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Sinhgad Institutes

Sinhgad Technical Education Society's
Sinhgad College of Engineering, Pune 41.
First Year Engineering
Subject: Engineering Chemistry

Unit 6: CORROSION SCIENCE

Q1. What is dry corrosion? Explain mechanism of oxidation corrosion with suitable figure & reactions. 6M (marking scheme: Definition-1M, Mechanism-2M, and Fig-1 M, reactions-2 M).

Ans: Dry corrosion-It occurs mainly due to direct chemical action of atmospheric gases like CO_2 , O_2 , H_2S , SO_2 , Halogens like Cl_2 and Br_2 with metal or alloy surface.

Mechanism-it involves four steps

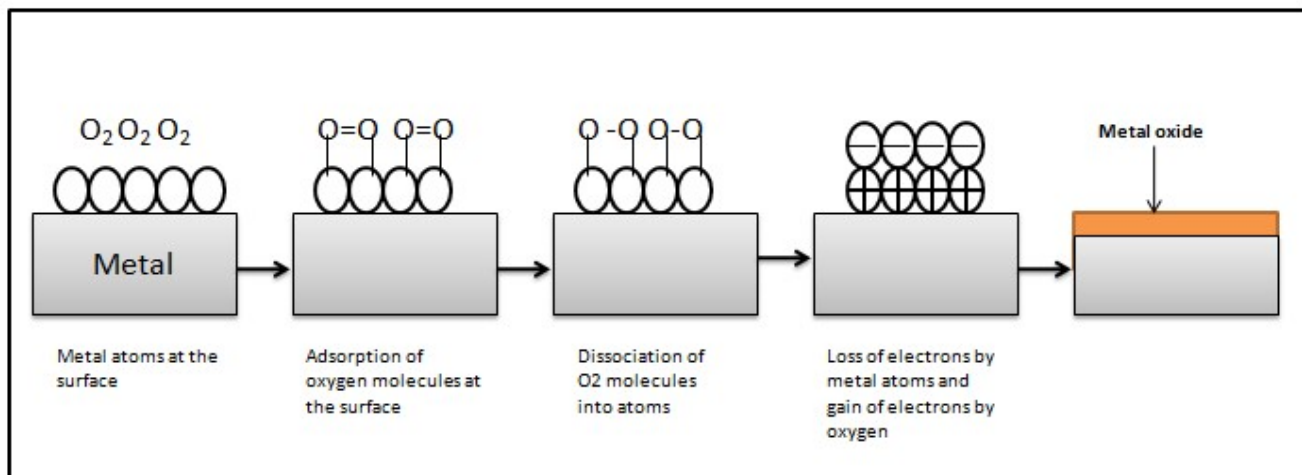
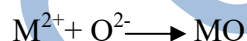
1) Adsorption of atmospheric oxygen at the metal surface:-oxygen molecules are adsorbed by the surface of the metal through their free valencies very firmly

2) Dissociation of oxygen molecules into atom:-At elevated temperature adsorbed oxygen gas molecules dissociate into atoms.

3) Oxidation of metal atoms and reduction of oxygen atoms-



4) Formation of metal oxide at the surface-Metal ion combine with oxide ion & form metal oxide film on the surface of metal.



Reactions: $2M \rightarrow 2M^{n+} + 2ne^-$ (oxidation)

$\frac{n}{2} O_2 + 2ne^- \rightarrow nO^{2-}$ (reduction)

Net reaction: $2M + \frac{n}{2} O_2 \rightarrow 2M^{n+} + nO^{2-} \rightarrow MO$ (rust)

Q2. Define oxidation corrosion .What are the different types of metal oxide formed? Give suitable example for each type.

5M (Marking scheme: Definition-1M, each type of oxide film with example-1M each)

Ans: Oxidation corrosion- it is brought about by direct action of oxygen on metal surface at low & high temperature in absence of moisture.

-On the basis of PBR metal oxide film is classified as protective oxide film & non protective oxide film.

$$P.B.R. = \frac{\text{volume of metal oxide formed}}{\text{volume of metal consumed}}$$

If $PBR \leq 1$, the film is porous and non-protective

If $PBR \geq 1$, the film is non-porous and protective

Types of oxide film

- 1) Porous oxide film-E.g. alkali & alkaline earth metal(Na, K, Mg, Li) forms oxide having less volume than volume of metal .as a result oxide layer faces stress & strain ,thereby develops cracks, pores in the film through which oxygen easily come in contact with metal & corrosion continues
- 2) Non-porous oxide film- E.g. Al, Cr, Cu etc.metals forms oxide film whose volume are greater than volume of metal exposed therefore these oxides films do not have any cracks, pores & forms barrier between Oxygen & metal. As a result corrosion stop once oxide film is formed.
- 3) Unstable oxide film-when oxide film is unstable it decomposes back into metal & Oxygen. As a result net corrosion is zero .e.g. metal like **Ag,Au,Pt** etc. forms this type of oxide film
- 4) Volatile oxide film-when oxide film volatile it vaporizes as soon as it is formed. As a result continues & excessive corrosion of metal.
E.g. metal like Mo, Sn etc.

