
DEPARTMENT OF BASIC SCIENCES AND HUMANITIES

Module 1: Corrosion Science and Coating Technologies

Corrosion: Introduction, electrochemical theory of corrosion, types of corrosion differential metal, differential aeration.

Corrosion control: metal coating; galvanization, surface conversion coating; anodization and cathodic protection; sacrificial anode method. Corrosion penetration rate (CPR)-numerical problems.

Metal finishing: Introduction, technological importance, electroplating - electroplating of chromium-decorative and hard chromium, electro-less plating - electroless plating of Nickel, difference between electroplating and electroless plating.

CORROSION

It is a common experience that, most of the metals (except the least reactive like Gold, platinum) are slowly destructed on long exposure to the atmosphere.

Definition:

“Destruction or Deterioration of metals or alloys and consequent loss through a chemical or electrochemical attack from the environment is called as corrosion”.

Example: Rusting of Iron.

Dry corrosion (chemical corrosion) :

This involves the direct attack of metals by corrosive gases such as carbon dioxide, sulphur dioxide, ammonia, hydrogen chloride, etc. present in the corrosion environment. Since this is observed in the absence of moisture or conducting electrolytes, it is called dry corrosion.

Wet Corrosion or Electrochemical corrosion or Immersed corrosion:

The corrosion of the metal takes place through the ionic reaction in the presence of moisture or electrolytes is called wet corrosion. *Ex.* Dry chlorine is non-corrosive to steel, but moist chlorine leads to corrosion.

Why do metals undergo corrosion?

Metals are originally in the form of ore (oxidized state), which is the most stable form. Pure metals are extracted from ore, and the pure metal thus obtained is less stable (more reactive), thus pure metals always naturally tend to revert to stable form (corrosion).

Electrochemical theory of corrosion [Theory or Mechanism of rusting of iron]:

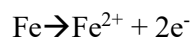
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According to this theory corrosion of the metals takes place through the formation of anodic or cathodic regions within the same metal surface in the presence of conducting medium.

Corrosion reactions:

a. Anodic reaction (i.e. at anodic area)

Oxidation of metal takes place resulting in the corrosion of iron.



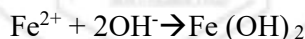
b. Cathodic reaction

The cathodic reaction consumes electrons by (a) the Evolution of Hydrogen (b) the Absorption of oxygen depending on the nature of the environment.

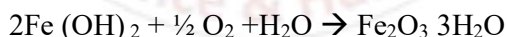
Cathodic reaction

Medium	Evolution of Hydrogen	Absorption of oxygen
Acidic	$2\text{H}^{+} + 2\text{e}^{-} \longrightarrow \text{H}_2$	$2\text{H}^{+} + 2\text{e}^{-} + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$
Basic / Neutral	$2\text{H}_2\text{O} + 2\text{e}^{-} \longrightarrow 2\text{OH}^{-} + \text{H}_2$	$\text{H}_2\text{O} + 2\text{e}^{-} + \frac{1}{2}\text{O}_2 \longrightarrow 2\text{OH}^{-}$

Corrosion of iron produces Fe^{2+} ions and OH^{-} ions at the anode and cathode sites respectively these ions diffuse towards each other since smaller Fe^{2+} ions diffuse more rapidly than OH^{-} ions their combination forms insoluble $\text{Fe}(\text{OH})_2$



In an oxidizing environment, it is oxidized to ferric oxide and yellow rust is hydrated ferric oxide.



Types of Corrosion

Galvanic Corrosion [Differential Metal corrosion]:

“The corrosion of metals when two dissimilar metals are in contact with each other in a corrosive environment is called galvanic corrosion”.

One of the metals having lower reduction potential acts as an anode and hence undergoes oxidation and the metal corrodes. The other metal has a high reduction potential and acts as a cathode hence undergoes reduction and the metal is protected.

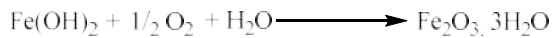
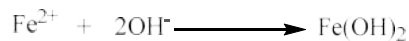
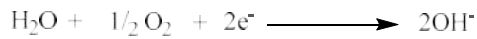
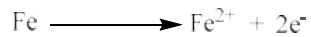
Example: As shown in the figure, if the two different metals (Fe & Cu) are placed in a corrosive environment. Iron corrodes and copper is protected. Because Iron has a lower reduction potential hence undergoes corrosion.

