
UNIT III: ELECTROCHEMICAL CELLS AND CORROSION

Galvanic cells - Reversible and irreversible cells – Single electrode potential – Electrochemical series and uses of this series- Standard electrodes (Hydrogen and Calomel electrodes) - Concentration Cells – Batteries: Dry Cell - Ni-Cd cells - Ni-Metal hydride cells - Li cells - Zinc – air cells.

Corrosion :- Definition – Theories of Corrosion (chemical & electrochemical) – Formation of galvanic cells by different metals, by concentration cells, by differential aeration and waterline corrosion – Passivity of metals – Pitting corrosion - Galvanic series – Factors which influence the rate of corrosion - Protection from corrosion – Design and material selection – Cathodic protection - Protective coatings: – Surface preparation – Metallic (cathodic and anodic) coatings - Methods of application on metals (Galvanizing, Tinning, Electroplating, Electroless plating).

1. Introduction

A system in which two electrodes are in contact with an electrolyte is called as cell. There are two types of cells,

- i) Electrolytic Cell
- ii) Electrochemical cell.

(i). Electrolytic cell:

Electrolytic cell is a device which produces chemical change by supplying electric current from outside source. Here, electrical energy is converted into chemical energy.

(ii). Electrochemical cells:

Electrochemical cell is a device in which chemical energy from a redox reaction is utilized to get electrical energy. Here, chemical energy is converted into electrical energy.

Example: Daniel cell.

2. Galvanic cells –

Galvanic cells are electrochemical cells in which the electrons transferred due to redox reaction, are converted into electrical energy. A galvanic cell consists of two half-cells with each half-cell contains an electrode. The electrode at which oxidation takes place is called anode and the electrode at which reduction occurs is called cathode. The electrons liberated to the electrolyte from the metal leaves the metal ions at anode. The electrons from the solution are accepted by the cathode metal ion to become metal. Galvanic cell is generally represented as follows.

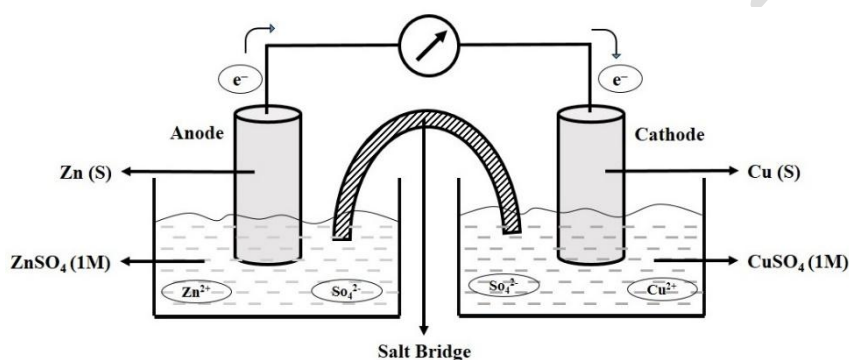


Where, M_1 & M_2 are Anode and Cathode respectively and M_1^+ & M_2^+ are the metal ions in respective electrolyte. The symbol \parallel denotes salt bridge. The above representation of galvanic cell is known as galvanic cell diagram.

Example: The typical example for galvanic cell is Daniel cell.

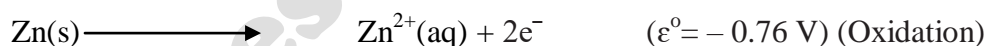
Daniel Cell:

This cell consists of a zinc rod as anode dipped in zinc sulphate solution (electrolyte) in a glass tank and copper rod as cathode dipped in copper sulphate (electrolyte) in another glass tank. Each electrode is known as half-cell. The two half cells are inter-connected by a salt bridge and zinc and copper electrodes are connected by a wire through voltmeter. The salt bridge contains saturated solution of KCl in agar-agar gel. The cell diagram of Daniel cell is

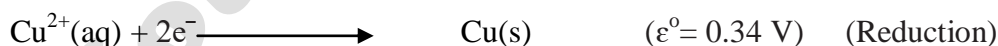


Redox reaction occurs at Daniel cell:

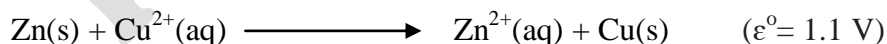
At anode:



At cathode:



Overall Cell reaction:

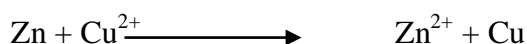


When the zinc rod is connected to copper wire, the chemical reaction starts at both the electrodes. Therefore the zinc rod transfer electrons to copper rod through external circuit. Thus the zinc rod (At anode) starts formation of Zn^{2+} ions and increase the concentration of Zn^{2+} ions in the solution. Whereas at the copper electrode (At cathode) Cu^{2+} ions in the solution takes electrons from copper rod and coats Cu on the electrode.

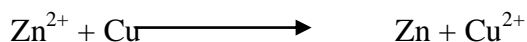
3. Reversible and irreversible cells –

Reversible electrochemical cells: are the cells whose cell reactions can be get reversed when an external emf greater than its capacity is applied. (A cell which obeys thermodynamic conditions of

reversibility is known as reversible cells). For example 3 Daniel cell with Capacity 1.1 V, when an external emf of 1.1 V is applied, the cell reaction stops.

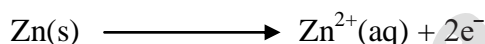


But when an increased amount of emf greater than 1.1 V is applied, the cell reaction is get reversed.

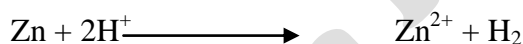


A cell of this type can be termed as Reversible cell.

Irreversible electrochemical cells: are the cells whose cell reactions cannot be get reversed when an external emf greater than its capacity is applied. (A cell which does not obey thermodynamic conditions of reversibility is known as irreversible cells). For example, a cell which has Zn as an anode and Ag as a cathode with sulphuric acid as an electrolyte. The cell reaction at the anode is (Zn/H+/Ag)



In the presence of electrolyte (H₂SO₄)



When an external emf is applied to the cell, the chemical reactions are not reversed because one of the products of the reaction H₂ gas is escaped from the reaction system. Dry cells are another familiar example for this type of cells.

4. Single electrode potential –

The measure of tendency of a metallic electrode to lose or gain electrons when in contact with a solution of its own salt in a half cell of an electrochemical cell is called as single electrode potential.

5. Electro chemical series and uses of this series-

When various metals as electrodes are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

Metal ion	Potential in volts
$\text{Li}^{+} + \text{e}^{-} \longrightarrow \text{Li}$	-3.05 Anode
$\text{K}^{+} + \text{e}^{-} \longrightarrow \text{K}$	-2.93
$\text{Ca}^{2+} + 2\text{e}^{-} \longrightarrow \text{Ca}$	-2.90
$\text{Na}^{+} + \text{e}^{-} \longrightarrow \text{Na}$	-2.71

$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.37	
$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66	
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.76	
$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	-0.74	
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.44	
$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	-0.23	
$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.14	
$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	-0.13	
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}$	-0.04	
$\text{H}^+ + \text{e}^- \longrightarrow \text{H}$	0.00	Reference
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34	
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.80	
$\text{Pt}^{4+} + 4\text{e}^- \longrightarrow \text{Pt}$	+0.86	
$\text{Au}^+ + \text{e}^- \longrightarrow \text{Au}$	+1.69	
$1/2\text{F}_2 + \text{e}^- \longrightarrow \text{F}^-$	+2.87	Cathode

Significance and applications of electrochemical series:

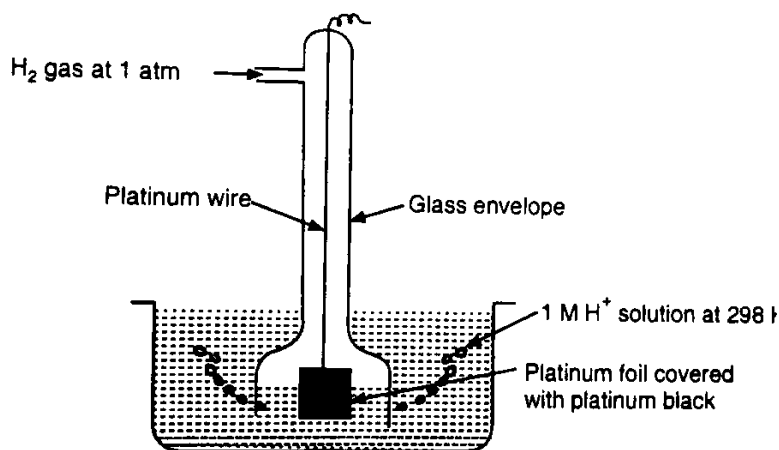
- Calculation of standard EMF of a cell: Standard electrode potential of any cell can be calculated using this series.
- Relative ease of oxidation and reduction: Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. Thus, metals on the top having more negative (-ve) values are more easily ionized (oxidized).
- Displacement of one element by another Metals: which lie higher in the series can displace those elements which lie below them in the series.
- Determination of equilibrium constant for the reaction: The equilibrium constant for the cell can be calculated from the standard electrode potential.
- Hydrogen displacement behaviour: Metals having more -ve potential in the series will displace hydrogen from acid solutions.
- Predicting spontaneity of redox reactions: Spontaneity of redox reaction can be predicted from the standard electrode potential values of the complete cell reaction.