Q3.What is wet corrosion? What are different conditions under which wet corrosion occurs? 3M (Marking scheme: Definition-1M, each type of oxide film with example-1M each)

Ans: Wet corrosion-this type of corrosion occurs mostly under wet or moist conditions through electrochemical reaction with formation of cathodic and anodic areas.

Conditions- 1) when two dissimilar metals are in contact with each other in presence of conducting medium, cathodic & anodic area develop due to difference in electrode potential.

2) When single metal is dipped partially in conducting medium, cathodic & anodic area develops on metal surface due to differential aeration

Q4. Define corrosion. Explain hydrogen evolution mechanism of wet corrosion.5M (Marking scheme: Definition-1M, each type of oxide film with example-1M each)

Ans: This type of corrosion occurs when conducting medium is acidic

-example: A small piece of copper is in steel tank (in contact with each other) in presence of acidic medium ($\text{pH} < 7$)

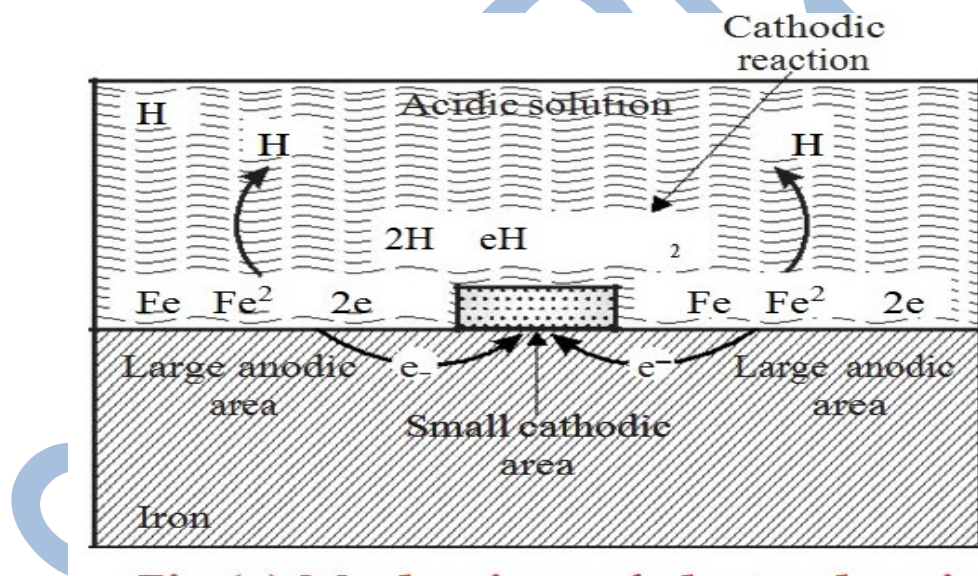


Fig.(a) Mechanism of electrochemical Corrosion with evolution of hydrogen

At anode- $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (oxidation /corrosion)

At cathode- $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ↑

Overall reaction $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$ ↑

- Iron and copper two metals are in contact with each other, as iron(steel)tank which is more active than copper, acts as an anode undergoes corrosion i.e. corrosion. ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$)

-Free electrons accumulate at cathode i.e. on copper metal. Hydrogen ions present in acidic solution take up these electrons forming H₂ gas as shown in the reaction above. H₂ gas liberates in the form of bubbles near the cathode.

-Thus, hydrogen evolution type of corrosion is nothing but displacement of H⁺ from acidic solution by metal ions

-All the metals above H₂ in the electro chemical series get dissolved in acidic solution with simultaneous evolution of hydrogen

-In hydrogen evolution type of corrosion anode has a large area (like metallic tank) and cathode has a smaller area.

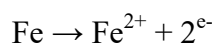
Q.5 Explain with suitable example oxygen absorption mechanism of wet corrosion.3M (Marking scheme: mechanism with reaction with cathode and anode-2M, figure-1M).

Ans:

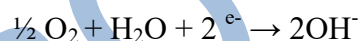
-This type of corrosion occurs when conducting medium is neutral solution or alkaline solution containing dissolved oxygen.

-The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some crack anodic areas are created on the surface; while the well metal parts acts

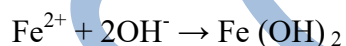
- Anode: Metal dissolves as ferrous ions with liberation of electrons.



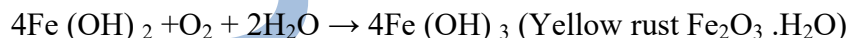
At Cathode: The liberated electrons are intercepted by the dissolved oxygen.



