CEMENT

A material possesing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc.

The principle constituents of cement used for constructional purposes are compounds of Ca and Al+Si.

The cements have properties of setting and hardening under water.

Classification:

1) **Natural cement:**

   It is made by calcining a naturally occuring lime stone at high temperature and subsequently pulverising the calcined mass. During calcination, silica and alumina combine with calcium oxide to form the corresponding calcium silicates and aluminates.

   Properties:

   1. It is of quick setting and relatively of low strength
   2. Used for laying stones and setting stones.
   3. Used for construction of dams and foundations.

2) **Puzzolona cement:**

   These are materials which when mixed with lime, without the use of heat, form hydraulic cementing materials. These are made by simply mixing and grinding natual puzzolona consisting of glassy material, produced by rapid cooling of lava and slaked lime.

3) **Slag cement:**

   This is produced by mixing blast furnace slag and hydrated lime and grinding with small quantity of gypsum.

4) **Portland cement:**

   This is produced by the mixing of calcarious matter(lime containing matter) and argillacous matter(clay containing matter) and powdered with addition of 2-3% gypsum.

Properties:

It most important and reliable cementing material, used for constructional work.

Chemical composition of Portland cement:

It is finely powedered mixture of calcium silicates and calcium aluminates of varying compositions.

- Ratio percentage of lime to that of silica, alumina and iron oxide when calculated by formula

$$\frac{CaO}{2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3}$$

1. Should be greater than 1.02 and not less than 0.66
2. Ratio percentage of alumina to that of iron oxide should not be less than 0.66
3. Weight of insoluble residue should not exceed 2%
4. Weight of magnesia shiuld not be more than 6%
5. Total sulphur contents, calculated as SO_3 should not be more than 2.75%
6. Total loss on ignition should not exceed 4%

Manufacture of portland cement:

Raw materials:

- Calcarious matter, CaO(lime stone, chalk, marl etc)
- Argillacous matter, Al_2O_3 and SiO_2(clay,slate etc)
- Powdered coal or fuel oil
- Gypsum

Functions of the ingredients of cement:

- lime:

Its proportion must be properly regulated. Excess or lesser amount of lime reduces strength of cement and makes it quick setting

- Silica:
  Gives strength to cement
- Alumina:
  Makes the cement quick setting
- Gypsum:
  It enhances the initial setting time of cement.
- Iron Oxide:
  Provides color, strength, hardness to the cement.
- Alkalies:
  If present in excess, causes cement efforescent.

Manufacture of portland cement involves the following steps:

1) Mixing of raw materials:

a**). Dry process:**

The raw materials and clay are crushed into small pieces,then these are ground to fine powder. Each separate powdered ingredients is stored in a separate hopper. Then, the powdered materials are mixed to get dry raw mix, which is stored in storage bins and kept ready to be fed in a rotary kiln.

b). wet process:

The calcareous raw materials are crushed , powdered and stored in a big storage tanks. The argilaceous material is thouroughly mixed with water in wash mills and made into slurry. The powdered lime and clay slurry are mixed in requisite proportions and then fed to a rotary kiln.

2). Burning:

It is done in rotary kiln, which is a steel tube lined inside with refractory bricks. The kiln is laid in slightly inclined position towards the lower end. Theupper part of kiln temperature is 400^{o}C but the temperature gradually increases upto 1750 ^{o}C at the bottom. The raw slurry from the wet process and the dry process is passed into the rotary kiln through the lower end. The following reactions takes place in the rotary kiln.

a). Drying zone:

The upper part of the kiln where the temperature is only 400^{o}C and the slurry gets dried.

b). Calcination zone:

It is the central part of kiln where the temperature is around 1000^{o}C. lime stone of dry mix or slurry undergoes decomposition to form quick lime and CO_2

$$CaCO3 \text{----------} \rightarrow CaO + CO_2$$

c). Clinkering zone:

In the lower part of the rotary kiln, the temperature is between 1500-1700 ^{o}C. here the lime and clay combine to form calcium silicates and aluminates

$$2CaO+SiO_2 \text{--------------------} \rightarrow 2CaO.SiO_2 \text{(dicalcium silicates)}$$

$$3CaO+SiO_2 \text{--------------------} \rightarrow 3CaO.SiO_2 \text{(tricalcium silicates)}$$

$$3CaO+Al_2O_3 \text{--------------------} \rightarrow 3CaO.Al_2O_3 \text{ (tricalcium aluminates)}$$

$$4CaO+Al_2O_3+Fe_2O_3 \text{-----------} \rightarrow 4CaO.Al2O3.Fe2O3 \text{(tetra calcium alumino ferrite)}$$

