



BansilalRamnathAgarwal Charitable Trust's

VISHWAKARMA INSTITUTE OF INFORMATION TECHNOLOGY

Department of Engineering & Applied Sciences

F.Y.B.Tech

Course Material (A brief reference version for students)

Course: Engineering Chemistry

Unit 4: Corrosion Science (AY 2020-21)

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Unit 4 - Corrosion Science

Objective: To study corrosion of metals and methods for its prevention

Contents:

Introduction, Types of corrosion, Mechanism of chemical and electrochemical corrosion,

Galvanic corrosion and Concentration cell corrosion,

Factors influencing corrosion- nature of metal, nature of environment,

Methods of corrosion control: cathodic and anodic protection

Protective coatings: surface preparation, types of protective coatings: a) metallic coatings: types of coatings, methods of applications, (hot dipping, cladding, electroplating & cementation), electro less coatings, b) non-metallic coatings: chemical conversion coatings, powder coatings
Practical problems of corrosion

4.1 Introduction

Any iron article if exposed to moist air, gets rusted or if brass article is exposed to atmosphere gets covered with green oxide film. These common observations are due to natural phenomena called corrosion. The chemical or electrochemical reactions between metals and environment that includes air, water, sea water, acid, alkali, gas etc. leads to corrosion. These reactions occur at different rate, at different temperature and give rise to different forms of products consuming metal. This consumption of metal slowly leads to decay or deterioration of metals.

Corrosion

Corrosion is a general term that refers to the deterioration or destruction of metal.

The destruction of a metal by chemical or electrochemical attack of environment, starting at surface, is known as corrosion.

Although corrosion is slow, still the losses due to corrosion are over 2500 million dollars per annum. The problem of corrosion of metals is severe in the localities rich with humidity.

- To control the problem of corrosion of metals, one should know completely the mechanism of corrosion under different situations and the various factors responsible for corrosion.
- It may be noted that steels (iron-carbon alloys) are used commonly and on large scale for various metallic designs and the steels have no any natural way of protection mechanism to save from corrosion. Therefore our discussion will be more pertinent to steel regarding corrosion and corrosion control.

4.2 Types of corrosion

Corrosion of metal occurs in many ways depending upon the environment.

On the basis of corrosive environment, corrosion is classified into two ways –

I) Direct chemical or Dry or Atmospheric corrosion: It occurs due to chemical reaction between metal and atmospheric gases to which it is exposed.

II) Electrochemical or Wet or Immersed corrosion: It occurs due to electrochemical reaction between metal and electrolyte which can be an aqueous salt solution, acid or alkali.

4.3 Dry or Direct chemical or Atmospheric corrosion

This type of corrosion occurs due to direct attack of atmospheric gases like oxygen, carbon dioxide, sulphur dioxide, hydrogen sulphide, moisture, ammonia, chlorine, nitrogen oxides, etc and by hot flowing liquids.

Rate of this type of corrosion depends upon:

- i) Temperature
- ii) Chemical affinity between metal and gas
- iii) Nature of oxide film on surface of metal.

- At higher temperature, the corrosion takes place faster. If the metal is higher placed in galvanic series, it is chemically active and gets corroded rapidly by the gases in atmosphere. Further some gases are more reactive than others e.g. H_2S is more reactive than O_2 and CO_2 .
- If surface of metal or alloy is attacked by oxygen then further corrosion of the underlying metal depends upon the nature of oxide film formed on the surface of metal.
- If the film is porous, then corrosion continues and if film is non porous, strong, well adhered then further corrosion stops.
- It is also found that gases like O_2 , CO_2 , are less active in the absence of moisture.
- The flowing hot liquids corrode the pipes or pots by chemical reaction or dissolution, combined with **erosion**.

4.3.1 Mechanism of Corrosion by Oxygen

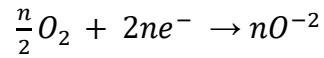
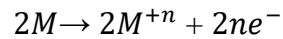
Amongst the corroding gases oxygen is largest in amount in atmosphere and it is present everywhere. Gases like H_2S , NH_3 , SO_2 , N_2O are not in large amounts and they are present in considerable amounts in some localities i.e. areas nearby gutters, industries, laboratories, waste disposal areas etc.

Oxidation corrosion is brought about by direct action of oxygen on metal surface at low or high temperature usually in absence of moisture.

The corrosion of metal/alloy, by oxygen takes place in following steps:

- i) Adsorption of O_2 molecules on metal surface.
- ii) Dissociation of O_2 molecule into atoms.
- iii) Loss of electrons by metal atom (being electropositive) to oxygen atom, resulting in the formation of metal ion and oxide ion.

iv) Formation of metal oxide by union of the ions, and leading finally to form thin layer or film of metal oxide on the surface of metal.



Iron forms Fe_2O_3 , chromium forms Cr_2O_3 , zinc forms ZnO , aluminium forms Al_2O_3 , copper forms CuO , on corrosion by oxygen.

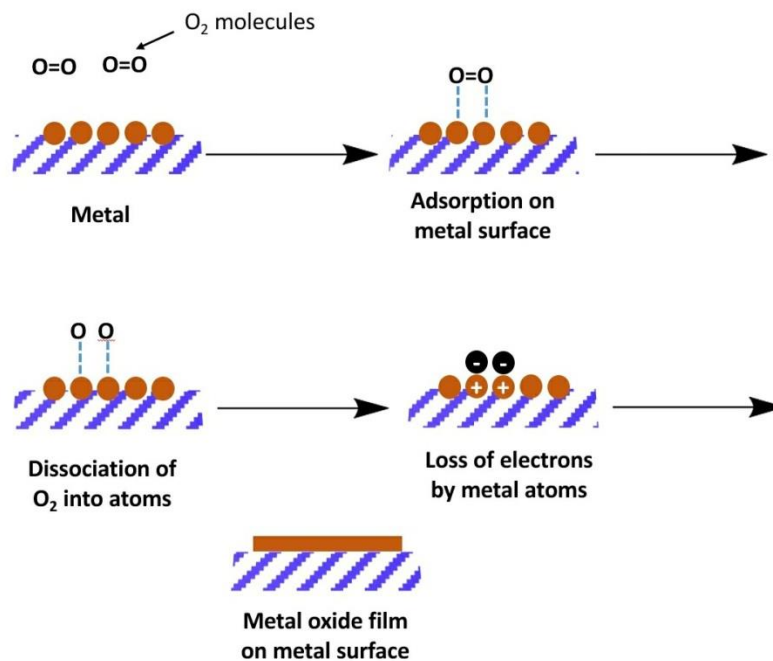


Fig. : Mechanism of O_2 attack

Nature of Oxide Film

The nature of oxide film plays an important part in the further corrosion to continue or not. Oxide films occur in following forms:

i) Porous film

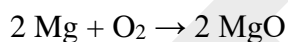
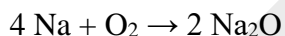
ii) Non porous film

iii) Unstable oxide film

iv) Volatile oxide film

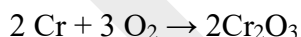
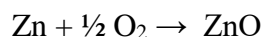
i) Porous film:

If the oxide film is porous, then through the pores, oxygen gas molecules penetrate and **continue** the corrosion of the underlying metal until whole metal gets destructed. e.g. oxide films of **iron(steel), magnesium, sodium, potassium, calcium** metals are porous.



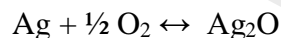
ii) Non porous film:

If the oxide film is stable, nonporous, strong, well adhered to the metal surface and self-healing, then further corrosion **stops**, as the oxide film formed after some initial corrosion of surface, acts as a barrier and detaches the underlying metal from the corroding oxygen or other gases. Various metals can safeguard themselves by such impervious metal oxide films e.g. **chromium, tin, zinc, lead, aluminium, nickel, copper, stainless steels, bronze, aluminium alloys**, etc.



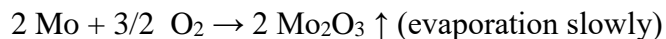
iii) Unstable oxide film:

When the oxide film formed is unstable and it decomposes back into the metal and oxygen, then there is no corrosion taking place. e.g. metals like **gold, platinum and silver**.



iv) Volatile oxide film:

If the metal oxide film is volatile, then its evaporation takes place simultaneously. The underlying fresh metal is exposed for the further attack by oxygen. e.g. molybdenum oxide (Mo_2O_3) film is volatile.



Pilling Bedworth Rule:

It states as

Oxide film is nonporous if the volume of oxide is more than volume of metal consumed for oxide formation

Oxide film is porous if volume of oxide formed is less than volume of metal consumed.

