

LECTURE NOTES

UNIT-3

**ELECTROCHEMISTRY,
CORROSION
&
CEMENT**

ENGINEERING CHEMISTRY

B.Tech 1st year

By

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Introduction

ELECTROCHEMISTRY: “Electrochemistry is defined as the branch of physical chemistry which deals with the inter- conversion of chemical energy of spontaneous redox reaction into electrical energy and use of electrical energy to govern non-spontaneous chemical reaction”.

For example, in a battery, chemical energy is converted to electrical energy whereas in electroplating / electrolysis electrical energy is converted to chemical energy.

Terms Used In Electrochemistry:

Electrodes: When a metal rod is dipped in its own aqueous salt solution, it either oxidized or get reduced such a metal rod is called electrode.

Anode: The electrode where oxidation takes place is called anode. It is also called negative electrode. Or the electrode which is connected with the positive terminal of the battery or external source of electricity is called anode.

Cathode: The electrode where reduction takes place is called cathode. It is also called positive electrode. Or the electrode which is connected with the negative terminal of the battery or external source of electricity is called cathode.

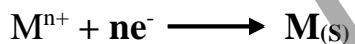
Electrode Potential: The tendency of a metal electrode to lose electron (oxidized) or gain electrons (reduced) is called electrode potential. It is also called EMF of the cell. It is denoted by E_{cell} .

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{\text{cathode}} - E_{\text{anode}}$$

Where E_{cathode} = reduction potential of cathode (reduction half cell)

E_{anode} = reduction potential of anode (oxidation half cell)

Reduction Potential: The tendency of a metal electrode to gain electrons or get reduced is called reduction potential.



Oxidation Potential: The tendency of a metal electrode to lose electrons or get oxidized is called oxidation potential.



Standard Hydrogen Electrode: If hydrogen gas is adsorbed at 1 atm-pressure over a platinum electrode & dipped in 1 M HCl at 25 °C, it neither oxidized nor reduced and its electrode potential is $E^{\circ} = \pm 0$ volt. Such electrode is called standard hydrogen electrode (S.H.E.) or Normal hydrogen electrode (N.H.E.) or reference electrode.

Standard electrode potential: If the metal electrode is suspended in an ionic solution of 1M (molar) concentration or unit activity and temperature is kept at 25 °C under 1atm pressure, then potential develop between electrode and ionic solution is known as standard electrode potential. It is represented by E°_{cell} .

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Where $E^{\circ}_{\text{cathode}}$ = standard reduction potential of cathode (reduction half cell)

E°_{anode} = standard reduction potential of anode (oxidation half cell)

EMF of the Cell: The electromotive force (EMF) is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element or a compound or an ion to acquire (i.e. gain) or release (lose) electrons.

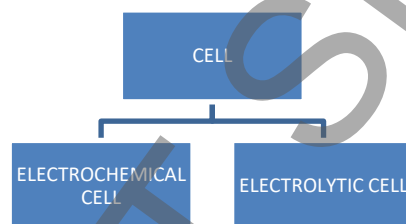
Calculation of EMF of the cell:

EMF of the cell = [reduction potential of R.H.S. electrode] –
[reduction potential of L.H.S. electrode]

$$E_{\text{cell}} = E_R - E_L = E_{\text{cathode}} - E_{\text{anode}}$$

Cell: The cell is a device which is used to convert chemical energy of spontaneous redox reaction into electrical energy and use of electrical energy to govern non-spontaneous chemical reaction.

Types of Cell: Generally there are two types of cells.



Electrochemical Cell: The cell in which chemical energy of spontaneous redox reaction is converted into electrical energy is called electrochemical cell. For Example: Galvanic cell, voltaic cell, Dry cell, Laclanche cell.

Electrolytic Cell: The cell in which electrical energy is used to govern non-spontaneous chemical reaction is called electrolytic cell.

Differences between Electrolytic Cell and Electrochemical cell:

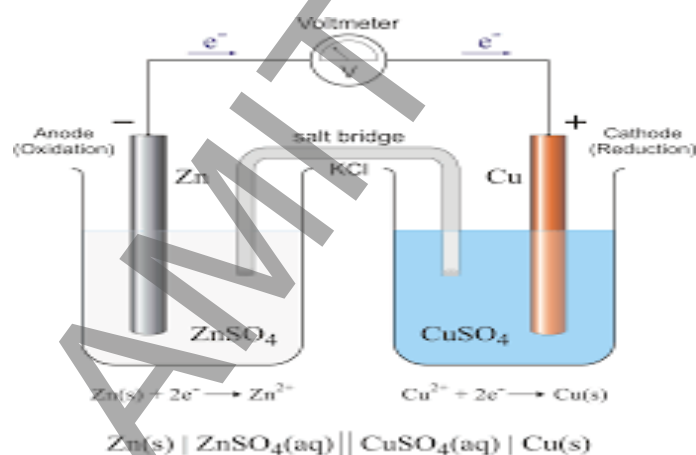
Differences between electrolytic cell and electrochemical cell.

Electrolytic Cell	Electrochemical cell
1. Electrical energy brings about a chemical reaction.	1. Electrical energy is produced at the expense of chemical energy.
2. Anode is positively charged.	2. Anode is negatively charged.
3. Cathode is negatively charged.	3. Cathode is positively charged.
4. Electrons move from anode to cathode through external circuit.	4. Electrons move from cathode to anode through external circuit.
5. The extent of chemical reaction at the electrode is governed by Faraday's laws of electrolysis.	5. The emf of the cell depends on concentration of electrolyte and nature of the metal electrode.
6. The amount of electricity passed is measured by a coulometer.	6. The emf of the cell is measured by a potentiometer.
7. One electrolyte and two electrodes of the same element are generally used in these cells.	7. Two different electrolytes and two different electrodes are

Galvanic cell: Galvanic cell is a device which is used to convert chemical energy of spontaneous redox reaction into electrical energy which can be used to perform work. These cells are known as electrochemical cells or voltaic cells. The best example of Galvanic cell is Daniel cell.

Construction of Galvanic Cell:

- This cell is formed by combination of two half cells.
- One is oxidation half cell or anodic half cell
- Other one is reduction half cell or cathodic half cell.
- The oxidation half cell consists of 'Zn' electrode dipped in ZnSO_4 solution
- Reduction half cell consists of 'Cu' electrode dipped in CuSO_4 solution.
- Both the half cells are externally connected by metallic wire through voltmeter.
- Both the electrolyte are internally connected by 'salt bridge'.
- Salt bridge is a U shaped tube containing solution of K_2SO_4 , KNO_3 , KCl or NH_4NO_3 in agar-agar gel contained porous site. It maintains the electrical neutrality between two solutions & complete the internal circuit.
- Oxidation takes place at Anode and Reduction takes place at cathode.
- The movement of electrons from Zn electrode to Cu electrode produces a current in the reverse direction.



Cell Reactions: The following reactions take place in the cell.

At anode: $\text{Zn}_{(s)} - 2e^- \rightarrow \text{Zn}^{+2}_{(aq)}$ (oxidation half cell)

At cathode: $\text{Cu}^{+2}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$ (Reduction half cell)

The overall cell reaction is: $\text{Zn}_{(s)} + \text{Cu}^{+2}_{(aq)} \rightarrow \text{Zn}^{+2}_{(aq)} + \text{Cu}_{(s)}$

Representation of Galvanic Cell:



E° of Galvanic Cell:

$$E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{(\text{Cu}^{2+}/\text{Cu})} - E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = 0.34 - (-0.76)$$

$$E^\circ_{\text{cell}} = 1.10 \text{ V}$$

Nernst Equation: The mathematical equation which gives the relation between concentration of electrolyte and electrode potential of the cell is called Nernst Equation. Mathematically it can be written as:

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303 RT}{nF} \log \frac{[products]}{[reactants]}$$

Where E_{cell} = electrode potential of the cell (EMF of the cell)

E°_{cell} = standard electrode potential of the cell

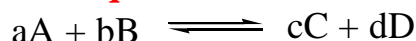
R = Rydberg's constant = $8.314 \text{ JK}^{-1}\text{mol}^{-1}$

F = Faraday Constant = 96500 C

T = Temperature in Kelvin

n = no. of electrons loss or gain.

Derivation of Nernst Equation: Lets us consider a hypothetical cell reaction



Applying Van't Hoff reaction isotherm

$$\Delta G = \Delta G^{\circ} + RT \ln Q_c \dots\dots \text{eq.1}$$

Where Q_c is the reaction co-efficient

We know that $\Delta G = -nFE_{cell}$

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

Put these values in Equation 1

$$-nFE_{cell} = -nFE^{\circ}_{cell} + RT \ln Q_c \dots\dots \text{eq.2}$$

Divide eq-2 Both side by $-nF$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q_c$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log Q_c \dots\dots \text{eq.3}$$

At Equilibrium $Q_c = K_c = \frac{[products]}{[reactants]}$

Put this value in Eq-3

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[products]}{[reactants]} \dots\dots \text{eq.4}$$

R = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T = 298K, F = 96,500 C

Put these values in eq-4

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[products]}{[reactants]} \dots\dots \text{eq.5}$$

For the given Reaction At Equilibrium $Q_c = K_c = \frac{[products]}{[reactants]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Put this value in eq-5

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \dots\dots \text{eq.6}$$

Eq-5 & Eq-6 are different forms of Nernst Equation.

Nernst Equation Applications: The Nernst equation can be used to calculate

- Single electrode reduction or oxidation potential at any conditions
- Standard electrode potentials
- Comparing the relative ability as a reductive or oxidative agent.
- Finding the feasibility of the combination of such single electrodes to produce electric potential.
- Emf of an electrochemical cell
- Unknown ionic concentrations
- The pH of solutions and solubility of sparingly soluble salts can be measured with the help of the Nernst equation.

Nernst Equation for Galvanic Cell: Galvanic cell can be represented as:



The cell potential, $E_{\text{cell}} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$(1)

Applying Nernst Equation

For Cathode:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} - \frac{2.303RT}{nF} \log \frac{1}{[\text{Cu}^{2+}_{(aq)}]}$$

For Anode:

$$E_{(\text{Zn}^{2+}/\text{Zn})} = E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})} - \frac{2.303RT}{nF} \log \frac{1}{[\text{Zn}^{2+}_{(aq)}]}$$

Put the values in equation (1)

$$E_{\text{cell}} = E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} - \frac{2.303RT}{nF} \log \frac{1}{[\text{Cu}^{2+}_{(aq)}]} - E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})} - \frac{2.303RT}{nF} \log \frac{1}{[\text{Zn}^{2+}_{(aq)}]}$$

$$= (E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} - E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})}) - \frac{2.303RT}{nF} \log \frac{1}{[\text{Cu}^{2+}_{(aq)}]} - \log \frac{1}{[\text{Zn}^{2+}_{(aq)}]}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \dots \dots \dots (2)$$

R = 8.314, F = 96500 C, and at 298 K

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Electrochemical series: The series in which elements are arranged in increasing order of their standard electrode potential is known as electrochemical series.

Electrode	Half cell reaction	E° volts (standard reduction potential)
Li^{+}/Li	$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	-3.04
K^{+}/K	$\text{K}^{+} + \text{e}^{-} \rightarrow \text{K}$	-2.9
Ca^{+2}/Ca	$\text{Ca}^{+2} + 2\text{e}^{-} \rightarrow \text{Ca}$	-2.8
Na^{+}/Na	$\text{Na}^{+} + \text{e}^{-} \rightarrow \text{Na}$	-2.7
Mg^{+2}/Mg	$\text{Mg}^{+2} + 2\text{e}^{-} \rightarrow \text{Mg}$	-2.3
Zn^{+2}/Zn	$\text{Zn}^{+2} + 2\text{e}^{-} \rightarrow \text{Zn}$	-0.76
Fe^{+2}/Fe	$\text{Fe}^{+2} + 2\text{e}^{-} \rightarrow \text{Fe}$	-0.4
$\text{H}^{+}/\text{H}_2, \text{Pt}$	$\text{H}^{+} + \text{e}^{-} \rightarrow \frac{1}{2} \text{H}_2$	+ 0
Cu^{+2}/Cu	$\text{Cu}^{+2} + 2\text{e}^{-} \rightarrow \text{Cu}$	+0.15
Ag^{+}/Ag	$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	+ 0.7
$\text{Pt}, \text{Cl}_2/\text{Cl}^{-}$	$\text{Cl}_2 + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}$	+ 1.3
$\text{Pt}, \text{F}_2/\text{F}^{-}$	$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	+ 2.8

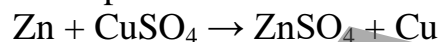
Application of Electrochemical series:

i) Comparison of relative oxidizing and reducing power:

The greater the reduction potential, greater the tendency of the element or ions to get reduce. For example, the reduction potential of Fe^{2+} (-0.41 V) is higher than the Li^+ (-3.04 V), therefore Fe^{2+} ion is easily reduce and Li^+ ion is easily oxidized.

ii) Relative reactivity of metals:

Greater the oxidation potential of the element, greater will be the tendency to lose electrons (greater tendency to get oxidized). A metal with higher oxidation potential can displace the metal with lower oxidation potential. For example, the oxidation potential of Zn^{2+} (-0.76 V) is higher than Cu^{2+} (0.34 V), therefore Zn replace Cu from its salt solution.



iii) Spontaneity of reaction:

If EMF of the cell is positive then redox reaction is spontaneous and if EMF of the cell is negative then redox reaction is non-spontaneous.

Question 1:

Write the half cell and net cell reactions for the following cell, $\text{Zn} / \text{ZnSO}_4 (\text{aq}) // \text{CuSO}_4 (\text{aq}) / \text{Cu}$.

Calculate the standard emf of the cell given: $E^\circ_{(\text{Cu}^{2+}/\text{Cu})} = 0.34 \text{ V}$,

$E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$

Solution:

Half cell reactions

At anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ At

cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

Net cell reaction = $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{(\text{Cu}^{2+}/\text{Cu})} - E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = 0.34 - (-0.76)$$

$$E^\circ_{\text{cell}} = 1.10$$

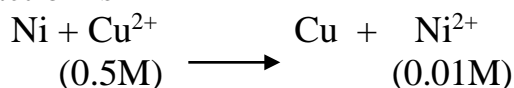
Question 2: Consider a cell $\text{Ni}/\text{Ni}^{2+} (0.01\text{M}) // \text{Cu}^{2+} (0.5\text{M})/\text{Cu}$. The standard reduction potential of Ni and Cu are -0.25 and 0.34 V, respectively. Calculate the EMF of the cell.

Solution:

At anode, $\text{Ni} \longrightarrow \text{Ni}^{2+} + 2\text{e}^-$ $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$

At cathode, $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$

The net cell reaction is



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} - E^{\circ}_{(\text{Ni}^{2+}/\text{Ni})}$$

$$= 0.34 - (-0.25) = 0.59 \text{ V}$$

EMF of the cell can be written as

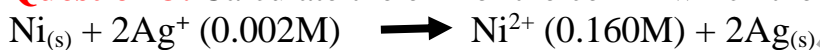
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E_{\text{cell}} = 0.59 - \frac{0.0591}{2} \log \frac{[0.01]}{[0.5]}$$

$$= 0.59 + 0.05$$

$$= 0.64 \text{ V}$$

Question 3: Calculate the emf of the cell in which the following reaction takes place:



Given that $E^{\circ}_{\text{cell}} = 1.05 \text{ V}$ at 298 K.



Given that $E^{\circ}_{\text{cell}} = 1.05 \text{ V}$ at 298 K.

Acc. To Nernst Equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[0.160]}{[0.002]^2}$$

$$E_{\text{cell}} = 1.05 - 0.13599 = 0.914 \text{ V}$$

Question 4: Can we store copper sulphate solution in zinc vessel? Give reason.

Solution: Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.



Hence, **copper sulphate solution cannot be stored in a zinc pot.**

Question 5: Depict the galvanic cell in which the reaction



(i) Which of the electrode is negatively charged?

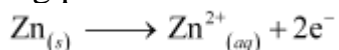
(ii) Individual reaction at each electrode.

Solution: The galvanic cell in which the given reaction takes place is depicted as:

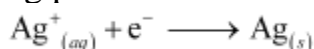


(i) Zn electrode (anode) is negatively charged.

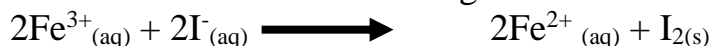
(ii) The reaction taking place at the **anode** is given by,



The reaction taking place at the **cathode** is given by,



Question 6: The cell in which the following reactions occurs:



Given $E^{\circ}_{\text{cell}} = 0.236 \text{ V}$ at 298 K.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Solution: For Cell Reaction:



Given $E^{\circ}_{\text{cell}} = 0.236 \text{ V}$ at 298 K.

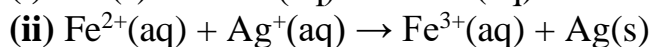
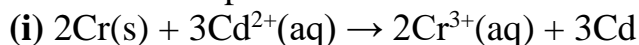
$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -2 \times 96500 \times 0.236 = -45548 \text{ J} = -45.548 \text{ KJ}$$

$$\Delta G^{\circ} = -2.303 RT \log K_c = -2.303 \times 8.314 \times 298 \log K_c$$

$$\log K_c = \Delta G^{\circ} / -2.303 \times 8.314 \times 298 = -45548 / -2.303 \times 8.314 \times 298 = 7.9827$$

$$K_c = \text{Antilog } 7.9827 = 9.609 \times 10^7$$

Question 7: Calculate the standard cell potentials of galvanic cells in which the following reactions take place:



Calculate the $\Delta_r G^{\circ}$ and equilibrium constant of the reactions. If, $E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = 0.74 \text{ V}$, $E^{\circ}_{\text{Cd}^{3+}/\text{Cd}} = -0.40 \text{ V}$, $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = 0.80 \text{ V}$

Solution: The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$\begin{aligned} E^{\ominus}_{\text{cell}} &= E^{\ominus}_{\text{R}} - E^{\ominus}_{\text{L}} \\ &= -0.40 - (-0.74) \\ &= +0.34 \text{ V} \end{aligned}$$

$$\Delta_r G^{\ominus} = -nFE^{\ominus}_{\text{cell}}$$

In the given equation,

$$n = 6$$

$$F = 96487 \text{ C mol}^{-1}$$

$$E^{\ominus}_{\text{cell}} = +0.34 \text{ V}$$

$$\text{Then, } \Delta_r G^{\ominus} = -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196833.48 \text{ CV mol}^{-1}$$

$$= -196833.48 \text{ J mol}^{-1}$$

$$\Delta_r G^{\ominus} = -196.83 \text{ kJ mol}^{-1}$$

Again,

$$\Delta_r G^{\ominus} = -RT \ln K$$

$$\Rightarrow \Delta_r G^\ominus = -2.303 RT \ln K$$

$$\begin{aligned}\Rightarrow \log K &= -\frac{\Delta_r G^\ominus}{2.303 RT} \\ &= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298}\end{aligned}$$

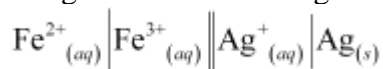
$$= 34.496$$

$$\therefore K = \text{antilog}(34.496) = 3.13 \times 10^{34}$$

$$(ii) E^\ominus_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$$

$$E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$$

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$\begin{aligned}E^\ominus_{\text{cell}} &= E^\ominus_{\text{R}} - E^\ominus_{\text{L}} \\ &= 0.80 - 0.77 \\ &= 0.03 \text{ V}\end{aligned}$$

Here, $n = 1$.

$$\begin{aligned}\text{Then, } \Delta_r G^\ominus &= -nFE^\ominus_{\text{cell}} \\ &= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V} \\ &= -2894.61 \text{ J mol}^{-1}\end{aligned}$$

$$\Delta_r G^\ominus = -2.89 \text{ kJ mol}^{-1}$$

$$\text{Again, } \Delta_r G^\ominus = -2.303 RT \ln K$$

$$\begin{aligned}\Rightarrow \log K &= -\frac{\Delta_r G^\ominus}{2.303 RT} \\ &= \frac{-2894.61}{2.303 \times 8.314 \times 298}\end{aligned}$$

$$= 0.5073$$

$$\therefore K = \text{antilog}(0.5073) = 3.2 \text{ (approximately)}$$

Battery: A battery is a device in which a number of electrochemical cells are connected in series. It transformed chemical energy into electrical energy. And it is used as a source of electricity.

Classification of Batteries:

- i) Primary battery
- ii) Secondary battery

i) Primary batteries:

Those batteries which can not be recharged after discharge and can be used only once in their life are called primary batteries. These batteries become dead after some time. These are non rechargeable batteries. In these batteries cell reaction takes place in one direction so these are also called irreversible batteries.

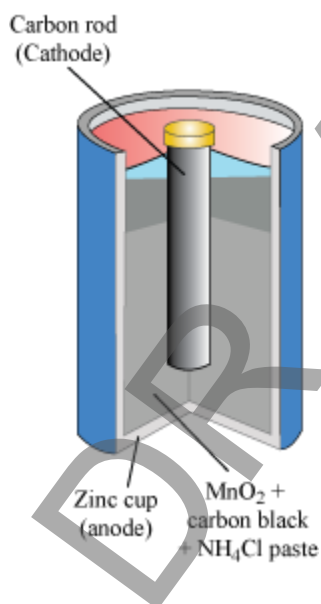
For example: lithium cell, dry cell, mercury cell, button cell etc.

ii) Secondary batteries:

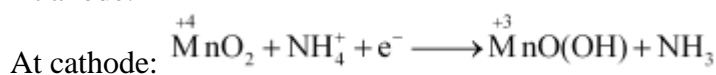
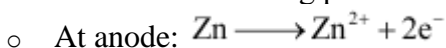
Those batteries which can be recharged after discharge by passing an electric current from external source in opposite direction are called secondary batteries. These are also called rechargeable batteries. They can be used again and again. In these batteries cell reaction takes place in both directions so these are also called reversible batteries.

For example: Lead acid battery, Lithium ion battery, Nickle cadmium battery etc.

- Dry cell



- The reactions taking place at the anode and cathode are –



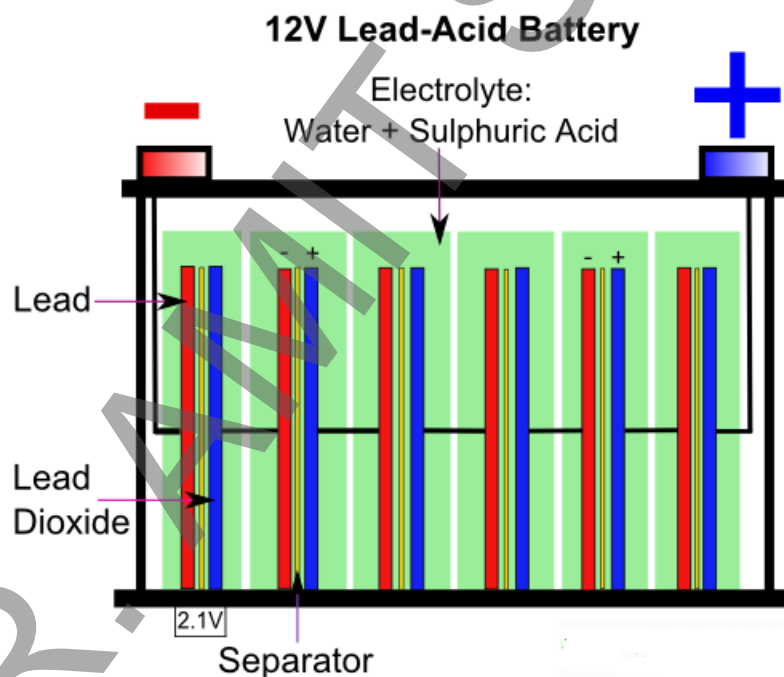
NH_3 formed in the reaction combines with Zn^{2+} to form a complex $[\text{Zn}(\text{NH}_3)_4]^{2+}$

- Cell potential is nearly 1.5 V.

Lead Storage Battery: Lead acid battery is an example of secondary battery it can be recharged after discharge by passing an electric current from an external source in opposite direction. It is also called rechargeable batteries. It can be used again and again. In this battery cell reaction takes place in both directions.

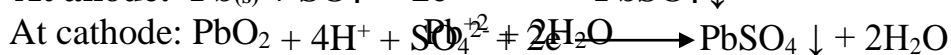
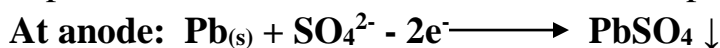
Construction:

- It consists of PVC container.
- Spongy metallic lead rods (Pb) behave like anode.
- Lead grid filled with Lead dioxide (PbO_2) behaves like cathode.
- 38% dil. H_2SO_4 behaves like electrolyte.
- A number of spongy lead plates (anode) and a number of lead dioxide (PbO_2) plates (cathode) are connected in parallel.
- The spongy lead plates are fit alternatively between lead dioxide plates.
- All the plates are separated from adjacent plates by insulators like wood strips, glass fiber etc.
- The entire combination is immersed in approximately 38 % dil. H_2SO_4 of specific gravity 1.2 to 1.3 g/cm^3 solution.

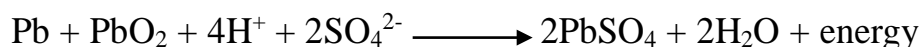


Discharging:

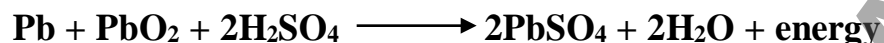
Battery is said to be discharge when used for production of electrical energy. In this process the lead electrode loses electron and get oxidized into Pb^{+2} which react with SO_4^{2-} and form PbSO_4 . The released electrons from anode are used up by cathode to reduce PbO_2 into Pb^{+2} which react with SO_4^{2-} and form PbSO_4 . In this process PbSO_4 deposited on both the electrode and cell stop working.



The net cell reaction

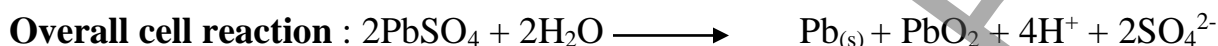
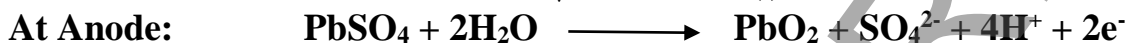


OR



Charging:

A battery needs charging when the specific gravity of H_2SO_4 falls below 1.2 g/cm^3 . This can be achieved by applying external direct current so as to reverse the cell reaction.



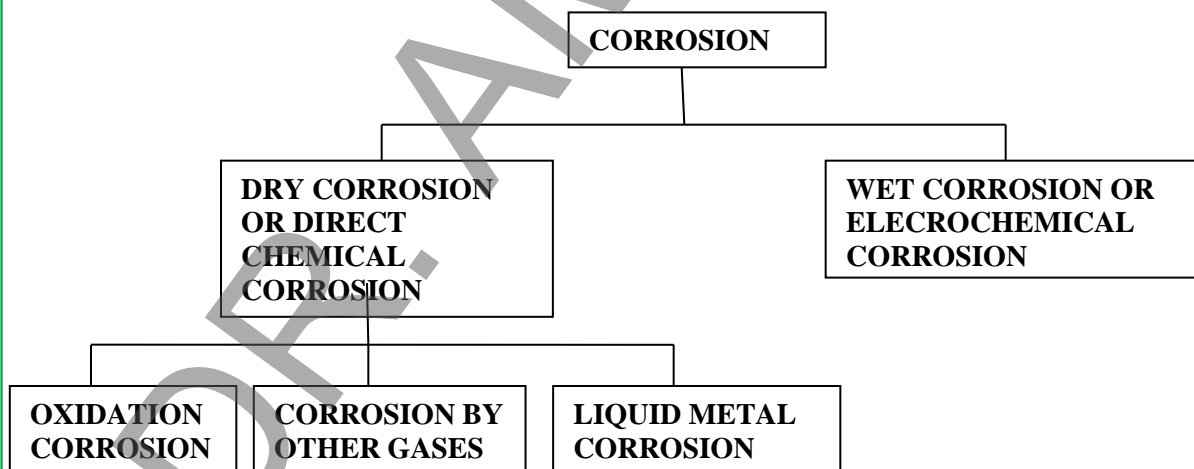
CORROSION: The process of slow conversion of metals into their undesirable compounds due to their reaction with oxygen, water, moisture, acids, gases etc. present in the atmosphere is called corrosion.

Corrosion is the reverse process of metallurgy.

Examples: Rusting of iron, Tarnishing of copper, Development of a green coating on copper and bronze.

Causes of Corrosion: Metal corrodes when it reacts with another substance such as oxygen, hydrogen, an electrical current or even dirt and bacteria. Corrosion can also happen when metals like steel are placed under too much stress causing the material to crack.

Types of Corrosion: Generally corrosion can be divided into two parts.



1. DRY CORROSION OR DIRECT CHEMICAL CORROSION: The process of slow conversion of metals into their undesirable metal oxide or metal compounds due to their reaction with oxygen, & other gases in absence of moisture or water is called dry corrosion or direct chemical corrosion.

It is further divided into three parts:

A. Oxidation Corrosion: The process of slow conversion of metals into their undesirable metal oxide due to their reaction with oxygen in absence of moisture or water is called oxidation corrosion.

During oxidation corrosion metal get oxidised and oxygen get reduced and they form metal oxide.

At Anode: $M_{(s)} - ne^- \longrightarrow M^{n+} \text{ ions}$

At Cathode: $O_2 + 4e^- \longrightarrow 2O^{2-} \text{ ions}$

The net reaction: $M_{(s)} + O_2 \longrightarrow M^{n+}nO^{2-}$

The metal oxide layer formed at the surface of metal decide the further corrosion.

Metal oxide layer may be of four type on the basis of nature.

(i). Stable metal oxide layer: A stable metal oxide layer is fine grained in structure and can get adhered tightly to the metal surface. Such a layer is impervious in nature, and prevents the metal from further oxygen coating, thereby shielding the metal surface from further corrosion.

Eg: The oxide films of Al, Sn, Pb etc are stable, adhering and impervious in nature.

(ii). Unstable metal oxide layer: They are mainly produced on the surface of noble metals (Ag, Au & Pt) which decomposes back to the metal and the oxide is liberated in the form of oxygen.

Metal oxide \longrightarrow Metal + Oxygen.

(iii). Porous metal oxide layer: In case of alkali and alkaline earth metals (Na, K & Mg, Li etc), the volume of oxide film formed on the surface is less than that of the metal, consumed. Hence, the oxide film formed is **porous and non-protective**. It results further corrosion of metal.

(iv). Volatile metal oxide layer: Volatile oxide layers volatilize as soon as they are formed, thereby leading to further corrosion directly. Eg. Molybdenum Oxide (MoO_3) is volatile.

B. Corrosion by other Gases: The process of slow conversion of metals into their undesirable metal salts due to their reaction with other gases except oxygen in absence of moisture and water is called corrosion by other gases.

At Anode: $M_{(s)} - ne^- \longrightarrow M^{n+} \text{ ions}$

At Cathode: $Cl_2 + 2e^- \longrightarrow 2Cl^- \text{ ions}$

The net reaction: $M_{(s)} + Cl_2 \longrightarrow M^{n+}nCl^-$

C. Liquid Metal Corrosion: The process of corrosion of metal due to the action of flowing liquid metal at high temperature during metallurgical operations is called liquid metal corrosion.

2. WET CORROSION OR ELECTROCHEMICAL CORROSION: The process of slow conversion of metal into their undesirable **hydrated metal oxide** by the attack of atmospheric oxygen and moisture is called wet corrosion or electrochemical corrosion. For example rusting of iron.

Rusting of iron: The process of slow conversion of iron into unwanted **hydrated ferric oxide** (rust) by the attack of atmospheric oxygen and moisture is called rusting of iron.

The molecular formula of rust is **$Fe_2O_3 \cdot xH_2O$**

It is chemically known as **hydrated ferric oxide**.

Mechanism: The mechanism of rusting of iron is an example of electrochemical corrosion. It takes place by the setup of an electrochemical cell on the surface of metal. One spot at the surface of metal behaves like anode and other surface of the metal behaves like cathode.

Oxidation takes place at anode and reduction takes place at cathode.

At anode: $\text{Fe} - 2\text{e}^- \longrightarrow \text{Fe}^{2+}$

At cathode: Chemical reaction at cathode takes place in different medium. It can take place in acidic medium in neutral medium or in weakly alkaline medium.

At cathode either **evolution of hydrogen** gas takes place or **absorption of oxygen** takes place.

During Hydrogen Evolution: It takes place in absence of oxygen.

In acidic medium: $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

In neutral medium: $2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$

During Absorption of Oxygen: It takes place in presence of oxygen.

In acidic medium: $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$

In neutral or weakly alkaline medium: $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \longrightarrow 4\text{OH}^-$

Overall Reaction: $2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$

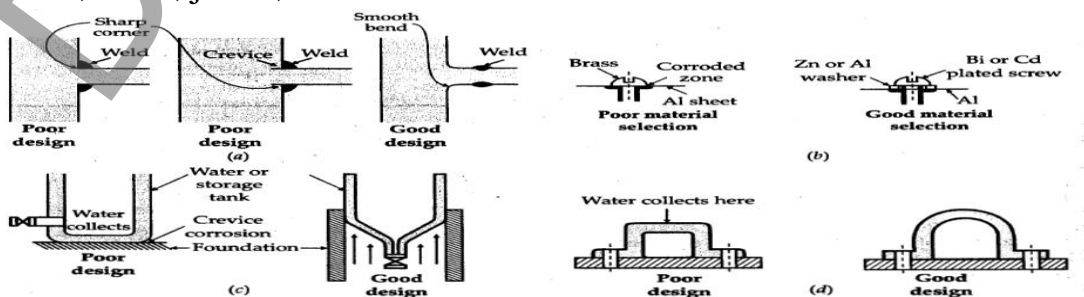
$2\text{Fe}^{2+} + 4\text{OH}^- \longrightarrow 2\text{Fe}(\text{OH})_2$

$4\text{Fe}(\text{OH})_2 + \text{O}_2 \longrightarrow 2[\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}]$

Rust (hydrated ferric oxide)

Prevention of corrosion: Corrosion can be prevented by applying following methods

- By coating the metal surface with paint.
- By coating the metal surface with red oxide.
- By coating the metal surface with organic substances or chemicals, grease or oil.
- **Galvanization:** The corrosion of metal can be prevented by coating metal surface with zinc metal. This process is called galvanization.
- **Electroplating:** The corrosion of metal can also be prevented by coating the metal surface by other less reactive metals. This process is called electroplating.
- **Tinning:** The process of coating tin on the metal surface to prevent metal from corrosion is called tinning.
- **By proper designing:** The corrosion of metal can also be prevented by proper designing of utensils, roofs, joints, bents etc.



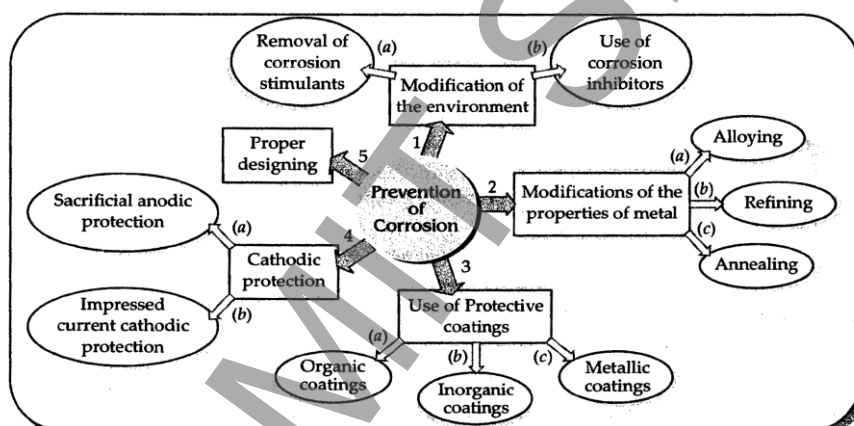
- Corrosion can also be prevented by using extra pure metals or by using metal alloys.
- **Cathodic protection or electrochemical protections method:** The corrosion of metal can also prevented by cathodic protection or electrochemical protection methods
Cathodic protection can be achieved by two ways

(i) **By sacrificial anodic protection:** The process of protection of metal from corrosion by attaching a highly reactive metal wire with anode, which itself oxidizes and protect the anodic metal from oxidation is called sacrificial anodic protection.

For example magnesium wire is attached with the iron anode in ships for protection of iron from oxidation with saline water magnesium itself oxidises and protect the iron from oxidation.

(ii) **Impressed current cathodic protection:** The process of protection of metal from corrosion by passing an electric current in opposite direction from an external source, which is greater than E_{cell} is called impressed current cathodic protection. Due to which anode is converted into cathode and cathode is converted into anode therefore anodic metal get prevented from oxidation.

Prevention of corrosion can be outlined below :



Differences between dry chemical corrosion and electrochemical:

Dry chemical corrosion	Electrochemical corrosion
It takes place in dry conditions	it takes place in presence of water or moisture or in wet conditions.
it takes place by direct chemical attack of environment on the metal.	it takes place through the formation of a series of galvanic cell on the metal surface.
It takes place in absence of water or moisture.	It requires Oxygen and moisture.
It can takes place on homogeneous and heterogeneous surface.	It takes place on heterogeneous metal surface only.
Corrosion product accumulates at the same spot where corrosion has occurred.	Corrosion product accumulates at the cathode whereas corrosion occurs at the anode.
It takes place uniformly.	It takes place non uniformly.

Cement

Portland cement is a very important building material. It was first discovered in England. It got its name because on setting, it hardened to a stone-like mass and was compared to the famous Portland Rock of England. It is a mixture of calcium and aluminium silicates with gypsum.

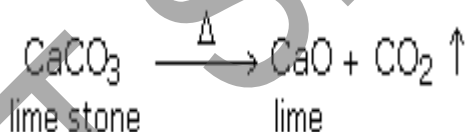
Composition of Portland cement

The approximate composition of cement is	
Calcium oxide (CaO) =	50 - 60%
Silica (SiO ₂) =	20 - 25%
Alumina (Al ₂ O ₃) =	5 - 10%
Magnesium oxide (MgO) =	2 - 3%
Ferric oxide (Fe ₂ O ₃) =	1 - 2%
Sulphur trioxide (SO ₂) =	1 - 2%

Raw Materials

Limestone and clay are the chief raw materials used in the manufacture of Portland cement.

- Limestone provides calcium oxide.



- Clay gives silica, alumina and ferric oxide.

Note: If lime is in excess, the cement cracks during setting and if it is less, the cement is weak in strength. Free lime is present in negligible quantity in cement; Almost the entire quantity of lime is present in the combined state as calcium silicates and aluminates.

Manufacture

Limestone and clay are first crushed separately. They are then mixed together in the required quantities and ground together finely. This grinding can be done either by the dry or the wet process. Wet process is suitable if limestone and clay are soft. If the raw materials are hard, dry process is preferred. Dry process is cost effective because fuel consumption is less when the raw materials are burnt in a rotary kiln.

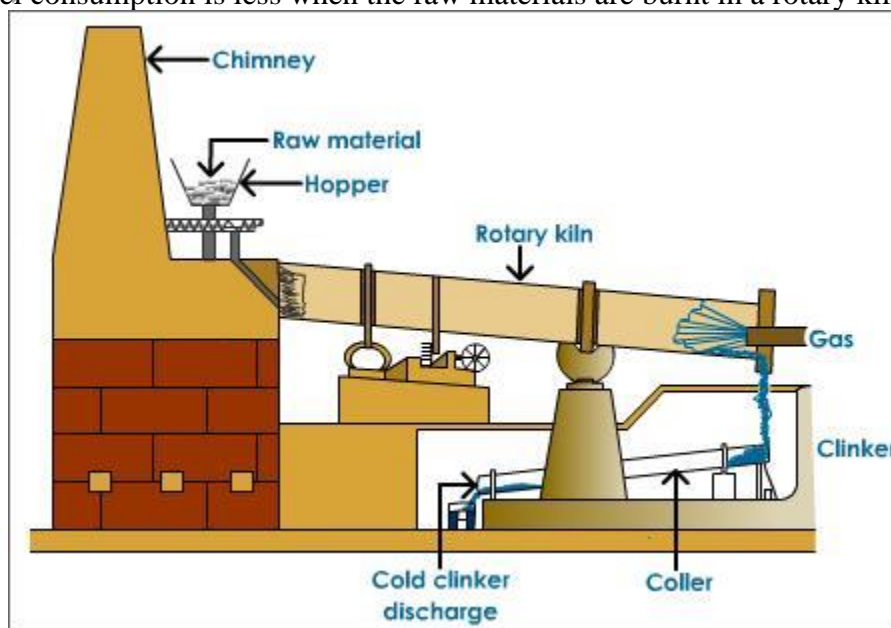
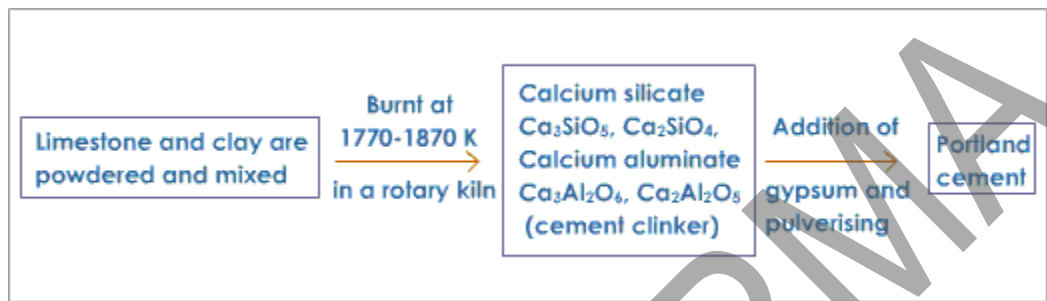


Fig: Manufacture of Cement



Process

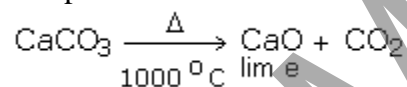
- The clay is first washed with water in wash mill to remove the foreign materials.
- Powdered lime is added to clay and the mixture is finely ground and homogenised.
- The clay-lime slurry (40% water present) or the dry pulverized mixture (in the case of dry process) is introduced into the upper end of the rotary kiln.
- The rotary kiln is a brick-lined, inclined, steel rotating cylinder, 150 - 200 feet long and 10 feet in diameter.
- Water evaporates at the upper end of the kiln with the help of hot gases, in the wet process.
- The dry material gravitates down and comes into contact with a flame produced by burning powdered coal.

Upper Part of the Kiln

Raw material heated $\xrightarrow[750^{\circ}\text{C}]{\Delta}$ Complete elimination of moisture

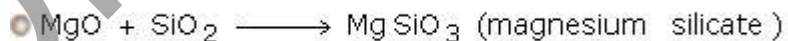
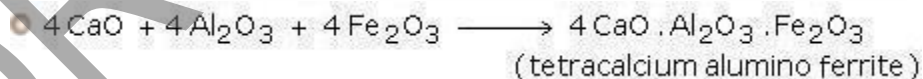
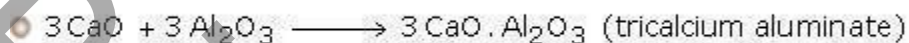
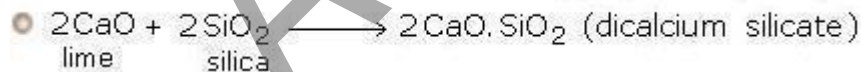
Middle Part of the Kiln

Temperature: 1000°C . Limestone decomposes to calcium oxide.



Lower End of the Kiln

Temperature: 1600°C . The partly fused and sintered mixture undergoes a series of chemical reactions to form calcium aluminates and silicates.



All these reactions are exothermic releasing heat. Proper temperature control is a must to avoid excessive vitrification (conversion into a glasslike substance by heat) of the mass.

The resulting mixture of all these silicates and aluminates is called cement clinker. After cooling, it is mixed with 2-3% gypsum and ground to a fine powder. Gypsum slows down the setting of cement so that cement is adequately hardened.

Setting Properties of Silicates and Aluminates

- Tricalcium silicate - sets quickly and develops considerable strength in a few days. Constitutes 50% of cement.
- Dicalcium silicate - sets slowly and becomes strong after a month or so.
- Tricalcium aluminate - sets instantaneously in the presence of water. Cement's internal strength is mainly because of this.
- Tetracalcium aluminoferrite sets rapidly but not as fast as tricalcium aluminate.

Setting of Cement

When mixed with water, cement sets to a hard mass. It first forms a plastic mass which hardens after some time due to 3-dimensional cross-links between the --Si-O-Si-- and --Si-O-Al-- chains. The first setting

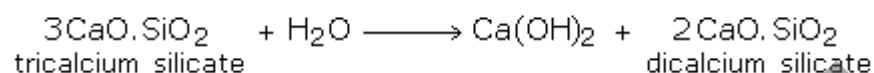
occurs within 24 hours whereas the subsequent hardening requires a fortnight, when it is covered by a layer of water. This transition from plastic to solid state is called setting.

Reactions Involved in Setting of Cement

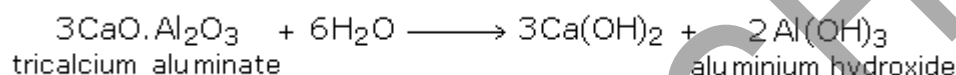
- On hydration silicates and aluminates of calcium get converted to their respective hydrated colloidal gels.



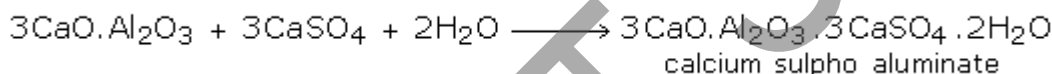
- At the same time, hydrolysis precipitates calcium hydroxide and aluminium hydroxide.



This calcium hydroxide binds calcium silicate particles together. On the other hand, aluminium hydroxide fills the interstices (an intervening space) rendering the mass impervious (not affording passage to a fluid).



- Role of gypsum - Gypsum reacts with tricalcium aluminate.



Note: The fast-setting tricalcium aluminate is removed to slow down the setting process. A quick setting will give rise to crystalline hydrated calcium aluminate. A slower setting yields the colloidal gel that imparts greater strength to the set mass. Thus gypsum helps in regulating the setting time of cement.

Concrete

It is a mixture of cement with sand and ballast (a mixture of coarse and fine aggregate for making concrete). Water is added to get a proper consistency. When set, a hard solid mass is formed.

Uses

- Concrete is used in foundations, flooring and walls.
- It is also used in paving roads.
- It also finds use in building roofs, piers for bridges, dams and canals.

Reinforced Cement Concrete (RCC)

Reinforced concrete is nothing but concrete allowed to set on structures having iron rod framework. This gives extra strength to the structures.

Review Questions

1. Iron corrodes faster than aluminium, even though iron is placed below aluminium in the electrochemical series. Why ?

Or

Aluminium is a highly corrosive metal, even then it is used freely in electrical lines for long time. Justify.

Ans. This can be explained by the fact that aluminium forms a non-porous, very thin, tightly adhering protective oxide film (Al_2O_3) on its surface and this film does not permit corrosion to occur.

2. Wire mesh corrodes faster at the joints. Why ?

Ans. We know that areas under stress tend to be anodic and corrosion takes place at these stressed areas. Due to welding, the joints of wire mesh are stressed so these becomes anodic. Hence, oxidation takes place easily at such joints leading to faster corrosion at the joints of wire mesh.

3. How is galvanization different from cathodic protection ?

Ans. In galvanization, the iron article is protected from corrosion by coating it with a thin layer of zinc. But in cathodic protection, the iron is made cathodic by connecting it with a more anodic metal like Al and Zn.

4. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

Or

Why metals corrode faster near sea-shores ?

Ans. Water is saline near sea-shores. Saline water has sodium chloride in it, which leads to increased conductivity of water. When such a water is in contact with the iron surface, corrosion current increases and rusting is speeded up.

5. Why does corrosion occur in steel pipe connected to copper plumbing ?

Or

Why a steel screw in a brass marine hardware corrodes ?

Or

Why a copper equipment should not possess a small steel bolt ?

Ans. Because steel (or iron) is higher in the electrochemical series so it forms the anode and undergoes corrosion when steel pipe connected to copper plumbing is exposed to a corroding environment. This type of corrosion is called galvanic corrosion.

6. Bolt and nut made of the same metal is preferred in practice. Why ?

Ans. Because such a combination will not permit galvanic corrosion to take place.

7. State the two conditions for wet corrosion to take place.

Ans. Condition (i) : Immersion or partial dipping of two dissimilar metals or alloys in a solution.

Condition (ii) : A metal in contact with the conducting liquid.

8. Why does part of a nail inside the wood undergoes corrosion easily ?

Ans. Corrosion is due to differential aeration. The part of the nail inside the wood is not exposed to atmospheric conditions, whereas the remainder part of it is exposed directly to atmospheric air. Thus, the nail inside the wood becomes anodic while the remaining part of the nail becomes cathodic. Due to differential aeration, a differential current starts flowing, whereby the nail inside the wood, the anodic part gets corroded easily.

9. *Why should nickel plated steel articles be free from pores and pin holes ?*

Ans. With respect to nickel, steel is anodic and if there are pores and pin holes in nickel plated steel article, they will expose the anodic steel to atmosphere. A galvanic cell is set up and an intense localized corrosion at these small exposed parts occur.

10. *Why is deposition of extraneous matter on metal surface for a long period is undesirable ?*

Ans. Extraneous matter like sand, dirt and scale when deposit on the surface of metal, restrict the access of oxygen below it. And the unexposed surface of metal becomes anodic with respect to well-aerated exposed surface of the metal. A differential current consequently starts flowing, which results in the localized corrosion of the metal surface, which is covered by extraneous matter.