Unit 4
Engineering Materials

PORTLAND CEMENT

DEFINITION

"An extremely finely ground product by calcinating together, at above 1500°C, an intimate and properly proportioned mixture of argillaceous (clay) and calcareous(lime) raw materials, without the addition of anything subsequent to calcination, excepting the retarder gypsum."

Clinker	CCN	Mass %
Tricalcium Silicate $(CaO)_3 \cdot SiO_2$	C_3S	45–75%
Dicalcium Silicate $(CaO)_2 \cdot SiO_2$	C_2S	7–32%
Tricalcium Aluminoferrite $(CaO)_3 \cdot Al_2O_3$	C_3A	0–13%
Tetra calcium Alumino Ferrite $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	0–18%
Gypsum $CaSO_4 \cdot 2H_2O$		2–10%
Calcium Oxide – CaO		2%
Magnesium Oxide - MgO		4%

Chemical Composition of Portland Cement

MANUFACTURING BY PORTLANT CEMENT

Raw Materials of Portland Cement and It's Use

Calcareous Materials, CaO [E.g. Limestone]

- Principal Constituent and its proportion can be regulated.
- Excess of lime reduces the strength and makes the cement expand & disintegrate.
- Lesser amount of lime also reduces the strength by quick setting.

Argillaceous Materials, Al_2O_3 and SiO_2 [E.g. Clay]

- Imparts strength.
- Makes quick setting.
- Excess of alumina weakens the cement.

Powdered Coal or Fuel Oil

- For burning

Gypsum ($CaSO_4$ $2H_2O$)

- Retards and enhances quick setting.

ROTARY KILN PROCESS

1. **Mixing and Crushing**
   (a) *Dry Process*
   - Raw materials are crushed, powdered and mixed in right proportion (Dry Raw mix).
   - Stored in silos.
   - Burning of dry raw mix is carried out in rotary kiln.
   - Klin rotates at speed of 1.

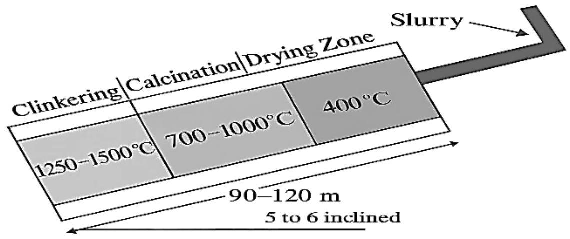
- RPM and is slightly inclined in position of 5 – 6°C.
- Hot clinkers are cooled with atmospheric air and pulverized together with 2-3% of gypsum in ball mills.

(b) Wet Process

- Limestone is crushed, powdered and stored in silos.
- Clay is washed with water to remove organic matter and stored in basin.
- Both these materials are mixed in grinding mill to form slurry.
- Slurry contains 38-40% water stored in correcting basin.

2. Burning Process

(a) Zones of Rotary Klin



Drying Zone

- Upper part of the kiln
- About 400°C
- Most of the water in the slurry gets evaporated

Calcination Zone

- Centre part of the kiln
- About 700°C – 1000°C
- Lime gets decomposed into CaO and CO_2

Clinkering Zone

- Lower part of the kiln
- About 1250°C - 1600°C
- Reacts with clay to form various bougee compounds

(b) Chemical Reactions in Rotary Klin Zones

- Calcination Zone:

$$CaCO_3 \longrightarrow CaO + CO_2$$

- Clinkering Zone:

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4 \text{ (Dicalcium silicate – } C_2S)$$

$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 \text{ (Tricalcium silicate – } C_3S)$$

$$3CaO + Al_2O_3 \longrightarrow Ca_3Al2O_6 \text{ (Tricalcium aluminate – } C_3A)$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10} \text{(Tricalcium aluminoferrite – } C_4AF)$$