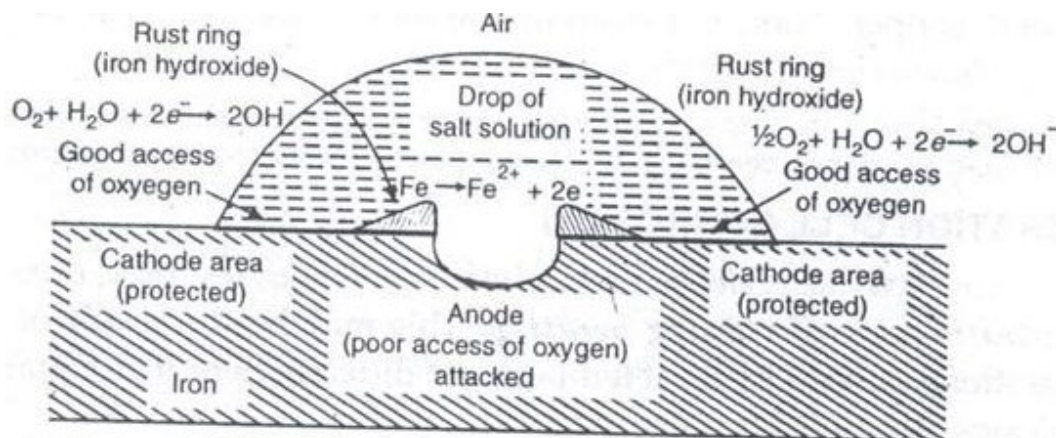
The Fe²⁺ ions and OH⁻ ions diffuse and when they meet, ferrous hydroxide is precipitated.



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



If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe₃O₄.



Mechanism of wet corrosion by oxygen adsorption (rusting of iron)

Q.6 Explain any three factors influencing the rate of corrosion with respect to nature of metal .3M (any 3 points- 1 each)

Ans. Purity of metal: As pure metal have high resistance for corrosion as compared to impure metal. Impurities in metal cause heterogeneity and form minute/tiny electrochemical cells and the anodic parts get corroded.

Physical state of the metal: The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

Relative areas of the anodic and cathode: Corrosion will be severe if the anodic area is small and the cathodic area is large. Larger cathodic area of the cathode will increases demand of more electrons, which can met by the smaller area of anode only by undergoing more corrosion. If anodic area is larger than cathodic area corrosion proceeds with slow rate.

Nature of the oxide film : If volatile oxide film formed by metal ,corrosion rate is very high .If porous oxide film formed by metal ,as this is non protective oxide film, corrosion rate is moderate but if non porous oxide film is formed by metal ,it is protective against corrosion.

Nature of corrosion product: In electrochemical corrosion if corrosion product is soluble in corroding medium, corrosion proceeds at faster rate. If corrosion product is insoluble in medium it stops further corrosion. And if corrosion product is volatile it causes rapid & continuous corrosion.

Electrode potential (oxidation potential): The extent of corrosion depends on the position of metal in galvanic series, metal which is placed higher in galvanic series get corroded fast than the lower metal.

The rate, extent of corrosion depends upon the potential difference between the two metals, the greater will be difference in their oxidation potential faster will be the corrosion of anodic metal

Q.7: Explain any three factors influencing the rate of corrosion with respect to nature of environment.3M(any three -1M each)

Ans-Temperature: The rate of corrosion is directly proportional to temperature i.e., rise in temperature increases the rate of corrosion. This is because the rate of diffusion of ions increases with rise in temperature

Humidity: The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, and sulphur dioxide gases etc. in the air to produce the electrolyte which is required for setting up a electrochemical cell.

pH of the medium: Generally acidic media (i.e. $\text{pH} < 7$) are more corrosive than alkaline and neutral media.

Nature of ions present: If anions like silicate is present in medium-which form barrier & inhibit further corrosion. Whereas if chloride ions is present in medium –corrosion is rapid

Conductance of the corroding medium: Corrosion in case of underground & submerged structure ,the mineralized & clayey soil is more conductive than sandy soil. Therefore corrosion rate is high in clayey soil thus rate of corrosion is high in highly conducting medium

Q.8 what is pilling Bedworth rule? How P.B ratio affects the rate of corrosion, explain with suitable example.4M (Marking scheme: PBR Difinition-1M, explanation with example-3M)

Ans. Pilling Bedworth rule: It is the ratio of volume of metal oxide formed to the volume of metal atom consumed.

$$\text{PBR} = \frac{\text{volume of metal oxide formed}}{\text{volume of metal atom consumed}}$$

PBR <1: the oxide coating layer is too thin, likely broken and provides no protective effect.

Example: Na, K, Mg.

