

Unit-III

Chapter- 1

Advance Engineering Materials & its application

1. Liquid Crystal

(A) Introduction :

Liquid crystals (LCs) are matter in a state which has properties between those of conventional liquids and those of solid crystals. It is observed that many long chain organic molecules when heated undergo one or more phase transitions in passing from the solid to the liquid phase, indicating one or more intermediate phases.

(B) Classification of Liquid crystal

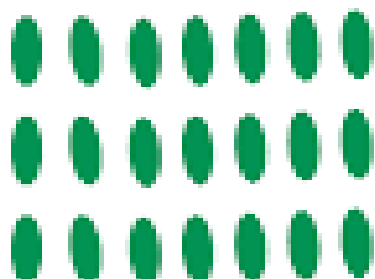
Liquid crystals can be divided into thermotropic and lyotropic. Thermotropic and lyotropic liquid crystals consist mostly of organic molecules,

1. Thermotropic LC:

- ➔ When long chain organic solids are heated, they undergo sharp phase transition at particular temperature yielding liquid crystal. The phase transitions involving these intermediate phases are most naturally effected by the changing temperature and hence, they are called thermotropic liquid crystal. Example: Ethyl -p-azoxy cinnamate, p-cholesteryl benzoate.
- ➔ Thermotropic LCs are divided into three types, namely **Nematic**, **Cholesteric** and **Smectic**. These three classes are distinguished by the different kinds of molecular order they exhibit.

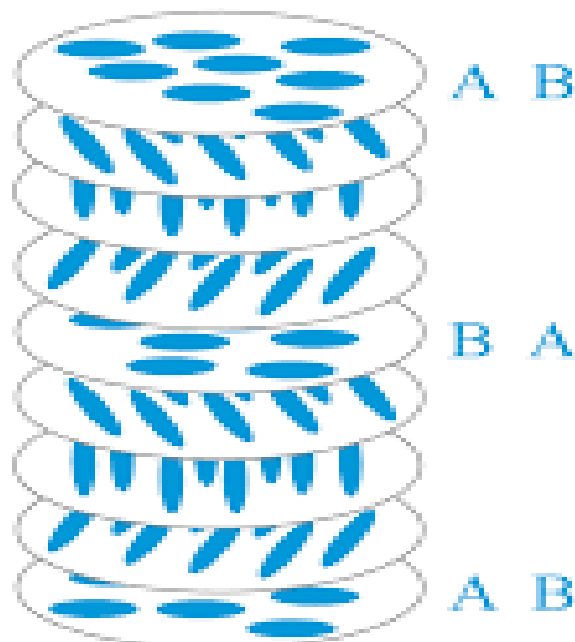


nematic



smectic

major orientation of the molecules
axes direction - director, n



cholesteric

recurrence period of the structure

Structure of Nematic, smectic, and cholesteric

[A] Nematic Structure :

The molecules in the nematic structure possessing only orientational but no positional long range order.

The behavior of nematic liquid crystal is closer to the true ‘**anisotropic**’ liquids. This liquid crystal exhibit normal liquid flow characteristic having low viscosity, they flow smoothly, yet is turbid and anisotropic.

The nematic structure is the highest temperature mesophase in thermotropic liquid crystal. In this structure, the molecules have no particular positional order, but tend to point vertically in same direction.