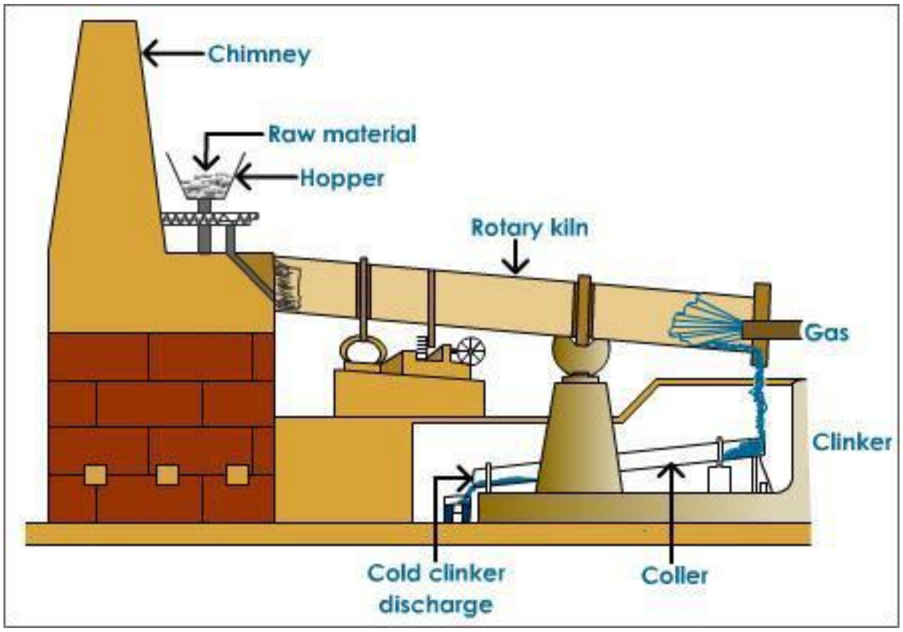
The aluminates and silicates of calcium fuse together to form hard greyesh stones called clinkers. The cooled clinkers are collected in trolleys.

3). Grinding:

The cooled clinkers are ground to fine powder in ball mills together with 2-3% gypsum. The mixture of clinkers and gypsum powder is called cement. Here,gypsum acts as a retarding agent for easily setting cement.

4). Packing.

The ground cement is stored in silos, from which it is fed into automatic packing machine.



Setting and Hardening 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.

The term '**Hardening'** refers to the gain of strength of a set cement paste, although during setting the cement paste acquires some strength.

Reactions Involved in Setting of Cement

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

$$\underset{\text{tricalcium aluminate}}{3CaO.Al_2O_3} + 6H_2O \longrightarrow \underset{\text{hydrated colloidal gel of tricalcium aluminate}}{3CaO.Al_2O_3.6H_2O}$$

$$2CaO.SiO_2 + xH_2O \longrightarrow \underset{\text{hydrated colloidal gel of dicalcium silicate}}{2CaO.SiO_2.xH_2O}$$

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

$$\underset{\text{tricalcium silicate}}{3CaO.SiO_2} + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{dicalcium silicate}}{2CaO.SiO_2}$$

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).

$$\underset{\text{tricalcium aluminate}}{3CaO.Al_2O_3} + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\text{aluminium hydroxide}}{2Al(OH)_3}$$

Role of gypsum - Gypsum reacts with tricalcium aluminate.

$$3CaO.Al_2O_3 + 3CaSO_4 + 2H_2O \longrightarrow \underset{\text{calcium sulpho aluminate}}{3CaO.Al_2O_3.3CaSO_4.2H_2O}$$

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.

Refractories

Refractories are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metals; slag's and gases, without suffering a deformation in shape. The main objective of a refractory is to confine heat.

On the basis of the chemical properties of their constituent substances, refractories are classified into three categories:

i. Neutral refractories

ii. Acid refractories

iii. Basic refractories

i. **Neutral refractories:** like graphite, zirconia and SiC refractories. These refractories are made from weakly basic/acidic materials like carbon, zirconia (ZiO2) and chromite (FeO.CrO2)

ii. **Acid refractories:** like alumina, silica and fire clay refractories. These refractories consist of acidic materials like alumina (Al_2O_3) and silica (SiO_2). These refractory materials are resistant to acidic slag (like silica) and are often used as contaminant vessel for them. On the other hand, they are readily attacked by basic slag's (like CaO, MgO etc.) and contact with these oxide materials should be avoided.

iii**. Basic refractories:** like Magnetite and Dolomite refractories. These refractories consist of basic materials like CaO, MgO etc. and are especially resistant to basic slags. That's why they find extensive use in some steel making open hearth furnaces. The presence of acidic materials like silica is deleterious to their high-temperature performance.