PBR >2: oxide formed chips off or cracks .thus provides no protective effects

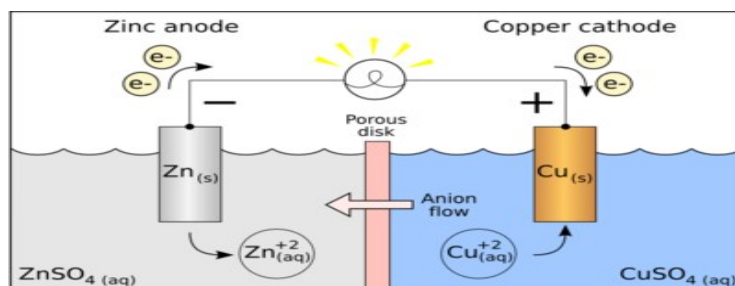
Example: Fe

1 < PBR < 2: Consequently, an extremely tightly-adhering non-porous layer and protective layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

Example: Al, Ti Cr.

Q.9 Explain galvanic corrosion as a type of wet corrosion with suitable example. 4M (Marking scheme: figure-1M, explanation with example-3M)

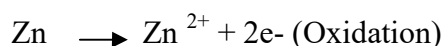
Ans:



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

In this process, the more active metal (with more negative electrode potential) acts as a anode while the less active metal (with less negative electrode potential) acts as cathode

In the above example, zinc (higher in electrochemical series) forms the anode and will dissolve& get corroded.



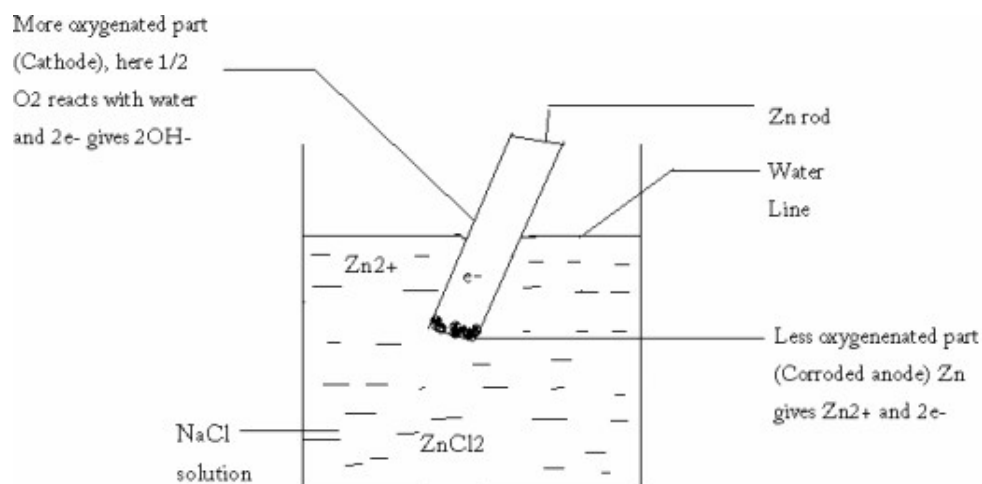
Whereas copper (lower in electrochemical series or more noble) acts as cathode. The nature corrosive environment decides the type of cathodic reaction.

If acidic medium, the corrosion occurs by the hydrogen evolution mechanism; while in neutral or slightly alkaline solution, corrosion occurs by oxygen absorption mechanism.

Q.10 Explain oxygen concentration cell corrosion (differential aeration corrosion) as a type of wet corrosion with suitable example. 3M (Marking scheme: explanation -2M, example-1M)

Ans- It occurs when one part of same metal is exposed to differential aeration (i.e. different air concentration) from the other part. This causes a difference in potential between differently aerated areas. Poor-oxygenated parts are anodic.

Examples: i) The metal part immersed in water or in a conducting liquid is called water line corrosion.



Explanation: If a metal is partially immersed in a conducting solution, the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.

Q.11 Explain cathodic protection method using sacrificial anode with respect to principle, method & application. 5M (Marking scheme: Principle-1M, method-2M, figure-1M, application-1M)

Ans: Principle: In electrochemical corrosion, anode is the one which undergoes corrosion & cathode remains protected from corrosion. **In cathodic protection, the metal to be protected is forced to behave like a cathode**

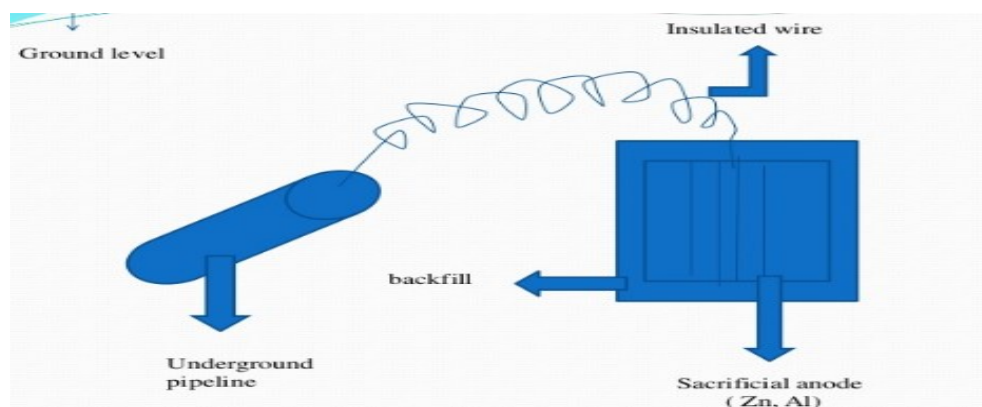


Fig: sacrificial anodic protection by underground pipeline.