6. Standard electrodes (Reference Electrodes)

The electrode of standard potential with which we can compare the potentials of another electrodes is called a reference electrode. The best reference electrode used is standard hydrogen electrode whose electrode potential at all temperature is taken as zero.

7. Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE) –

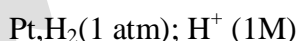
It consists of a small piece of platinum foil electroplated with platinum black, over which hydrogen gas is passed. The platinum black surface exhibits a strong absorption power towards hydrogen gas, as a result the metal surface remains continuous contact with the hydrogen gas. The electrode will act as if it were an electrode of metallic hydrogen. When in use, therefore, only a part of the foil is immersed in 1N HCl; the remainder is surrounded by hydrogen gas at atm pressure. This is standard hydrogen electrode. The e.m.f. of the electrode has been arbitrarily assigned to be zero and all other electrode potential are expressed in comparison with this value.



The reactions occurring in this electrode is as follows:



Standard hydrogen electrode is represented as follows

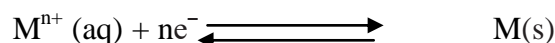


The pH of the solution can be measured with the help of hydrogen electrode.

The tendency of an electrode to lose electrons is called oxidation potential while the tendency of an electrode to gain electrons is called reduction potential.

Expression for electrode potential:

The electrode potential for an electrode reaction



Now for a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter-related as;

$$\Delta G = RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \dots\dots\dots(i)$$

Where ΔG° is known as the standard free energy change (i.e., the change in free energy, when re unity each). The above equation, is known popularly as Van't Hoff's reaction isother. In a reversible reaction, the electrical energy is produced at the expense of the free energy decrease, i.e.,

$$\Delta G^\circ = nEF \quad \text{and} \quad \Delta G^\circ = -nE^\circ F \quad \dots\dots\dots(ii)$$

Where E is the electrode potential; E° is the standard electrode potential; F is Faraday (96,500 coulombs), from equation (i) and (ii)

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nEF = -nE^\circ F + RT \ln \frac{1}{[M^{n+}]} \quad (\text{Concentration of metal, M is unity})$$

$$-nEF = -nE^\circ F - RT \ln [M^{n+}]$$

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] = E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

This expression, is known as Nernst's equation for electrode potential. At 25 °C

$$\frac{2.303 RT}{nF} = \frac{0.0592 V}{n}$$

$$E = E^\circ + \frac{0.0592 V}{n} \log [M^{n+}]$$

From the above equation, it is cleared that (i). If the concentration of solution $[M^{n+}]$ is increased, the electrode potential increases and vice versa. (ii). If the temperature increased, the electrode potential increases and vice versa.

8. Calomel electrode –

It consists of a tube in the bottom of which is a layer of mercury, over which is placed a paste of $\text{Hg} + \text{Hg}_2\text{Cl}_2$. The remaining portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire, dipping into the mercury layer, is used for making electrical contact. The side-tube is used for making electrical contact with a salt bridge.

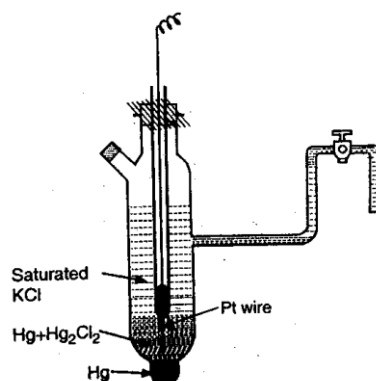
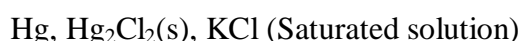
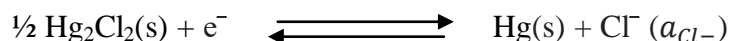


Figure: Saturated calomel electrode

The saturated calomel electrode is formulated as:



The electrode reaction is:



The electrode potential (E) is given by

$$E = E^\circ + \frac{RT}{F} \ln a_{\text{Cl}^-} \quad (\text{Where } n=1)$$

The standard electrode potential of calomel electrode

For (0.1 N) KCl = +0.28 V

Saturated KCl = +0.2422V

Any electrode whose standard potential is to be determined is connected to calomel electrode by means of KCl salt bridge. The e.m.f. of the set-up cell is determined potentiometrically from which the standard electrode potential of the electrode is calculated.

To determine pH of a solution: The electrode is coupled with hydrogen electrode containing solution of unknown pH,

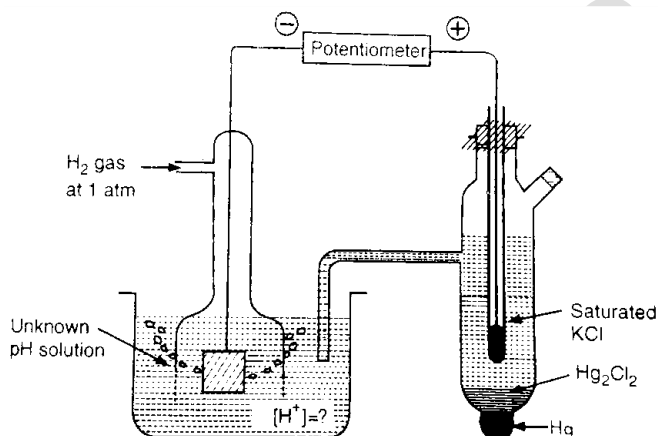
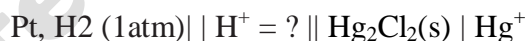


Figure: Determination of pH value of a solution using calomel electrode



$$E_{\text{obs}} = E (\text{Calomel}) - E(\text{H}_2 \text{ electrode})$$

$$E_{\text{obs}} = E (\text{Calomel}) - 0.059 \log[\text{H}^+]$$

$$E_{\text{obs}} = 0.28 + 0.059 \text{ pH} \quad \text{Or} \quad \text{pH} = \frac{E_{\text{obs}} - 0.28}{0.059}$$

9. Concentration Cells –

The cell which produces electrical energy by transfer of a substance from the solution of higher concentration to the solution of lower concentration is called concentration cell.

This is also an electrochemical cell. The difference in concentration may be brought about by the difference in concentration of the electrodes or electrolytes. The concentration cells are classified into two types.

- i) Electrode concentration cell
- ii) Electrolyte concentration cell.

Electrode concentration cell:

Two identical electrodes of different concentrations are dipped in the same electrolytic solution of the electrode metal in a cell is called electrode concentration cell.

Example: Amalgam concentration cells.

Amalgam electrodes are produced by mixing various proportions of lead and mercury. It is represented as,



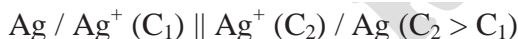
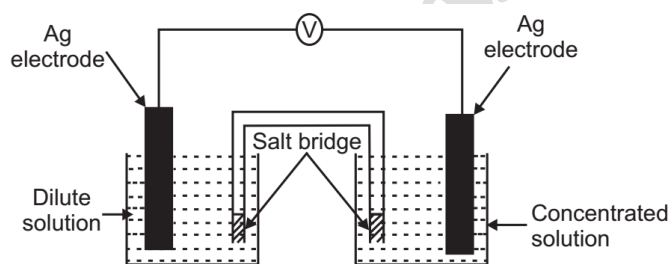
Where, C_1 & C_2 are concentrations of electrolytes.

Electrolyte concentration cell:

Two identical electrodes of same concentrations are dipped in the electrolytic solutions of different concentration in a cell is called electrolyte concentration cell.

Example: Silver ion concentration cell

The diagram of an electrolytic concentration cell is



10. Batteries:

A device that stores chemical energy and releases it as electrical energy is called as battery or storage battery. A battery is an electrochemical cell which is often connected in series in electrical devices as a source of direct electric current at a constant voltage. Batteries are classified as follows,

- (i) Primary Battery
- (ii) Secondary Battery
- (iii) Flow Battery

Primary Battery (or primary cells):

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. They are use and throw type.

Example: Dry cell, Laclanche cell etc.

Secondary Battery (or secondary cells):

Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged.

Example: Nickel-Cadmium cell, Lead-acid cell (storage cell), etc.

Flow Battery and Fuel Cell:

Flow battery is an electrochemical cell that converts the chemical reaction into electrical energy. When the reactants are exhausted, new chemicals replace them.

Example: Hydrogen-oxygen cell, Aluminium-air cell, etc.

In Aluminium-air cell, when the cell is exhausted, a new aluminium rod is used and the solution is diluted with more water as the electrochemical reaction involves aluminium and water.

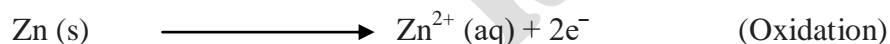
11. Dry Cell – (or Leclanche cell): A cell without fluid component is called as dry cell.

Example: Daniel cell, Alkaline Battery

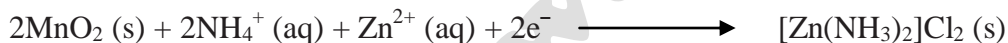
Construction and working:

The anode of the cell is zinc container containing an electrolyte consisting of NH_4Cl , ZnCl_2 and MnO_2 to which starch is added to make it thick paste-like so that is less likely to leak. A graphite rod serves as the cathode, which is immersed in the electrolyte in the centre of the cell. The electrode reactions are given below.