Criteria of good refractory material or essential properties of good refractory materials:

The important properties are:

a. **Refractoriness:** is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions. The refractory material should have a softening temperature higher than the operating temperature of the furnace in which it is to be used.

b. **Refractoriness-under-load:** Temperature resistance and load bearing capacity are the two essential qualities of a refractory. This is due to the fact that commercial refractory which are used for lining high temperature furnace are expected to withstand varying loads of the charge. Hence they should possess high strength and excellent temperature resistance.

c. **Dimensional stability:** Dimensional stability is the resistance of a material to any change in volume when it is exposed to high temperatures, over a prolonged time.Dimensional changes are permanent contraction and permanent expansion.

Dimensional stability is the resistance of a material to any volume changes, which may occurs on its exposure to high temperature, over a prolonged time. These dimensional may be permanent or reversible.

d. **Chemical inertness:** The refractory material which is used as linear for furnace walls should be chemically inert to the chemicals charged into a furnace. It should be react with the reactants, slags, furnace gases, fuel ashes and the products involved inside the furnace. Such reactions can contaminate the product and gradually corrode the furnace.

e. **Thermal expansion and contraction:** A good refractory material should have least possible coefficient of thermal expansion. The refractory material expands when heated and contract when cooled. Repeated expansion and contraction contribute much towards rapid wear and tear of the refractory structure and its rapid breakdown.

In a furnace design, allowance has to be made for thermal expansion, since practically all solids expands, when heated and contract, when cooled. The expansion affects all dimensions of a body. So, it is necessary that a refractory material should have least possible thermal expansion, because;

1. Expansion of a refractory decreases the capacity of the furnace.

2. Repeated expansion and contraction contributes much towards rapid breakdown, and wear and tear of the refractory material structure.

f. **Thermal conductivity:** It is one of the important properties of refractory material since it determines the amount of heat transmission or heat loss due to radiation through it.

Refractories with low thermal conductivity are used for lining the walls of blast furnace, copper hearth furnace etc. because they minimize the heat losses to outside radiation and help in the maintenance of high temperatures inside the furnace.

g. **Resistance to corrosion and erosion:** The higher temperatures at which the furnace is operated, viscosity of slag decreases which accelerated the chemical reaction between the slag and refractory lining. This might lead to corrosion of refractory lining.

h. **Electrical conductivity:** a refractory material of low electrical conductivity is desired for lining the walls of electrical furnace. For proper selection of refractory material it should be always remembered that electrical conductivities of these material increases with rise in temperature.

i. **Porosity:** Porosity of a refractory material is the ratio of its pore's volume to the bulk volume. Porosity can also increase the thermal shock resistance. The least porous bricks have the highest thermal conductivity, strength, resistance to abrasion and corrosion.

All refractories contain pores, either due to manufacturing methods or deliberately by incorporating saw-dust or cork during manufacture. The pores may be open or closed; the latter are encountered in an oven-fired refractory. Porosity in the ratio of its pore's volume to the bulk volume. Thus, porosity,

$$P = [(W - D)/(W - A)]*100$$

W= Weight of saturated specimen

D= Weight of dry specimen

A = weight of saturated specimen submerged in water.

j. **Thermal spalling:** Rapid changes in temperature, cause uneven expansion and contraction of refractory material, thereby leading to development of internal stresses and strains. This is in turn are responsible for cracking, breaking or fracturing of a refractory brick or block under high temperature, collectively known as thermal spalling. Thermal spalling can also caused by the variation in the coefficient of expansion due to slag penetration in the refractory brick. A good refractory must show a good resistance to thermal spalling. Spalling can be decreased by

1. Avoiding sudden temperature changes.

2. Over firing the refractories.

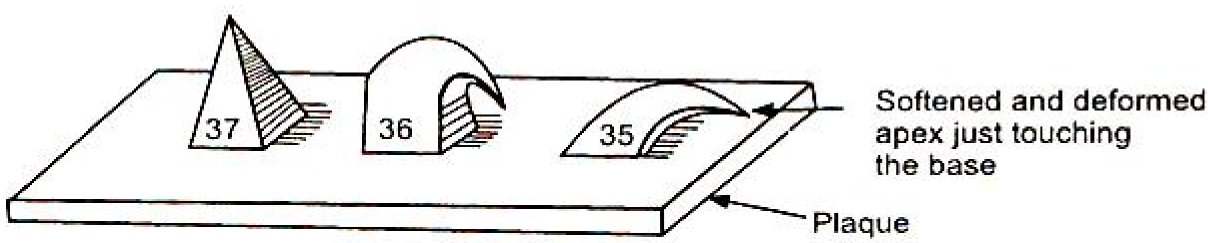
3. Modifying the furnace design.