Method: In this method, the metallic structure to be protected is made cathode by connecting it with more active metal (anodic metal).

-Hence, all the corrosion will be concentrated only on the active metal. The parent structure is thus protected. By any reason if coating formed on cathode gets broken/ruptured in this situation also only more active metal gets corroded by giving complete protection to cathode. Thus it

shows sacrifice by behaving as anode in any condition. Therefore the more active metal so employed is called sacrificial anode.

-The corroded sacrificial anode block is replaced by a fresh one after its complete consumption

-Metals commonly employed as sacrificial anodes are-**magnesium, zinc, aluminum** and their alloys.

Applications: For the protection of-1) Buried pipelines

2) Underground cables, ship hulls, pillars etc.

Q.12 Explain cathodic protection method using impressed current with respect to principle, method, & application.5M

(Marking scheme: Principle-1M, method-2M, figure-1M, application-1M)

Ans- Principle- In electrochemical corrosion, anode is the one which undergoes corrosion & cathode remains protected from corrosion. In cathodic protection, the metal to be protected is forced to behave like a cathode,

Method-In this method, an impressed external current is applied in opposite direction to nullify the corrosive current and convert the corroding metal from anode to cathode.

- Usually the impressed current is derived from a direct current sources (like battery or rectifier on AC line)

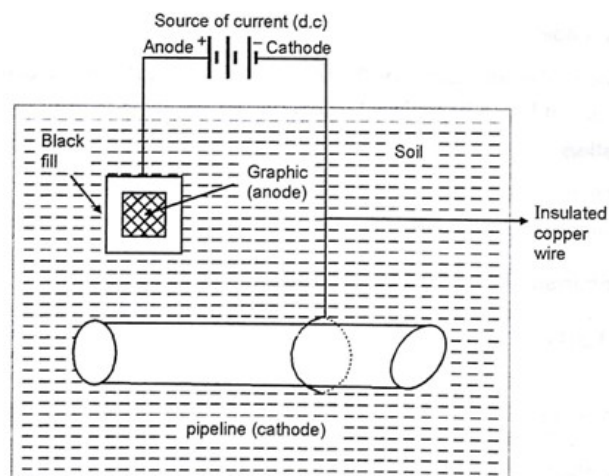
This DC source is connected with an insoluble, inert anode (+ve terminal of DC is connected to anode) (like graphite, scrap iron, stainless steel, and platinum)buried in the soil &-ve terminal of DC is connected to cathode i.e. the metallic structure to be protected

The anode is generally placed in a backfill (mixt of salt+coal) so as to increase the electrical contact with surrounding soil

Applications:-For the protection of -

1) Water tank

2) Buried oil & water pipes, condensers ,transmission line towers.



Q.13 Describe anodic protection method used for prevention of corrosion on the basis of principle, method & application. 5M (Marking scheme: Principle-1M, method-2M, figure-1M, application-1M)

Ans: principle: The part of 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, thin oxide film is formed which protects the surface from further corrosion.

Method: metallic part which is to be protected from corrosion is connected to potentiostat. Potentiostat maintain a constant potential & has a reference electrode attached to it

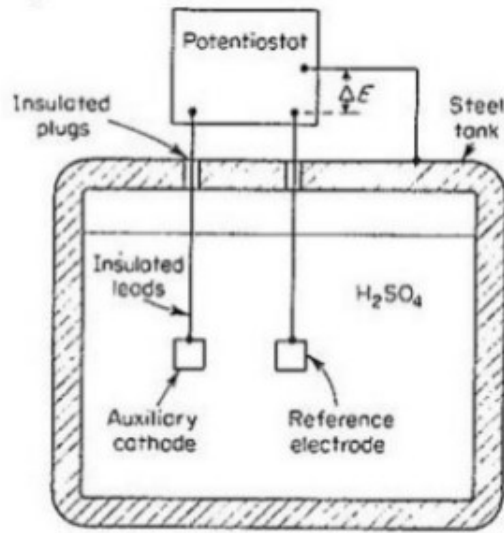
-an auxiliary electrode which does not suffer much corrosion in the oxidizing environment acts as cathode. The tank to be protected acts as anode.

-the potentiostat is adjusted for particular current & so that anodic metal tank gets oxidized & gets passivated. There is a formation of thin corrosion resistant oxide layer which protects the metal from corrosion.

-Once the metal becomes passive, the potential abruptly change to a positive value. This reduces current and reduces further corrosion of metal.