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GALVANIC CORROSION/ BIMETALLIC CORROSION



Reaction is



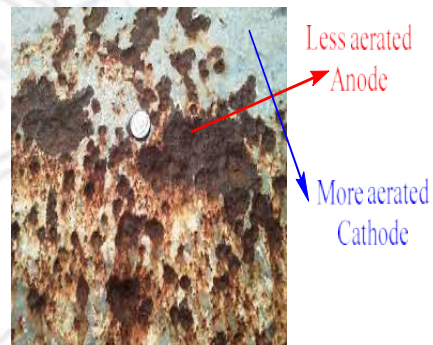
Differential aeration corrosion [Concentration cell corrosion]:

“Corrosion of metal due to difference in air or oxygen concentration on the surface is called differential aeration corrosion”.

- The area in which less oxygen concentration becomes anode and hence undergoes corrosion.
- More oxygen concentration areas act as cathode hence it is unaffected.

Pitting corrosion: *“Pitting corrosion occurs when dust or oil particles get deposited on the metal surface”.*

The area of the metal below the deposit (dust) is exposed to less oxygen and hence acts as an *anode*, the more oxygenated uncovered region acts as a *cathode*. Hence, the area below the deposit undergoes corrosion leading to small pinholes. Because of the small anodic and large cathodic area, the rate of corrosion is severe leading to a pit.



Water-Line corrosion:

When water is stored in a metallic tank as shown in figure, it is observed that corrosion takes place just below the water level in the container. The area above water is more oxygenated, acts as cathode. Area below the water level is less oxygenated, acts as anode. Therefore, area below the water level is corroded and area above water level is protected. Hence, a distinct brown line is formed below the water line due to corrosion.



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Corrosion control

Corrosion can be controlled by protecting the surface of the metal or by preventing the formation of galvanic cells. Thus, the corrosion rate can be controlled.

Metal coatings:

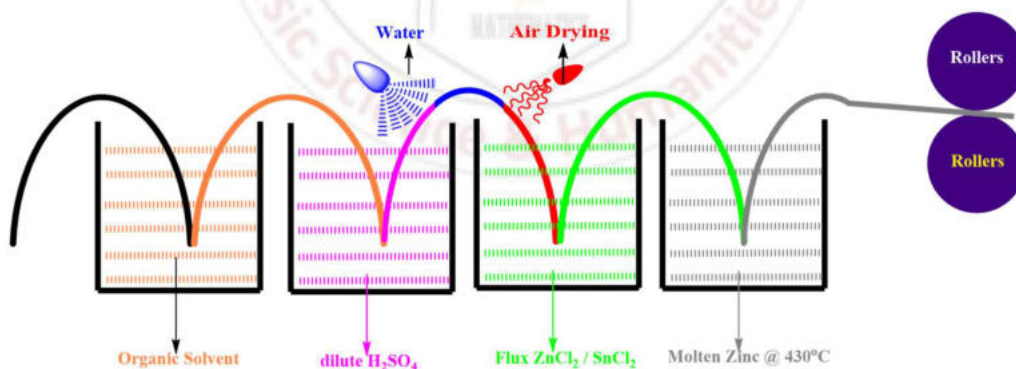
In this method protective metal is coated on the surface of the base metal which can be done by electroplating, flames spray, hot dipping, etc. The coating can be an anodic coating or cathodic coating.

Galvanization

Galvanization is a familiar example of an *anodic coating*.

“The process of coating base metal like steel, copper, etc. with zinc is called galvanization”. It consists of the following steps as shown in figure 2.6:

1. Articles to be galvanized are dipped in an organic solvent to remove dust or grease.
2. Then dipped in dilute sulphuric acid to remove any rust formed. Washed with water and dried.
3. Then dipped in a solution of zinc chloride (ZnCl_2) and ammonium chloride (NH_4Cl) which acts as a flux to have a firm coating.
4. Then dipped in molten zinc at 430°C .
5. Excess zinc is removed by rolling over rollers.



Uses: It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. Zn coating is not done for storing food stuffs because it readily dissolves in acid which is toxic.

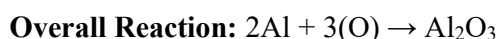
Surface conversion coating; Anodization:

In this protective coating of inorganic metal oxide is formed on the surface which prevents the metal from corrosion acting as a barrier between the metal surface and corrosion environment. Such coatings are particularly used as an excellent base for paints, lacquers oils and enamels.