Pilling Bedworth Rule takes into consideration **Pilling Bedworth Ratio (PBR)**

$$\text{Pilling – Bedworth Ratio(P. B. R.)} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal consumed}}$$

Relation of PBR and nature of oxide film:

- $\text{PBR} < 1$: the oxide coating layer is too thin, likely broken and provides no protective effect. e. g. Mg
- $\text{PBR} > 2$: the oxide coating peels off and provides no protective effect. e.g Fe
- $1 < \text{PBR} < 2$: the oxide coating is passivating and provides a protecting effect against further surface oxidation. e.g. Al, Ti, Cr

4.3.2 Corrosion by Other Gases

i) Halogens/ Chlorine :

Chlorine attacks the metals to form metal chlorides. The metal chloride deposited on surface is generally forms a porous film. Dry chlorine gas has slower action but the presence of moisture enhances the corrosion, with of formation of HCl. Zirconium is resistant to dry Cl_2 but not to wet chlorine gas and titanium is more resistant to wet chlorine but not to dry chlorine, silver, gold, platinum resist the action of halogens at ordinary temperature but are attacked at higher temperatures than 100°C . Al and Mg form protective fluoride films. First row transition metals except iron and chromium are resistant to halogens.

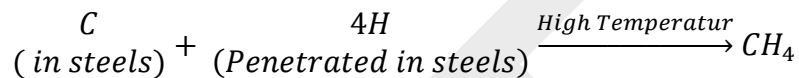
ii) Corrosion by gases containing sulphur:

Such gases are SO_2 , SO_3 , H_2S , etc. Attack of these gases on metals, particularly at higher temperatures has become a problem. Fossil fuels (coal, crude oil) contain sulphur compounds and the corrosive gases of sulphur are produced by combustion of the fuels. These gases attack the machinery, metal of refinery, and cracking units. Gaseous sulphur also corrodes the metals. H_2S , SO_2 and SO_3 are acidic gas and they are more corrosive in the presence of moisture. Nickel is highly susceptible to attack by H_2S , SO_2 .

iii) Decarburization and hydrogen embrittlement:

a) Decarburization:

The gas streams from refinery, cracking systems, combustion of oil, etc. at high temperature are mixture of gases containing certain amount of H_2 . The H_2 at high temperature penetrates into steel, stainless steel, in the form of atomic hydrogen. This atomic H reacts with the carbon or carbide which is used to strengthen the metal; to form CH_4 . The process of removal of carbon or carbide from the metal by action of hydrogen, at higher temperatures, is called as decarburisation. Decarburisation of steels or stainless steels results in decreasing the mechanical strength.



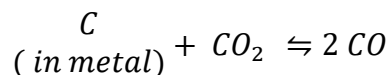
The CH_4 deposits in the internal voids in the steel, decreases cohesive force between iron atoms, produces minor cracks in steel. The reverse process, carburization, can also occur in H_2 – hydrocarbon gas mixture, at high temperature in petroleum refining operations. Chromium and Mo additions to Fe for increasing strength is preferable rather than carbon or carbide alloying, if the metal is to be used at high temperature and in contact with H_2 .

b) H_2 embrittlement:

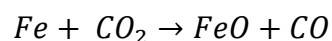
At room temperature, the hydrogen penetrates within the metal in voids or intergranular space or at the crack tip, leading to localized weakening and lowering the cohesive strength. The cracks propagate by mechanical fracture of the weakened region, **This breaking of metal at weakened region by H_2 accumulation in metal, is known as hydrogen embrittlement.**

iv) CO and CO_2

CO_2 and other carbonaceous gases are frequently encountered in petroleum refining and during combustion of fuels. A CO – CO_2 atmosphere is capable of decarburing or carburing steels and other alloys, at high temperature.



CO_2 can attack iron very slowly



In the presence of moisture, the acidic CO_2 can corrode the metal faster, to form finally metal carbonate.

v) By liquid metals:

The attack of a liquid metal on other metals is primarily a physical effect. The effect happens by,

- i) Dissolution of metal in liquid metal.
- ii) Diffusion of liquid metal into the solid metal.
- iii) Formation of intermetallic compound (surface reaction or subsurface precipitation).

4.4 Mechanism of Wet or Electrochemical or Immersed Corrosion

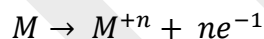
Corrosion of a metal by aqueous conducting medium, with the formation of anodic and cathodic areas, is known as wet or electrochemical or immersed corrosion.

Wet corrosion occurs under following conditions:

1. When conducting liquid is in contact with metal
2. When 2 dissimilar metals are immersed or single metal is dipped partially, in aqueous solution of acid, base or salt and involve transfer of electrons

Electrochemical corrosion involves flow of electrons between anodic and cathodic areas. The anodic reaction involves dissolution of metal as corresponding metal ions with liberation of electrons.

Anodic reaction :



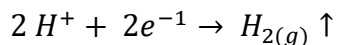
The electrons liberated flow from anode to cathode through an electrolyte.

The electrons which flow towards cathode are responsible for the reaction at cathode which depend upon the nature of environment.

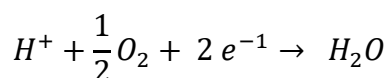
Cathodic reaction:

i) In acidic medium (Absence of oxygen)

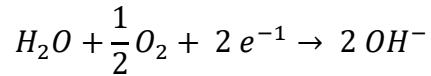
Hydrogen ions combine with electrons and form hydrogen gas.



ii) In acidic medium (Presence of oxygen)



iii) In neutral or alkaline medium (Presence of oxygen) : Dissolved oxygen combines with electrons and forms hydroxyl ions.



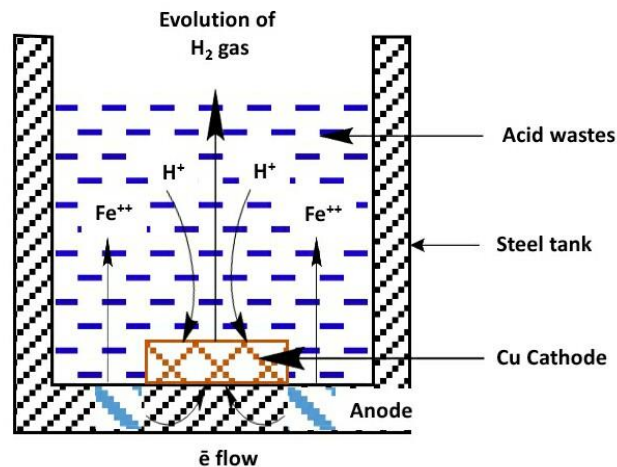
Electrochemical corrosion involves any one of the following two mechanisms depending upon the nature of environment

I) Hydrogen evolution mechanism II) Oxygen absorption mechanism.

4.4.1 Hydrogen evolution mechanism:

This type of electrochemical corrosion occurs usually in acidic environment like industrial waste, solution of non-oxidising acids.

For example, a steel tank containing acid industrial waste and a small copper scrap are in contact is considered. Refer to Fig.

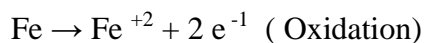


The piece of copper and steel tank in contact with each other in presence of acidic electrolyte form electrochemical cell. In this cell, steel act as anode and copper act as cathode. It is observed that the steel tank portion in contact with copper piece is corroded.

This can be explained on the basis of following reactions.

At anode: At steel tank

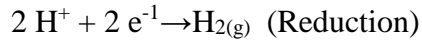
Iron passes into solution as Fe⁺² ions.



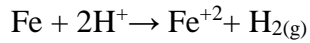
The free electrons are accumulated at cathode.

At cathode: At copper piece

Hydrogen ions from acidic electrolyte take up the free electrons and hydrogen gas formed is liberated in the form of bubbles at cathode.



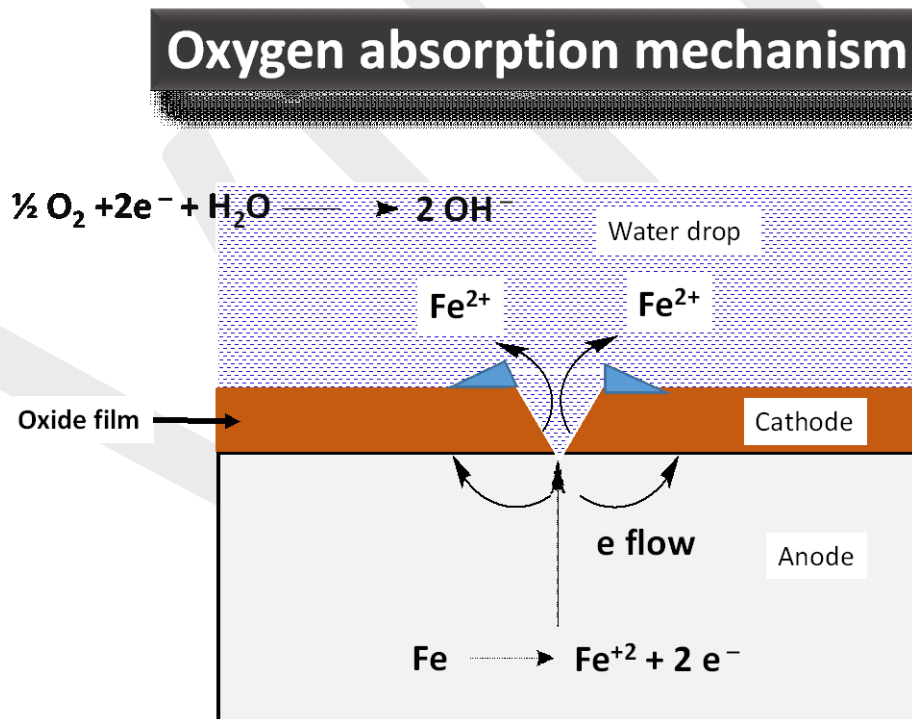
Net cell reaction:



4.4.2 Oxygen absorption mechanism:

This type of electrochemical corrosion occurs when electrolyte is neutral aqueous solution or alkaline solution containing dissolved oxygen.