Example: P-methoxybenzylidene P1-N-butyl-aniline, P-n-Hexyl-P1-cyano Biphenyl



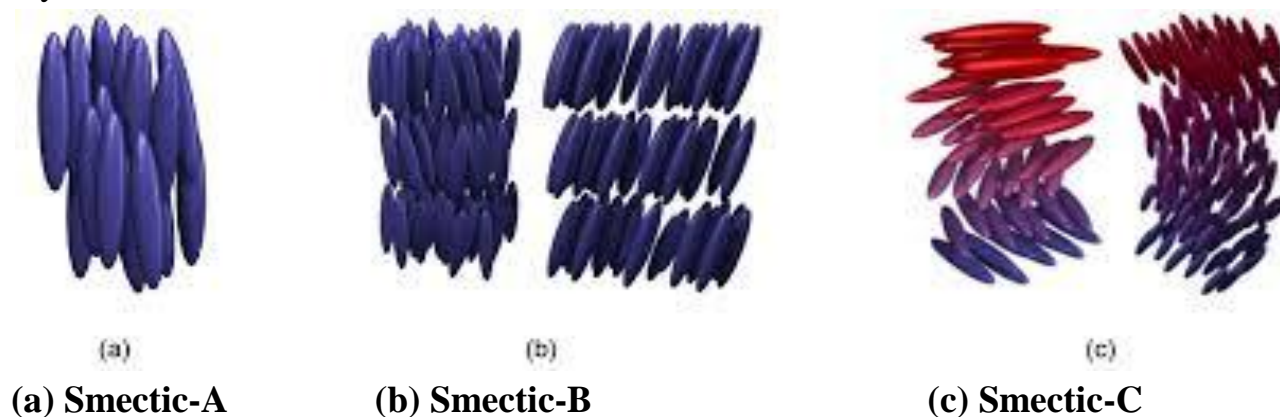
Nematic Structure

[B] Smectic Structure:

The word “Smectic” is derived from the Greek word which means soap. The origine is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually type of smectic liquid crystal.

Another distinct mesophase of liquid crystal substance is the smectic state. In this phase, the molecules maintain the general orientational order not present in the nematic state. The smectic LC does not flow as normal liquids.

The optical observations indicated different structures for these smectic phases and therefore, there are A, B and C type of smectic liquid crystal.



(i) Smectic Liquid Crystal-A:

There are the few characteristics of Smectic-A :

- They do not show layered structure. The thickness of layer is very close to the full length of the constituent molecules.
- There is no long –range molecular order.
- It is optically active.

Example: EthylP-(P1-Phenyl benzalamine) benzoate

(ii) Smectic Liquid Crystal –B:

There are the few characteristics of Smectic-B :

- They formed layered structure and these layers appear to have a ‘periodicity’ and ‘rigidity’ of two dimentional liquids.

→Molecular order is found in each layer of the LC.

→The layers of smectic- B are not flexible.

Example: Ethyl P-ethoxy benzal-P1-aminocinnamate

(iii) Smectic Liquid Crystal-C:

There are the few characteristics of Smectic-C :

→ They formed layered structure.

→Each layer is still two dimensional liquid.

→It is optically biaxial.

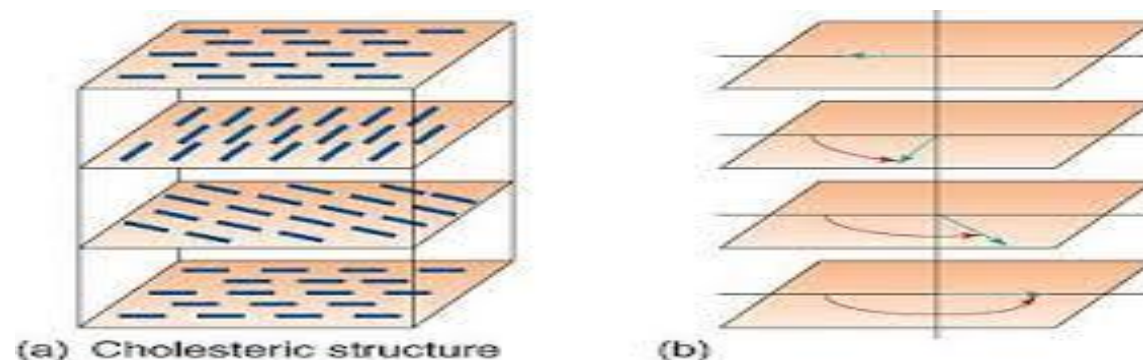
Example: P-n-octyloxy benzoic acid

[C] Cholesteric Liquid Crystal :

→The cholesteric LC phase is typically composed of nematic mesogenic molecules containing chiral centre which produces intermolecular forces that favor alignment between molecules at a slight angle to another.

→This leads to the formation of a structure which can be visualized as a stack of very thin 2-dimensional nematic-like layers with the director in each layer twisted with respect to those above and below.