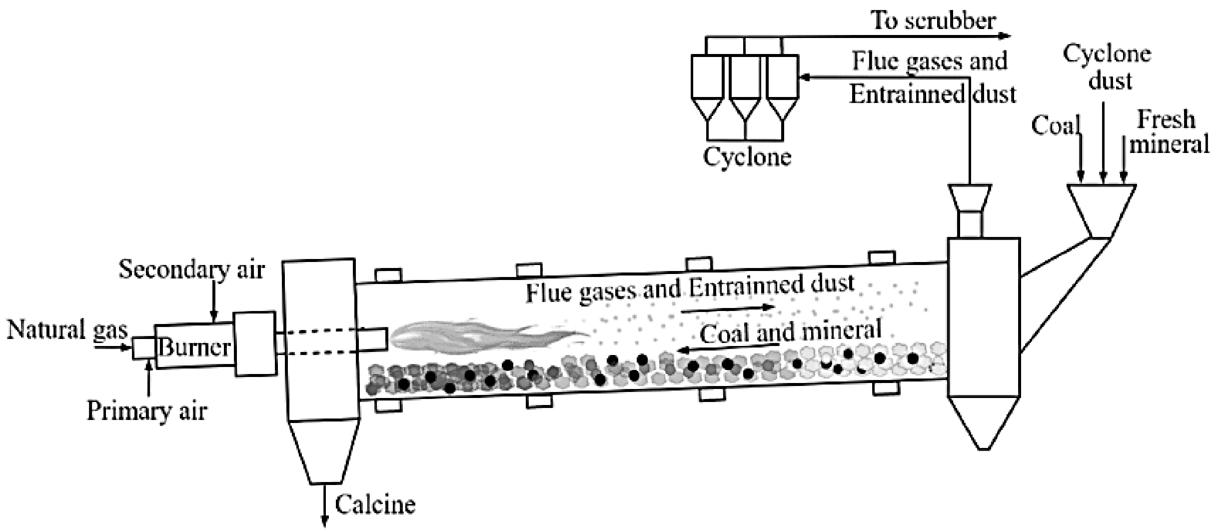
3. Grinding

- Cooled clinkers are ground to fine powder in ball mills.
- At final stages of grounding about 2-3% of powdered gypsum is added (This is to avoid setting of cement quickly when it comes in contact with water).
- Gypsum acts as a retarding agent for early setting of the cement.

$$\underbrace{3CaO + Al_2O_3}_{\text{After initial set}} + \underbrace{x\,CaSO_4.\,7H_2O}_{\text{Gypsum}} \longrightarrow \underbrace{3CaO.\,Al_2O_3.\,xCaSO_4.\,7H_2O}_{\text{Tricalcium sulphoaluminate (Insoluble)}}$$

4. Packaging

- Ground cement is stored in silos.
- From silos they are automatically packaged into bag which are about 50 Kg.



ROLE OF GYPSUM ($CaSO_4 \cdot 2H_2O$)

- Tricalcium aluminate (C3A) combines with water very rapidly with the evolution of large amount of heat.

$$C_3A + 6H_2O \longrightarrow C_3A.\ 6H_2O + \text{Heat}$$

- After the initial set, the paste becomes stiff.
- Adding gypsum retards the dissolution of C3A by forming *insoluble calcium sulpho-aluminate.*

$$3CaO.\ Al_2O_3.\ xCaSO_4.\ 7H_2O$$

- The above reaction shows how gypsum retards the early initial set of cement.

CHEMISTRY OF SETTING AND HARDENING OF CEMENT

- When the cement is mixed with water, hydration and hydrolysis reactions of Bogue compounds of cement begin, resulting in formation of gel and crystalline products.
- These products have the ability to surround inert materials like sand, bricks, crushed stones, etc.

"Setting is the stiffening of original plastic mass due to the formation of torbernite gel". It can be divided into 2 stages:

(a) *Initial Set:* Initial Set is when paste being to stiffen

(b) *Final Set:* Final Set is when the paste beginning to harden and able to sustain some loads

"Hardening is the development of strength due to formation of crystals."

Cement + Water Paste → 1st day → Hydration of C_3A and C_4F → 7th day → Gelation of C_3S → 28th day → Gelation of C2S and C3S

Chemical Reactions

Day 1:

- When cement is mixed with water, hydration of tricalcium aluminate (C_3A) takes place within a day.
- The paste becomes rigid, which is known as Initial set or Flash set.

$$\underset{\textit{Tricalciumaluminate}}{3CaO.\ Al_2O_3} + 6H_2O \longrightarrow \underset{\textit{Hydrated tricalcium aluminate (Crystalline)}}{3CaO.\ Al_2O_3.\ 6H_2O} + 880\ kJ/Kg$$

OR

$$C_3A + 6H_2O \longrightarrow C_3A.\ 6H_2O + 880\ kJ/Kg$$

- To avoid early setting of C_3A, gypsum is added which acts as retarding agent.

$$C_3A + 3CaSO_4.\ 2H_2O \longrightarrow \underset{\textit{Calcium sulpho aluminate}}{C_3A.\ 3CaSO_4.\ 2H_2O}$$

Day – 2 to 7:

- After hydration of C_3A, C_3S beings to hydrate to give tobermonite gel and crystalline Ca $(OH)_2$, which is responsible for initial strength of the cement.
- The hydration of C_3S gets completed within 7 days.

$$\underset{\text{Tricalcium silicate}}{2[3CaO.\ SiO_2]} + 6H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO.2SiO_2.\ 3H_2O} + \underset{\text{Crystalline}}{3Ca\ (OH)_2} + 500\ kJ/Kg$$

OR

$$2C_3S + 6H_2O \longrightarrow C_3S_2.\ 3H_2O + 3Ca\ (OH)_2 + 500\ kJ/Kg$$

Tobermonite gel possesses a very high surface area and very high adhesive property.