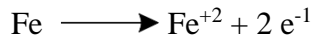
For example, consider a steel plate lying on the ground and is exposed to the atmosphere. In due course of time, oxide layer will form on the surface of the steel plate and drops of water may be collected over a small crack on the oxide film present on the surface of steel as shown in fig. In this case water act as an electrolyte, iron plate underlying through the crack act as anode where as scale on steel surface act as cathode.



Reactions involved in this type of corrosion at anode and cathode are as follows:

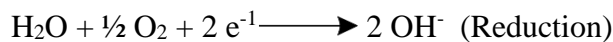
At anode:

The steel goes into solution as ferrous ions(Fe^{+2})

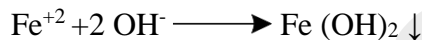


At cathode:

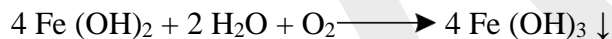
The electrons flow from anode to cathode that is from crack to the oxide scale on the surface of steel plate. These electrons are interrupted by dissolved oxygen present in the electrolyte, forming hydroxyl ions as follows.



The Fe^{+2} ions at anode and OH^{-} ions at cathode diffuse and combine to form ferrous hydroxide. It is observed that outward diffusion of Fe^{+2} ions is more rapid as they have small size as compare to OH^{-} ions. Therefore although corrosion takes place at anode, rust deposition takes place at cathode.



If enough oxygen is present in the electrolyte, ferrous hydroxide is easily oxidized to ferric hydroxide.



If supply of oxygen is limited, the corrosion product may be black anhydrous Fe_3O_4 .

It should be noted that, increase in dissolved oxygen content of electrolyte has two effects on corrosion reaction.

- i) It forces the cathodic reaction to the right i.e. producing more OH^{-} ions.
- ii) It removes more electrons and therefore accelerate the corrosion at the anode.

In oxygen absorption reaction mechanism of corrosion, cathodes usually have larger area than anode.

4.5 Different Forms of Wet Corrosion:

I) Galvanic corrosion:

Galvanic corrosion

Two dissimilar metals in contact and exposed to electrolyte

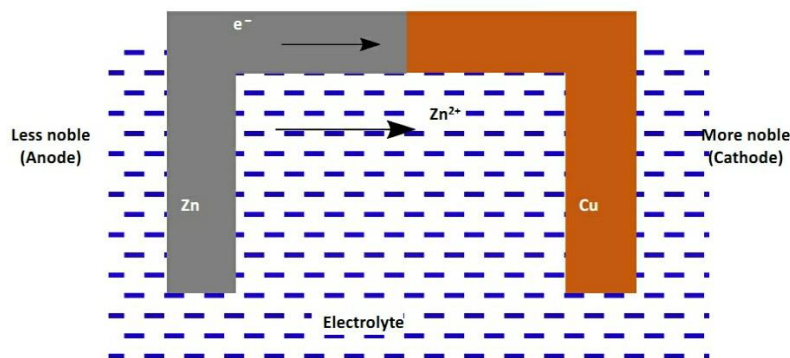


Fig. Galvanic corrosion

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.

For example, when two metals, zinc and copper are electrically connected and exposed to an electrolyte. Zinc being less noble metal will dissolve and act as anode, whereas copper being more noble metal, will act as the cathode. The nature of the corrosive environment decides the type of cathodic reactions.

Common examples of galvanic corrosion:

- Rusting of fencing wire under joints.
- Copper sheets joined by iron nails.
- Steel pipe connected to copper plumbing.
- Lead-antimony solder around copper wire.

II) Concentration cell corrosion:

This type of corrosion occurs when a single piece of metal is exposed to an electrolyte of varying concentration or varying aeration.

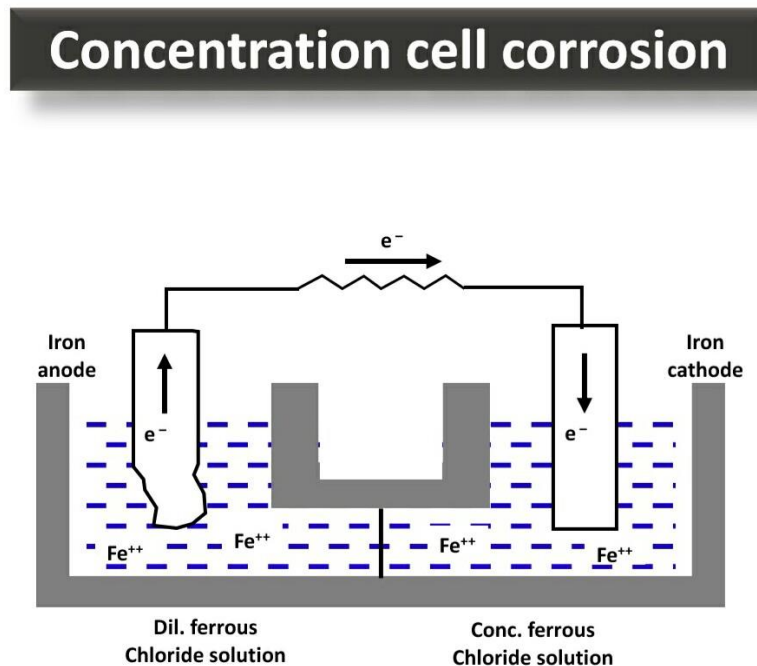
Concentration cells are of two types:

1. Metal-ion concentration cell
2. Oxygen concentration cell

1. Metal ion concentration cell corrosion:

The electrode potential of a metal depends upon the electrolyte results in the potential difference of the two electrodes. Electrode potential of metal in dilute solution is more negative than in a concentrated solution. The metal ion concentration in the electrolyte vary due to insufficient agitation or slow diffusion of metal ions produced by corrosion.

When two electrodes of the same metal are immersed into two solutions of different concentrations of same electrolyte are joined externally, they form a metal ion concentration cell as shown in fig.



In fig. it is noted that two iron electrodes are dipped in electrolyte of ferric chloride having varying concentration i.e. one iron rod is dipped in dilute ferric chloride and other in

concentrated ferric chloride solution. It is noted that iron electrode dipped in low concentration of Fe^{+2} ions become anode and undergoes corrosion. The electrons flow to other side of the cell towards cathode. The electrode dipped in concentrated solution of ferrous ions (Fe^{+2} ions) becomes cathode and is protected.

This type of corrosion is very common in chemical plant.

2. Oxygen concentration cell corrosion:

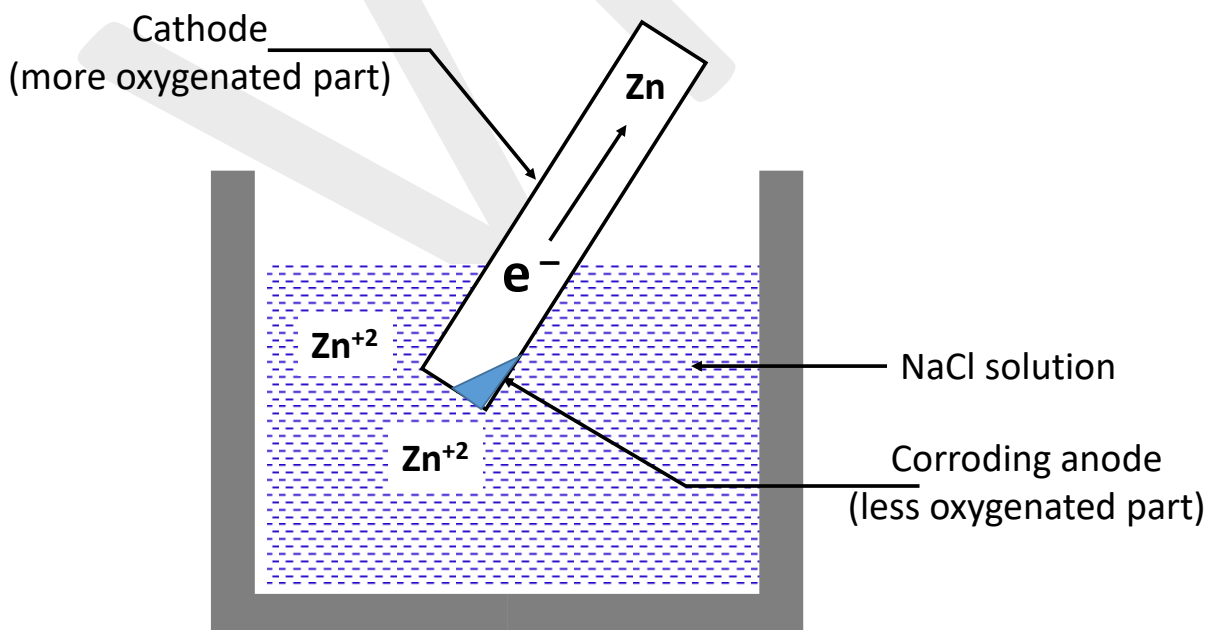
The electrode potential of a metal depends upon the aeration of the electrolyte surrounding the electrode. That is when two parts of the same metal are exposed to different aeration, then the potential difference is caused due to differential aeration. Electrode potential of a less aerated part on the metal is more negative than that of a more aerated part on the metal. Thus, less aerated part on the metal behaves as anode and more aerated part behaves as cathode (as shown in figure). At anode, metal dissolves forming metal ions and liberate electrons as



The electrons so released flow to cathode through electrolyte. Depending on nature of electrolyte, cathodic reaction occurs.