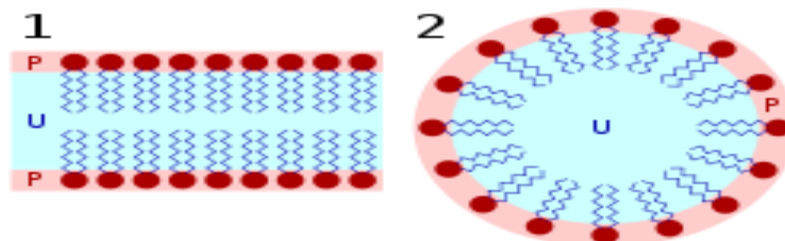
→**Example:** Cholesterylnonanoate



Cholesteric Structure

2. **Lyotropic LC:** When a high concentration of long organic molecules of rod-like shape is dissolved in an isotropic solvent like water, lyotropic liquid crystals are

formed. The long ranges ordering in these lyotropic LC are mainly due to the solvent –solute interaction. Example: Deoxyribonucleic acid , Tobacco mosaic virus ,synthetic polypeptides,Sodium stearate.



1 . Lamellar structure 2 . . Miscelle structure

(B)Applications :

→LCD device like Liquid crystal thermometer: Cholesteric LC reflect light with a wavelength equal to to pitch. Because the pitch is dependent upon temperature, the colour reflect also is dependent on temperature. LC makes it possible to accurately gauge temperature just by looking at the color of the thermometer.

→Auto Dashboards, Radios & Clocks ,Computers ,Blood Pressure Indicators, Calculators Cameras, Digital Meters, Electronic Billboards, Exercise Equipment, Gasoline Pump Indicators ,Highway Signs.

→ Non-destructive Testing: Cholesteric LC s are color sensitive with temp.

→Biological Systems and Medicine: In medical thermography which provides information on the normal and abnormal functioning of the sensory and nervous system, vascular dysfunction

→Radiation sensing: Thermal imaging as well as specialized LC thermal detectors has grown into an important technology that is applied directly by users on the ground or from flying aircraft. Using thermal sensors coupled with optical systems

one is able to see in the dark by detecting varying temperatures from different objects in the scene.

→ Analytical Instruments

2. Organic electronic materials

(A) Introduction

- ➔ Organic electronics is a field of science concerning the design, synthesis, characterization, and application of organic small molecules or polymers that show desirable electronic properties such as conductivity.
- ➔ Unlike conventional inorganic conductors and semiconductors, organic electronic materials are constructed from organic (carbon-based) small molecules or polymers using synthetic strategies developed in the context of organic and polymer chemistry.
- ➔ One of the promised benefits of organic electronics is their potential low cost compared to traditional inorganic electronics. Organic electronics have been promising on account of their low-cost, low temperature and fast manufacturability in addition to their compatibility with various kinds of substrates that are thin, large in area, transparent or mechanically flexible.

(B) Classification : Organic electronics are classified in main three types

- Conductive organic materials**
- Organic light emitting diode (OLED)**
- Organic Field effect transistor (OFET)**

(1.) Conductive organic materials

- ➔ Conductive polymers are often typically intrinsically conductive or at least semiconductors. They sometimes show mechanical properties comparable to those of conventional organic polymers.
- ➔ Both organic synthesis and advanced dispersion techniques can be used to tune the electrical properties of conductive polymers.
- ➔ The most well-studied class of conductive polymers include polyacetylene, polypyrrole, polyaniline, and their copolymers.
- ➔ Poly (p-phenylene vinylene) and its derivatives are used for electroluminescent semiconducting polymers. Poly(3-alkylthiophenes) are also a typical material for use in solar cells and transistors.

(2) Organic light emitting diode (OLED)

An OLED (organic light-emitting diode) consists of a thin film of organic material that emits light under stimulation by an electric current. A typical OLED consists of an anode, a cathode, OLED organic material and a conductive layer.

OLED organic materials can be divided into two major families:

(i) Small-molecule-based OLED

- ➔ Small molecule OLEDs (SM-OLEDs) include organometallic chelates, fluorescent and phosphorescent dyes, and conjugated dendrimers. Fluorescent dyes can be selected according to the desired range of emission wavelengths; compounds like perylene and rubrene are often used.