Anodic reaction:



Cathodic reaction:



Overall reaction:

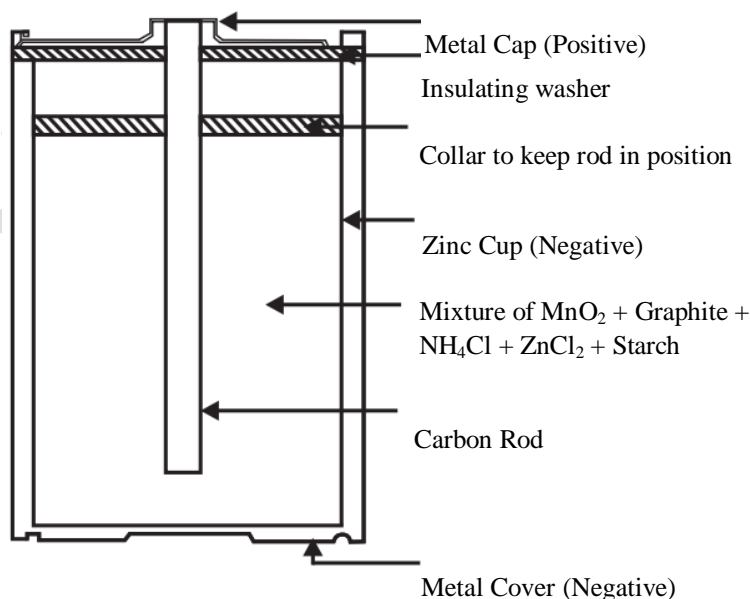


Figure: Construction of a dry cell

The dry cell is a primary battery, since no reaction is reversible by supplying electricity. Dry cell is very cheap to make. It gives voltage of about 1.5V.

Limitations: i) When current is drawn rapidly, drop in voltage occurs. ii) Since the electrolyte is acidic, Zn dissolves slowly even if it is not in use.

Uses: Dry cells are used in flash-lights, transistor radios, calculators, etc.

12. Ni-Cd cells –

A nickel – cadmium storage cell consists of Cadmium as anode and NiO paste as cathode and KOH as the electrolyte.

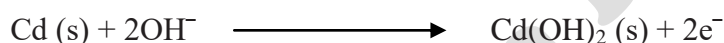
The cell is represented as...



Construction and Working:

When the nickel battery operates, Cd is oxidized to Cd^{2+} ions at anode and the insoluble Cd(OH)_2 is formed. NiO(OH) is reduced to Ni ions which further combines with OH ions to form Ni(OH)_2 . It produces about 1.4 V. The following cell reactions occur.

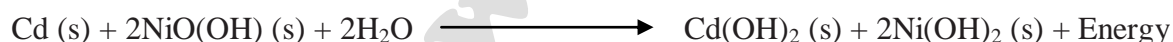
Anodic reaction:



Cathodic reaction:

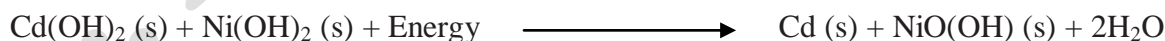


Overall cell reaction during discharging:



From the above cell reactions, it is clear that Cd(OH)_2 and Ni(OH)_2 are deposited at both the anodes and cathodes respectively. So, this can be reversed by recharging the cell.

Overall cell reaction during recharging: The cell can be charged by passing electric current in the opposite direction. The electrode reactions get reversed. As a result, Cd is deposited on the anode and NiO on the cathode.



Advantages of Ni-Cd battery:

1. It is portable and rechargeable cell.
2. It has longer life than lead – acid battery.
3. It can be easily packed like dry cell since it is smaller and lighter.

Uses:

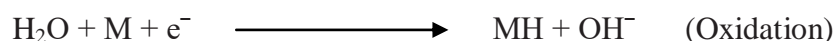
1. It is used in calculators.
2. It is used in gas electronics flash units.
3. It is used in transistors, cordless electronic appliances, etc.

13. Ni-Metal hydride cells –

These are abbreviated as NiMH or Ni-MH, these are reversible cells. The chemical reaction at the positive electrode is similar to that of the nickel-cadmium cell (NiCd), with both using nickel oxyhydroxide (NiOOH). However, the negative electrodes use a hydrogen-absorbing alloy instead of cadmium. A NiMH battery can have two to three times the capacity of an equivalent size Ni-Cd battery.

The cell reaction is

At Cathode:

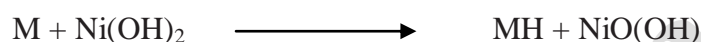


The charge reaction is read left to right and discharge reaction is read right to left.

At Anode:



Overall cell reaction during discharging:



The metal M in the negative electrode of a NiMH cell is an intermetallic compound. Many different compounds have been developed for this application.

When overcharged at low rates, oxygen produced at the positive electrode passes through the separator and recombines at the surface of the negative. Hydrogen evolution is suppressed and the charging energy is converted to heat. This process allows NiMH cells to remain sealed in normal operation and to be maintenance-free.

Uses: It is used in calculators, electronic flash units etc.,

14. Li cells –

In the Li batteries, Li is used as anode and different types of compounds have been used for the cathode and electrolyte. The common setup in these cells is Li as anode, MnO₂ as cathode salt of lithium dissolved in an organic solvent.

Three principal types of lithium organic electrolyte battery are currently available; the lithium-thionyl chloride system, the lithium-vanadium pentoxide system and the lithium-sulphur dioxide system. These batteries all have high-rate capabilities.

Example: Lithium-sulphur dioxide batteries.

At Anode:



At Cathode:



Overall cell reaction:

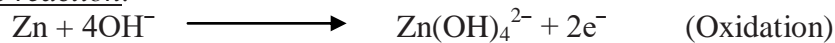


Uses of Li cells:

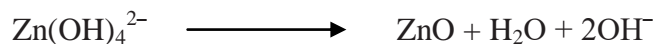
15. Zinc – air cells.

Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate ($\text{Zn}(\text{OH})_4^{2-}$), releasing electrons to travel to the cathode. The zincate decays into zinc oxide and water returns to the electrolyte. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed.

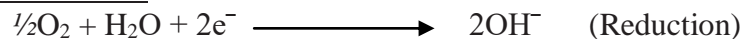
Anodic reaction:



Fluid:



Cathodic reaction:



Overall cell reaction:



Zinc–air batteries cannot be used in a sealed battery holder, because it need the oxygen from atmosphere.

16. Fuel Cells

Fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is,



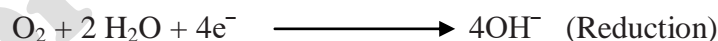
17. Hydrogen Oxygen Fuel Cell:

It consists of fuels Hydrogen, oxygen and consists of 25% KOH as electrolytic solution and two inert porous electrodes. Hydrogen oxygen gases are bubbled through the anode and cathode compartment respectively.

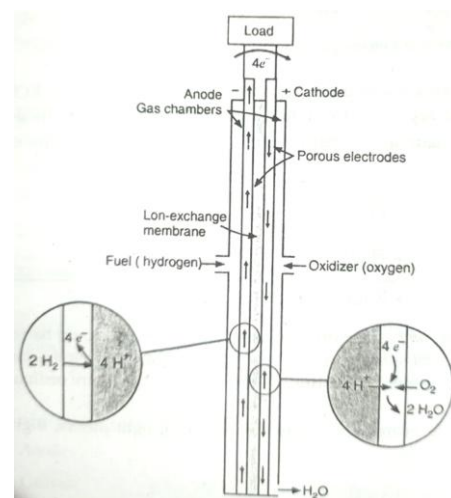
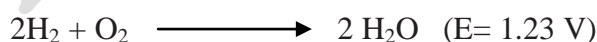
Anodic reaction:



Cathodic reaction:



Overall cell reaction:



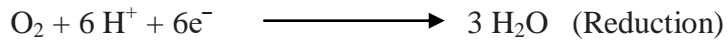
18. Methanol – Oxygen Fuel Cell

It consists of fuels Methanol and Oxygen, at anode methanol undergoes oxidation and liberates electrons; at cathode oxygen takes the electrons and undergoes reduction. It produces 1.06 V electricity, the half cell reactions are as follows,

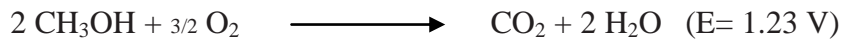
Anodic reaction:



Cathodic reaction:



Overall cell reaction:



CORROSION

19. Corrosion :-

Corrosion is a 'billion dollar thief'. Even though it is a natural phenomenon in which the gases present in the atmosphere react chemically with metals to convert them into their salts, it results in loss of material and money. Metals have a strong crystalline structure and when they are converted into their salts they lose the metallic strength resulting in the damage to machineries in which they are used. Thus corrosion causes damage to metals and thereby to the society. The estimate of loss due to corrosion is approximately 2.5 billion dollars / annum all over the world. Hence it is necessary to understand the mechanism of corrosion. In this lesson we are going to study about the causes and the mechanism of corrosion so that we can find ways to prevent this social enemy.

Corrosion is defined as the deterioration of a metal by chemical or electro chemical reactions with its environment.