Common examples are:

- Buried electrical pole
- Lower part of ship hull
- Cross over of fencing wires



Difference in dry corrosion and wet corrosion:

Sr. No.	Dry corrosion	Wet corrosion
1	It occurs in dry conditions.	It occurs in wet conditions such as presence of electrolyte or moisture.
2	It takes place by direct chemical attack of atmospheric gases such as O ₂ , CO ₂ , Cl ₂ , H ₂ S, SO ₂ .	It takes place by electrochemical attack of corrosive environment on the surface of metal. This involves setting up of a large number of galvanic cells.
3	Corrosion is uniform.	Corrosion is non-uniform. When anodic area is small, pitting corrosion takes place more frequently.
4	It is a slow process.	It is a fast process.
5	It involves chemical reactions of atmospheric gases.	It involves electrochemical reactions.
6	Corrosion products accumulate at the place where corrosion occurs.	Corrosion take place at anode but products accumulate near the cathode.

4.6 Factors influencing corrosion

The rate and extent of corrosion, depends upon the following two main factors.

I) Nature of metal and II) Nature of environment

4.6.1 Nature of Metal

i) Position of metal in galvanic series:

- When two metals or alloys are in electrical contact in a conducting medium, then the higher placed metal/ alloy in galvanic series (more active) acts as anode and get corroded.
- The rate and severity of corrosion further depends upon their difference in positions. More the metals are apart in galvanic series faster is the corrosion of anodic metal and more is the current generated during corrosion. Dry corrosion is also faster in more active metals.

ii) Relative areas of anode and cathode:

- If the ratio of cathodic area to anodic area is greater, then the rate of wet corrosion is faster, severe and localised on anodic area.
- Relatively larger cathode area has high demand for electrons and it can be met by smaller anode only by undergoing rapid corrosion.

- Hence a better design by use of two metals is the one in which anodic area is much larger than cathodic area i.e. the metal lower placed in galvanic series is used on smaller proportion than the metal placed higher in galvanic series.

iii) Purity of metal:

- Impurities in metal form large number of minute or tiny galvanic cells when there is conducting medium around the impure metal.
- If the impurity is passive (lower position in galvanic series) then the metal undergoes corrosion but if impurity is more active, then faster corrosion of impurity takes place with small pits with small pits formation on surface, due to local action.

However, most of the alloys are homogeneous solid solutions and do not suffer corrosion by the tiny galvanic cells formation.

iv) Physical state of metal:

- Smaller the grain size of the metal or alloy, greater is the found the rate of corrosion (wet or dry) e.g. steels get corroded more easily than cast irons because grains in steels are of smaller size.
- Further, areas under stress in the same metal, tend to be anodic.

v) Nature of oxide film:

- If the oxide film formed on metal surface is protective, nonporous, strongly adhered, then neither dry corrosion nor electrochemical corrosion will take place.
- But if the film is porous, loosely adhered (steels) then the corrosion of the metal takes place until complete destruction, by dry or wet mechanism.

vi) Over voltage:

- In the case of metals having higher position in EMF series than hydrogen, the corrosion of the metal in acidic medium liberates hydrogen gas.
- The tiny bubbles of the hydrogen gas adhere to the metal surface and the acidic solution is not in well contact of the metal. This fact leads to decrease in the rate of corrosion of metal after initial corrosion reaction begins.
- In other words, such metal develops corrosion resistance to some extent or the metal behaves as if it is placed lower than its actual position in EMF series.
- To restore the position of metal, some extra voltage is necessary. This extra voltage is known as 'overvoltage'.

- However all metals do not have hydrogen adsorption and their corrosion takes place in usual way. The metals having the ‘overvoltage’ nature are, zinc, lead, chromium, nickel, etc.
- The rate of corrosion depends upon the value of overvoltage. Higher the over voltage, slower or lesser is the corrosion.

4.6.2 Nature of environment

i) Temperature:

- The rate of atmospheric or dry corrosion is faster at higher temperature because the attacking gas as well as metal get activated at the higher temperature.
- In the case of electrochemical corrosion, the corrosion of anode depends upon the temperature. As per Nernst’s equation for electrode potential, the potential of a metal is higher at higher temperature. Hence rate of electrochemical corrosion increases with increase of temperature.

ii) Moisture:

- The corrosion of metal is fast in humid atmosphere than in dry atmosphere.
- High relative humidity, fog, mist in air provides the aqueous conducting medium and causes galvanic or differential aeration cells formation. The rate of corrosion (anodic part) by cells formation is fast. Moisture in soil, water, aqueous solutions also causes such cells formation and corrosion of metals.

iii) pH:

- Generally acidic media have more corrosive effect on metals. Amphoteric metals are more attacked by alkaline media Al, Zn, Pb, etc. in general. Corrosion of iron or steel is minimum at pH 5.0 in the oxygen free water and at lower pH its corrosion rate increases.
- Zn gets minimum corroded at pH 11, tin gets minimum corroded at pH 8.5, Al gets corroded minimum at 5.5 pH. Thus every metal gets corroded minimum at certain pH medium and at the pH of medium higher or lower than that, the corrosion of the metal is faster.

iv) Conductivity of corroding medium:

- Higher the electrical conductivity of the soil, water or any aqueous corroding medium, higher is the rate of the electrochemical corrosion.

v) Nature of ions in medium:

- The Cl^- , NO_3^- like ions ability to break the nonporous oxide films on metals surface and cause enhanced wet corrosion.
- On the contrary the presence of oxalate ions, phosphate ions, silicate ions etc. have ability to slow down the rate of wet corrosion.

4.7 Methods of corrosion control

There are various methods of corrosion control. Any one method, most suitable is adopted for the corrosion control of a metal.

A) Cathodic protection :

- Sacrificial anodic protection
- Impressed current cathodic protection

B) Anodic protection

C) Metallic coatings:

- Hotdipping (Galvanising, Tinning)
- Electroplating
- Cladding
- Cementation

D) Chemical conversion coatings (inorganic coatings)

- Anodized coating
- Chemical Oxide coating
- Phosphate coating
- Chromate coating

E) Powder coating

4.7.1 Cathodic protection:

Principle:

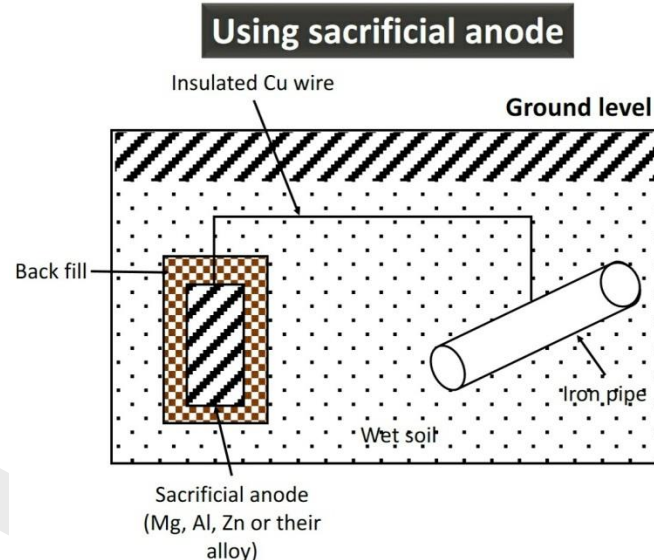
Principle of this method is, the metal to be protected is forced to behave as cathode. There are two ways of doing so:

- i) Using sacrificial anode
- ii) Using impressed current

I) Using Sacrificial Anode (Sacrificial anodic protection/Galvanic protection)

(i) Method:

The metallic structure to be protected from corrosion is connected to anodic metal (active) by an insulated wire. The more active metal like Zn, Al, Mg, etc. acts as anode and gets corroded, protecting the main metal, hence it is called as sacrificial anode. For the purpose of increasing electrical contact, the active metal is placed in back fill (coal and NaCl). When the sacrificial metal is consumed completely, it is replaced by fresh piece.



(ii) Application: Method can be used for protection of

- Buried steel pipelines
- Ship hull
- Hot water tanks
- Buried cables, etc.