Application: For the protection of:

- 1) Stainless steel containers used for transporting corrosive chemicals like acids
- 2) Chemical reactors, tanks

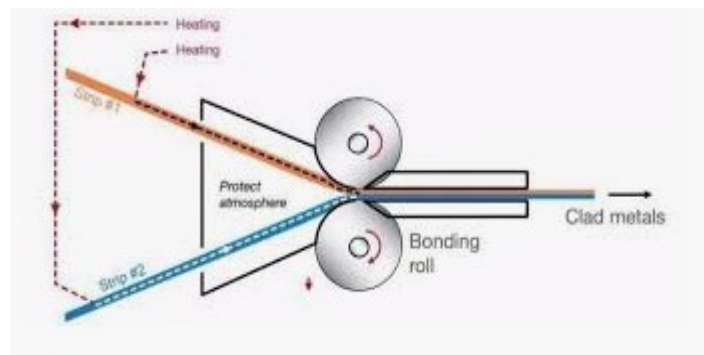


Q.14) What is metal cladding? Which is the commonly used cladding material? Describe the process of metal cladding with suitable figure.

4M(Marking scheme: Definition-1M, cladding material-2M, and process with figure-2 M)

Ans- Metal cladding: metal cladding is the process by which coating metal is bonded firmly & permanently to base metal on one or both sides.

Cladding material: metals like Ni, Cu, Pb, Pt & alloy like stainless steel, nickel alloy copper alloy etc.



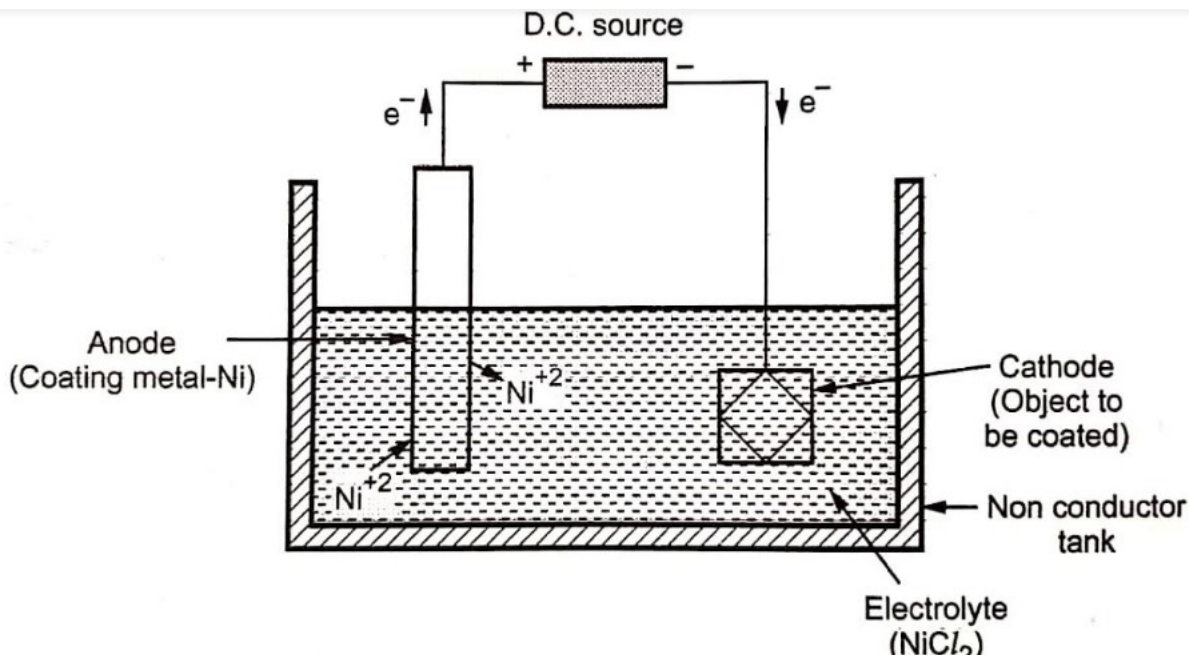
Process: It is done by performing a sandwich of protecting layer & the base metal, which are passed through rollers & bonded under the action of heat & pressure.

Example: Duralumin is sandwiched between two layers of 99.5% pure Al, this sheet is called **Alclad** used in Aircraft industry.

Q.15 What is electroplating? Explain the process with suitable diagram. Give any two applications of electroplating. 5M (Marking scheme: Definition-1M, process-2M, diagram-1M, two applications-1M)

Ans: Electroplating: It is the process of coating metal is deposited on base metal by passing a direct current through electrolytic solution of an electrolyte, containing the soluble salt of coating metal.

Diagram:



Process:- The base metal article to be coated, is cleaned to remove oils, oxides, scales etc

-the metal article to be plated is made cathode.

-coating metal is made anode

-cathode & anode are dipped in the electrolyte. (Salt solution of coating metal) containing suitable mineral acid which increases electrical conductivity.