Definition – Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at its surface, is called corrosion. Thus, corrosion is a process “reverse of extraction of metals”.

The most familiar example of corrosion is rusting of iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide (Fe_3O_4) is formed, and the iron becomes weak. Another common example is formation of green film of basic carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$] on the surface of copper, when exposed to moist-air containing carbon dioxide.

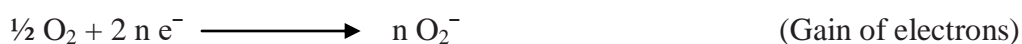
Theories of Corrosion (chemical & electrochemical) –

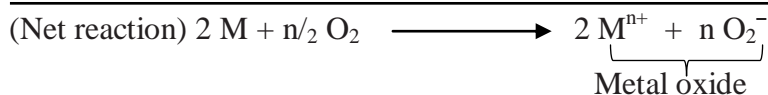
Types of corrosion

(I) Chemical Corrosion or Dry Corrosion: The direct chemical action of atmospheric gases like oxygen, halogen, H_2S etc in a dry environment on metals, a solid film of the Corrosion produced is formed on the surface of the metal. This is known as chemical Corrosion. There are three main types of corrosion.

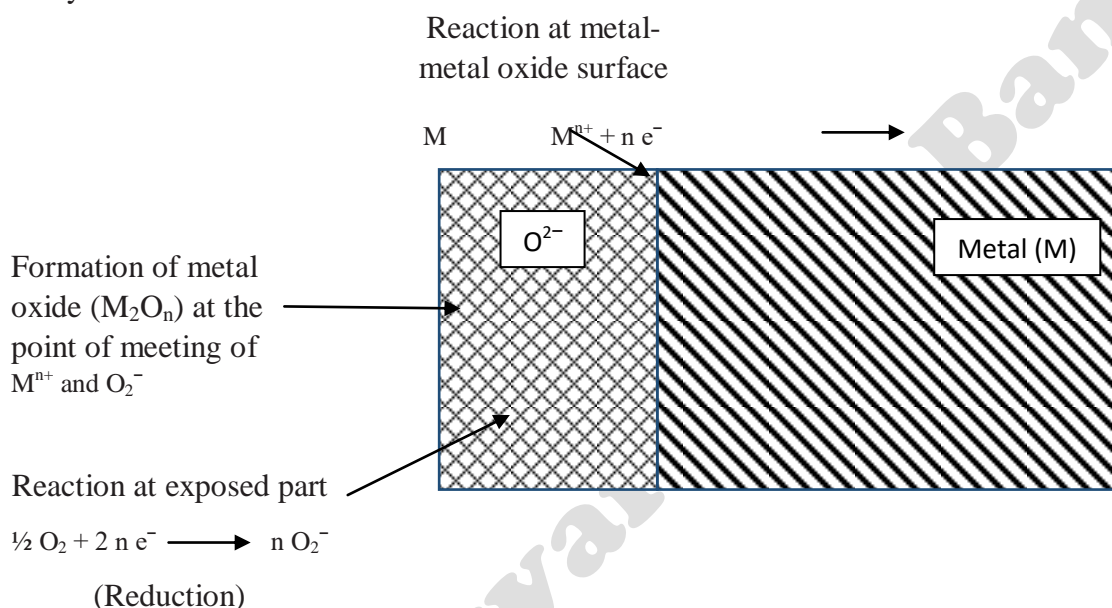
(Ia) **Oxidation corrosion**: is brought about by the direct action of oxygen at low or high temperatures on metals, usually, in the absence of moisture. At ordinary temperatures, metals, in general, are very slightly attacked. However, alkali metals (Li, Na, K, Rb, etc.) and alkaline-earth metals (Be, Ca, Sr, etc.) are even rapidly oxidised at low temperatures. At high temperatures, almost all metals (except Ag, Au, and Pt) are oxidised.

The reactions in the oxidation corrosion are:





Mechanism: oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier, that tends to restrict further oxidation. For oxidation to continue, either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion of metal is, generally, much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxygen ion and consequently, of much higher mobility.



Nature of the oxide formed plays an important part in oxidation corrosion process.

(Ib) Corrosion by other gasses like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc.

(Ic) Liquid metal corrosion is due to chemical action of following liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either: (a) dissolution of a solid metal by a liquid metal or (b) internal penetration of the liquid metal into the solid metal both these modes of corrosion cause weakening of the solid metal.

(II) Wet or Electrochemical corrosion:

Wet corrosion occurs due to the electrochemical action of moisture and oxygen on metals. Corrosion of very important metal, iron takes place due to electrochemical attack.

At anodic area: $\text{M} \longrightarrow \text{M}^{n+} + n \text{e}^{-}$ (Oxidation)

On the other hand, the cathodic reaction consumes electrons with either by (IIa) evolution of hydrogen or (IIb) absorption of oxygen.

(IIa) evolution of hydrogen: Corrosion occurs, usually, in acidic environments.

Example: Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.



These electrons flow through the metal, from anode to cathode, when H^+ ions (of acidic solution) are eliminated as hydrogen gas.

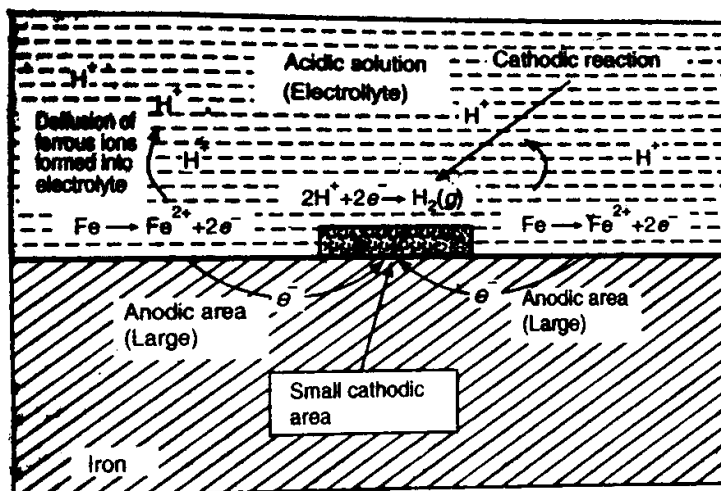
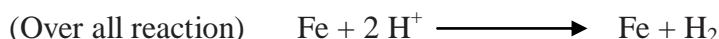


Figure: Mechanism of wet corrosion by hydrogen evolution

Thus, this type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions”.

(IIb) absorption of oxygen: Rusting or iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is, usually, coated with a thin film of iron oxide.

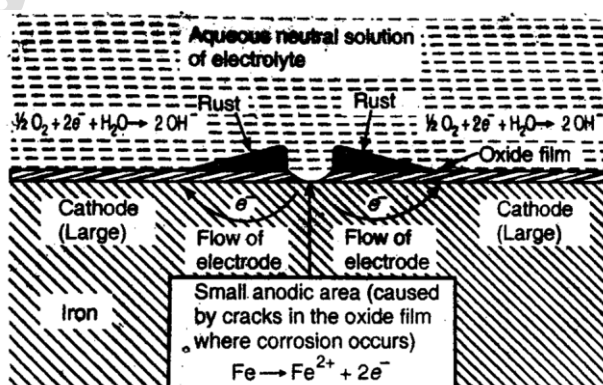
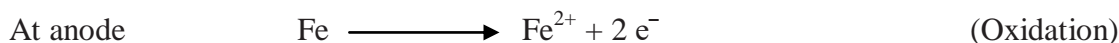


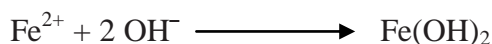
Figure: Mechanism of wet corrosion by oxygen absorption.



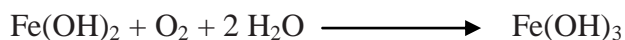
These electrons flow from anode to cathodic areas, through iron metal, where the electrons are intercepted by the dissolved oxygen as:



The Fe^{2+} ions and OH^- ions diffuse and when they meet, ferrous hydroxide is precipitated.



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



This product, called yellow rust, actually corresponds to $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

20. Formation of galvanic cells by different metals: (Galvanic (Or Bimetallic) Corrosion):

When two dissimilar metals (e.g., Zinc and copper) are electrically contacted and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion. In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved. Whereas copper (lower in electrochemical series or more noble) acts as cathode.

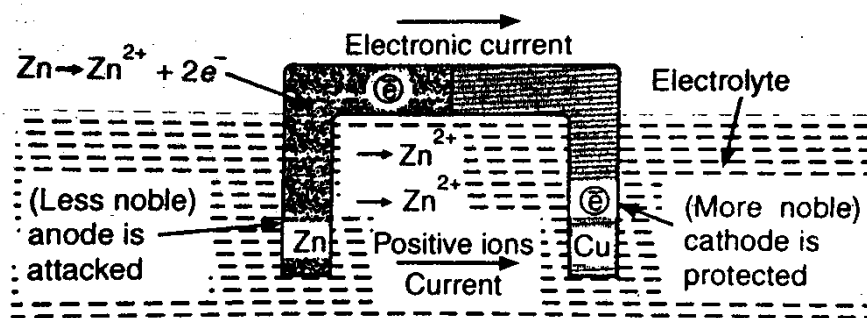
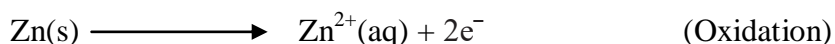


Figure: Galvanic corrosion

Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process. While in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anodic metal (zinc) to the cathodic metal (copper). Thus, it is evident that the corrosion occurs at the anodic metal. While the cathodic part is protected from the attack.