(iii) Advantages of Sacrificial anodic protection:

- No external power is required
- Easy to install
- Anodes can be readily added

- Minimum maintenance is required

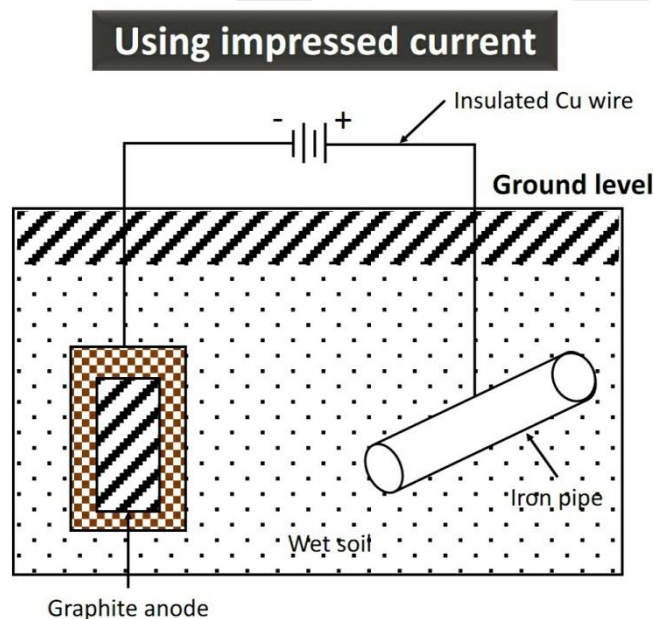
(iv) Limitations:

- Limited driving potential
- Poorly coated structures may require many anodes
- Can be ineffective in high resistivity environment

II) Using Impressed Current (Impressed current cathodic protection)

(i) 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 derived from a D.C. Source and given to insoluble anode like graphite, stainless steel or scrap iron, buried in soil. The negative terminal of D.C. is connected to pipeline to be protected. The anode is kept in back – fill (composed of gypsum or coke breeze), to increase electrical contact with surrounding soil.



(ii) Applications:

This type of cathodic protection is applicable to :

- Open water box coolers
- Water tanks
- Buried water or gas pipeline
- Condensers

- Transmission line towers
- Laid – up ships
- Marine piers, etc.

This method is particularly useful where current requirements and resistivity are high. This is suited to large structures and long operation.

(iii) Advantages of Impressed current cathodic protection:

- Large structures can be protected for long term operations
- Can be designed for wide range of voltage and current
- Can be applied in high resistivity environment
- Effective in protecting uncoated and poorly coated structures

(iv) Limitations:

- Require periodic maintenance
- Require external power
- Over protection can cause coating damage
- Are subject to power failure

Limitations of Cathodic Protection

- High capital investment and maintenance costs.
- Because of stray currents, a pipe line or metallic installation near by the protected metallic structure, gets corroded rapidly.
- Special care needs to be taken to see the structure is not over protected, otherwise problems associated to H_2 liberation or OH^- formation are more.

4.7.2 Anodic protection

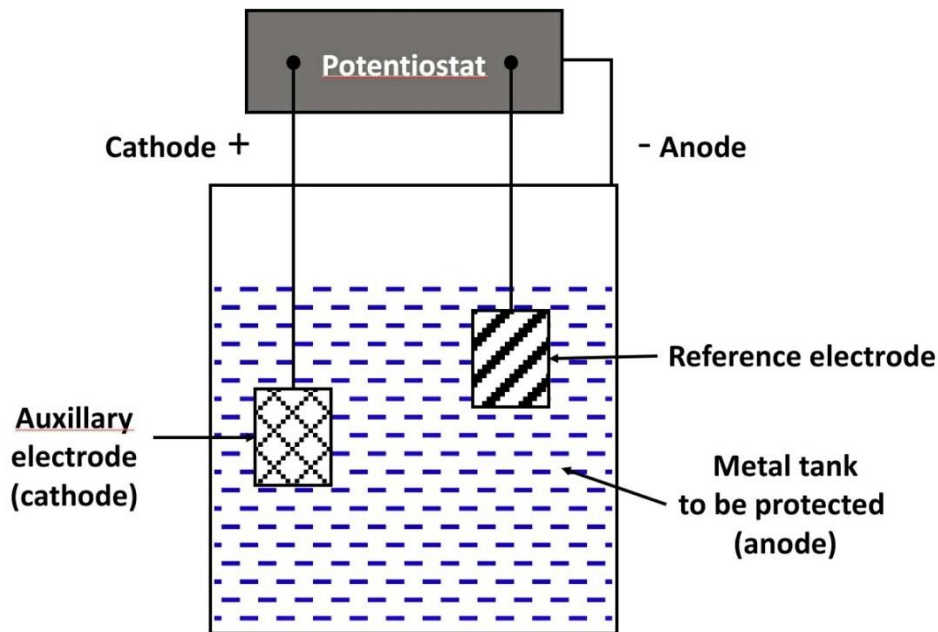
Principle:

A metal or alloy having wider range of passivity voltage, is made anodic and the voltage in the passivity range is applied over it to control its corrosion even by strongly corroding media

In anodic protection method, the metal to be protected from corrosion is made more anodic by applying external impressed direct current in the same direction as that of corrosion current, thus making it more anodic. As a result, a thin oxide film is formed which protects the surface from further corrosion.

Construction and Working:

- The metallic installation (reactor, water tank, industrial water coolers, industrial condensers, etc.) is made anodic by use of reference electrode (calomel electrode) and auxiliary electrode (platinum) which does not suffer much corrosion, acts as the cathode, as shown in fig.
- There is potentiostat for applying the desired voltage and an ammeter to watch the corrosion current. The potentiostat is adjusted for particular current and potential so that anodic metal tank gets oxidized and gets passivated. There is a formation of thin corrosion resistant oxide layer which protects metal from corrosion. Once metal becomes passive, current reduces. The minimum or negligible current indicates that anodic protection is taking place successfully.



- If system goes out of the corrosion control any time, the corrosion current will be high and the electrical connections are removed immediately.

Applications:

- Chemical reactors
- Complex metallic installations on ground or under sea water
- Industrial water coolers
- Industrial metal condensers
- Pipe lines for carrying corrosive liquids or solutions etc.

Advantages:

- Low operating cost
- Applicable to highly corrosive media
- Reliable to protect complex structures
- Feasibility of method can be predicted in laboratory
- Protection current gives idea about corrosion rate

Limitations:

- Applicable to only those metals which show active – passivity
- High installation cost
- High starting current required
- In case system goes out of control, then very high corrosion rate occurs

Comparison of Cathodic and Anodic Protection:

Sr.No.	Cathodic protection	Anodic protection
1	Method applicable to all metals	Method applicable to only those metals which show active – passivity
2	Used for metal protection in less electrical conductance of environment	Useful for metal protection in highly conducting environments
3	Installation cost low	Installation cost higher
4	Operating cost higher	Operating cost lower
5	If system goes out of control, slower corrosion of metal	If system goes out of control quite fast corrosion of metal
6	Feasibility can not be predicted by laboratory experiments	Feasibility and design can be predicted by laboratory experiments

4.7.3 Application of Protective Coating

Metals can also be protected by coating their surface with some protective material. A coated surface isolates the underlying metal from the corrosive environment. The metal to be coated is called base metal while the protective material is called coating.

Protective coating can be metallic or nonmetallic.

Surface treatment –

Long life of any protective coating on metal surface can be achieved when the metallic surface is well cleaned and properly treated before application of coating material.

Surface treatment involves 3 steps –

- a) Removal of grease and other contaminations

b) Removal of oxide scale, rust and corrosion products

c) Etching treatment for better adhesion of coat.

The surface of the base metal should be clean and somewhat rough.

Metal surface should be cleaned and prepared before coating in the following ways:

i) **Solvent cleaning** is made to remove oily/ greasy matter by use of organic solvents or detergents.

ii) **Alkali cleanings** are used to remove old coatings, some type of rusts, by use of alkali solution or Na_3PO_4 , followed by **acid cleaning and finally water washing and drying**.

iii) **Mechanical cleaning** is employed to remove rust by use of wire- brushes abrasives, scrapers, grinders, etc.

iv) **Flame cleaning** is made to remove loose scale and moisture, followed by wire brushing.

v) **Sand blasting** is used to remove loose scales particularly when roughened surface is required. The operation consists of impact of high pressure sand on hot surface.

vi) **Pickling** is immersing the metal in acidic or alkaline solution to provide clean, smooth coating

4.7.3.1 Metallic Coatings

Protective coatings of metals function as a barrier between coated metal and environment. Before applying a thin coat of a corrosion resistant metal (**coating metal**) on the surface of the metal which is to be protected from corrosion (**base metal** or coated metal), the surface of the metal coated should be thoroughly prepared by surface cleaning.