-pH of electrolyte is adjusted and suitable current density is chosen for electrolysis.

-when electric current passed through electrolyte, anode metal gets oxidized & dissolves in electrolytic solution as a metal ion

-These metal ion get deposited on cathode surface form uniform coating.

	Reaction at anode	Reaction at cathode	Salts for electrolyte
For nickel plating	$\text{Ni} \rightarrow \text{Ni}^{+2} + 2\text{e}^-$	$\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni}$	NiCl_4 , NiSO_4
For copper plating	$\text{Cu} \rightarrow \text{Cu}^{+2} + 2\text{e}^-$	$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$	CuSO_4
For silver plating	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	AgCN

Application: It is used for protecting surface against corrosion

2) Electroplating is done on non-metallic surface like wood, paper, glass, leather for decoration & preservation of surface.

Q.16) What is galvanizing? Explain the process of galvanizing of steel with diagram.4M

(Marking scheme: Definition-1M, process-2M, diagram-1M,

Ans: Galvanizing: It is process coating steel or iron with a thin coat of zinc by hot dipping to prevent base metal from corrosion is called galvanizing.

Process: -In this process iron or steel is first cleaned by acid pickling with dil. H_2SO_4 for 15-20 minutes and 60-90 °C to remove rust & scale.

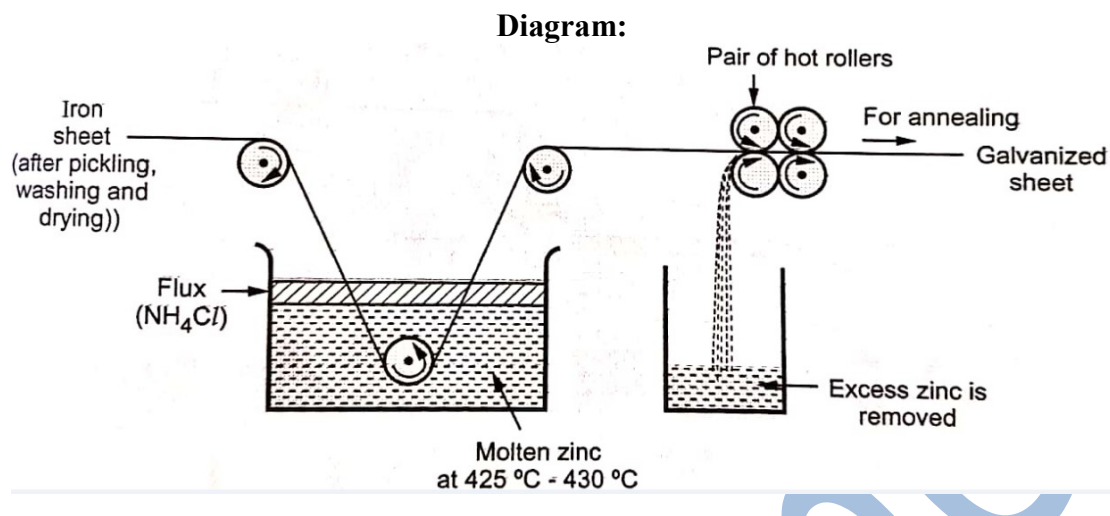
The article is then washed with water and dries in a dry chamber.

It is then dipped in bath of molten Zinc at 425-430°C.

The surface of the bath is kept covered with NH_4Cl flux to prevent oxide formation.

When the article is taken out, the article is coated with a thin layer of Zinc. It is then passed through a pair of hot rollers to remove any excess of Zinc& produce thin uniform coating

-it is then annealed at 625°C & cooled at room temp.



Q.17) what is hot dipping? Explain the process of tinning of steel with help of suitable diagram.4M (Marking scheme: Definition-1M, process-2M diagram-1M)

Ans: Hot dipping: It is the process of coating of low melting metals such as Zn, Sn on the surface of high melting metal like iron, steel.

Process: It is coating of Tin over the iron or steel articles

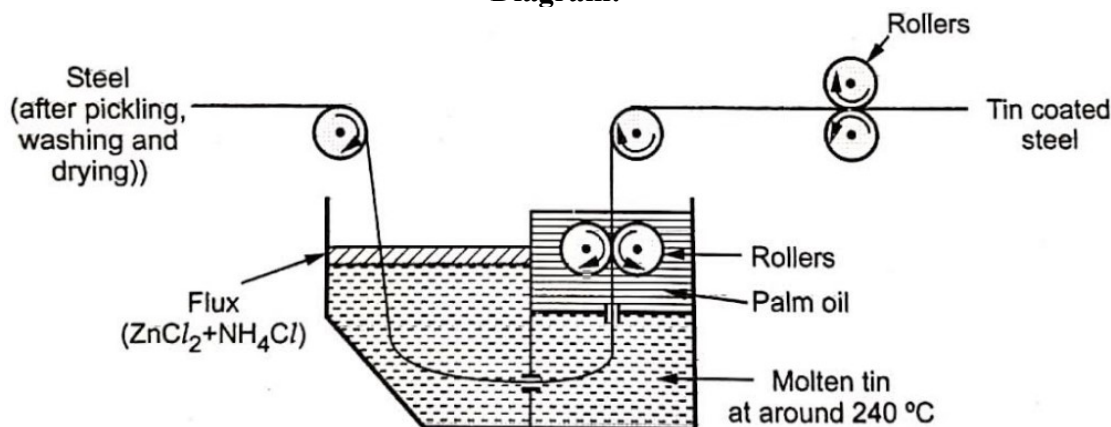
In this process first treating steel sheet in $\text{Dil. H}_2\text{SO}_4$ to remove any oxide film after this it is passed through a bath of molten tin maintained at 240°C