(ii) Polymer light-emitting diodes (PLEDs),

- ➔ Similar to SM-OLED, emit light under an applied electric current. Polymer-based OLEDs are generally more efficient than SM-OLEDs requiring a

comparatively lower amount of energy to produce the same luminescence. Common polymers used in PLEDs include derivatives of poly(p-phenylene vinylene) and polyfluorene. The emitted color can be tuned by substitution of different side chains onto the polymer backbone or modifying the stability of the polymer.

(3) Organic field-effect transistor (OFET)

- ➔ It is a field-effect transistor using an organic semiconductor in its channel. OFETs can be prepared either by vacuum evaporation of small molecules, by solution-casting of polymers or small molecules onto a substrate.
- ➔ These devices have been developed to realize low-cost, large-area electronic products and biodegradable electronics. OFETs have been fabricated with various device geometries.
- ➔ The most commonly used device geometry is bottom gate with top drain and source electrodes, because this geometry is similar to the thin-film silicon transistor (TFT) using thermally grown SiO_2 as gate dielectric. Organic polymers, such as poly(methyl-methacrylate) (PMMA), can also be used as dielectric.

➤ **Comparison between Organic Electronics and Inorganic Electronics**

➤ **Organic Electronics**

- ✓ Flexible
- ✓ Foldable
- ✓ Light weight
- ✓ Low cost
- ✓ Low processing temperature

Inorganic Electronics

- ➔ Rigid
- ➔ Hard
- ➔ Heavy
- ➔ Expensive
- ➔ High processing temperature

➤ Applications of Organic Electronics

- ✓ Television
- ✓ Cell phone screens
- ✓ Wrist watch
- ✓ Foldable smart phones
- ✓ Roll top touch screen laptop
- ✓ Automobiles
- ✓ OLED lenses

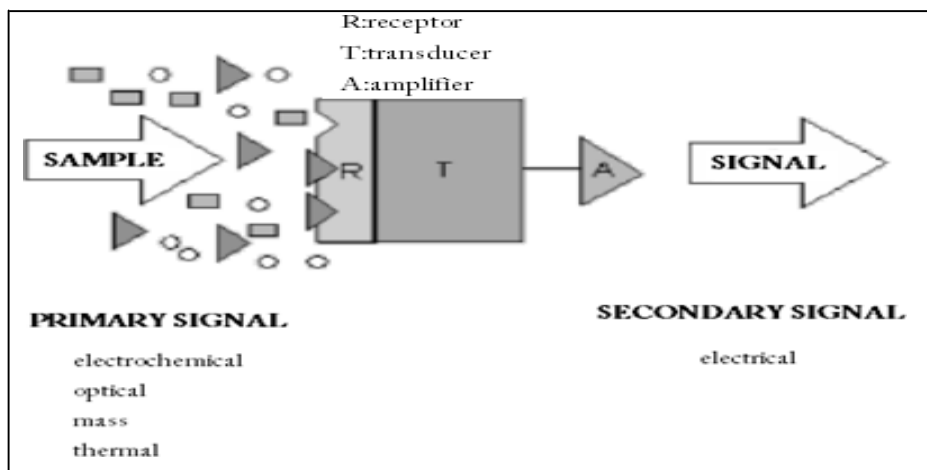
3. Chemical Sensor

➔ DEFINITION:

- **A chemical sensor is a device that transforms chemical information (composition, presence of a particular element or ion, concentration, chemical activity, partial pressure...) into an analytically useful signal.**
- The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated. They can have applications in different areas such as medicine, home safety, environmental pollution and many others.

➔ COMPOSITION

- Chemical sensors usually contain two basic components connected in series: a chemical (molecular) recognition system (receptor) and a physicochemical transducer. In the majority of chemical sensors, the receptor interacts with analyte molecules. As a result, its physical properties are changed in such a way that the appending transducer can gain an electrical signal.