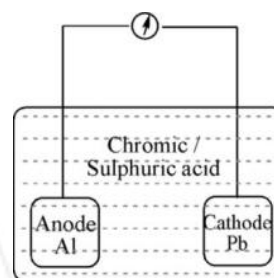
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Anodized oxide coatings [Non-Ferrous method]:

Metals like Al, Zn and Mg are made to develop protective metal oxide coating artificially on their surfaces. Anodized coating is obtained as shown in figure, in which the base metal is made *anode* and inert metal like lead is made *cathode*. The electrolytic bath containing oxidizing agent with an acid is taken. On passing current the oxide film is formed on the base metal. These oxide coatings prevent the further corrosion of the base metal.



E.g. Anodization of Aluminum is carried out by making it an anode in an electrolytic bath containing acid 5-10% of chromic acid at 35 to 40°C. A plate of lead is made as cathode. On passing electric current a thin oxide layer is formed on the surface of the metal. Thus, aluminum is protected from corrosion. *Ex. Anodized articles are used as soap boxes, tiffin carriers, window frames, etc.*

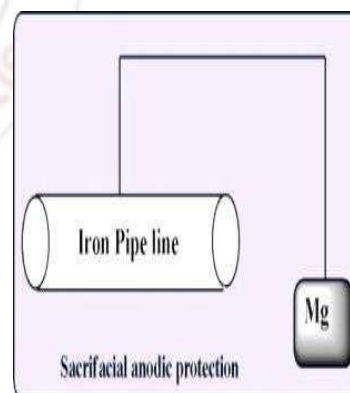


Cathodic protection:

It is a technique of protecting metal from corrosion by converting it to a cathode. It can be done by,

Sacrificial anodic method:

Metal to be protected is converted into a cathode by connecting it to a more active metal. The active metal acts as an auxiliary anode. The more active metal itself gets corroded slowly while the parent structure (cathodic) is protected. Metals like zinc, Aluminium are generally used as auxiliary anodes. Metallic blocks of Al, zinc, or Mg are connected to the metallic structure of iron to be protected. Since the anode is sacrificed to prevent the corrosion of the Cathode, it is called the sacrificial anode method.



Eg. When Magnesium blocks are connected to the sides of the ship, it acts as anode, prevents ship from corrosion. Magnesium blocks are connected to buried pipelines to prevent structure from corrosion, by acting as anode.

Corrosion rate

Corrosion rate is the speed at which any metal in a specific environment deteriorates. It also can be defined as the amount of corrosion loss per year in thickness. The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under reference.

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Corrosion Penetration Rate (CPR)

The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment. The amount of corrosion loss per year in thickness. The speed at which corrosion spreads to the inner portions of a material.

$$\text{CPR} = \frac{k \times w}{p \times A \times T}$$

Where

k = Constant

w = Total weight loss

T = Time taken

A = Surface area of exposed metal

p = Metal density in g/cm³

CPR Numerical Problems

A thick brass sheet of area **24 inch** is exposed to air near the ocean. After a one-year six months period, it was found to experience a weight loss of **1.2 kg** due to corrosion. If the density of the brass is **6.5 g/cm³**, calculate the corrosion penetrating rate in mpy and mm/y.

Given Data

$$A = 24 \text{ inch} = 24 \times 2.54 \text{ cm} = 60.96 \text{ cm}$$

$$W = 1.2 \text{ kg} = 1200 \times 10^3 \text{ mg}$$

$$d = 6.5 \text{ g.cm}^3$$

$$K = 534 \text{ mpy} / 87.6 \text{ mmpy (Constant)}$$

$$T = 1.6 \text{ year} = (24 \text{ hr} \times (365 + 180) \text{ days})$$

$$\text{CPR} = ?$$

WKT

$$\text{CPR} = \frac{k \times w}{p \times A \times T}$$

$$\text{CPR} = \frac{534 \times 1200 \times 10^3}{6.5 \times 60.96 \times 13080}$$

$$\text{CPR} = 123.64 \text{ mpy}$$

$$\text{CPR} = \frac{87.6 \times 1200 \times 10^3}{6.5 \times 60.6 \times 13080}$$

$$\text{CPR} = 20.40 \text{ mmpy}$$

A thick steel sheet of area **400 cm²** is exposed to air near the ocean. After a one-year period, it was found to experience a weight loss of **375 g** due to corrosion. If the density of the steel is **7.9g/cm³**, calculate the corrosion penetrating rate in mpy and mm/y (given K= 534 in mpy and 87.6 in mm/y)