Metallic coatings are of two types:

(i) Anodic coatings

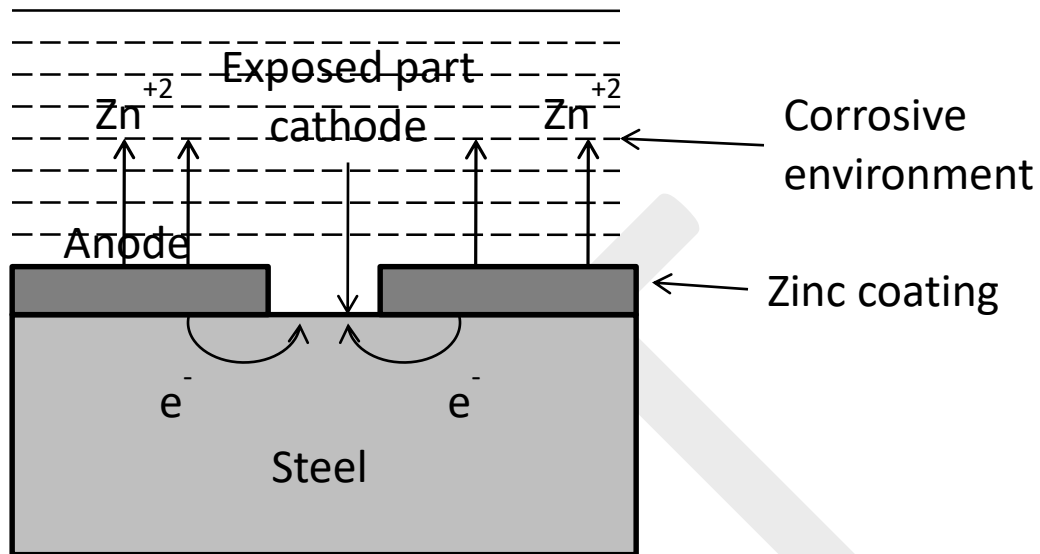
(ii) Cathodic coatings

(i) Anodic coatings/ Sacrificial coatings

- **If the coating metal is higher placed in galvanic series than the base metal, then the coating is called as anodic coating.** e.g. Zn, Al, Cr coated on steel.
- If any pores, breaks, or discontinuities occur in such anodic coating and there is a conducting medium around it, then a galvanic cell sets up. In the galvanic cell, coating metal being anode, starts getting corroded. As long as the coating metal is on surface, the base metal remains protected. As, even after the coating gets ruptured, the base metal

does not get corroded, therefore, **the anodic coatings are preferred over cathodic coatings.**

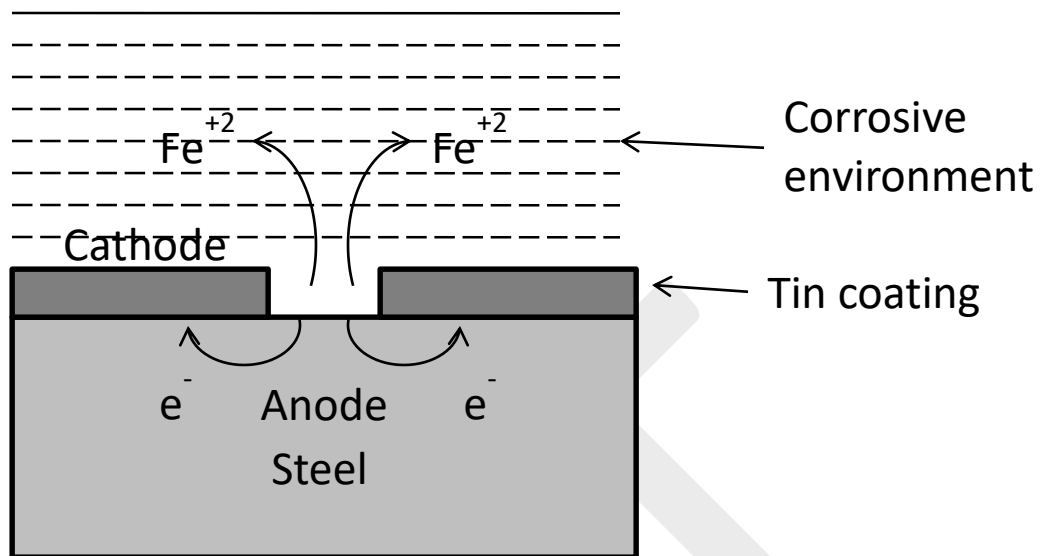
Anodic coating



(ii) Cathodic coatings/ Noble coatings

- If the coating metal is lower placed in galvanic series than the base metal, then the coating is called as cathodic coating. e.g. coating of tin on steel, silver or gold on brass, etc.
- As long as coating is uniformly present on base metal surface, the base metal is protected from corrosion. But if the cathodic coating is ruptured the base metal acts as anode and gets corroded, in the galvanic cell set up. It causes the intense local attack on exposed part resulting in pitting/cracking.

Cathodic coating



Comparison between anodic coating and cathodic coating

Sr.No.	Anodic coating	Cathodic coating
1	It protects the underlying base metal by scarifying itself	It protects the underlying base metal due to its noble character offering higher corrosion resistance
2	Coating metal has higher oxidation potential than base metal	Coating metal has lower oxidation potential than base metal
3	In case of any cracks or pores in the coating, the base metal is not corroded till the coating metal is consumed	In case of cracks or pores in the coating, there will be faster corrosion of base metal
4	e.g. Coating of zinc on iron (galvanized steel)	e.g.Coating of tin on iron (tin coated steel)

4.7.3.2 Methods of Applying Metallic Coatings

- A) Hot dipping
- B) Metal cladding

C) Electroplating

D) Cementation

E) Electroless plating/Immersion plating

They are discussed in detail below

A) Hot dipping

Hot dipping is used for producing a coating of low melting metals such as Zinc (419 °C) or tin (232 °C), lead, etc. on metal like steels, copper, brass, etc. The process consists of immersing the base metal in a bath of molten coating metal, covered by a molten flux layer (usually ZnCl_2). The flux prevents oxidation of molten coating metal.

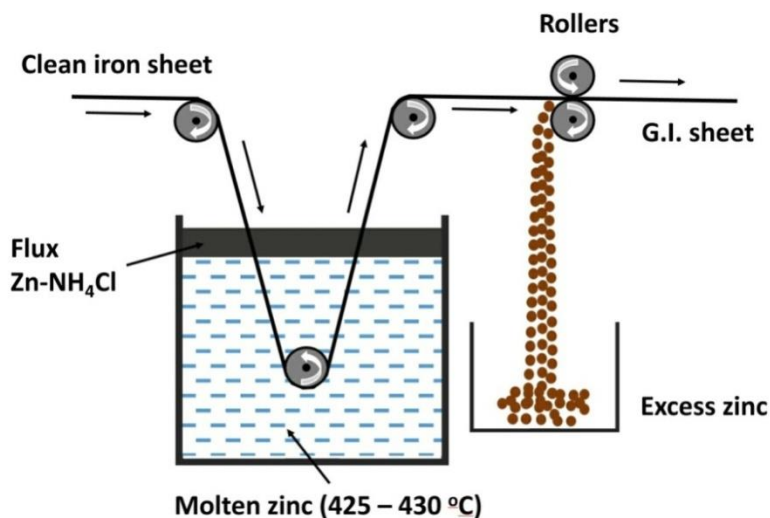
For a good adhesion, base metal should be clean and well prepared.

a) Galvanising:

(i) Definition: The process of coating of iron or steel (base metal) with a thin coat of zinc by hot dipping to prevent base metal corrosion is called galvanizing.

(ii) Method:

- The steel article is cleaned well with dil. H_2SO_4 to remove any rust or scale, washed well with water and dried.
- Then it is dipped in bath of molten zinc maintained at 425-430 °C. Surface of bath is covered with flux like NH_4Cl . Flux clean the metal surface before coating for better adhesion and prevents the oxidation of molten coating metal after coating.
- It is then passed through pair of hot rollers to remove excess of zinc and produce coating of uniform thickness.
- Article is then annealed at 650°C and cooled to room temperature slowly.



(ii) Applications of galvanizing:

It is used widely for protection of iron. Various galvanized iron (G.I.) articles are in use. e.g. G.I. sheets (plane or corrugated), wires, pipes, buckets, tubes, screws, nails, etc. G.I. vessels cannot be used for storing foods as there is formation of poisonous products by action of foods on zinc.

b) Tinning:

(i) **Definition:** The process of coating of iron or steel (base metal) with a thin coat of tin by hot dipping to prevent base metal corrosion, is called tinning

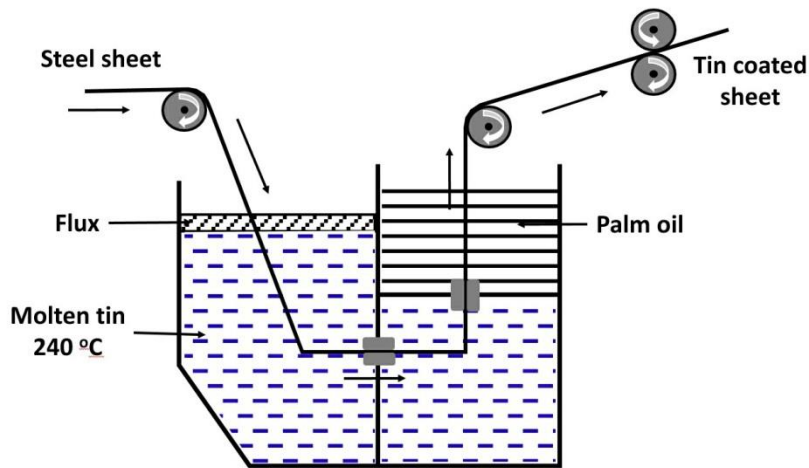
(ii) Method:

- The steel article is cleaned well with dil. H₂SO₄ to remove any rust or scale, washed well with water and dried.
- It is immersed in flux (ZnCl₂ and NH₄Cl) which will facilitate better adhesion of coating
- The cleaned steel article (sheet) is then passed through molten tin bath maintained at about 240°C and then through palm oil. Palm oil protects the hot tin-coated surface against corrosion.
- The rollers finally remove excess of tin and make uniform coating.

ii) Application of tinning:

Tin has greater corrosion resistance and better glaze.