Examples:

(a). Steel screws in a brass merine hardware; (b). lead-antimony solder around copper wire; (c). Steel pipe connected to copper plumbing.

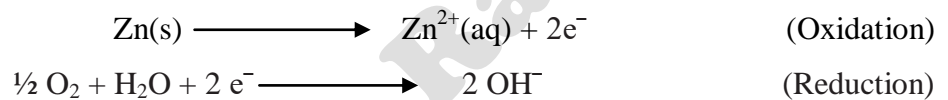
21. By concentration cells: (Concentraion Cell Corrosion):

This type of corrosion is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentration or of varying aeration. This may be the result of local difference in metal-ion concentrations, caused by local temperature differences or inadequate agitation or slow diffusion of metal-ions, produced by corrosion.

22. By differential aeration: (Differential aeration corrosion):

(The most common type of concentration cell corrosion) occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that "Poor oxygenated parts are anodic". Consequently, a differential aeration of metal causes a flow of current, called the differential current.

Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline. Thus, if a metal (say Zn) is partially immersed in a dilute solution of a neutral salt (Say NaCl) and the solution is not agitated properly, then, the parts above and closely adjacent to the waterline are more strongly aerated (because of the easy access of oxygen) and hence, become cathodic. On the other hand, parts immersed to greater depth (which have less access of oxygen) show a smaller oxygen concentration and thus, become anodic (see figure). So, a difference of potential is created, which causes a flow of current between the two differentially aerated areas of the same metal. Zinc will dissolve at the anodic areas, and oxygen will take up electrons at the cathodic areas to form hydroxyl ions.



The circuit is completed by migration of ions, through the electrolyte and flow of electrons, through the metal, from anode to cathode.

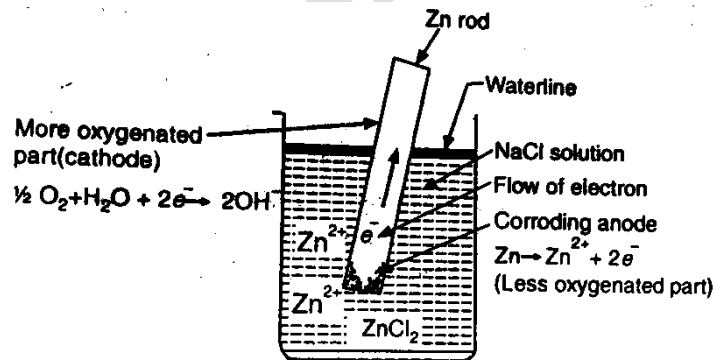


Figure: Mechanism of differential aeration attack caused by partial immersion of a metal.

Example-2:

In a similar way, iron corrodes under drops of water (or salt solution). Areas covered by droplets, having no access of oxygen, become anodic with respect to the other areas, which are freely exposed to air.

From the above, it is clear that oxygen concentration cell increases corrosion, but it occurs where the oxygen concentration is lower.

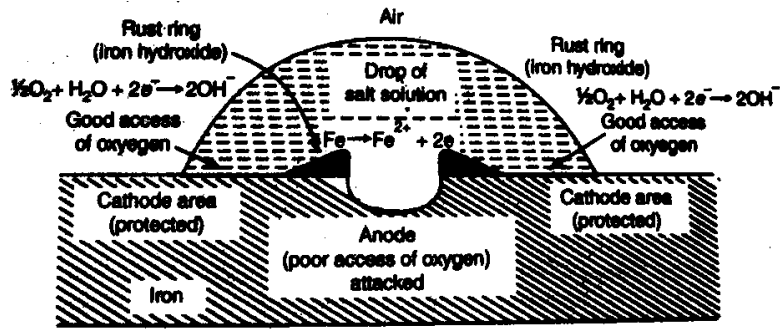


Figure: Mechanism of differential aeration attack, caused by the presence of drops of salt solution on the iron surface. Metal dissolves at the less-aerated anodic areas; whereas corrosion product (iron hydroxide) is deposited at the cathodic areas.

General facts about differential aeration corrosion:

- (i) Corrosion may be accelerated in apparently inaccessible places, because the oxygen-deficient areas serve as anodes and therefore cracks or crevices serve as foci for corrosion.

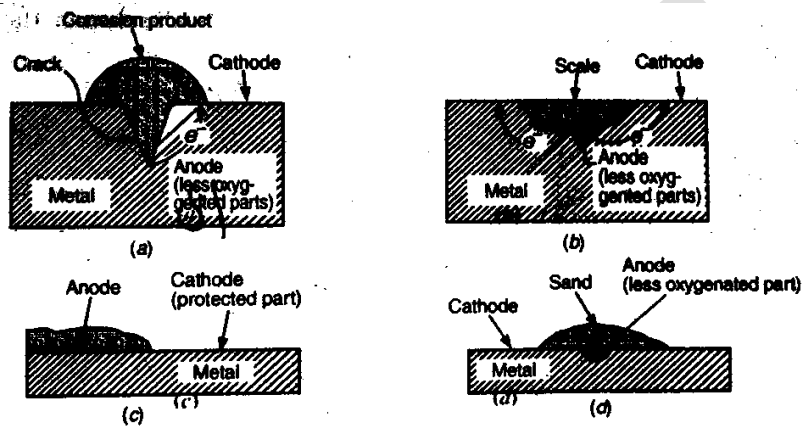


Figure: Oxygen concentration corrosion. Anode is formed at inaccessible location, where oxygen is less available. The cathode forms, where oxygen is freely available.

- (ii) Corrosion is accelerated under accumulation of dirt sand, scale or other, contamination. This is because accumulation of rust or scale or sand, etc. restricts the access of oxygen and establishes an anode to promote still greater accumulation. The result is localized corrosion, due to non-uniform corrosion.

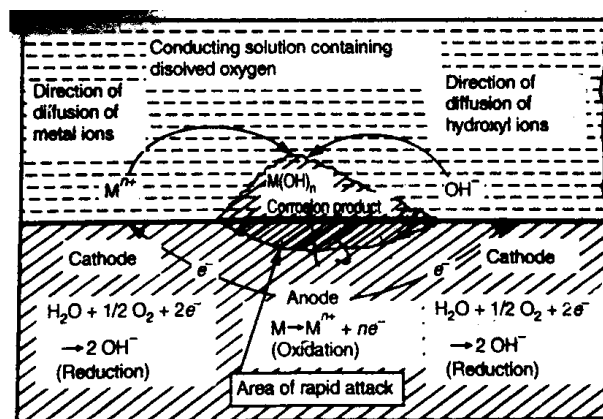


Figure: localized corrosion of oxygen-deficient areas.

- (iii) Metals exposed to aqueous media corrode under blocks of wood or pieces of glass, which screen that portion of metal from oxygen access. The differential aeration type of corrosion is a localized attack on some oxygen-deficient areas, resulting in characteristics localized pitting. This attack becomes more intensified with the time, because the corrosion products accumulate around a small anodic area, thereby making inaccessibility of that part more effective.

23. waterline corrosion:

When water is stored in a steel tank it is generally found that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus (see Figure). The area above the waterline (Highly-oxygenated) acts as the cathodic and is completely unaffected by corrosion. However, if the water is relatively free from acidity, little corrosion takes place.

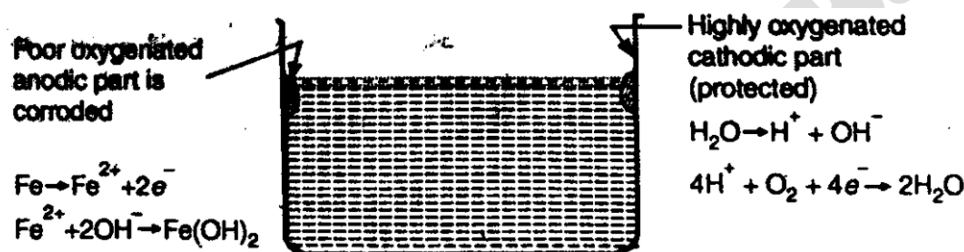


Figure: Waterline corrosion occurs just underneath the meniscus and the water level.

The problem of waterline corrosion is also that concerns marine engineers. In the case of ships, this kind of corrosion is often accelerated by marine plants attaching themselves to the sides of ships. The use of special antifouling paints restrict this to some extent.

24. Passivity of metals: (Passivity or Passivation):

Passivity or passivation is the “phenomenon in which a metal or an alloy exhibits a much higher corrosion-resistance than expected from its position in the electrochemical series”. Passivity is the result of the formation of a highly protective, but very thin (about 0.0004 mm thick) and quite invisible film on the surface of metal or an alloy, which makes it more noble. This film is insoluble, non-porous and of such a “self-healing nature”. That when broken, it will repair itself on re-exposure to oxidising conditions.