4. Using high porosity, low coefficient of expansion, and good thermal conductivity refractory bricks.

k. **Permeability:** It is a measure of rate of diffusion of molten solids, liquids and gases through the connected pores of refractory. The higher the porosity is a refractory brick, the more easily it is penetrated by gases and molten fluxes. A good refractory material should show low permeability

i. **Refractoriness** is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions. It is generally measured as the softening temperature. It is necessary that a refractory material should have a softening temperature higher than the operating temperature of the furnace in which it is to be used. Sometimes, it can be employed to withstand a temperature higher than its softening temperature since the outer part of refractory is at a lower temperature and still in solid state, providing strength. Thus, refractory material does not melt away although inner refractory lining in a furnace is at a much higher temperatures than the outer ones. Most of the commercial refractories do not exhibit sharp melting points and they soften gradually over a range of temperatures.

Measurement of refractoriness: The softening temperatures of refractories are generally determined by seger cones also called pyrometric cones test.



In this test, behaviour of heat on cone of refractory and series of seger cones of standard dimensions are compared. These cones are small pyramid shaped with triangular base, 38 mm high with 19 mm long sides. The test refractory in the form of a cone is kept along side similar sized standard cones and all are heated uniformly at 20^0C/hour or 100^0C/hour or 150^0C/hour or occasionally at 600^0C/hour. As seger cones are made of a particular refractory of a definite softening temperature so they are assigned ascending seger cone numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard seger cones also softens and loses its shape provided its refractoriness is close to that of the test cone. The serial number of this standard seger cone is noted and this number is the pyrometric cone equivalent (PCE) of the refractory under that test. When the test cone softens earlier than one standard cone, but later than the previous one, the PCE value of the test sample is approximated as average of the two.

The temperature at which the softening or fusion of the test-cone occurs is indicated by its apex touching the base.

Conditional for failure of a refractory material:

i. Using a refractory material which does not have required heat, corrosion and abrasion resistance;

ii. Using refractory material of higher thermal expansion;

iii. Using a refractory of refractoriness less than that of the operating temperature;

iv. Using basic refractory in a furnace in which acidic reactants and/or products are being processed and vice-versa;

v. Using lower-duty refractory bricks in a furnace than the actual load of raw materials in products;

vi. Using refractories which undergo considerable volume changes during their use at high temperature.

Lubricants

A **lubricant** is a substance introduced to reduce friction between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move. It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the surfaces. The property of reducing friction is known as lubricity.

In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats in use in frying pans, in baking to prevent food sticking), bio-medical applications on humans (e.g. lubricants for artificial joints), ultrasound examination, medical examinations, and the use of personal lubricant for sexual purposes.

The lubricant oil must have following characteristics:-

1. It should have long hydrocarbon chain.
2. It should have active group or atoms.
3. It should have good oiliness.
4. It should have high viscosity index.
5. It should have low pour point.
6. It should have good resistance to heat & oxidation

Classification of Lubricants

Based on its physical states, you can classify lubricants as:

- Liquid lubricants, which include:
    1. Vegetable oil and animal oil
    2. Mineral oil from petroleum
    3. Blended oil, doped oil, or compound oil
    4. Synthetic oils

- Semisolid lubricants
- Solid lubricants
- Synthetic Lubricants

Liquid Lubricants or Lubricating Oils

Liquid lubricants reduce friction and wear between two moving or sliding metallic surfaces by providing a continuous fluid film in between them. They act as a cooling medium, a sealing agent, and a corrosion preventor. Liquid lubricants are classified into many types, depending on the type of base oil used.

a) Vegetable Oil and Animal Oil

These oils are the most commonly used lubricants. They are quite oily and are absorbed by all the metallic surfaces. However, they decompose at high temperature, undergo oxidation easily, forming gummy and acidic hydrolyzed products, and thicken on coming in contact with air, restricting the smooth movement of moving surfaces. Consequently, these oils are blended with mineral oils to overcome these restrictions.

b) Mineral Oil from Petroleum

Mineral oils that are used as lubricants are obtained by fractional distillation of petroleum. Petroleum oils have long-chain hydrocarbons, ranging between 12-50 Carbon atoms. The shorter chain oils have lower viscosity than the longer chain hydrocarbons do. Shorter chain hydrocarbons are widely used as lubricants because they possess good stability. At very high pressure and speed, petroleum oil possesses poor oiliness but the oiliness of these oils can be improved by adding oils, such as Oleic and Stearic acid.