Day – 7 to 28:

- Dicalcium silicate (C_2S) reacts with water very slowly and gets completed in 7 to 28 days.

$$\underset{\text{Dicalcium silicate}}{2[2CaO.\ SiO_2]} + 4H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO\ .2SiO_2.\ 3H_2O} + \underset{\text{Crystalline}}{Ca\ (OH)_2} + 250\ kJ/Kg$$

OR

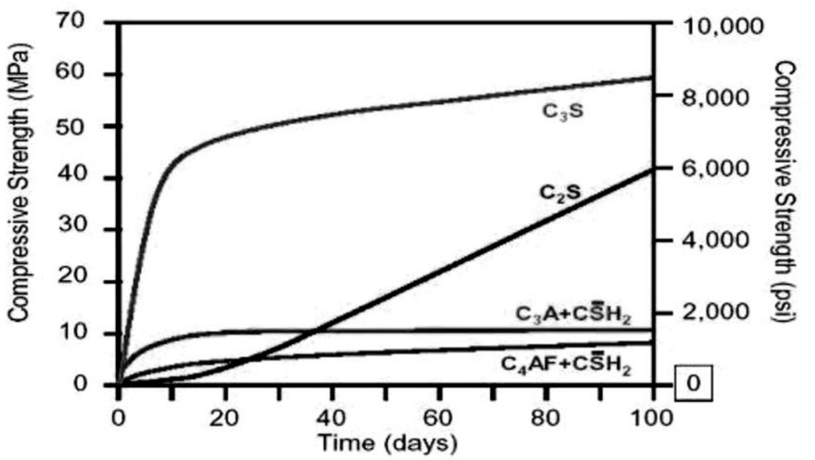
$$2C_2S + 4H_2O \longrightarrow C_3S_2.\ 3H_2O + Ca\ (OH)_2 + 250\ kJ/Kg$$

- Increase of strength is due to formation of tobermonite gel and crystalline Ca $(OH)_2$ of both C_2S and C_3S.
- After initial hydration of tetra calcium alumino ferrite (C_4AF), hardening takes place through crystallization, along with C_2S.

$$\underset{\text{Tetra calcium alumino ferrite}}{4CaO.\ Al_2O_3.\ Fe_2O_3} + 7H_2O \longrightarrow \underset{\text{Crystalline}}{3CaO.\ Al_2O_3.\ 6H_2O} + \underset{\text{Gel}}{CaO.\ Fe_2O_3.\ H_2O} + 420\ kJ/Kg$$

OR

$$C_4AF + 7H_2O \longrightarrow C_3A.\ 6H_2O$$



"Hydration and Hydrolysis of Bogue compounds causes cement to develop compressive strength" (Shown in the figure).

GLASS

DEFINITION

Glass is a solid material, usually transparent or translucent, that is formed by the fusion of inorganic substances and subsequent cooling to a rigid state without crystallization. This means that although glass appears solid, it does not have a long-range ordered crystalline structure, making it an amorphous solid or a supercooled liquid. The primary constituent of most glass types is silicon dioxide (SiO_2), commonly obtained from sand.

Chemically, glass is a mixture of metallic silicates or borates, with varying proportions of alkali and alkaline earth metals. These compositions can be adjusted to achieve specific properties like chemical resistance, thermal stability, optical clarity, and mechanical strength.

Scientific Definition

Glass is an amorphous, homogeneous, non-crystalline solid obtained by cooling a fused mixture of inorganic oxides and other substances to a rigid condition without crystallization.