- Receptor: The function of the receptor is fulfilled in many cases by a thin layer which is able to interact with the analyte molecules, catalyze a reaction selectively, or participate in a chemical equilibrium together with the analyte. The receptor layer can respond selectively to particular substances or to a group of substances.
- The term molecular recognition is used to describe this behavior. Among the interaction processes, the most important for chemical sensors are adsorption, ion exchange and liquid-liquid extraction. Primarily these phenomena act at the interface between analyte and receptor surface.
- Transducer: Nowadays, signals are processed almost exclusively by means of electrical instrumentation. Accordingly, every sensor should include a transducing function, i.e. the actual concentration value, a non-electric quantity must be transformed into an electric quantity, voltage, current or resistance. Some of them develop their sensor function only in combination with an additional receptor layer. In other

types, receptor operation is an inherent function of the transducer.

- The characteristics of a sensor developed for a given application are strongly shaped by the requirements of the application and by existing sensor science and technology. Using the descriptors developed in , limiting features of many existing chemical sensors include:

- **sensitivity;**
- **selectivity**
- **limit of detection;**
- **response time**
- **packaging size.**

→ **Examples:**

- **Carbon monoxide detector**
- **Glucose detector**
- **Mosquito**
- **Nanotechnology and chemical sensors**

→ **Application:**

- Gas chromatograph-mass spectroscopy;
- Ion mobility spectrometer;
- Patch chemical reactions showing color change;
- Fiberoptic and related methods;
- Electrochemical sensors;
- Acoustic-wave chemical sensors; and
- Immunochemical assays.

4. Chromic Materials

Introduction:

Chromic material is made by a process that induces a change in the colors of compounds. The process is called as a Chromism. In most cases; chromism is based on a change in the electron states of molecules.

➤ Classification of chromic materials :

- **Thermochromic material** is induced by heat, that is a change of temperature. Example: Cu_2Hgl_4 is red at 20°C but black at 70°C , ZnO is white at room temperature but yellow at higher temperatures
- **Photochromic material** is induced by light irradiation. This phenomenon is based on the isomerization between two different molecular structures, light-induced formation of color centers in crystals, precipitation of metal particles in a glass, or other mechanisms. Example : piropyrans, spirooxazines
- **Electrochromic material** is induced by the gain and loss of electrons. This phenomenon occurs in compounds with redox active sites, such as metal ions or organic radicals. Example : arbazoles, methoxy biphenyls, fluorenones, benzoquinones, naphthoquinones and anthraquinones

- **Solvatochromic material** is depends on the polarity of the solvent. Most solvatochromic compounds are metal complexes.

Applications:

- ✓ Plastic lenses for sunglasses
- ✓ children's toys
- ✓ logos on T-shirts, lunch boxes, crayons, jelly shoes, hair clips, craft beads,
- ✓ PVC belts, watchbands,
- ✓ Drinking straws, spoons, cups, combs,
- ✓ Greeting cards, stickers and business cards.
- ✓ Environmental control of the temperature of a building using smart glazing in windows.