- Tinned containers can be used for storing foods, ghee, oils, pickles, medicines because it has high corrosion resistance and does not form poisonous products after action by foods.
- Copper wires before insulation by rubber, are tinned to avoid attack of sulphur of rubber.
- Tinned copper or brass vessels or sheets are used for cooking utensils and refrigeration equipments.



Comparison of Galvanising and Tinning

Sr.No.	Galvanising	Tinning
1	Zn coating on iron	Tin coating on iron
2	Temperature for coating is about 450°C	Temperature for coating is about 250°C
3	Anodic coating	Cathodic coating
4	Applicable for general use like sheets, pipes, wires, angles	Applicable for containers for storage of edible material.
5	Reliable, Zn is higher placed in galvanic series.	Less reliable, lower placed in galvanic series.
6	Cheaper	Costlier

B) Metal Cladding:

(i) Defination:

Metal cladding is the process in which a thin sheet of coating metal is firmly bonded to the base metal on one or both sides.

Clad metal: Lead, Nickel, Copper, Silver, Chromium, Aluminium.

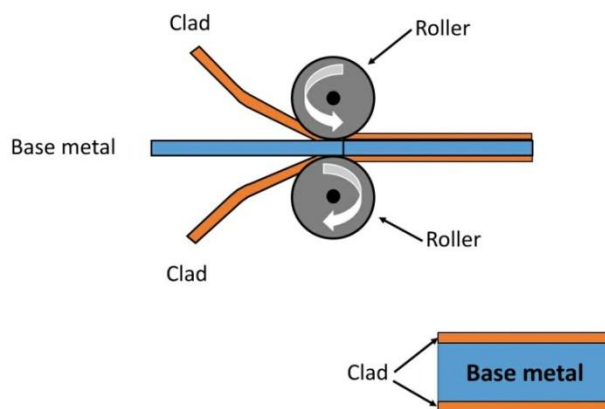
Base metal: Duralumin, Mild steel, Brass.

(ii) Process:

Base metal sheet is sandwiched between the sheets of cladding metal. Such set of sheets is then passed through roller, under the action of heat and pressure. The clad metal thus fix mechanically on the base metal.

(iii) Application:

Cladding can be done on regular surfaces of base metal. The base metal on cladding is not getting exposed to corroding atmosphere. Examples of cladding are, steel table tops, mild steel doors cladded with brass, window panels, mild steel pipe cladded internally and externally with brass, aluminium clads on duralumin base used for aeroplane body, stainless steel clad on mild steel sheets for body of buses, etc.



C) Electroplating:

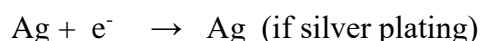
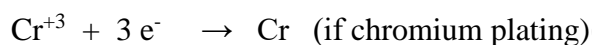
(i) Definition:

Electroplating is the method in which coating metal is coated on a base metal by passing a direct current through the solution of electrolyte, containing the soluble salt of coating metal.

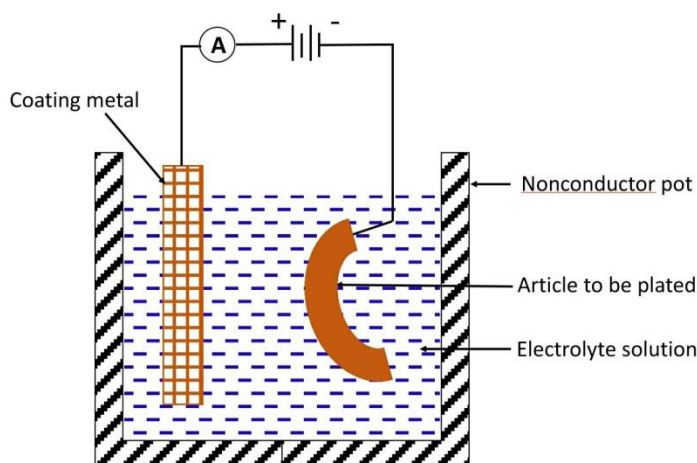
(ii) Method:

The article to be electroplated is cleaned well. There is a nonconducting (plastic or concrete) tank containing solution of salt of the coating metal. The article is connected to negative terminal of D.C. supply to make it cathode. Anode is the coating metal rod/strip. After adjusting the suitable pH and current density on article surface, the electroplating begins.

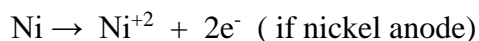
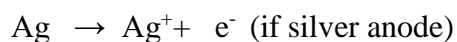
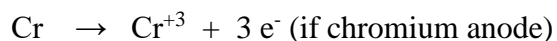
At Cathode (article):



The metal ions in solution migrate towards article and capture electrons on reaching there to get discharged as metal atoms.



At anode:



The coating metal (anode) passes in solution as its ions. The quantity of metal ions discharged on article in certain time, is equal to the quantity anode metal ions passing in the solution. The decrease in weight of anode is equal to increase in weight of article due to plating (coating) formed.

(iii) Applications:

- Electroplating can be used for getting decorative surface. e.g. gold, chromium coating on steel for ornaments, wrist watches, belts, pens etc.
- Used for protective surface against corrosion e.g. chromium plating on steel.
- Non metallic materials like wood, paper, glass can be electroplated for decoration, preservation of surface, for obtaining conductive surface, increasing strength.

(iv) Advantages of electroplating:

- Coating thickness can be controlled
- Coating metals having high melting points like Cr, Ni, Ag, Au etc. can be easily applied
- Process is non expensive
- Fine coating can be obtained with improved hardness

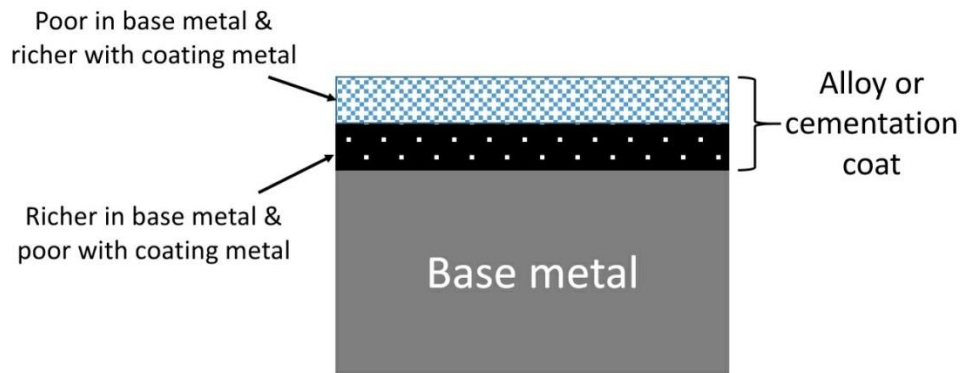
D) Cementation:

(i) Principle:

In the cementation technique, there is formation of strong layer of alloy of coating metal and base metal, on the surface of base metal.

(ii) Method:

In this method, the base metal articles are packed in powder of coating metal and heated to a temperature just below the melting point of lower melting component of them. An alloy of the two metals is formed by diffusion of coating metal into the base metal. The composition of alloy is varying i.e. on the surface layer coating metal is larger while the layer adjacent to the base metal is richer in base metal. The cementation process is called as **sherardizing** if the coating metal is zinc; as **colorizing** if coating metal is aluminium and **chromizing** if coating metal is chromium.



(iii) Applications:

The method is suitable for coating small articles like nuts, bolts, screws, spanners, screw drivers, threaded parts, tools, furnace parts, turbine blades, etc. The coatings are strong and have good abrasion resistance.

E) Electroless plating

(i) Principle: Any metal will displace any other metal with lower position in electrochemical series (noble metal) from the solution of its salt and precipitate it in metallic form.

(ii) Method: It involves immersing the base metal article in the bath of noble salt used for coating. The noble metal is displaced from the salt solution in the presence of a suitable reducing agent by the base metal ion and forms a thin but uniform coating on the base metal without using electrical energy.

