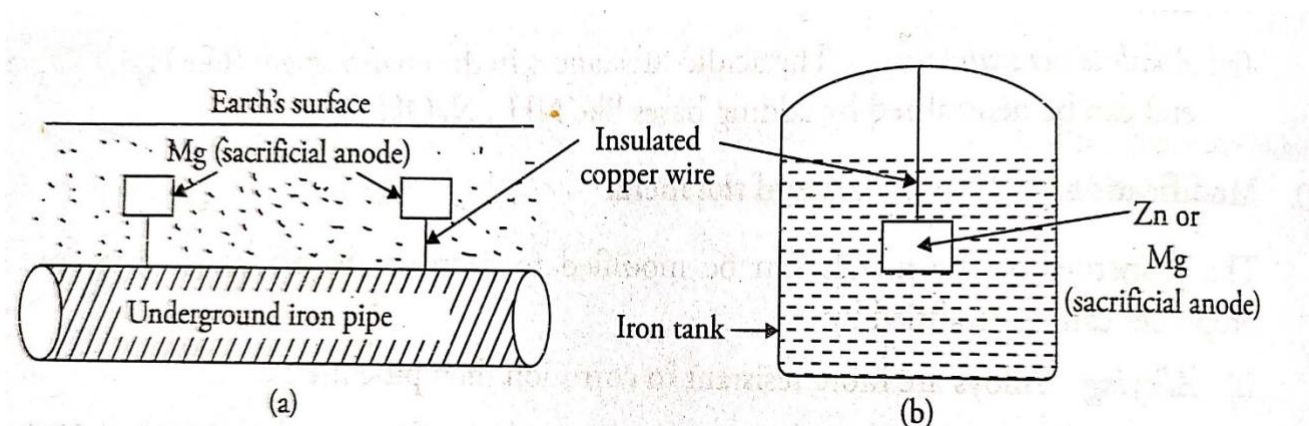
2) Cathodic Protection :

The main principle involved in this method is to force the metal to be protected to behave like a cathode. Thereby corrosion does not occur. There are two types of cathodic protections.

- a) **Sacrificial anodic protection method:** In this method the metallic structure to be protected is connected by a wire to more so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly while the parent metallic structure (which becomes cathode) is protected.

The more active metal so used is called as 'sacrificial anode'. The corroded sacrificed anode can be replaced by a fresh anode when consumed completely.

Diagram:

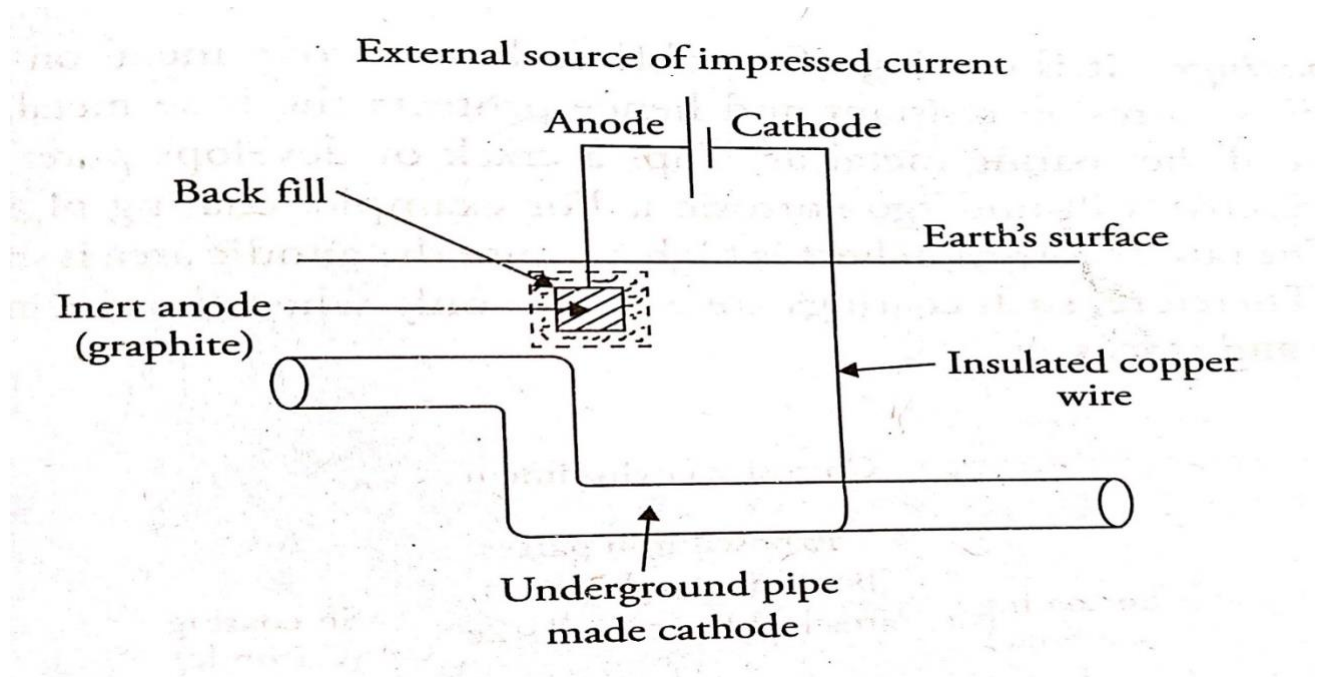


The sacrificial anode generally used are Zn, Mg, Al and their alloys. This method can be used for the protection of iron pipelines, underground cables, industrial hot water tanks etc.

b) Impressed current cathodic protection :

In this method an impressed current is passing in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Generally D.C. source is used to pass impressed current with an insoluble anodes like Graphite, Stainless steel, Platinum etc.

Diagram:



A sufficient direct current is applied to an insoluble anode immersed in the corroding medium, connected to the metallic structure which is to be protected. This type of cathodic protection can be used in water box coolers, water tanks, pipeline, condenser etc.