SEMI-SOLID LUBRICANTS OR GREASES, EMULSION LUBRICANTS

SEMI-SOLID LUBRICANTS OR GREASES: - Greases are semi-solid lubricants which consist of metallic soap in lubricating oil.

Preparation: - They are made by Saponification of fat with alkali followed by addition of hot lubricating oil with constant stirring. Consistency of grease is governed by amount of oil added.

Conditions for using semi-solid lubricants:

- When it is necessary to seal the bearing or joint against the dirty & dust particles.

- When the machine is worked at low speed under high load.
- When the contamination of lubricating oil is unacceptable and harmful for products.
- When the lubricating oil is not suitable for machines.

On the basis of soap used in manufacture of semi solid are classified as:-

1. **CALCIUM BASED GREASE: -** These greases are prepared by mixing of calcium soap with petroleum oil. They are insoluble in water. These can be used upto 80^0C. These are also called 'Cup grease'.
2. **SODA-BASED GREASE**: - These grease are prepared by mixing of sodium soap with petroleum oil. They are soluble in water. These can be used upto 175^0C. These greases are used in ball bearings.
3. **LITHIUM-BASED GREASE: -** These greases are prepared by mixing of lithium soap with petroleum oil. They are water resistant. They have high stability and suitable for use at high temperature.

AXLE GREASE:-These are prepared by adding lime or any metal hydroxide to fatty acids. They are water resisting and suitable for high temp and low speed. These are used in tractor rollers and machines bearings.

SOLID LUBRICANTS:-"The lubricants that exist in solid form are called solid lubricants". E.g.: - graphite,molybdenum disulphide etc. They are used in heavy machines under high load and low speed.

Conditions for using Solid Lubricants:-

- Machines that are under high load and low speed.
- When liquid and semi-solid lubricants are highly combustible.
- In machines where liquid and semi-solid lubricants can't work.
- When contamination of oil and grease with dust particles is noticed.

Graphite as solid lubricant:-

- It is soapy in touch.
- It is non – inflammable.
- It is not oxidized in air up to 3750C
- It is used either in powdered form or in suspension form.

- When graphite is dispersed in oil, it is called 'oil dag' and when it is dispersed in water; it is called 'aquadag'. Oil dag is useful in internal combustion engine and aquadag is useful in food stuffs industry.

Molybdenum disulphide as solid lubricant:-

- It has sand-witch like structure. The layer of molybdenum atoms lie between two layers of sulphur atom. These layers are held together by very weak vander Waals forces. Due to these forces, it is soft & smooth in nature.
- It possesses very low coefficient of friction
- It is stable in air up to 400^0C.
- It has high specific gravity than graphite.
- It is used as either in powdered form or in additives

Mechanism of lubrication:

1. **Extreme pressure lubrication:-**

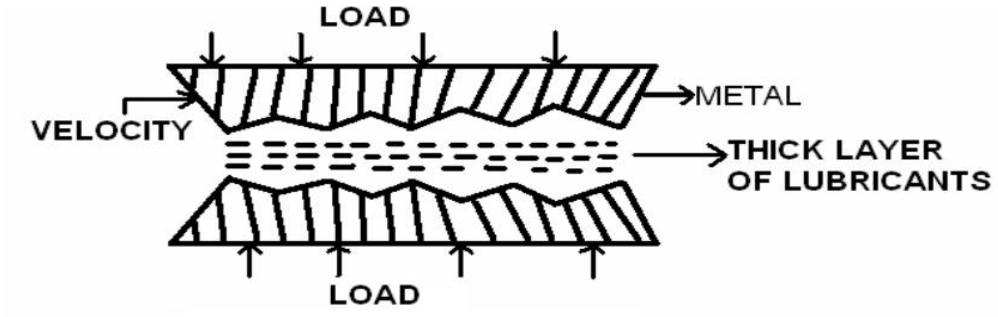
When the moving surfaces are under very high pressure and speed, high temperature is attained. This high temperature can change properties of lubricants due to decomposition & lubricant may evaporate also. Here any normal lubricants don't work, here EPL works.