For e.g. metals and alloys like Al, Cu, Fe, brass can be directly plated with nickel by dipping them in the bath of nickel sulphate or nickel chloride and sodium hypophosphite (reducing agent) at pH = 4.5 – 5.6 and temperature about 93°C.

(iii) Applications:

1. Electroless nickel plating is extensively used in

- Electronic appliances (knobs of hi-fi equipments)
- Hydraulic compressors, pressure vessels, pumps etc.
- Jewellery
- Shock absorbers, gears, cylinders in automobile.

- Satellite and rocket components.
- Moulds and dies for plastic moulding.
- Electroless copper plating is used in making printed circuit boards (PCBs)

4.7.3.3 Nonmetallic Coatings

A) Chemical conversion coating / Surface conversion coatings

Definition: Chemical/ Surface conversion coatings are the inorganic surface barriers, produced by chemical or electrochemical reactions taking place at the surface of base metal.

Surface conversion coatings remain as an integral part of base metal. These coatings protect the base metal against corrosion and provide excellent base for application of paints, lacquers, oils and enamels.

They can be applied to the metals like Fe, Al, Zn and their alloys.

The different types of chemical conversion coatings commonly used are

1. Phosphate coating.
2. Chromate coating.
3. Chemical oxide coating.
4. Anodized coating.

1. Phosphate Coatings

Phosphate coatings are produced by the chemical reaction of base metal with aqueous solution of phosphoric acid and phosphate.

Phosphates generally used are of iron, manganese and zinc. Some copper salts are used as accelerators which accelerate the otherwise slow reaction. Such coatings are frequently applied to iron, steel and zinc. The chemical reaction between the phosphating solution and the base metal results in the formation of a surface film consisting of crystalline zinc-iron or manganese-iron phosphate.

Phosphate coating is applied by immersion, spraying or brushing. Such coats do not offer complete resistance to corrosion and are used as base coat/primer coat for paints, lacquers etc.

2. Chromate coatings

They are produced by immersing the article in a bath of acidic potassium chromate followed by immersion in a bath of neutral chromate solution. Protection is provided by formation of a surface film, consisting of mixture of trivalent and hexavalent chromium.

Chromate coatings can be used for the protection of zinc, aluminium, magnesium and some cadmium plated parts.

Chromate films are amorphous, nonporous and more corrosion resistant than phosphate coat, but they have comparatively low abrasion resistance. They are used as base for paints, lacquers and enamels.

3. Chemical oxide coatings

They are produced by treating the base metal with alkaline oxidizing solution or gas.

The base metal has its own original oxide film formed due to atmospheric corrosion. The above treatment increases the thickness of the original oxide film on the metal thereby increasing the corrosion resistance.

Oxide coating on steel is available in variety of colours from straw yellow to light blue. The coatings themselves are not corrosion protective, but they serve as a good base for oils, greases and waxes.

4. Anodized coatings

The coating are produced on non ferrous metals like Al, Zn and Mg and their alloy by anodic oxidation process in which the base metal is made as anode. The process is carried out by electrolysis in which the base metal is suspended from anode. The electrolytic bath usually contains sulphuric, chromic, phosphoric, oxalic or boric acid.

For e.g. Aluminium coatings are formed by electrolysis in suitable acid electrolyte (sulphuric, chromic, phosphoric acid) at 35-40°C and moderate current density. The film so formed is porous in nature which is sealed by exposing the oxide film to boiling water to form corresponding monohydrate which occupies more volume or it can be sealed with dyes.

Anodized coatings are about 100 times thicker than the natural oxide films, so they possess improved resistance to corrosion and mechanical injury.

B) Powder coating

(I) Definition: Powder coating is the process of application of coating which is applied as free flowing dry powder of thermoplastic or thermosetting polymer on the surface of metal.

(II) Powder coating materials

Powder coatings are homogenized mixture of number of raw materials like resins (thermoplastics or thermosetting), fillers or extenders (to reduce price), pigments (to give colour), additives (to improve properties)

(III) Types of powder coatings

There are 2 main categories of powder coatings

a) Thermosetting coating – While baking (curing), they may undergo cross linkage between the molecules to improve its molecular weight and hence performance. Resins that are used to make thermosetting powders are epoxy, polyesters and acrylic polymers.

b) Thermoplastic coating - These, on baking, do not undergo cross linkage but melt to form final coating. Resins that are used to make thermoplastic powders are polyvinyl chloride (PVC), nylons, polypropylene etc.

(IV) Powder coating processes

It involves 3 steps:

i) Pre-treatment

It involves cleaning and preparing surface for powder coating. It includes removal of oil, grease, soil, metal oxides, scales etc. by mechanical and chemical methods. (like sand blasting, phosphating, chromating, etching etc.)

ii) Powder application –

It is possible by following methods-

a) Electrostatic spraying – In electrostatic spraying, an electrical charge (+ve) is applied to the dry powder particles by electrostatic gun while the component to be coated is electrically grounded. The charged powder and grounded workpiece create an electrostatic field that pulls the powder particle to workpiece. The coating deposited on the workpiece retains its charge, which holds the powder to workpiece.

The coated workpiece is placed in curing oven, where the paint particles are melted onto the surface and charge is dissipated.

b) Fluidized bed method – In this method, powder particles are kept in suspension by an air stream. A preheated workpiece is placed in the fluidized bed (aerated powder filled bed) where the powder particles coming in contact with the workpiece melt and adhere to its surface. Thickness of coat depends on temperature and the residence time in the bed.

Curing may not be required for thermoplastic but required for thermosetting.

c) Electrostatic fluidized bed method – It has similar design as fluidized bed. Here, air stream is electrically charged, which charges the powder particles. These particles move upward in the bed forming a cloud of charged particles. The grounded workpiece is covered by charged particles. No preheating of workpiece is required. Curing is however necessary.

iii) Curing-

Thermoplastic powders require heat only to fuse the powder together into continuous film. However, thermosetting powders often require additional heat to cure the film by forming cross linkage. Curing is done by heating at certain temperature and for certain period of time in order to achieve film formation.

(V) Application of powder coating

Powder coating are used mainly for **decoration** and corrosion **resistance**.

For e.g.

- 1) Epoxy powder coatings are known for their superior mechanical performance and corrosion resistance. They are used in office furnitures, domestic appliances, industrial machines, electrical components etc.
- 2) Epoxy polyester powder coating are known for decorative and anticorrosive finishes. They find applications in office furnitures, domestic appliances, industrial shelving, hand and power tools, heating and air conditioning units, computers, cars etc.
- 3) Polyester powder coatings have high gloss and used for outdoor furniture, galvanized windows, electrical components etc.

4.8 Practical problems of corrosion:

(Ref: Corrosion Reviews Special Issue: India)

Case study1: Iron contamination of white clay powder, making it unusable.

SERVICE	White Clay manufacturing involves handling of clay slurry through bleaching, filtering and conveying the filter cake.
PROBLEM	Iron oxide (rust) flakes liberated due to corrosion of structures associated with filter presses and conveyors, fall into the process media, wet cake, and contaminate the product
MATERIAL	Carbon steel plates
OBSERVATIONS	Peeling-off of the paint coating followed by corrosion of the underlying steel resulting in brownish rust flakes.
DIAGNOSIS	GENERAL UNIFORM CORROSION by the process aqueous solution of pH 4.5/5.0, at a very slow rate of about 0.025mm/year. This rate is quite acceptable from structural integrity point, but not from product purity point for the specific application
REMEDY	Replace the structures with solid FRP or with Galvanized Steel.

Case study 2: Instrumentation tube in an offshore platform of an Oil & Gas Plant

SERVICE	Instrumentation tube in a off-shore platform producing oil & gas. Contains produced gas under pressure at ambient temperature
PROBLEM	Minor leak after 5 years of operation under one of the support clamps.
MATERIAL	Stainless steel
OBSERVATIONS	Highly localized corrosion on the outside surface of the tube below the tight fit plastic support clamp. No general corrosion elsewhere due to the overall marine atmosphere. No corrosion on the inside surface.
DIAGNOSIS	CREVICE CORROSION under the tight fit plastic support clamp.
REMEDY	Keep the plastic support clamps under loose fit so that free air and moisture flows during winds is ensured.

Case study 3: VIIT, D-Building, Corrosion of a grill



SERVICE	Grill for protection of a window glass
PROBLEM	Grill has become weak due to corrosion
MATERIAL	Mild steel
OBSERVATIONS	Electrochemical corrosion observed wherever the paint was peeled off
DIAGNOSIS	Grill is corroded with oxygen absorption mechanism
REMEDY	Frequent cleaning of corrosion product and painting

Reference books:

1. Engineering Chemistry- Jain and Jain
 2. Engineering Chemistry – Wiley India
 3. Engineering Chemistry - O. G. Palanna, Tata McGraw Hill Education Pvt. Ltd.
 4. A Textbook of Engineering Chemistry – Dr S .S. Dara and Dr. S. S. Umare, S. Chand publication
 5. A textbook of Engineering Chemistry – Shashi Chawla, DhanpatRai Publications
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