Given Data

$$A = 400 \text{ cm}^2$$

$$W = 375 \text{ g} = 375 \times 10^3 \text{ mg}$$

$$d = 7.9 \text{ g.cm}^3$$

$$K = 534 \text{ mpy} / 87.6 \text{ mmpy}$$

$$T = 1 \text{ year} = (24 \text{ hr} \times 365 \text{ days} \times 1 \text{ yr})$$

$$\text{CPR} = ?$$

WKT

$$\text{CPR} = \frac{k \times w}{p \times A \times T}$$

$$\text{CPR} = \frac{534 \times 375 \times 10^3}{7.5 \times 400 \times 8760}$$

$$\text{CPR} = 7.23 \text{ mpy}$$

$$\text{CPR} = \frac{87.6 \times 375 \times 10^3}{7.5 \times 400 \times 8760}$$

$$\text{CPR} = 0.0118 \text{ mmpy}$$

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A sheet of carbon steel **one meter** wide by **three meters** long has lost **40 g** to corrosion over the past **six months**. Convert that mass loss to a penetration rate of the steel in **mpy and mmpy**. What would be the total corrosion rate associated with such a corrosion rate? (carbon steel density = **7.8 g/cm³**)

Given Data

$$A = 1\text{m} \times 3\text{m} = (1 \times 1000\text{ cm}) \times (3 \times 1000\text{ cm}) = 3 \times 10^6\text{ cm}^2$$

$$W = 40\text{ g} = 40 \times 10^3\text{ mg}$$

$$d = 7.8\text{ g.cm}^3$$

$$K = 534\text{ mpy} / 87.6\text{ mmpy (constant)}$$

$$T = 6\text{ months} = (24\text{ hr} \times 30\text{ days} \times 6\text{ months})$$

$$\text{CPR} = ?$$

WKT

$$\text{CPR} = \frac{k \times w}{p \times A \times T}$$

$$\text{CPR} = \frac{87.6 \times 40 \times 10^3}{7.8 \times 3 \times 10^6 \times 4320}$$

$$\text{CPR} = \frac{534 \times 40 \times 10^3}{7.8 \times 3 \times 10^6 \times 4320}$$

$$\text{CPR} = 3.47 \times 10^{-5}\text{ mmpy}$$

$$\text{CPR} = 2.11 \times 10^{-4}\text{ mpy}$$

A piece of corroded metal alloy plate was found in a submerged ocean vessel, it was estimated that the original are plate was **800 cm²** and that approximately **7.6 Kg** had corroded away during the submersion, assuming a corrosion penetration rate of **4 mm/yr** for this alloy in seawater, estimate the time of submersion in years, the density of alloy is **4.5 g/cm³**.

Given Data

$$A = 800\text{ cm}^2$$

$$W = 7.6\text{ kg} = 7.6 \times 10^3\text{ g} = 7.6 \times 10^3 \times 10^3\text{ mg}$$

$$d = 4.5\text{ g.cm}^3$$

$$K = 87.6\text{ mmpy}$$

$$T = ?$$

$$\text{CPR} = 4\text{ mmpy}$$

WKT

$$\text{CPR} = \frac{k \times w}{p \times A \times T}$$

$$T = \frac{k \times w}{p \times A \times \text{CPR}}$$

$$T = \frac{87.6 \times 7.6 \times 10^6}{4.5 \times 800 \times 4}$$

$$T = 46233.33\text{ hr}$$

$$T = \frac{46233.33\text{ hr}}{24 \times 365}$$

$$T = 5.28\text{ years}$$

Practice Numerical problems

A thick brass sheet of area **12 inch** is exposed to air near the ocean. After a 9 months, it was found to experience a weight loss of **600 g** due to corrosion. If the density of the brass is **3.25 g/cm³**, calculate the corrosion penetrating rate in mpy and mm/y.

A thick steel sheet of area **800 cm²** is exposed to air near the ocean. After a 2 years, it was found to experience a weight loss of **1500 g** due to corrosion. If the density of the steel is **15.8 g/cm³**, calculate the corrosion penetrating rate in mpy and mm/y (given K= 534 in mpy and 87.6 in mm/y)

A sheet of carbon steel **one meter** wide by **two meters** long has lost **20 g** to corrosion over the past **three months**. Convert that mass loss to a penetration rate of the steel in **mpy and mmpy**. What would be the total corrosion rate associated with such a corrosion rate? (carbon steel density = **3.9 g/cm³**)

A piece of corroded metal alloy plate was found in a submerged ocean vessel, it was estimated that the original are plate was **400 cm²** and that approximately **3.8 Kg** had corroded away during the submersion, assuming a corrosion penetration rate of **2 mm/yr** for this alloy in seawater, estimate the time of submersion in years, the density of alloy is **2.25 g/cm³**.