Extreme pressure lubricants contains organic compounds having active groups such as chlorine, sulphur and phosphorus, such compound react with surface at high temperature and form metallic chloride, sulphide or phosphide. These layers can withstand high temperature, high pressure because of their strength and high melting point.

2. **Fluid film, Thick film or Hydrodynamic Lubrication**

This type of lubrication is done with liquid lubricants. In this method lubricant fills the irregularities of sliding surface and forms a thick layer ($1000A^0$) in between them and keep the material surface away from each other. Here the lubricant should have minimum viscosity during working condition and it should remain inside and separate the surface.

This friction is quite common in the case of shaft running at a fair speed in a well lubricated bearing with moderate load. This type of lubrication is done in delicate Instruments like watch, clock, guns, and sewing machines and in scientific instruments.



FLUID-FILM LUBRICATION

3. **Boundary lubrication & Thin film lubrication:-**

This type of lubrication is done when continuous film of lubricants cannot persist and direct metal to metal Contact is possible**.**

This will happen when:-

- Shaft starts moving
- Viscosity of oil is very low
- Speed is very low & Load is very high

In this thin layer lubricant binds with the molecule of metal surface & can't be removed easily.. These adsorbed layers avoid direct metal to metal contact. Mineral oil, blended oil with some vegetable or animal oils are used for thin film lubrication.

Vegetable oil and their soaps have good property of adsorption but they break at high temp and mineral oil have of oiliness therefore blended oil is used for thin film lubrication..

PROPERTIES OF LUBRICANTS

1 OILINESS: - It is capacity of lubricants to stick on surface of machine parts under high pressure & load.

- A good lubricant should have good oiliness
- A good lubricant should have low volatility

2 VOLATILITY: - It is property by which oil evaporates at high temperature. A good lubricant should have low volatility.

3 EMULSIFICATION:-It is property of an oil by which it gets mixed with water & form emulsion. Emulsions have tendency to collect dirt particles & protect machine parts.

4 CORROSION STABIITY: - A good lubricant should not take part in corrosion. Corrosion occurs when oil contains some chemicals.

5 CLOUD-POINT AND POUR POINT:-

CLOUD POINT: - When oil is cooled slowly the temperature at which it becomes cloudy in appearance is called ‘cloud point’.

POUR POINT: - Pour point of oil is the temperature at which the oil ceases to flow or pour**.**

Significance:-It indicates the suitability of lubricants in cold conditions. A lubricant used in machine working at low temperature should have low pour point, otherwise it will cause jamming of machine.

6 FLASH AND FIRE POINT:-

Flash point: The lowest temperature at which an oil lubricant gives off enough vapours that ignite for a moment when flame is brought near to it.

Fire point: It is the lowest temp. of lubricant at which the lubricant gives off sufficient vapor that ignite continuously for at least 5 seconds when a flame is brought near it.

Generally, the fire point is 5-10^{0}C higher than the flash point for any lubricant.

Significance:

- It tells the maximum temperature up to which a lubricant can be used.
- A good lubricant should have flash and fire point above its working temperature.

Factors affecting the flash point and fire point of oil

- **Low molecular weight constituents:** which tends to decrease the flash point.
- **Contamination with small amounts of volatile:** Because of their presence irregular flashes can be observed below the true flash point of lubricating oil. It is called **"freaky flash point". Moisture:** It may prevent the oil vapor from igniting and hence raise the flash point.
- **Experimental factors:**

1. Frequency of application of test frame
2. Rate of heating
3. Rate of stirring
4. Size of test flame
5. Time of opening the shutter.

7 VISCOSITY: - It is the resistance offered by liquid towards its flow. It is

determined by Red Wood Viscometer.

8 VISCOSITY INDEX (V.I):-

- The rate of change of viscosity with temperature is called viscosity index(V.I
- Viscosity generally decreases with increase in temperature.
- If the viscosity of oil falls rapidly with temperature it is said to have a low viscosity index.
- If the viscosity of the oil does not fall rapidly with temperature it is said to have a high viscosity index.
- Good lubricant oil should have a high viscosity index.

DIAGRAM:-

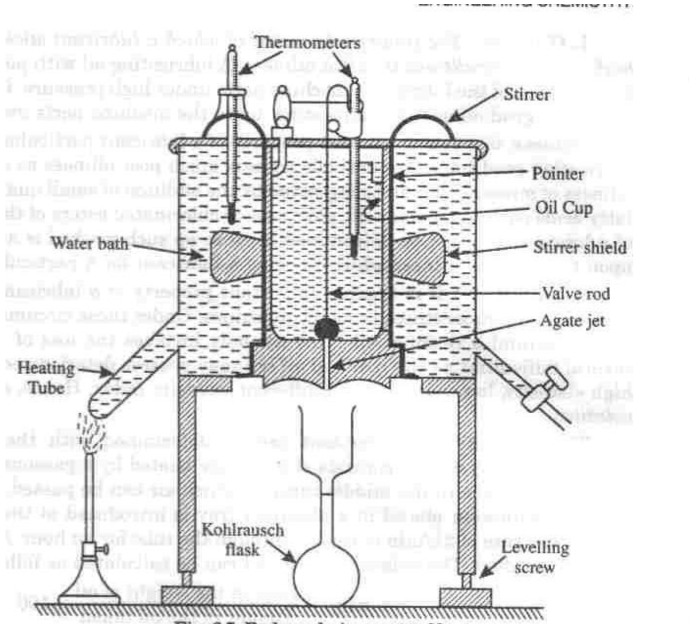


Fig. 6.7. Redwood viscometer No. 1

DETERMINATION OF VISCOSITY INDEX:-

- Test oil is compared with two standard oils with viscosity index 0 & 100
- Oil with viscosity index =0(Gulf coastb oil) (L)
- Oil with viscosity index =100(Penssylvanian oil) (H)
- V.I of test oil= $\frac{V_L - V_U}{V_L - V_H} * 100$

Where, V_L=viscosity of Gulf oil at 100^0C.

V_H=viscosity of Penssylvanian oil at 100^0C

V_u=viscosity of oil under test

VISCOSITY INDEX AND MOLECULAR STRUCTURE:-

1. Molecules with linear structures, with flexibility have high V.I.
2. An oil of high mol. wt possesses a high B.P and high viscosity.

NEUTRALIZATION NUMBER (ACID VALUE):-

Lubricating oils acidity or alkalinity is determined in terms of neutralization number. The neutralization number represents the total acid number (TAN) .

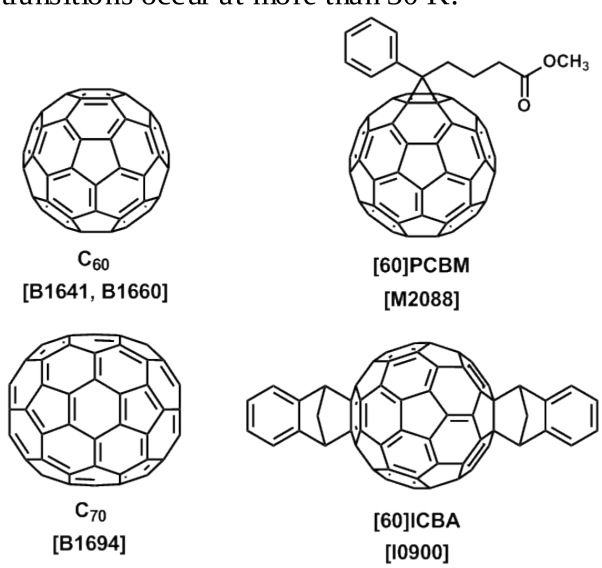
"It is defined as the number of milligrams of KOH required to neutralize the free acid in 1gram of the oil".

Acid value gives an idea about the age of the oil because the acid content or value of fatty acids increases with time due to hydrolysis with moisture.

NANO CHEMISTRY

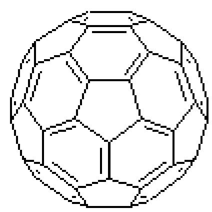
FULLERENS

- Fullerene is a spherical carbon compound and is an allotrope of carbon such as diamond, graphite and carbon nanotubes.
- Fullerenes of C_{60}, C_{70} and C_{84} are well known. They are isolable carbon compounds in a sole molecular species.
- Among them, the C_{60} is a representative species. Kroto, Smalley and Curl *et al.* first observed the C60 in which the 60 carbon atoms consist of 12 five-membered rings and 20 six-membered rings.
- Kroto, Smalley and Curl won their joint Nobel prizes in chemistry in 1996 for their contributions. Osawa predicted existence of fullerene in 1970, earlier than the first observation of fullerene.
- The most specific feature of fullerene is that it is an excellent electron acceptor.
- Any fullerenes are n-type semiconductors, which are suitable for organic electronic materials with electron carriers. Rubidium- and cesium-doped fullerenes can be superconductors with electron carriers. These superconducting transitions occur at more than 30 K.



PROPERTIES

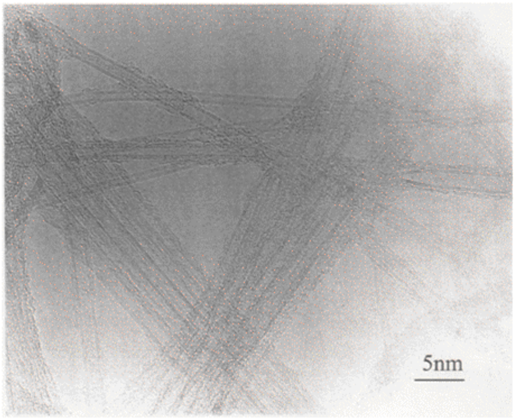
1. Addition reactions and other chemical modifications of fullerenes easily produce fullerene derivatives.
2. Non-derivatized fullerenes are poorly soluble in similarity to the other nanocarbon materials.
3. However, we can introduce soluble functional groups to form solution-processible electronic materials. Phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) and indene-C_{60} bisadduct (ICBA) are useful organic semiconductors for fabricating a solution-processible electronic device. These fullerene derivatives are n-type organic semiconductors for organic photovoltaics (OPV) by mixing with a p-type conjugated polymer.
4. An application of a fullerene derivative for organic transistors was also reported.
5. A complexation of C_{60} with tetrakis(dimethylamino)ethylene (TDAE) gives a charge transfer complex (TDAE-C_{60}), which is an organic magnet at low temperature.
6. Although a chemical modification of the outer surface of fullerene provides PCBM or ICBA, we can introduce a small component to the inner side of fullerene. For instance, fullerenes can encapsulate a metal atom on the inner side, when the fullerenes are produced in the presence of the metal. This is the so-called metal-encapsulated fullerene described as $M@C_{60}$.
7. The encapsulation modifies the electronic state and chemical reactivity of fullerene.
8. On the other hand, water-encapsulated fullerene ($H_2O@C_{60}$) was also reported.

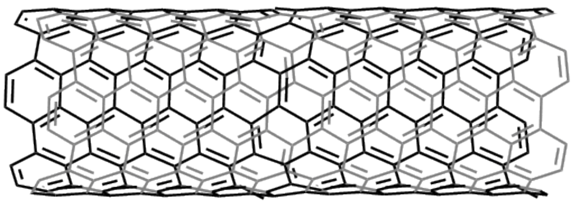


Carbon Nanotubes (Nanocarbon Materials):

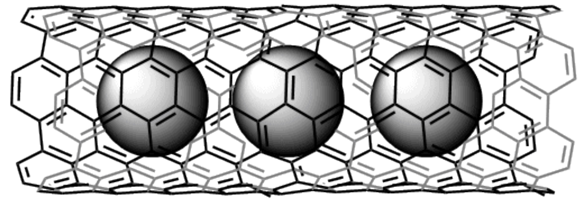
1. A carbon nanotube (CNT) has a cylindrical structure with a nanoscale diameter that is like a rolled graphene sheet.
2. Limija first observed a CNT in 1991.
3. A CNT consists of only sp2 carbons similar to fullerenes.
4. CNTs have high physical durability, high electrical and thermal conductivity, and are light and flexible. On the basis of such excellent characteristics, CNTs are expected to be field-effect transistor (FET) materials, nanoscale wire materials, electron emission sources, optical communication switches, chemical sensors, high strength composites, and thermal devices.
5. CNTs can enclose nanoscale molecules and atoms in the internal space, because of the cylindrical structure.

6. For instance, there is a fullerene-enclosed CNT, the so-called ‘peapod’. In addition, CNTs can enclose metal, water, and molecular oxygen. Properties of the enclosed water

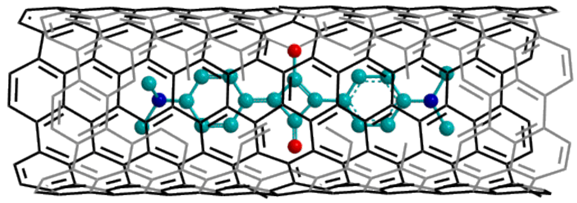




Single-Walled Carbon Nanotube (SWCNT)



C_{60} Peapod



Squarylium@CNT