Raw Materials Used in Glass Manufacturing

The composition of glass can vary significantly depending on the desired end-use. However, the following are the typical raw materials used in glass manufacturing:

Basic Raw Materials:

1. $Silica\ (SiO_2)$:
   - It is the main component and constitutes about 60–80% of glass.
   - Obtained from quartz sand.
   - Provides hardness, chemical resistance, and transparency.
2. $Soda\ (Na_2CO_3\ or\ Sodium\ Nitrate)$:
   - Acts as a flux, reducing the melting point of silica.
   - Improves workability but decreases chemical resistance.
3. $Lime\ (CaCO_3\ or\ CaO)$:
   - Provides stability and durability.
   - Prevents glass from being soluble in water.
4. $Alumina\ (Al_2O_3)$:
   - Enhances mechanical strength and thermal resistance.
5. $Boron\ Oxide\ (B_2O_3)$:
   - Added to produce borosilicate glass.
   - Provides excellent thermal resistance.
6. $Lead\ Oxide\ (PbO)$:
   - Added in optical and lead glass for better refractive index and electrical insulation.
7. $Coloring\ Agents$:
   - Used to impart colors:
     - $Fe_2O_3\ (Green\ or\ brown)$
     - $MnO_2\ (Removes\ green\ tint)$
     - $CoO\ (Blue)$
     - $CuO\ (Blue/green)$
     - $Cr_2O_3\ (Green)$
8. $Fining\ Agents$:
   - Arsenic trioxide (As_2O_3) and antimony trioxide (Sb_2O_3) help remove gas bubbles.

MANUFACTURING BY TANK FURNACE

The tank furnace is a continuous glass-melting furnace widely used in large-scale industrial glass production. It is constructed using refractory bricks and can operate non-stop for several months. The tank furnace allows the continuous input of raw materials (batch) and continuous withdrawal of molten glass, making it efficient, economical, and consistent in quality.

The glass manufacturing process in a tank furnace involves the following stages:

Step 1: Mixing or Batching

- Accurately calculated amounts of raw materials such as silica (SiO_2), soda ash (Na_2CO_3), limestone $(CaCO_3)$, alumina (Al_2O_3), and boron compounds (B_2O_3) are weighed, crushed, and mixed thoroughly.

- The resulting homogeneous mixture is called the glass batch.
- *Function:* Ensures the correct chemical composition and quality of the final glass product.

Step 2: Melting

- The glass batch is continuously fed into the melting zone of the refractory-lined tank furnace, which is heated to a temperature range of 1400°C to 1600°C.
- The raw materials melt and fuse to form a viscous, homogeneous molten glass.
- Fuel sources may include natural gas, oil, or electricity.
- *Function:* Converts solid raw materials into a uniform molten phase suitable for forming.

Step 3: Fining (Purification)

- Molten glass contains air bubbles and undissolved particles that must be removed to ensure clarity and strength.
- Fining agents such as arsenic trioxide (As_2O_3) or antimony trioxide (Sb_2O_3) are added. These release gases that help small bubbles coalesce into larger ones which then rise to the surface and escape.
- Stirring may be used to aid purification.
- *Function:* Removes impurities and entrapped gases to ensure optically clear glass.

Step 4: Conditioning

- After fining, the glass is transferred to a cooler zone (1100°C–1200°C), called the conditioning zone.
- The temperature is adjusted to obtain the optimal working viscosity (neither too runny nor too hard).
- This stage ensures that the molten glass is in a uniform condition for shaping.
- *Function:* Prepares the glass for smooth and defect-free forming.

Step 5: Forming or Shaping

- The conditioned molten glass enters the working end (forehearth), where it is shaped into final products using different methods:
    - Blowing – for making bottles, bulbs, flasks
    - Pressing – for dishes, plates, lenses
    - Drawing – for glass fibers and filaments
    - Rolling – for glass sheets and flat panels
- Mechanical forming machines and molds may be used for mass production.
- *Function:* Converts molten glass into usable articles of desired size and shape.

Step 6: Annealing

- Freshly formed glass articles are passed through a lehr (annealing oven) where they are reheated to ~500–600°C and then slowly cooled.
- This gradual cooling process relieves internal thermal stresses caused by uneven cooling during shaping.
- If not annealed properly, glass may crack or shatter spontaneously—even days later.

Importance of Annealing:

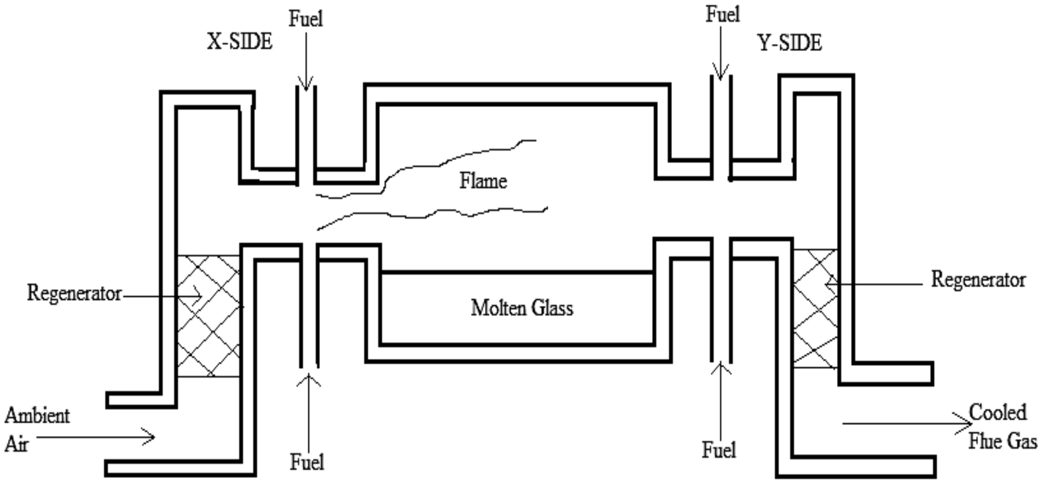
- Prevents thermal shock
- Improves mechanical strength
- Ensures long-term durability
- Makes glass safe for use and handling

Step 7: Finishing

- The cooled and annealed glass articles are inspected for defects (bubbles, cracks, warping).
- If needed, the following finishing operations are performed:
    - Cutting
    - Grinding

- Polishing
- Etching
- Tempering
- Coating

- Final products are then packed and stored for distribution.



SIGNIFICANCE OF ANNEALING

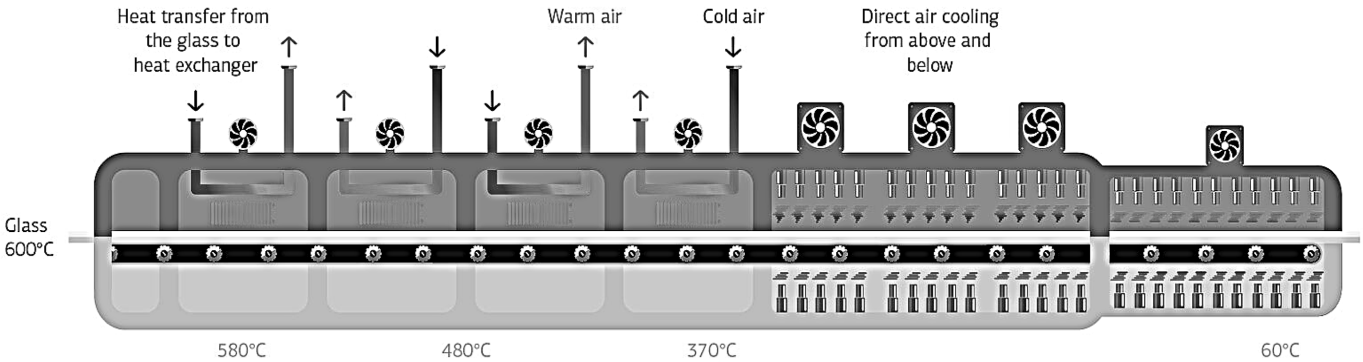
What is Annealing?

Annealing is the slow and uniform cooling of glass articles after forming, to allow internal stresses to equalize and avoid cracking or breakage.

Process of Annealing

1. Glass objects after shaping are placed into a lehr (annealing oven).
2. The glass is heated again (not melted) to a temperature called the annealing point (approx. 500–600°C depending on glass type).
3. The temperature is maintained uniformly so that internal stresses can relax.
4. The objects are then cooled very slowly, sometimes over several hours.

Note: The rate of cooling depends on:
- Thickness of the glass object
- Type of glass
- Desired properties



Importance / Significance of Annealing

1. *Removes Internal Stress*
    - Sudden cooling causes stress which can cause spontaneous cracking.
    - Annealing allows atoms to reorganize and stabilize, relieving tension.

2. *Improves Mechanical Strength*
    - Properly annealed glass is stronger and less prone to breakage.
3. *Ensures Dimensional Stability*
    - Without annealing, glass may warp or deform during use.
4. *Prepares for Secondary Processing*
    - Annealed glass is safer and more reliable for cutting, polishing, or tempering.
5. *Improves Quality and Reliability*
    - Products with internal stress may fail prematurely.
    - Annealing ensures long-term durability of glass products.

TYPES OF GLASS

A. Soda-Lime Glass *(Soft Glass)*

This is the most common type of glass, making up about 90% of manufactured glass worldwide.