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METAL FINISHING

Definition: It is a process in which a specimen metal (article) is coated with another metal or a polymer to modify the surface properties of the specimen.

Example: [a] Electroplating of metals or alloys.

[b] Electroless plating of metals or alloys.

Technological importance of metal finishing:

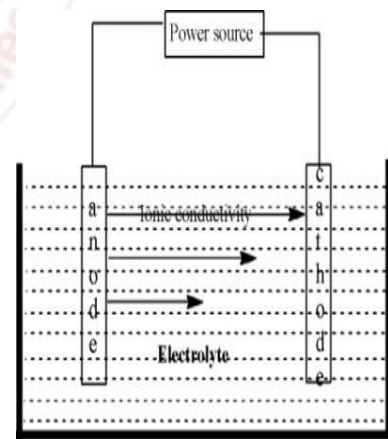
- To get a decorative surface. *Example:* Gold plating on copper.
- To prevent corrosion. *Example:* Zinc coating on iron.
- To modify the surface properties such as thermal resistance, hardness, brightness, brittleness, etc.
Example: Chromium or nickel coating on iron.
- To get thermal and electrical conductivity.
- Manufacture of Electronic components. Example PCB Circuits.

Electrolysis: The decomposition of electrolytes in an aqueous solution when current is passed is called electrolysis.

Electroplating:

It is the process in which base metal is uniformly coated with suitable metal by electrodeposition.

- Electroplating is achieved by passing an electric current through an electrolytic solution containing metal ions and the electrodes.
- The metal object to be plated serves as a cathode that attracts metal ions from the solution.
- In an electrolytic bath, the coating metal or an inert material of good conducting capacity may be used as the anode.
- If the anode used in electrolysis is other than the coating metal, the salt is to be added continuously to the electrolytic bath to maintain the optimum metal ion concentration in the solution.



Electroplating of chromium:

Electroplating of chromium is carried out on the pretreated Ni or Cu articles.

Decorative Chromium Coatings: Decorative chromium coating is the coating of the thin layer of chromium with thicknesses of 0.25 to 0.75 μm . thicker deposits look very dull.

Hard Chromium coating: Deposition of chromium with a thickness of 0.005 to 0.75mm is referred as hard chromium coating.

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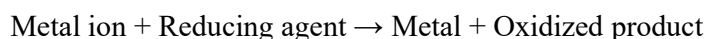
Plating Bath Condition	For Decorative Plating	For Hard Chrome plating
Plating bath	Chromic acid + Sulfuric acid (100:1) + Trivalent Chromium Cr^{3+}	Chromic acid + Sulfuric acid (100:1) + Trivalent Chromium Cr^{3+}
Temperature	45-55 °C	45-55 °C
Current density	100-200 mA/cm ²	290-580 mA/cm ²
Anode	Pb-Sn alloy or stainless steel	Pb-Sn alloy or stainless steel
Cathode	Object to be coated (article)	Object to be coated (article)
Applications	To obtain decorative and corrosion resistant coating like automotive wheel rims, taps etc.	Used to impact surface hardness and wear resistance to materials like cutting edges, handguns etc.

In chromium plating, sulphate ion acts as a catalyst. In the CrO_3 bath solution, Cr is in the Cr^{6+} state. This is converted into Cr^{3+} by a complex anodic reaction which is then coated as Cr on the cathode surface.

Note: Chromium anodes are not used in chromium plating for the following reasons:

- Chromium metal passivates strongly in an acid sulphate medium.
- Chromium anode gives Cr (III) ions on dissolution. In presence of Cr (III) ions in large concentrations, a black Cr deposit is obtained.

Electroless plating: The deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is known as 'electroless plating'.



Electroless plating of Nickel:

[1] Preparation of the surface: Initially the surface of the metal is washed with a dilute acid solution to remove scaling on the metal then it is degreased by treating it with an alkali solution and finally washed four to five times with distilled water. The cleaned metal surface is activated by treating with PdCl_2 whereas for polymers AgNO_3 is used for activation of the surface.

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[2] Composition of electroless bath:

Plating Bath	
Coating electrolyte	NiSO ₄ / NiCl ₂ 21g/L
Reducing agent	Sodium Hypophosphite 24g/L
Buffer	Tri sodium citrate 15g/L
Complexing agent	Sodium Acetate, Lead acetate
Wetting agent	Sodium Dodecyl sulphate
pH	9
Temperature	25 °C

[3] Reactions:

