

UNIT-V : MATERIAL CHEMISTRY

1.CEMENT: Concrete is most widely used non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is the essential bonding material which binds sand and rock when mixed with water.

Cement is a dirty greenish heavy powder and finds its importance as a building material. It can be described as material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc. Cement has the property of setting and hardening in the presence of water. So it is called as hydraulic cement. The essential constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al +Si (argillaceous).

Classification:- Cement is classified into four types, based on the chemical composition.

1. Natural cement
2. Puzzolona cement
3. Slag cement
4. Portland cement

Of these, Portland cement is the most widely used cement.

Portland cement: It is most widely used non-metallic material of construction. It is a mixture of calcium silicates and calcium aluminates with small amount of gypsum.

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock.

Properties:-All Portland cements are hydraulic in nature.

Composition of Portland cement:-

A good sample of Portland cement

- Calcium Oxide or lime (CaO) : 60-70%
- Silica (SiO₂) : 20-24%
- Alumina (Al₂O₃) : 5-7.5%
- Magnesia (MgO) : 2-3%
- Ferric Oxide (Fe₂O₃) : 1-2.5%
- Sulphur trioxide (SO₃) : 1-1.5%
- Sulphur Oxide (Na₂O) : 1%
- Potassium Oxide (K₂O) : 1%

Manufacture of Portland cement:-Raw materials:- The raw materials used for the manufacture of Portland cement are

(i)Calcareous materials:- Those which supply lime (CaO) such as lime stone cement, rock, chalk and waste calcium carbonate etc.

(ii)Argillaceous materials:- Those which supply silica(SiO₂), alumina and iron oxide such as clay, blast furnace slag ashes, cement rock, shale etc.

(iii)Powdered coal or fuel oil

(iv)Gypsum:-This is added during the final grinding and it controls the ratio of setting and hardening.

Functions of ingredients of cement:- During the manufacture of Portland cement, great care should be taken.

- Lime is the principal constituent of cement. Its proportion must be regulated properly. Excess of lime makes the cement to expand and disintegrate which reduces the strength. If the lime content is less, the strength of cement is reduced and sets very soon.
- Silica imparts strength to cement. So if the content of silica is more, it produces a slow hardening cement.
- Alumina makes the cement quick setting. But excess of alumina weakens the cement.
- Gypsum helps to retard the setting action of cement and it enhances the initial setting time of cement.
- Iron oxide provides colour, strength and hardness t the cement.
- Sulphur trioxide is desirable in small proportions.
- Presence of excess of alkali oxides causes cement efflorescent

The manufacture of cement involves the following steps.

Mixing of raw materials:- A mixture of finely ground lime stone and clay in the ratio of 3:1 is done by the following methods.

- (a) Dry process
- (b) Wet process

- (a) Dry process:-** The dry process is used if the lime stone and clay are hard. In this process, the lime stone is crushed into pieces and then it is mixed with clay in the proportion of 3:1. This mixture is pulverised to a fine powder and is stored in storage bins. Then it is introduced into upper end of the rotary kiln.
- (b) Wet process:-**The wet process is used if lime stone and clay are soft. In this process, the clay is washed with water in wash mills to remove any foreign materials. Powdered lime stone is then mixed with the clay in a proportion of 3:1. The mixture is then finely ground and homogenised to form a slurry containing 40% of water. This is also stored in the storage bins and can be introduced into the rotary kiln.

Merits and demerits of dry and wet process

Dry process	Wet process
(1) This process is adopted when the raw materials are quite hard.	(1) This process is preferred when the raw materials are soft.
(2)It is a slow and costly process.	(2)It is a comparatively cheaper and fast process.
(3)The fuel consumption is low as the rotary kiln used is a smaller one.	(3) Fuel consumption is high as a longer kiln is needed to drive off the water.
(4)Since the fuel consumption is less, the cost of production of cement is less.	(4)Cost of production is high, since the fuel consumption is more for longer kiln.

(5)The quality of cement produced is inferior.

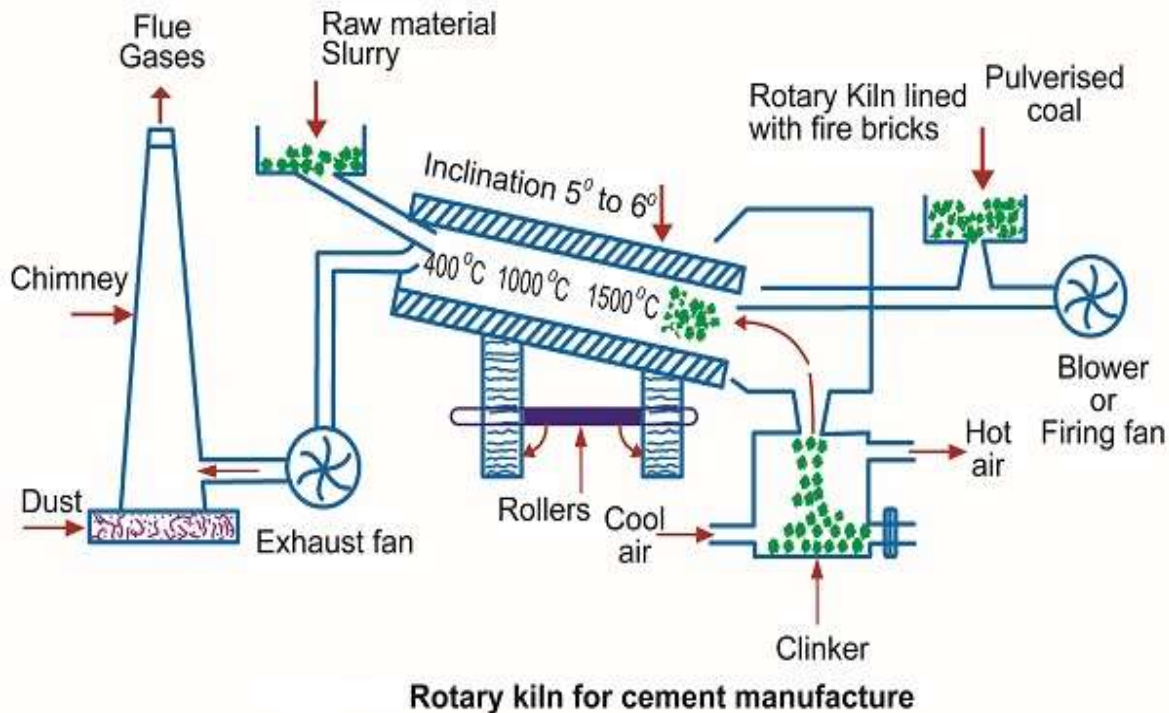
(6)This process is not suitable if the raw material has moisture content of 15% or more.

(5)The quality of cement produced is superior.

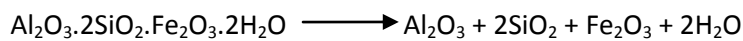
(6) This process is adopted even in wet conditions.

Burning the mixture in a rotary kiln:-

- The rotary kiln is an inclined steel cylinder of 90-120 m in length and 2.5-3.0 m in diameter and it is lined inside with fine bricks.
- The kiln is laid in slightly inclined position and can be rotated at one revolution per minute.
- Burning fuel and air are injected at the lower end.
- A long hot flame is produced that heats the interior of the kiln to a maximum temperature of 1750°C.
- As the kiln rotates, the raw materials are injected into the kiln at its upper end.
- The hot flames are forced into the kiln from the lower end.
- Due to the slope and slow rotation of the kiln, the materials move continuously towards the hottest end.
- As the mixture gradually descends, the temperature rises and creates different zones in the rotary kiln.



- (a) **Drying zone:-** This is present in the upper part of the kiln and the temperature is around 400°C. In this zone, most of the water in the slurry gets evaporated due to hot gases. The clay is broken as Al_2O_3 , SiO_2 and Fe_2O_3 .



(b) Calcination zone:- This is the central part of the kiln and the temperature is around 1000°C. In this zone, the lime stone is completely decomposed into quick lime.



(c)Clinkering zone:- This is the lower part of the kiln and is the hottest part.the temperature of clinkering zone is between 1400°C-1500°C.

In this zone, lime and clay undergo chemical interaction and form calcium aluminates and silicates.

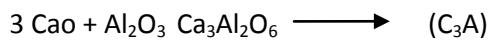
The aluminates and silicates of calcium are fused together and form small, hard, greyish stones called clinkers which are very hot.



Dicalcium silicate



tricalcium silicate



Tricalcium aluminate

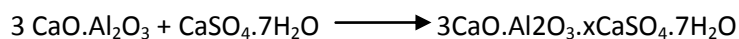


Tetra calcium alumino ferrite

Grinding of cement clinkers with gypsum:-

The clinkers are cooled and ground to a fine powder. The finely ground clinkers set very rapidly by absorbing moisture from the atmosphere. So gypsum is added which acts as retarding agent for early setting of cement.

After the initial setting, the cement water paste becomes stiff. But gypsum retards the dissolution of tricalcium aluminate by forming tricalcium sulpho aluminate which is insoluble.

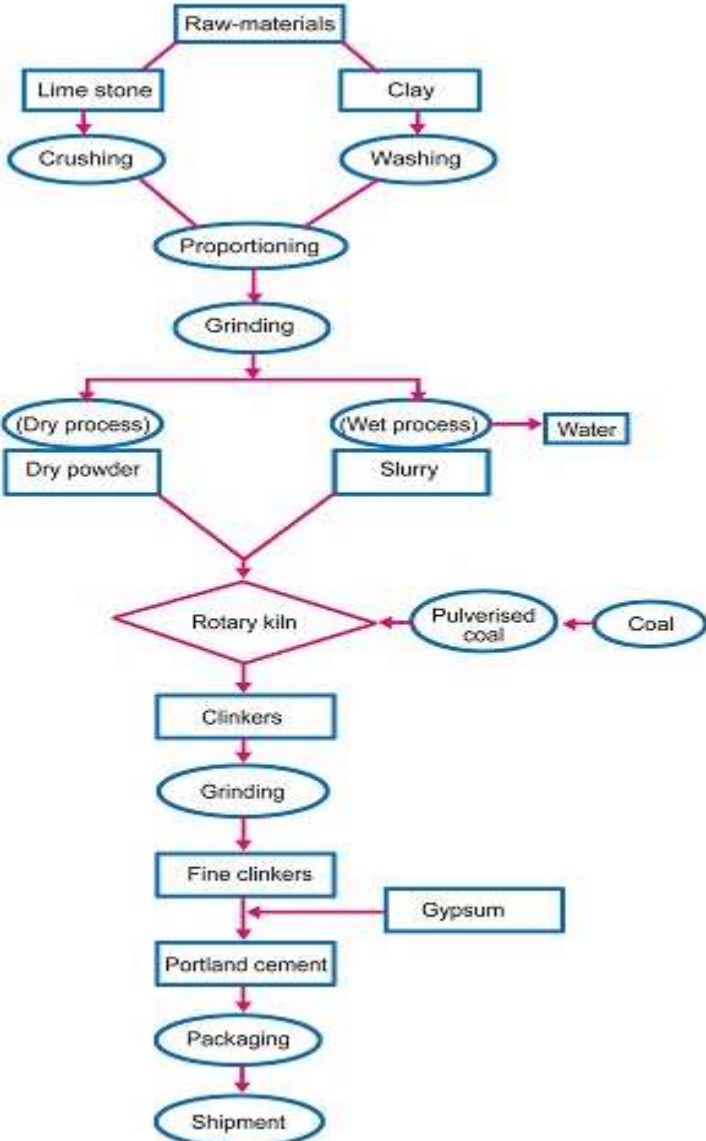


after initial set gypsum tricalcium sulpho aluminate

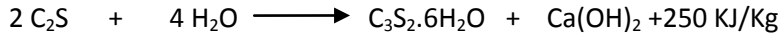
The formation of insoluble tricalcium sulpho aluminate prevents too early reactions of setting and hardening. This mixture of clinkers and gypsum powder is known as Portland cement.

Packing:-The ground cement is stored in silos from which it is fed to automatic packing machines.

Flow diagram for the manufacture of Portland cement

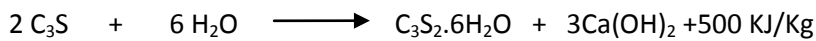


Flow diagram for the manufacture of Portland Cement



Dicalcium silicate tobermonite gel

Final setting and hardening of cement pasties due to the formation of tobermonite gel and crystallisation of calcium hydroxide and hydrated tricalcium aluminate.



tricalcium silicate tobermonite gel calcium hydroxide
(crystalline)

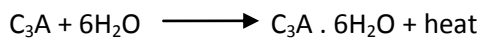
During setting and hardening of cement, some amount of heat is liberated due to hydration and hydrolysis reactions. The quantity of heat evolved during complete hydration of cement is 500 KJ/Kg.

Sequence of chemical reactions during setting & hardening:-

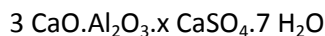
Cement	1 day	hydration of	7 days	gelation	28 days	gelation
+	----->	C ₃ A and	----->	of	----->	of
Water paste		C ₄ AF		C ₃ S		C ₂ S & C ₃ S

Function of gypsum in cement:-

Tri calcium aluminate (C₃A) combines with water very rapidly.



After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C₃A by forming insoluble calcium sulpho aluminate.



This reaction prevents the high concentration of alumina in the cement solution and hence retards the early initial setting of cement.

The physical changes occurring in the setting and hardening of cement can be summarised as follows:

2.Lubricants:-

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. This mutual rubbing of one part over the other leads to resistance of movement which is called as friction. Friction causes a lot of wear and tear of surfaces of moving parts and since heat is generated in this process, it reduces the efficiency of the machinery. The problems of frictional resistance can be minimised by using lubricants which forms a thin layer between the moving parts.

A lubricant is defined as a substance introduced between two moving or sliding surfaces and reduces the frictional resistance between them. This phenomenon of reducing frictional resistance between the two surfaces by the introduction of lubricants in between them is called lubrication.

Criteria of a good lubricant:-A good lubricant must have the following functions.

- The first and foremost function is to reduce friction.
- It reduces surface deformation, wear and tear because the direct contact between the rubbing surfaces is avoided.
- It reduces waste of energy. Hence the efficiency of the machine is enhanced.
- It reduces expansion of metal by local frictional heat.
- It avoids seizure of moving surfaces as the lubricant minimises the liberation of frictional heat.
- It avoids unsmooth relative motion of moving parts.
- It reduces the maintenance and running cost of machine, by preventing rust and corrosion.
- It also acts as a seal.

Mechanism of lubrication:-

There are mainly three types of mechanisms by which lubrication takes place. They are:

- (i) Fluid film or thick film or hydrodynamic lubrication
- (ii) Boundary lubrication or thin film lubrication
- (iii) Extreme pressure lubrication

(i) Fluid film lubrication:-

- In this type of lubrication, the moving or sliding surfaces are separated from each other by a thick film of fluid, so that there is no direct contact between them.

- The lubricant film covers the irregularities of the surfaces and reduces friction and wear and tear.
- The resistance to movement of sliding or moving parts is due to internal resistance between the particles of the lubricant moving over each other.
- For this, the lubricant should have minimum viscosity under working conditions. It should remain in place and separate the surfaces.
- The coefficient of friction which is a ratio of force required to cause motion to the applied load is as low as 0.001 to 0.03.

- Delicate instruments, light machines like watches, clocks, guns, sewing machines etc. are provided with fluid film lubrication.

The fluid film lubrication is done by hydrocarbon oils. These are blended with selected long chain polymers to maintain the viscosity of oil as constant in all

seasons. The viscosity of hydrocarbon oils increases with increasing molecular weight.

Hence appropriate fractions are blended from petroleum refining to meet the requirement for different applications. These fractions contain small quantities of unsaturated hydrocarbons which get oxidised under operating conditions and form gummy products. So antioxidants like amino phenols are used in hydrocarbon oils.

(ii) Boundary lubrication:-

- This type of lubrication occurs when a continuous film of lubricant cannot persist and direct metal to metal is possible.
- In these conditions, the space between the moving or sliding surfaces is lubricated so that a thin layer of lubricant is adsorbed on the metallic surfaces due to physical or chemical forces.
- This adsorbed layer helps to avoid the direct metal to metal contact between the rubbing surfaces.
- This load is carried by the layers of adsorbed lubricant on both the metal surfaces.
- The coefficient of friction varies from 0.05 to 0.15.

For boundary lubrication, the lubricant molecules should have

Long hydrocarbon chains

Polar groups to promote wetting or spreading over the surface

Lateral attraction between the chains

Active functional groups which can form chemical bonds with metals or other surfaces

High viscosity index

Good oiliness

Resistance to heat and oxidation

Low pour point

Solid lubricants, greases and oils with proper additives function as lubricants

in this type of lubrication. For example, graphite, molybdenum disulphide, mineral

oils with additives of fatty acids or fatty oils, vegetable and animal oils and their

soaps. These materials form films on the metal surfaces having internal friction. So they can bear compression and high temperatures.

(iii) Extreme pressure lubrication:-

- When the moving or sliding surfaces are under high pressure and speed, a special type of lubricants are used called high pressure lubricants.
- They withstand high temperatures generated due to friction.
- Under these conditions, liquid lubricants fail to stick and decompose and may vaporise.
- These problems are minimised by adding special additives to mineral oils.
- These additives form durable films on metal surfaces which can withstand high loads and high temperatures.
- Important additives are organic esters, sulphur as in sulphurised oils or phosphorous as in tricresyl phosphate.
- These compounds react with metallic surfaces at high temperatures and form metallic chlorides, sulphides or phosphides.
- These metallic compounds possess high melting points and serve as good lubricants at high temperatures and high pressures.

Mechanical properties of lubricants:-

Cloud and pour points:- The lubricating oils obtained from petroleum contains dissolved paraffin wax and asphaltic or resinous impurities which separate out of the oil at low temperatures. Further solidification of lubricant causes jamming of machine.

Cloud point:- When oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance is called its cloud point.

Pour point:- When oil is cooled slowly, the temperature at which it ceases to flow or pour is called its pour point.

The cloud and pour points indicate the suitability of lubricants in cold conditions. In machines working at low temperatures, the lubricants that are used should have low pour points. Examples are refrigerator plants and air-craft engines, which are required to start and operate at sub-zero temperatures.

Significance of cloud and pour point:-

(i) Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines become clogged because of separation of wax.

(ii) Pour point values of petroleum and non-petroleum lubricants are necessary under sub-freezing conditions.

Flash and fire points:-

- A good lubricant should have flash point above the temperature at which it is used.
- It should not volatilise under working temperature. If some volatilisation occurs, the vapours should not form inflammable mixture with air.
- This aids in precautionary measures against fire hazards during the use of lubricant.

Flash point:- The lowest temperature at which the oil lubricant gives off vapours that ignites for a moment, when a flame is brought near it.

Fire point:- The lowest temperature at which the vapours of the oil burn continuously for at least five seconds, when a flame is brought near it.

The fire points are mostly 5 to 40°C higher than the flash points. The fire and flash points do not have importance in lubricating properties but are important only when oil is exposed to high temperatures.

Viscosity:- Viscosity is the property of a fluid by virtue of which it offers resistance to its own flow. It is the indicator of flow ability of a lubricating oil.

Lower the viscosity, greater the flow ability. Viscosity helps in the selection of good lubricating oil.

Viscosity index:- The variation of viscosity of a liquid with temperature is called viscosity index.

The viscosity of a good lubricating oil should not change much with change in temperature. But in general, for every 1°C rise in temperature, the viscosity index decreases by 2%.

L-U

Viscosity Index(VI) = ----- X 100

L-H

where U = viscosity of test oil at 38°C.

L = viscosity of standard oil at 38°C having a VI of zero.

H = viscosity of standard oil at 38°C having a VI of 100.

3. Refractories:-

- A substance that is difficult to fuse is called a refractory.
- A refractory is a material which does not melt easily and its fusion temperature is very high. They are inorganic materials which can withstand high temperatures, abrasive and corrosive action without any deformation in shape.
- The main role of a refractory is to confine heat in it.
- Refractories are widely used for providing high temperature resistant lining for furnaces, kilns, crucibles etc.
- They are used in industries like glass, ceramic, oil-refining, power generation and cement.
- They are also used in the manufacture of rocket nozzles, launch pads and for domestic heating.
- Refractories are available in different shapes and sizes as crucibles, tubes, granules and cements.

Classification:-

Based on fusion temperature, they are of 3 types.

(a) Normal refractories:- They have fusion temperature in the range of 1580-1780°C.

Eg:- fire clay

(b) High refractories:- They have fusion temperature in the range of 1780-2000°C.

Eg:- chromite

(c) Super refractories:- They have fusion temperature in the range of about 2000°C.

Eg:- zircon

Based on chemical composition, they are of 3 types.

(a) Acidic refractories:- They consist of acidic materials like alumina and silica. These refractory materials are resistant to acid slags and are readily attacked by basic slags.

Eg:- alumina, silica and fire clay refractories

(b) Basic refractories:- They consist of basic materials like CaO, MgO etc. and are resistant to basic slags. They are widely used in steel making open hearth furnaces.

Eg:- magnesite and dolomite bricks

(c) Neutral refractories:- They are made from weakly basic or acidic materials like carbon, zirconia and chromite. Neutral refractories show resistance to the action of basic and acidic materials. They show good chemical stability.

Eg:- graphite, zirconia and carborundum

Based on oxide content, the refractories are classified into 3 types.

(a) Single oxide refractories:- Eg:- alumina, magnesia and zirconia

(b) Mixed oxide refractories:- Eg:- zircon, spinel

(c) Non oxide refractories:- Eg:- borides, carbides, silicides etc.

Characteristics of refractory materials:-

- A good refractory material should have a softening temperature higher than operating temperatures.
- They should be chemically inert.
- The refractoriness should be high for a good refractory.
- The refractories should not crack at operating temperatures.
- They should have low permeability.
- They should have low thermal coefficient of expansion and should expand and contract uniformly with increase and decrease of temperatures.
- They should withstand heavy loads.
- They should possess good physical, chemical and mechanical properties.

Properties of refractories:-

(i) Refractoriness:-

- It is the ability of a material to withstand high temperature without deformation under working conditions.
- It is the softening temperature of the material.
- Higher the softening temperature, more valuable is the refractory.

ii) Refractoriness under load (RUL):-

- Refractoriness determines the strength of a refractory.
- The essential qualities of a refractory are
 - Temperature resistance and
 - Load bearing capacity
- The refractory lined furnaces are generally charged with heavy reactants. So they should withstand heavy loads at high temperatures.

Eg:- Fire clay refractories collapse at temperatures below their fusion temperatures when heavy load is applied. Silica refractories with stand loads even at high temperatures.

RUL test is performed to know the safe upper temperature limit upto which the refractory can be used. The RUL test is done in rectangular container by applying a load of 75 kg/cm^2 on to the refractory and heating at a constant rate of 10°C per minute. During this process, the specimen will soften and its height will decrease under the load. This decrease in height is measured and when there is 10% decrease to that of original height, the temperature is noted. The RUL is then expressed as the temperature at which this 10% deformation occurs.

(iii) Porosity:- Refractories contain pores which result from manufacture methods and they can be opened or closed. Porosity affects the physical and chemical properties of refractory like chemical stability, strength, abrasion resistance and thermal conductivity.

A highly porous refractory allows slags, gases etc., and decreases the strength and resistance to abrasion and corrosion.

Thus a good refractory should have low porosity.

iv) Thermal spalling:- It is peeling, cracking, fracturing and breaking of refractories due to rapid fluctuations in temperature causing uneven stress and strain in the refractory. A good refractory should have good resistance to thermal spalling.

v) **Thermal expansion and contraction:-** All solids expand when heated and contract on cooling. So allowance has to be made in the furnace design for thermal expansion.

Expansion of a refractory material decreases the capacity of furnace and results in internal stress. Further expansion and contraction leads to rapid break down of refractory.

Hence lower the thermal expansion and contraction better is the quality of refractory. Heavy and dense refractory bricks have high heat capacity and are used in brick work of coke ovens, glass and blast furnaces. Light weight refractory bricks have low heat capacity and are used in intermittently operated furnaces to achieve working temperatures in a short time with less consumption of fuel.

Conditions leading to failure of refractory material:-

- Using a refractory of less refractoriness than that of operating temperature.
- Using refractories which cannot withstand load of raw materials and products.
- Rapid changes in temperatures of furnace.
- Using bricks which are not properly fired.
- Using bricks of high thermal expansion.
- Using bricks which undergo volume changes at high temperatures.
- Using acidic or basic refractory in a furnace in which basic or acidic reactants or products are processed.
- Using heavy weight refractory bricks.

4. BATTERIES:

Battery can be defined as a device which contains two or more electrochemical cells connected in series, that can be used as a source of direct electric current at a constant voltage. They are mainly of 2 types.

(1) PRIMARY CELLS (OR) PRIMARY BATTERIES : The cells in which the cell reaction is not reversible i.e, when the cell reaction is completed or all the reactants are exhausted, then no more electricity is produced and the battery becomes dead. Primary cells can't be recharged.

(2) **SECONDARY CELLS (OR) SECONDARY BATTERIES** : Cells in which the cell reaction can be reversed by passing direct electric current in opposite direction. Thus a secondary battery may be used through a large number of cycles of discharging and charging.

Primary batteries (non rechargeable) : They are non rechargeable and are less expensive and are often used in ordinary gadgets like torch lights, watches and toys. Commercially many kinds of primary batteries are available, the important ones are leclanche cell, alkaline cell and lithium cell.

Dry cell (Laclanche cell): A cell without fluid component is called as dry cell.

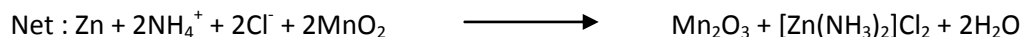
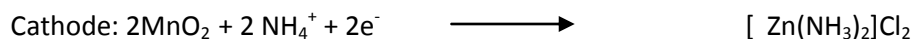
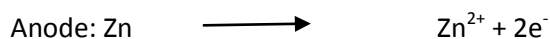
The anode of the cell is zinc can, containing an electrolyte consisting of NH_4Cl , ZnCl_2 and MnO_2 to which starch is added to make it thick paste to prevent leak. A carbon rod serves as cathode, which is immersed in the electrolyte in the centre of the cell.



However an acid base reaction between OH^- and NH_4^+ (derived from NH_4Cl) evolves NH_3 , which disrupts the current flow.



This is prevented by reaction of NH_3 with Zn^{2+} to form complex $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$



The dry cell is a *primary cell*, so, various reactions involved cannot be reversed by passing electricity back through the cell.

It gives a voltage of about 1.5V.

Disadvantages:

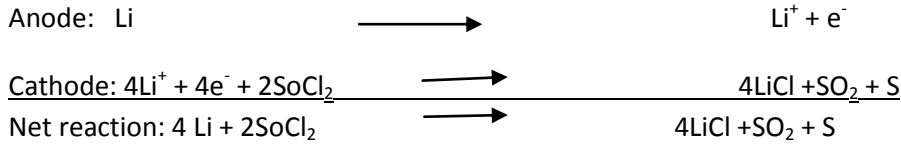
- 1) When current is drawn rapidly from it, products build up on the electrodes cause drop in voltage
- 2) Since the electrolytic medium is acidic, Zn metal dissolves slowly, thereby the cell run down slowly even if it is not in use.

Lithium cells : There are 3 types of lithium cells.

a) Liquid cathode lithium cells:

Anode: lithium , cathode: SoCl_2 , electrolyte: LiAlCl_2 .

These cells offer higher discharge rates because reactions occur at cathode surface. In a solid cathode the reactions take longer because the lithium ions must enter into cathode for discharge. The direct contact between the liquid cathode and lithium forms film over lithium, called solid electrolyte interface(SEI). This prevents further chemical reaction when not in use, thus it preserves the shelf life. This cell consists of long surface area carbon cathode. Thionyl chloride acts as electrolyte solvent and the active cathode material.

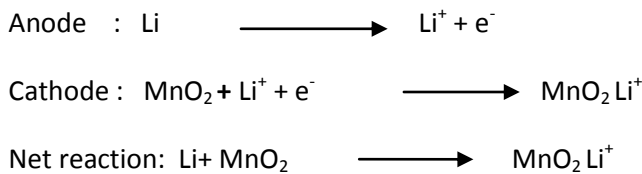


During discharge the anode gives off lithium ions. On the carbon surface the thionyl chloride reduces to chloride ions, SO₂ and sulphur. The lithium and chloride then form lithium chloride. The sulphur and sulphur dioxide dissolve in the electrolyte, but at a higher rate discharges SO₂ will increase the cell pressure. Thus system has very high energy density and an operating voltage of 3.3 to 3.5 V.

- Uses:**
1. these are used on electronic circuit boards for supplying fixed voltage for memory applications.
 2. they are used for military and space applications.
 3. they are used in medical devices such as neuro-stimulators, drug delivery systems.

b) Solid Cathode lithium cells (LiMnO₂) :

These cells can not be used in high drain applications and don't perform well under low temperature conditions. However they don't have same voltage delay as liquid cells. The cathode is Manganese dioxide and electrolyte is a mixture of Propylene carbonate and 1,2-Dimethoxyethane.

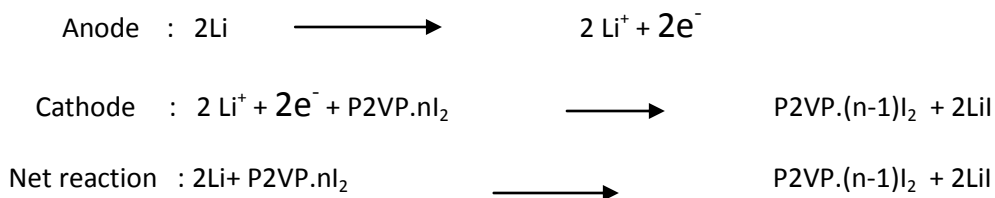


The cathode in this cell is carbon mono fluoride. Electrolyte is lithium tetrafluoroborate in a solution of propylene carbonate and dimethoxyethane.

Uses: The cells also have high voltage(3 V) and high energy density (250Wh/Kg). These are used in Watches, calculators and memory applications and portable electronic devices.

c) Solid electrolyte lithium cells: They perform best in low current applications and have very long service life.

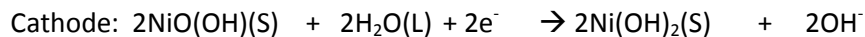
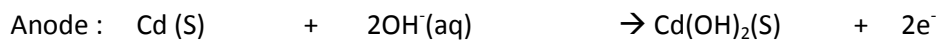
The electrolyte is solid lithium iodine. Cathode is poly-2-vinylpyridene (P2VP).



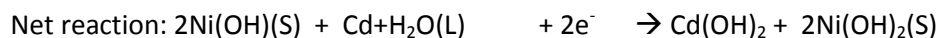
Uses: They are used in pacemakers.

Secondary Cells : - These cells are rechargeable and reversible.

- **Nickel cadmium battery:** It consists of a cadmium anode and a cathode composed of a paste of NiO(OH) (Nickel oxy hydroxide). The cell reactions are:



(Nickel oxy hydroxide)



The reaction can be readily reversed because the reaction products Ni(OH)₂ (S) and Cd(OH)₂ (S) add here to electrode surface.

Nickel – cadmium battery, recently developed is a potable, rechargeable cell and its cell voltage is fairly constant and is about 1.4v. It can be left for long periods of time without any appreciable deterioration, since the gases are produced during discharging.

USES: used in electronic calculations, electronic flash units, cordless electronic shavers, transistors etc.

LEAD – ACID CELLS :

Anode : sponge metallic lead

Cathode : Lead dioxide

Electrolyte :dil. H₂SO₄

Construction : A number of lead plates (- ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel. The lead plates are fit in between lead dioxide plates various plates are separated from adjacent plates by insulators like wood strips, rubber or glass fibre. The entire combination is immersed in approximately 20 – 21 % dil H₂SO₄ of density 1.2 to 1.3.

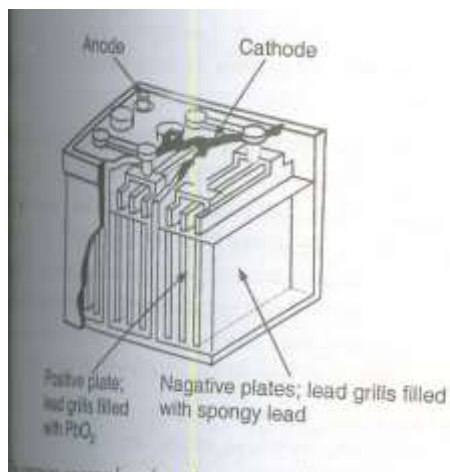
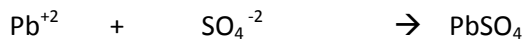


Fig. 26. A lead accumulator for car consists of six lead-acid storage cells in series and it is capable of delivering 12 V.

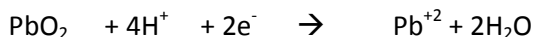
Discharging :- when the strong cell is operating as voltaic cell, it is said to be discharging, the lead electrode loses e^- s which flow through the wire. Thus at anode oxidation of lead takes place



Then it combines with SO_4^{-2} ions



The electrons flow to the cathode . here PbO_2 gains electrons and undergoes reduction from +4 to +2 and thus combines with SO_4^{-2} .

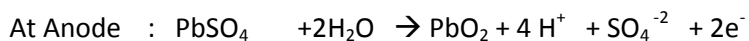
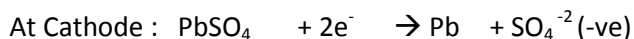


So, the net reactions during use is

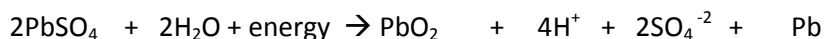


used in automobiles is a combination of six cells in series to form a battery with an e.m.f of 12 volts.(each cell is about 2 volts).

CHARGING: - when both anode and cathode become coated with PbSO_4 , the cell stops to function as voltaic cell to recharge it, the reactions taking place during charging are reversed by passing an external e.m.f greater than 2 volts from a generator and following reactions take place at the respective electrodes.



The Net reaction during charging is :



→ During charging, the lead acid strong cell acts as electrolytic cell.

→ During discharging, concentration of H_2SO_4 decreases while during charging, its concentration increases.

APPLICATIONS: Automobile and construction equipment, stand by backup systems.

ADVANTAGES: Low cost, ability to withstand mistreatment and also perform well in high and low temperatures.

DISADVANTAGES: They have low cycle life a quick self discharge and low energy densities.

FUEL CELLS: In a fuel cell, electrical energy is obtained without combustion from oxygen and a fuel gas that can be oxidized (like H_2 gas). Hence a fuel cell converts the chemical energy of the fuels directly to electricity.

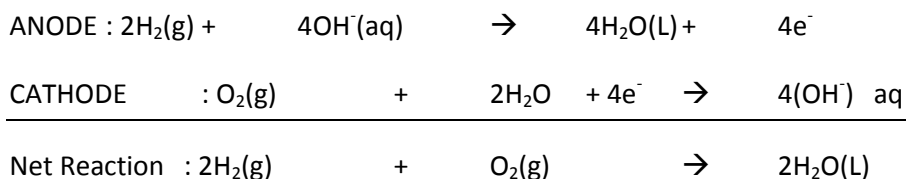
The essential process in a fuel cell is



In a fuel cell one or both of the reactants are not permanently contained in the cell, but are continuously supplied from a source external to the cell and the reaction products are continuously removed. This is called a fuel cell.

One of the most successful and simplest fuel cells is the hydrogen-oxygen fuel cell.

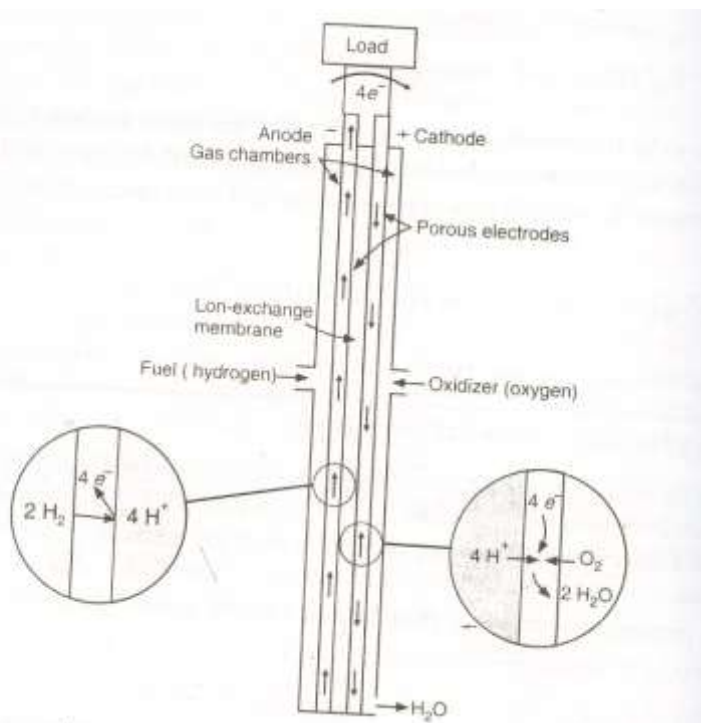
It consists of an electrolytic solution such as 25% KOH and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments respectively where the following reaction takes place.



It may be noticed that the only product that is discharged by the cell is H_2O .

Usually, large numbers of these cells are stacked together in series to make a battery, called a fuel cell battery or fuel battery.

Applications: H_2 / O_2 fuel cells are used as auxiliary energy sources in space vehicles, submarines or other military vehicles. The weight of the fuel battery sufficient for 15 days is 250 kg. In the case of H_2 / O_2 fuel cells, the product water proved to be a valuable source of fresh water by astronauts.



ADVANTAGES OF FUEL CELLS:

1. No emission of toxic gases or chemical wastes; they are in safe limits. The reactants and products are environmentally friendly.
2. High efficiency of conversion of chemical energy to electrical energy. So it can be used as an excellent renewable energy resource.

3. No noise pollution like generators.
4. Low maintenance and fuel transportation costs.
5. Unlike nuclear energy, fuel energy is economical and safe.
6. Fuel cells are operable to 200⁰c and so find applications in high temperature systems.

LIMITATIONS OF FUEL CELLS:

1. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs.
2. Large weight and volume of N₂ gas fuel storage system
3. High cost of H₂ gas
4. Lack of infrastructure for distributions and marketing of hydrogen gas.
5. Most alkaline fuel cells suffer from carbon dioxide linkage.
6. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs.
7. Large weight and volume of N₂ gas fuel storage system
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11. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs.
12. Large weight and volume of N₂ gas fuel storage system
13. High cost of H₂ gas
14. Lack of infrastructure for distributions and marketing of hydrogen gas.
15. Most alkaline fuel cells suffer from carbon dioxide linkage.

5. NANO TECHNOLOGY

Definition: The design ,characterization ,production and application of structures,devices and systems by controlled manipulation of size and shape at the nanometer scale that produces structures ,devices and systems with atleast one novel function because of their small structure. is nano technology.

Nano means one billionth part of a meter.

ex: human hair measures 50,000 nm

10 hydrogen atoms in a line make up 1 nm

NANO MATERIALS

These are materials with dimensions and tolerances in the range of 100 nm to 0.1 nm.

These are biological,inorganic or organic structures possessing unique properties.

These can be metals,ceramics,polymeric materials or composite materials.

ex:carbon nanotubes,bucky balls,quantum dots.

METHODS OF PREPARATION OF NANO MATERIALS

1) Top - down approach:

in this method ,small features are created on large substrates by repeated pattern transfer steps involving lithographic methods.

this approach is expensive ,slow and not suitable for large scale production.

ex: etching,lithography,erosion,mechanical grinding

this method is used in the microelectronics industry.

Bottom - up Approach:

This method starts with very small units, often individual molecules or atoms and assembles these

Building - block units into larger hierarchical and controlled structures.

This approach is less expensive and suitable for large scale production.

ex:molecular self assembly,dip pen nanolithography,gas phase agglomeration,chemical vapour deposition,molecular beam epitaxy, ion implantation

PROPERTIES OF NANO MATERIALS

Nanomaterials are unique .

Reason:

The physical behaviour of particals changes from classical physics to quantum physics with decreasing partical size to less than or equal to 100 nm.

1.size effect:

Only by varing the partical size of the material,properties like melting point,solubility,colour,transparecy,and catalytic behaviour changes.

2.composition effect:

Different physical and chemical behaviour of the material is observed by varing the particle compositions.

3.surface effect:

Properties like dispersibility,conductivity,catalytic behaviour,electrical and magnetic behaviour,reactivity strength and optical properties alter with different surface properties of the nanoparticle.

4.At high temperatures they are strong, hard,more ductile .

5They become wear resistant,errosion and corrosion resistant.

The principal factors which cause the properties of nanomaterials to difer significantly from other materials are:

1. Small particle sizes less than or equal to 100 nm.

2. Increased relative surface area

3. Quantum size effects

4.Size distribution

5.Specific surface feature.

NANO MATERIALS

Carbon nano tubes:

Carbon nano tubes are sheets of graphite rolled up to make a tube. They are about 100nm in diameter. they can be single walled carbon nanotubes or multi-walled carbon nanotubes. These are true examples of nanotechnology.

PROPERTIES:

1. They possess remarkable tensile strength and large surface area.
2. They can be insulating, semiconductors or conductors
3. They show good in electron emission and thermally stable in a vacuum up to 2800⁰C.
4. They exhibit excellent electrical and mechanical properties.
5. They are extremely strong, resistant, hydrophobic, flexible and

Applications;

1. Carbon nano tubes were used as needles to bring active agents into living cells which is used as a therapy for cancer.
2. Used in polymer LED, ultra-resistant materials for use as reinforcement fibers, electrical energy storage applications.

Fullerenes or carbon bucky balls:

Fullerenes or carbon bucky balls are a class of cage-like carbon compounds of fused, pentagonal sp² carbon rings

These are a class of allotropes of carbon in which sheets of graphite are rolled up to make a sphere.

These are classical three dimensional carbon nano materials made up of 60 carbon atoms arranged in a soccer ball like shape and are less than 1nm in diameter.

These are hollow interior.

There are now 30 or more forms of fullerenes up to and beyond C₁₂₀.

The important fact is that atoms can be placed inside a fullerene system i.e., a certain drug is fitted inside while outside, the bucky ball is resistant to interaction with other molecules so they can be safe functioning drug containers that can enter cancer cells without reacting with them.

Fullerenes of pure C₆₀ is the smallest member of fullerene family known as Buckminster fullerene or bucky ball.

PROPERTIES:

1. They are insoluble in water.
2. They exhibit excellent tribological properties like tensile strength and highest packing density.
3. They possess cage like structure.
4. They are impenetrable to all elements under normal circumstances.
5. Fullerenes of pure C₆₀ are only semiconducting materials.

Applications:

1. fullerenes can be used as fillers, drug deliverers, tracer molecules.
2. They are impervious to lasers, allowing for defences from future warfare.
3. They have been shown to be useful at fighting the HIV virus that leads to AIDS.

QUANTUM DOTS:

Quantum dots are often referred to as artificial atoms.

Size is in the range of 1-10nm.

PROPERTIES:

1. These are semiconductors that exhibit quantum confinement properties in all three dimensions.
2. These may be metallic. ex: gold or chalcogenide based cadmium selenide, lead selenide or cadmium sulphide.
3. These display any chosen colour in UV region, thus multicolour lasers are developed.

Applications:

1. Quantum dots have potential for photovoltaic applications.
2. Used in transistors, LED's and diode layers as agents for medical imaging.
3. Optical encoding and multiplexing applications in all trafficking tumour targeting and diagnostics.

Applications of Nanomaterials ;

As engineering materials

1. Fabrication of thin wires for communication technology.
2. Nano particles are processed to form light emitting devices.
3. Nano structure metals and ceramics are in exact shape without machining.
4. Improved colour printing brought by nm scale particles that have properties of both dyes and pigments.
5. Nano fabrication on chip with high levels of complexity and functionality.
6. In nano composition, one of the constituent phases have dimensions length, width or thickness in nm range.
7. The nano tubes by virtue of their electrical conductivity make the composite conductive as well.

In chemical industry:

1. Nano particles of barium hexa aluminate is used in catalysis where large surface area and catalytic activity are achieved.
2. The new nano catalysts designed and new nanochemical routes could pave way for environment friendly and atom economical green chemistry routes.

In biotechnology:

Combining nanoscale materials with enzymes improve durability of enzymes, create localized high concentrations of proteins and reduce costs by minimizing losses.

In medicine and health:

- 1.Rapid efficient genome sequencing ,revolutionizing diagnostics and therapeutics.
2. More durable , rejection resistant artificial tissues and organs.
3. Sensor systems that detect emerging diseases in the body.
- 4.tissue engineering
- 5.detection of proteins
6. probing of DNA structure
7. tumour destruction
8. cancer therapy
- 9.protein and peptide delivery.
10. improving the bio compatibility of an artificial bone implant.

In environment as solar cell:

- 1.nanomaterial sized solar cells could be developed to provide much of the energy needed , storage and production.

In computer technology:

- 1.nanoscale circuits and computers
2. nano strutured microprocessor devices
3. highertransmission frequencies.
4. Integratednanosensor systems for collecting, processing and communicating massive amounts of data.

In aeronautics and space exploration:

Nanostructured materials and nanocomposites will make them tunable,adaptive,selfhealing and stress smart sensing systems and enable a revolution in air and space travel by increasing intelligence in aerospace systems and vehicles while reducing mass.

In food science:

Used in agriculture,food safety,food processing , food packing ,biosecurity,ingredient technology and production development

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