It is covered by a ZnCl_2 flux. This flux helps the molten metal to adhere on the metal sheet and helps to prevent oxidation of molten tin

Finally the metal sheets passed through a series of rollers from underneath the surface of a layer of palm oil. The palm oil protect the hard tin coated surface against oxidation

The rollers remove any excess of tin and produce a tin film of uniform thickness on the steel sheet.

Diagram:



Q.18) what is cementation? Which are the different coating metals used in cementation process. Describe sherardizing as cementation.4M (Marking scheme: Definition-1M, metals used in the process-1M, process of sherardizing-2M)

Ans: Cementation: In which coating is obtained by heating base metal in a revolving drum containing a powder of the coating metal.

Coating metals used in cementation: Zn, Cr, Al.

Sherardizing process: It is process of cementation in which Zn powder is used as coating metal.

In this process, iron article is cleaned and packed with zinc dust in a drum

The drum is sealed tightly so that oxidation of zinc is minimum,

The drum is rotated for 2-3 hrs.& heated at 350-370°C

During this process Zn get diffused into iron forming Fe-Zn alloy.

Q.19) what is anodic & cathodic coating ? Which is more protective and why?4M

(Marking scheme: Definition-1M each, state better coating-1M, reason-1M)

Ans: Anodic coating:-Anodic coating are produced from coating metals which are anodic to base metal i.e. which have higher in position in galvanic series than base metal

E.g. -coating of Zn, Al, Cd on steel

Cathodic coating:-Cathodic coatings are obtained when the coating metal is cathodic to the base metal .i.e. coating metal which is lower in position in galvanic series than base metal.

E.g:- if Fe is a base metal ,Tin(Sn) is coating metal

Anodic coating is always better than cathodic coating.

Reason:- Because in case of anodic coating E.g. coating of Zn, on steel are anodic coating .if any pores , breaks occur in such anodic coating ,a galvanic cell is formed between coating metal & exposed part of base metal. Here coating metal Zn is more anodic to steel (Fe) and undergoes corrosion, coating metal get corroded & protecting underlying base metal.

But in case of cathodic coating E.g. coating of Tin on steel is cathodic coating. If coating is broken a galvanic cell is formed between coating metal & exposed part of the base metal then Tin is cathodic to iron therefore it acts as cathode base metal acts as anode undergoes corrosion. Thus in this case base metal get corroded

Cathodic coating provides effective protection to the base metal only when they are completely continues & free from pores, cracks.

Q.20) why surface preparation is carried out before applying metallic coating on metal surface? Explain the steps involved in surface preparation.5M

(Marking scheme: reason for surface preparation-1M, steps involved-4M)

Ans:- Reason:- To increase the life of protective coating on metal surface.

Three Steps involved surface preparation:-

Step1) Removal of grease & other contaminations:- For removal of grease other contamination like paints following cleaning procedure is used.

I) Solvent cleaning: Solvents like CCl_4 , toluene & acetone etc. is used to remove oils, greases, fatty substances from metal surfaces.

It is followed by cleaning with steam & hot water containing wetting agent

II) Alkali cleaning: It is used for removing old paint coating from metal surfaces .E.g. trisodium phosphate along with soaps & wetting agent like caustic soda are used for this purpose.

-followed by very mild rinsing with water further treated with slightly acidic solution to neutralize the traces of alkali left

Step2) Removal of oxide scale, rust & corrosion products:- following methods to remove oxide scale, rust & corrosion product

I) Mechanical cleaning:- By using chisel, wire brush, scrapers etc loose rust & other impurities removed from the metal surface .

II) Flame cleaning:- Metal surface is heated with hot flame to remove moisture & loosely held scales. followed by wire brushing.

III) Sand blasting:- the process consists of introducing the sand into air stream under pressure of 25 to 100 atm. to remove oxide scale

Step3) Etching treatment for better adhesion of coat.

In order to achieve better adhesion of metallic coating **pickling** method is widely used

Pickling: - Involve immersing the metal in acidic or alkaline solution to provide clean, smooth surface.

SCOE, Pune