Examples of passive metals and alloys are: Ti, Al, Cr, and a wide variety of stainless steel alloys, containing Cr. These exhibit outstanding corrosion resistance in oxidising environments, but in reducing environments, they become chemically active. Based on experiment conducted in aerated 0.5 M NaCl solution, the passivity of certain metals falls in the following order:

Ti → Al → Cr → Be → Mo → Mg → Ni → Co → Fe → Mn → Zn → Cd → Sn → Pb → Cu.

Passivation is not a constant state, but exists only in certain environment condition, which tend to maintain thin protective oxide films on their surfaces. In the presence of oxygen, the oxide

film is automatically repaired, whenever any damage occur. But in oxygen absence, the passive metals and alloys become chemically active and are rapidly corroded. For Example, the austenitic stainless steels are quite good resistant to the action of aerated dilute sulphuric acid, but show low resistance in air-free acid.

25. Pitting corrosion:

Pitting corrosion is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively unattached. Thus, pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting is, usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the correct environment, this produces corrosion current. Breakdown of the protective film may be caused by:

- (i) Surface roughness or non-uniform finish
- (ii) Scratches or cut edges,
- (iii) Local straining of metal, due to non-uniform stresses
- (iv) Alternating stresses
- (v) Sliding under load
- (vi) Impingement attack (caused by the turbulent flow of a solution over a metal surface)
- (vii) Chemical attack.

Metal owing their corrosion resistance to their passive state, show a marked pitting under all conditions, which lead to the destruction of their passivity. For example, stainless steel and aluminium show characteristic pitting in chloride solution.

The presence of the extraneous impurities (like sand, dust, scale, etc.) embedded on the surfaces of metals also lead to pitting. Owing to the differential amount of oxygen in contact with the metal (See figure), the small part (underneath the impurity) become the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion, therefore, start just underneath the impurity. Once a small pit is formed, the rate of corrosion will be increased.

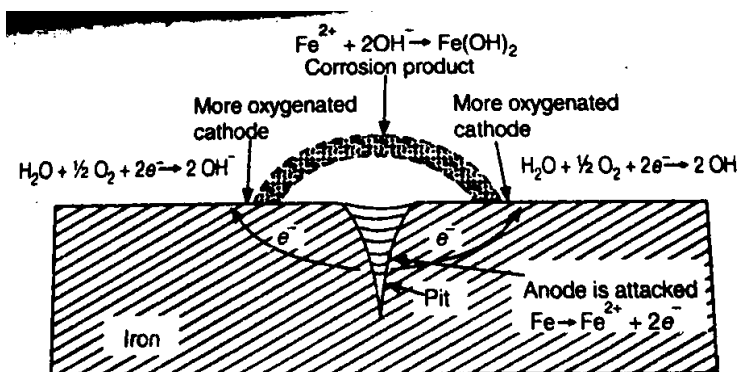


Figure: Pitting corrosion at the surface of iron.

26. Galvanic series:

In the electrochemical series (reduction electrode potential arranged down in an increasing order), a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example Li corrodes faster than Mg; Zn corrodes faster than Fe; Fe corrodes faster than Sn; Cu corrodes faster than Ag and so on. However, some exceptions to this generalization are known. For example, Ti (above Ag in the electrochemical series) is less reactive than Ag. In Zn-Al Couple, Zn (below Al in the electrochemical series) is corroded; while Al acts cathodic and is protected. These observations, exactly opposite to that predicted by the emf series, are due to the fact that metals like Ti and Al develop, strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more positive (or less negative).

From the above, it is clear that electrochemical series does not account for the corrosion of all metals and alloys. Consequently, a more practical series, called Galvanic series have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water. Thus, galvanic series give real and useful information for studying the corrosion of metals and alloys.

Active (or anodic)	Mg
	Mg alloys
	Zn
	Al
	Cd
	Al Alloys
	Mild steel
	Cast iron
	High Ni cast iron
	Pb-Sn solder
	Pb
	Sn
	Iconel
	Ni-Mo-Fe alloys
	Brasses
	Monel (7 = Ni, 30 = Cu, rest = Fe)
	Silver solder
	Cu
	Ni
	Cr stainless steel
	18-8 Stainless steel
	18-8 Mo Stainless steel
	Ag
	Ti
	Graphite
Noble (or cathodic)	Au
	Pt

27. Factors which influence the rate of corrosion:

The rate of extent of corrosion, depends on the following factors:

(I) Nature of Metal:**(a). Position in galvanic series:**

The type of impurity present in it and its electropositive nature decides the corrosion of a metal. For example when iron has impurities like copper, tin, etc. iron corrodes since iron is more electropositive than metals like copper and tin. On the other hand when iron is coupled with zinc, zinc corrodes since zinc is more electropositive than iron.

(b). Overvoltage:

The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v when zinc metal is placed in 1 M sulphuric acid and the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal.

(c). Relative areas of the anodic and cathodic parts:

When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

Corrosion is more rapid and severe, and highly localized, If the anodic area is small. Because the current density at a smaller anodic area is much greater and the demand for electrons can be met by smaller anodic areas only by undergoing corrosion more briskly.

(d). Purity of metal:

Generally pure metal does not corrode, as there is no cathode spot available to induce corrosion. Impurities in a metal, generally cause heterogeneity and form minute/tiny electrochemical cells (at the exposed parts), and the anodic parts get corrode.

(e). Physical state of metal:

The rate of corrosion is influenced by grain size, Orientation of crystals, stress etc. The smaller the grains size of the metal greater the rate of corrosion.

(f). Nature of surface film:

A rough surface corrodes readily as it collects more dirt and provides more cathode spot for corrosion. A polished surface does not corrode easily.

(g). Passive character of metal:

Metal like Ti, Al, Cr, Mg, Ni, and Co are passive and they exhibit much higher corrosion-resistance than expected from their positions in galvanic series, due to the formation of highly protective, but very thin film on the metal or alloy surface.

The corrosive-resistance of alloys is due to the passivating character of metal present in it.

(h). Solubility of corrosion products:

In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate. On the contrary product is insoluble in the medium or it interacts with the medium to form another insoluble product, then the corrosion product functions as physical barrier, thereby suppressing further corrosion.

(i). Volatility of corrosion products:

If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion.

(II) Nature of the corroding environment:

(a). 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.

(b). Humidity of air:

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, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up a corrosion cell.

(c). Presence of impurities in atmosphere:

Atmosphere in industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

(d). Presence of suspended particles in atmosphere:

In case of atmospheric corrosion: (i) if the suspended particles are chemically active in nature (like NaCl , Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion; (ii) if the suspended particles are chemically inactive in nature (eg., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.

(e). Influence of pH:

Generally acidic media (i.e., $\text{pH} < 7$) are more corrosive than alkaline and neutral media. However, amphoteric metals (like Al , Zn , Pb , etc.) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5. The corresponding corrosion rate in presence of oxygen is much higher. Consequently corrosion of metals, readily attacked by acid, can be reduced by increasing the pH of the attacking environment, eg., Zn (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at $\text{pH}=11$).

(f). Nature of ions present:

Presence of anions like silicate in the medium leads to the formation of insoluble reaction products (e.g., silica gel), inhibit further corrosion. On the other hand, chloride ions, if present in the medium, destroy the protective and passive surface film, thereby exposing the metal/alloy surface for fresh corrosion. Many metals undergo corrosion rapidly, if the corroding medium contains ammonium salts.

(g). Conductance of the corroding medium:

Conductance of dry sandy-soils is lower than those of clayey and mineralized soils. Consequently, stray currents will cause more severe damage to the metallic structures, buried under clayey and mineralized soils than those under dry sandy-soils.

(h). Formation of oxygen concentration cell:

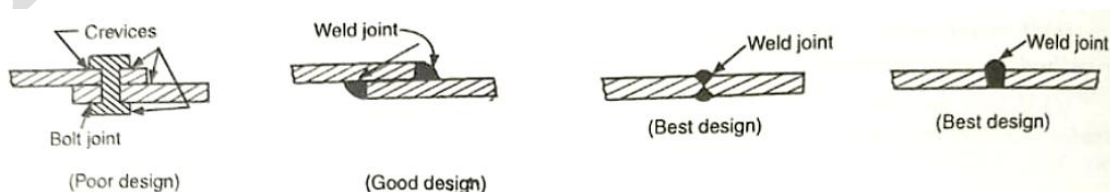
With the increase in supply of oxygen/air to the moist-metal surface, the corrosion is promoted. But it occurs where the oxygen concentration is lower.