Composition:

- SiO_2 $(Silica)$: $70 - 75\%$
- Na_2O $(Sodium\ Oxide)$: $12 - 15\%$
- CaO $(Calcium\ Oxide)$: $10 - 12\%$
- $Minor\ additives$: Al_2O_3, MgO

Properties:

- Soft and easy to mold at low temperature
- Melting point ~600–800°C
- Less resistant to chemicals and thermal shocks
- Highly transparent
- Brittle in nature

Uses:

- Windows, bottles, jars
- Drinking glasses, tumblers
- Light bulbs, mirrors
- Decorative glassware

B. Borosilicate Glass

This glass contains boron oxide (B_2O_3) in addition to silica. It is known for its superior resistance to heat and chemicals.

Composition:

- SiO_2: ~80%
- B_2O_3: $12 - 15\%$
- Na_2O: $4 - 5\%$
- Al_2O_3: $2 - 3\%$

Properties:

- Low thermal expansion coefficient
- High resistance to sudden temperature changes
- Excellent chemical resistance (against acids, salts)
- Durable and tough

Uses:

- Laboratory glassware (beakers, test tubes)
- Kitchenware (e.g., Pyrex dishes)
- Industrial chemical equipment

- Solar panels and telescope mirrors

C. Optical Glass

This specialized glass is designed to have precise optical properties such as high transparency, high refractive index, and low dispersion.

Composition:

- $Silica\ (SiO_2)$
- $Lead\ oxide\ (PbO)\ -\ enhances\ refractive\ index$
- $Barium\ oxide\ (BaO)$
- $Lanthanum\ oxide\ (La_2O_3)$

Properties:

- High refractive index and clarity
- Homogeneous structure with minimal distortion
- Low dispersion (to prevent chromatic aberration)
- Very low impurity content

Uses:

- Lenses (microscopes, telescopes, cameras)
- Fiber optics
- Laser and infrared equipment
- Spectacles and optical instruments

PROPERTIES AND USES OF SOFT AND HARD GLASS

Soft Glass (Soda-Lime Glass)

Properties:

- Melts at a lower temperature
- Easily molded and worked into various shapes
- Poor resistance to chemicals and high temperatures
- Brittle and more prone to thermal breakage
- Transparent and low-cost

Uses:

- Common household containers and packaging
- Beverage bottles and food jars
- Flat glass for windows and mirrors
- Light fixtures and low-temperature laboratory use

Hard Glass (e.g., Borosilicate Glass)

Properties:

- High thermal and chemical resistance
- Low expansion under heat (doesn't crack easily)
- Higher softening point (~800–1000°C)
- Stronger and more durable
- Suitable for rigorous scientific and industrial use

Uses:

- Laboratory glassware (high-temperature beakers, flasks)
- Medical and pharmaceutical containers (autoclavable)
- Cookware used in ovens and stovetops
- High-pressure chemical plants
- Solar collectors and telescope lenses

LUBRICANTS

Lubricants are defined as a substance which reduces the friction between two moving metallic surfaces, and the phenomena known as Lubrication.

Functions of Lubricants

- *Reduces Friction:* Minimizes resistance between moving surfaces.
- *Prevents Wear and Tear:* Protects surfaces from damage and extends equipment life.
- *Dissipates Heat:* Acts as a cooling agent by carrying away heat.
- *Prevents Corrosion:* Forms a protective layer to prevent rusting.
- *Seals Gaps:* Helps in sealing small gaps in machine parts (e.g. piston rings).
- *Cleans Surfaces:* Removes contaminants and debris from mechanical parts.
- *Enhances Efficiency:* Reduces energy loss due to friction, improving performance.

CLASSIFICATION OF LUBRICANTS

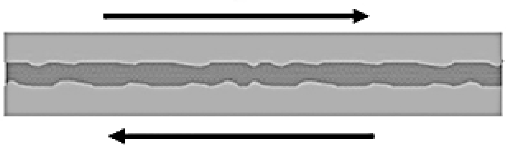
Liquid Lubricants	Semi-Solid Lubricants	Solid Lubricants
• Used in machinery, engines, and industrial applications. • Examples: Mineral oils (petroleum-based oils), synthetic oils, vegetable oils etc.	• Used in automobile wheel bearings, gears, and open mechanical parts. • Example: Calcium grease, Sodium grease, Lithium grease etc.	• Used in extreme conditions like high temperatures, vacuum environments. • Examples: Graphite, Molybdenum disulfide (MoS_2), Boron nitride etc.