28. Protection from corrosion: Some of the corrosion control methods are described as follows:

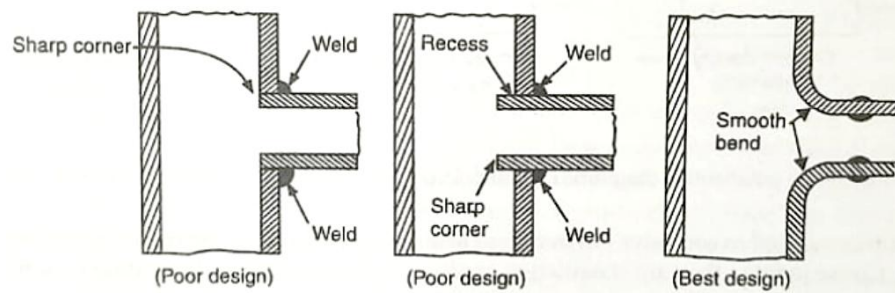
(I). Proper designing:

Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following:

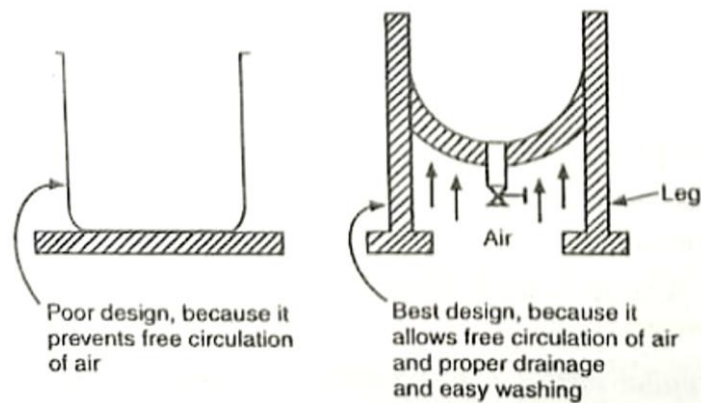
- (i) Use always simple design and structure.
- (ii) The design must avoid more complicated shapes having more angles, edges, corners etc.
- (iii) Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion. To overcome this, insulation can be used.
- (iv) When two dissimilar metals are to be in contact, the anodic area must be as large as possible and the cathodic area should be as small as possible.
- (v) As far as possible, crevices (gap or crack) should be avoided between adjacent parts of a structure.
- (vi) Bolts and rivets should be replaced by proper welding



- (vii) Metal washers should be replaced by rubber or plastic washers as they do not adsorb water. They also act as insulation.
- (viii) Corrosion in pipelines can be prevented by using smooth bends.



- (ix) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.



- (x) Heat treatment like annealing minimizes the stress corrosion.
- (xi) A good design of water storage container is the one from which water can be drained and cleaned easily. Such a design avoids accumulation of dirt etc.

(II). Using pure metal:

Impurities in metal cause heterogeneity, which decreases corrosion-resistance of the metal. Thus, the corrosion-resistance of a given metal may be improved by increasing its purity.

In many cases, it is not practical to produce a metal of high chemical purity, because:

- (i). Cost consideration in some cases
- (j). Very pure metal often possesses the disadvantages of inadequate mechanical properties like softness and low strength.

(III). Using metal alloys:

The first choice is to use noble metals such as gold and platinum. They are most resistant to corrosion. As they are precious, they cannot be used for general purposes.

The next choice is to use purest possible metal. But in many cases, it is not possible to produce a metal of high chemical purity. Hence, even a trace amount of impurity leads to corrosion.

Thus, the next choice is the use of corrosion resistant alloys. Several corrosion resistant alloys have been developed for specific purposes and environment. For example,

- a. Stainless steel containing chromium produce an exceptionally coherent oxide film which protects the steel from further attack.

- b. Cupro-nickel (70% Cu + 30%Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries.
- c. Highly stressed Nimonic alloys (Ni-Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

(IV). Cathodic protection:

The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur. There are two methods of applying cathodic protection to metallic structures.

[a]. Sacrificial anodic protection (galvanic protection)

[b]. Impressed current cathodic protection

Sacrificial anodic protection method:

In this method, the metallic structure to be protected is made cathode by connection it with more active metal (anodic metal). Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.

Applications:

- Protection as buried pipelines, underground cables from soil corrosion.
- Protection from marine corrosion of cables, ship hulls, piers etc.
- Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
- Calcium metal is employed to minimize engine corrosion.

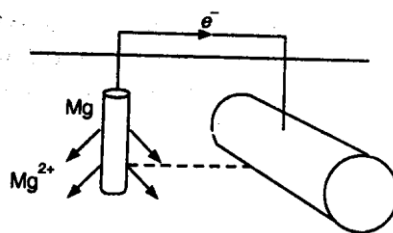


Figure: In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (e.g. a pipeline, bridge, ship hull or boat)

Advantages:

- Low installation and operating cost.
- Capacity to protect complex structures.
- Applied to wide range of severe corrodents.

Limitations:

- High starting current is required.
- Uncoated parts cannot be protected.
- Limited driving potential, hence, not applicable for large objects.

Impressed current cathodic protection 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.

Usually the impressed current is derived from a direct current sources (like battery or rectifier on AC line) with an insoluble, inert anode (like graphite, scrap iron, stainless steel, platinum or high silica iron).

A sufficient DC current is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is, usually, a back fill, composed of coke breeze or gypsum, so as to increase the electrical contact with the surrounding soil.

Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid up ships etc. This kind of protection technique is particularly useful for large structures for long term operations.

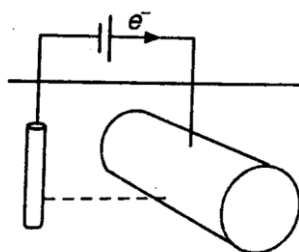


Figure: In impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

Comparison of Sacrificial anode method with impressed current cathodic method:

S.No	Sacrificial anode method	impressed current cathodic method
1	External power supply is not required.	External power supply is required.
2	The cost of investment is low.	The cost of investment is high.
3	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.

6	This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.
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(II). Modifying the environment:

Environment plays a major role in the corrosion of metals. Hence, we can prevent corrosion to a great extent by modifying the environment. Some of the methods are

- (a). Deaeration: Fresh water contains dissolved oxygen. The presence of increased amount of oxygen is harmful and increases the corrosion rate. Deaeration involves the removal of dissolved oxygen by increase of temperature together with mechanical agitation. It also removes dissolved carbon dioxide in water
- (b). Use of inhibitors: Inhibitors are organic or inorganic substances which decrease the rate of corrosion. Usually the inhibitors are added in small quantities to the corrosive medium. Inhibitors are classified into
 - Anodic inhibitors (chemical passivators)
 - Cathodic inhibitors (adsorption inhibitors)
 - Vapour phase inhibitors (volatile corrosion inhibitors)

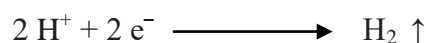
Anodic Inhibitors:

Inhibitors which retard the corrosion of metals by forming a sparingly soluble compound with a newly produced metal cations. This compound will then adsorb on the corroding metal surface forming a passive film or barrier. Anodic inhibitors are used to repair a) the crack of the oxide film over the metal surface b) the pitting corrosion c) the porous oxide film formed on the metal surface. Examples: Chromate, phosphate, tungstate, nitrate, molybdate etc.

Cathodic Inhibitors:

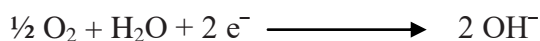
Depending on the nature of the cathodic reaction in an electrochemical corrosion, cathodic inhibitors are classified into

- (i) In an acidic solution: the main cathodic reaction is the liberation of hydrogen gas, the corrosion can be controlled by slowing down the diffusion of H^+ ions through the cathode. Eg., Amines, Mercaptans, Thiourea etc.



- (ii) In a neutral solution: in a neutral solution, the cathodic reaction is the adsorption of oxygen or formation of hydroxyl ions. The corrosion is therefore controlled either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic area. The dissolved oxygen can be eliminated by adding reducing agents like Na_2SO_3 . The diffusion of oxygen can

be controlled by adding inhibitors like Mg, Zn or Ni salts. Eg., Na₂SO₃, N₂H₄, Salts of Mg, Zn or Ni.

**Vapour phase inhibitors:**

These are organic inhibitors which are readily vapourised and form a protective layer on the metal surface. These are conveniently used to prevent corrosion in closed spaces, storage containers, packing materials, sophisticated equipments etc. Examples are Dicyclohexylammonium nitrate, dicyclohexyl ammonium chromate, benzotriazole, phenylthiourea etc.

(V). Application of protective coating:

Introduction: In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings. These coatings act as a physical barrier between the coated metal surface and the environment. They afford decorative appeal and impart special properties like hardness, oxidation resistance and thermal insulation.

Classification: Protective coatings can be broadly classified into two types.

- a. Inorganic coatings
- b. Organic coatings

Inorganic coatings: are further classified into two types. They are

- Metallic coating:
 - 1) Hot dipping- Galvanising, Tinning
 - 2) Metal cladding
 - 3) Cementation-Sherardising, Chromising, Calorising
 - 4) Electroplating.
- Non-metallic coating:
 - 1) Surface coating or chemical conversion coating – Chromate coating, Phosphate coating and Oxide coating.
 - 2) Anodising
 - 3) Enamel coating or Vitreous or Porcelain coating.
- Organic coatings consists of Paints, Varnishes, Lacquers and Enamels.

METALLIC COATINGS: Corrosion of metals can be prevented or controlled by using methods like galvanization, tinning, metal cladding, electroplating, cementation, anodizing, phosphate coating, enamelling, electroless plating. Some of the methods are

1) Hot dipping: It is used for producing a coating of low-melting metals such as Zn (m.p.=419 deg C), Sn (m.p.=232 deg C), Pb, Al etc., on iron, steel and copper which have relatively higher melting

points. The process in immersing the base metal in a bath of the molten coating-metal, covered by a molten flux layer (usually zinc chloride).

2) **Galvanizing**: It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. The process is iron or steel article is first cleaned with dil. Sulphuric acid and washed with distilled water and dried. The dried metal is dipped in bath of molten zinc, now the thin layer of zinc is coated on the iron or steel article.

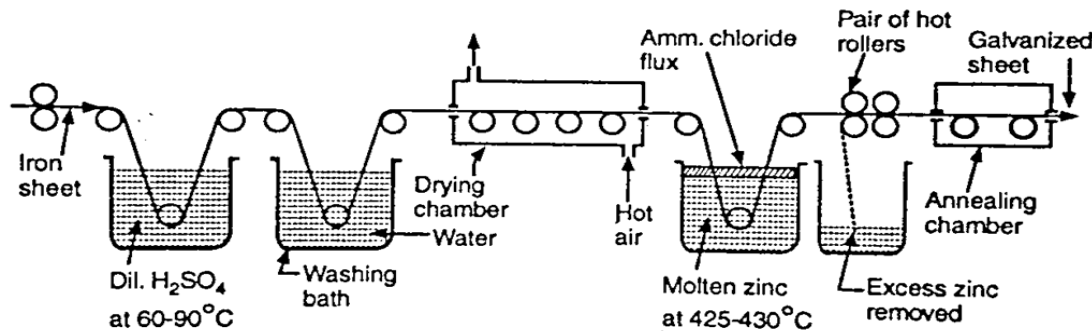
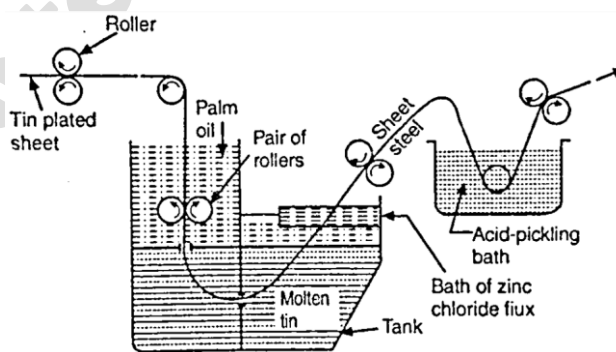


Fig. 3. Galvanizing of sheet steel.

3) **Metal cladding**: It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides. Corrosion resistant metals like nickel, copper, lead, silver, platinum and alloys like SS, nickel alloys, copper alloys, lead alloys can be used as cladding materials.

4) **Tinning**: It is a method of coating tin over the iron or steel articles. The process is first treating steel sheet in dilute sulphuric acid and it is passed through a flux (ZnCl_2), next steel passes through a tank of molten tin and finally through a series of rollers from underneath (bottom of) the surface of a layer of palm oil.



Electroplating:

It is a coating technique. It is the most important and most frequently applied industrial method of producing metallic coating.

Electroplating is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

The base metal to be plated is made cathode whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

Objectives: Electroplating is carried out for

- 1) Decoration or better appearance
- 2) Increasing the resistance to corrosion of the coated metal.
- 3) Improving the hardness of the metal
- 4) Increasing the resistance to chemical attack
- 5) Electro refining.

Procedure: The article is to be plated first treated with organic solvent like carbon tetrachloride, acetone, tetrachloro ethylene to remove oils, greases etc. Then it is made free from surface scale, oxides, etc. by treating with dil. HCl or H₂SO₄ (acid pickling). The cleaned article is then made as the cathode of the electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity. The electrolyte is a solution of soluble salt of the coating metal.

When direct current is passed, coating metal ions migrate to the cathode and get deposited there. Thus, a thin layer of coating metal is obtained on the article made as the cathode.

In order to get strong, adherent and smooth deposit, certain types of additives (glue, gelatin, boric acid) are added to the electrolytic bath.

In order to improve the brightness of the deposit, brightening agents are added in the electrolytic bath.

The favourable conditions for a good electrodeposit are

- (a). Optimum temperature
- (b). Optimum current density
- (c). Low metal ion concentrations.

Gold Electroplating:

Anode: Gold Cathode:

Metal article Electrolyte: Gold + KCN

Temperature: 60 deg C.

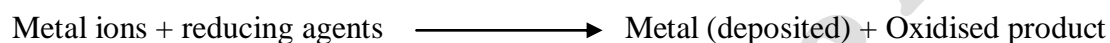
Current density (mA cm⁻²): 1-10

Use:

- This is used for electrical and electronic applications.
- It is used for high quality decorations and high oxidation resistant coatings
- Usually for ornamental jewellery, a very thin goldcoating (about 1×10^{-4} cm) is given.

ELECTROLESS PLATING:

Principle: Electroless plating is a newer technique of depositing a noble metal from its salt solution on a catalytically active surface of the metal to be protected by using a suitable reducing agent without using electrical energy. The reducing agent reduces the metal ions into metal which gets plated over the catalytically activated surface giving a uniform and thin coating.



ELECTROLESS NICKEL PLATING:

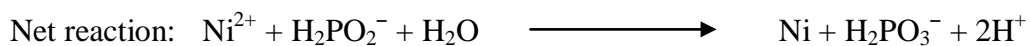
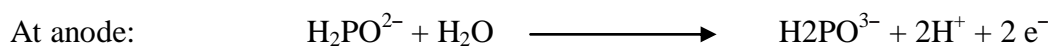
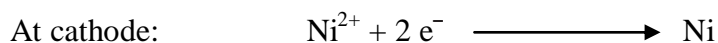
Pretreatment and activation of the surface: The surface to be plated is first degreased by using organic solvents or alkali, followed by acid treatment.

- The surface of the stainless steel is activated by dipping in hot solution of 50 % dilute sulphuric acid.
- The surface of magnesium alloy is activated by thin coating of zinc or copper over it.
- Metals (Al, Cu, Fe) and alloys like brass can be directly nickel plated without activation.
- Non metallic articles like plastics, glass are activated by dipping them in the solution containing $\text{SnCl}_2 + \text{HCl}$, followed by dipping in palladium chloride solution. On drying, a thin layer of palladium is formed on the surface.

Preparation of plating bath: The details of preparation of plating bath are:

Sl. No.	Nature of the compound	Name of the compound	Quantity (g/L)
1	Coating solution	Nickel chloride (NiCl_2)	20
2	Reducing agent	Sodium hypophosphite (NaH_2PO_2)	20
3	Complexing agent	Sodium succinate	15
4	Buffer	Sodium acetate	10
5	Optimum pH	4.5	-
6	Optimum temperature	93 °C	-

Procedure: The pre-treated object is immersed in the plating bath for the required time. The following reactions occur and nickel gets coated over the object.



Applications:

- It is used extensively in electronic appliances.
- It is used in domestic as well as automotive fields (eg. jewellery, tops of perfume bottles).
- Its polymers are used in decorative and functional works.
- Its plastic cabinets are used in digital as well as electronic instruments.

29. _____

Model Questions (2 Marks)

- 1) Define corrosion.
- 2) What is meant by rusting of iron?
- 3) What is wet corrosion?
- 4) State Pilling- Bedworth rule.
- 5) Define water line corrosion.
- 6) What is pitting corrosion?
- 7) What is galvanic corrosion?
- 8) The rate of metallic corrosion increases with increase in temperature. Give reason.
- 9) Differentiate chemical and electrochemical corrosion.
- 10) What is differential aeration corrosion?
- 11) Mention the factors influencing corrosion.
- 12) What is corrosion control and why is it required?
- 13) Write a small note on cathodic protection.

- 14) Write a small note on anodic protection.
- 15) What should be the nature of the corrosion product to prevent further corrosion?
- 16) What are the important constituents of paint?
- 17) Bolt and nut made of the same metal is preferred in practice. Why?
- 18) What is metal cladding?
- 19) Why coating of zinc on iron is called sacrificial anode?
- 20) During electroplating, pH of bath is strictly maintained. Give reasons.
- 21) Give any three functions of pigments in paints.

Model Questions (6 Marks)

- 1) What is corrosion of metals? Explain the mechanism of oxidation corrosion.
- 2) What are the factors that affect electrochemical corrosion rate? Discuss.
- 3) Differentiate chemical and electrochemical corrosion. Mention any four factors that affect electrochemical corrosion.
- 4) Describe the mechanism of electrochemical corrosion by hydrogen evolution and oxygen adsorption.
- 5) Explain water line corrosion.
- 6) How is galvanic corrosion occur.
- 7) Deposition of oil or dust on metal surfaces for a long period is undesirable. Give reasons.
- 8) Describe the mechanism of differential aeration corrosion taking pitting as example.
- 9) Explain the electrochemical theory of corrosion with suitable example.
- 10) Discuss the mechanism of chemical and electrochemical corrosion.
- 11) Explain the following: i) hydrogen embrittlement ii) decarburization iii) liquid metal corrosion iv) water line corrosion v) pitting corrosion vi) crevice corrosion vii) pipeline corrosion
- 12) Substantiate the statement that nature of the environment affects corrosion.
- 13) What is sacrificial anode? Mention its role in the prevention of corrosion.
- 14) Write short note on corrosion control by impressed current method.
- 15) What are corrosion inhibitors? How do they function?
- 16) Explain how corrosion of metals controlled by sacrificial anode technique.
- 17) Write a note on pitting corrosion and cathodic protection.
- 18) Mention the constituents of a paint. Explain the function of the various constituents.
- 19) Describe the mechanisms of drying of an oil.
- 20) How the Hot dipping process is carried out?

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