MECHANISM OF LUBRICATION

Lubrication mechanisms describe how lubricants reduce friction and wear between moving surfaces. The three main types of lubrication mechanisms are:

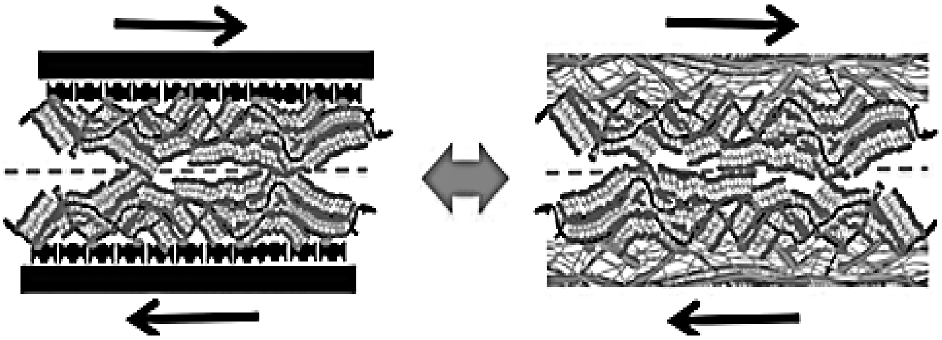
1. **Thick Flim / Fluid Film Lubrication**

- A thick layer of lubricant separates the moving surfaces, preventing direct contact.
  It is of two types:
  (a) *Hydrodynamic Lubrication*: A continuous lubricant film is formed due to relative motion (E.g., Journal Bearings).
  (b) *Electrohydrodynamic Lubrication:* The lubricant film is formed under high pressure, slightly deforming the surfaces (E.g. Gear Teeth, Rolling Bearings).



2. **Thin Flim / Boundary Lubrication**

- A thin molecular layer of lubricant is adsorbed on the surface, preventing metal-to-metal contact.
- Occurs in low-speed, high-load conditions.
- Example: Engine start-up and stop situations, where full fluid lubrication isn't achieved.



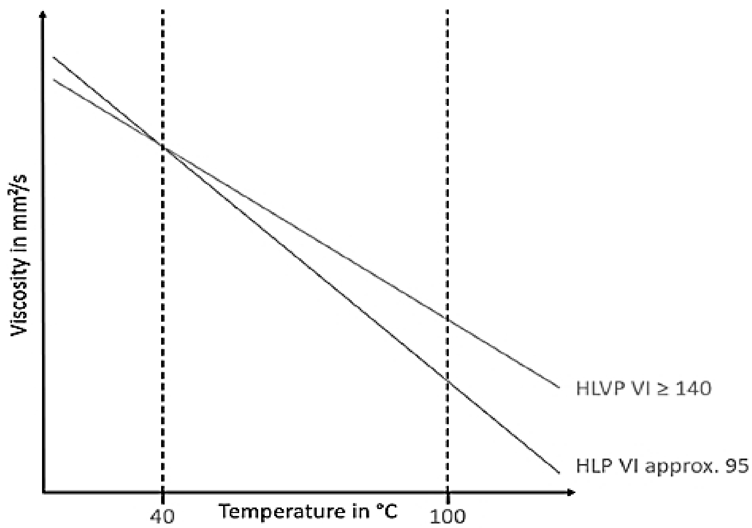
3. **Extreme - Pressure / Mixed Lubrication**

- A combination of fluid film and boundary lubrication.
- Some regions have full fluid separation, while others have metal-to-metal contact with boundary layers.
- Common in applications like automobile engines and machine tools.

PROPERTIES

1. **Viscosity and Viscosity Index**

- *Viscosity:* Viscosity is the measure of a lubricant's resistance to flow. It determines the ability of a lubricant to form a protective film between moving surfaces.
- A high-viscosity lubricant is thicker and provides better lubrication under heavy loads, while a low-viscosity lubricant flows more easily and is suitable for high-speed applications.
- *Viscosity Index:* The viscosity index (VI) indicates how much the viscosity of a lubricant changes with temperature. A higher viscosity index means the lubricant remains stable across a wide range of temperatures, ensuring better performance in extreme conditions.
- Example: Engine oils used in vehicles have a high viscosity index to perform well in both summer and winter.



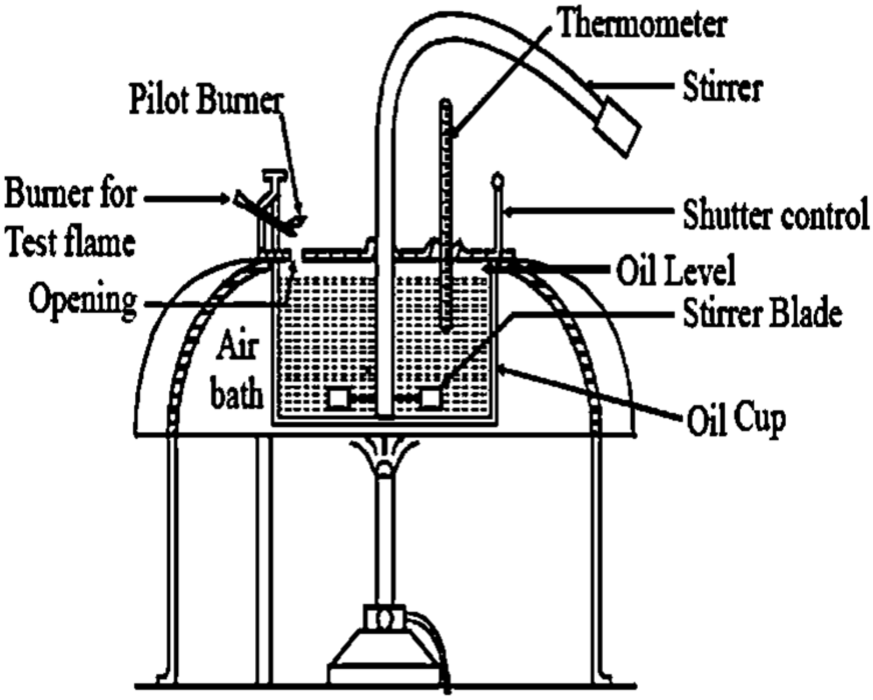
2. **Flash Point and Fire Point**

- *Flash Point:* The flash point is the minimum temperature at which a lubricant produces enough vapor to ignite momentarily when exposed to a flame.

- *Fire Point:* The fire point is the temperature at which the lubricant continues to burn for at least five seconds.

- Lubricants with higher flash and fire points are preferred in high-temperature applications because they reduce the risk of fire hazards.

- Example: Industrial lubricants used in turbines and engines require a high flash point to ensure safety during operation.



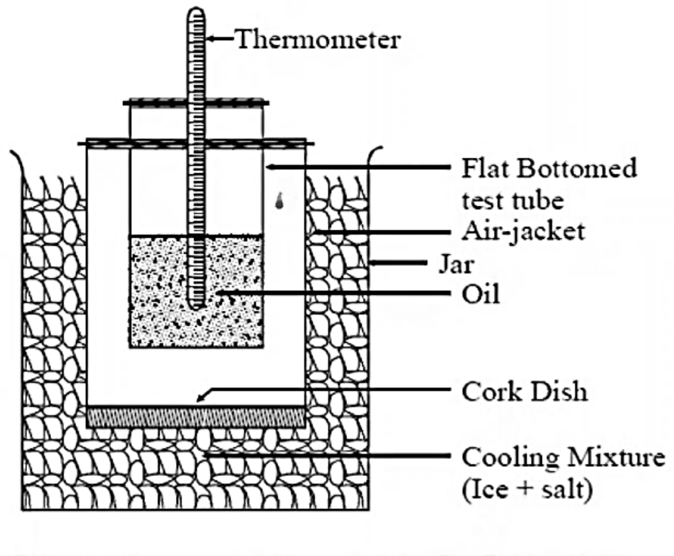
3. Cloud Point and Pour Point

- *Cloud Point:* When oil is cooled in a standard apparatus under standard condition, the temperature at which oil becomes cloudy / hazy/ foggy/turbid in appearance is called Cloud Point.
- *Pour Point:* The temperature at which the oil thickens and stops flowing due to complete solidification of oil is called Pour Point. Flowing ability of oil is lost completely. High pour point is generally associated with a high paraffin content.

It consists of following parts:

a) Flat-bottom glass tube (2 cm high and 3 cm diameter) is enclosed in an air jacket.
b) Air jacket glass tube is surrounded by air jacket.
c) Cooling bath: The air jacket containing glass tube is placed in a cooling bath containing freezing mixture. The freezing mixture is a combination of crushed ice and salt. The freezing mixture is prepared in following manner.

Freezing Mixture (Crushed Ice+ Salt)	**Temperature Range**
Ice+Water	Up to 10°C
Ice+NaCl	Up to-10°C
Ice+$CaCl_2$	Up to -25°C
Solid Co_2 + Acetone	Up to-60°C



Significance of cloud and pour point

- Cloud and pour point indicate the suitability of lubricant in cold conditions.
- Cloud point indicates the temperature at which wax crystals separate. These crystals may clog the filter screen in fuel tank.
- Machineries work below 0°C temperature, the pour point determines the suitability of oil for temperature installations e.g. air-craft engine, refrigerator plants.
- A high pour point causes early solidification of lubricant causing jamming of machine.

A lubricant should have low cloud and pour point to avoid early jamming of machine.