5. Ionic liquid

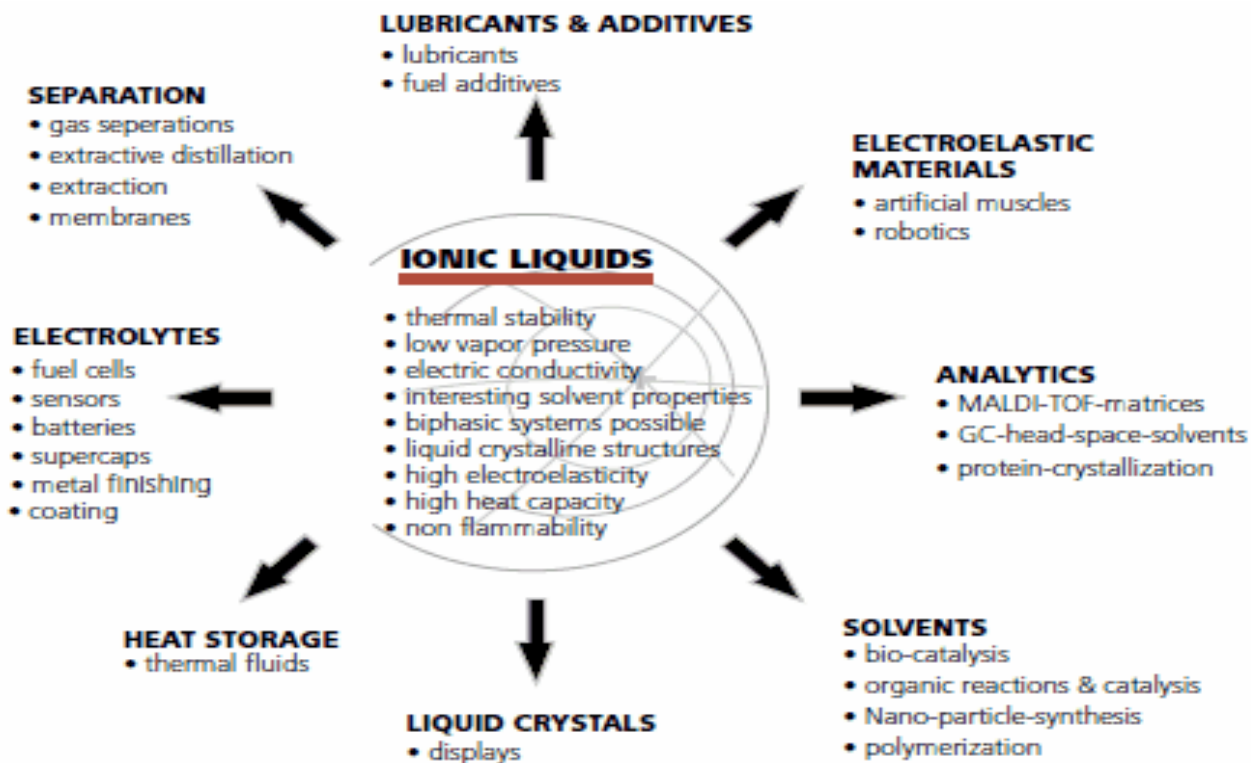
→ Introduction :

- Ionic Liquids are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures.
- These are ionic compounds which are liquid below 100 °C.” More commonly, these have melting points below room temperature; some of them even have melting points below 0 °C.
- Ionic liquids are, quite simply, salts that are liquid at, or near to, room temperature. Just like table salt, that consists only of ions (sodium cations, Na⁺, and chloride anions, Cl⁻), ionic liquids also consist only of ions (positively charged cations and negatively charged anions).

CLASSES OF IONIC LIQUIDS


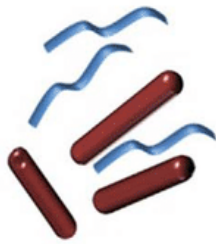
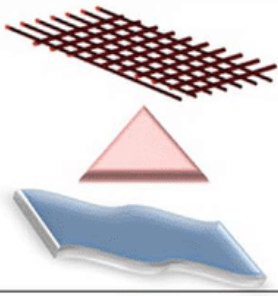
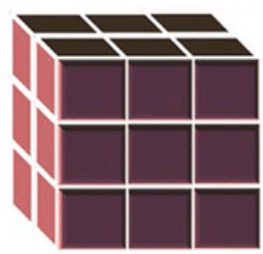
Protic ionic liquid	Aprotic liquid	Inorganic ionic liquids	Solvate (Chelate) ionic liquid
Proton transfer from a brønsted acid to a brønsted base	Liquids involving cations are organic molecular ions (contains no acidic protons)	Present in both protic and aprotic ionic liquid	Unexplored class of ionic liquids
High fluidity and conductivity Low melting points	Low fluidity and conductivity High melting points	Advantage of similar packing problem that result in low melting ILs of the organic cation type	Multivalent cation salts that does not satisfy the criteria of low melting points
Cheaper and easy to synthesis	Less ability to react quickly with fresh metallic surface	Aprotic example Lithium chlorate Melting point 115°C	Molten salt hydrates like calcium nitrate tetrahydrates, which forms ideal mixtures with alkali metals
Alkylammonium nitrate Ethanolammonium nitrate	Hexafluorophosphate Tetrafluoroborate	Protic example Hydrazinium nitrate Melting point 80°C	

→ Properties & Application of Ionic liquids



6. Nano Materials

- Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.
- Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Classification of nanomaterials based on structure.
- Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles).
- They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).
- According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

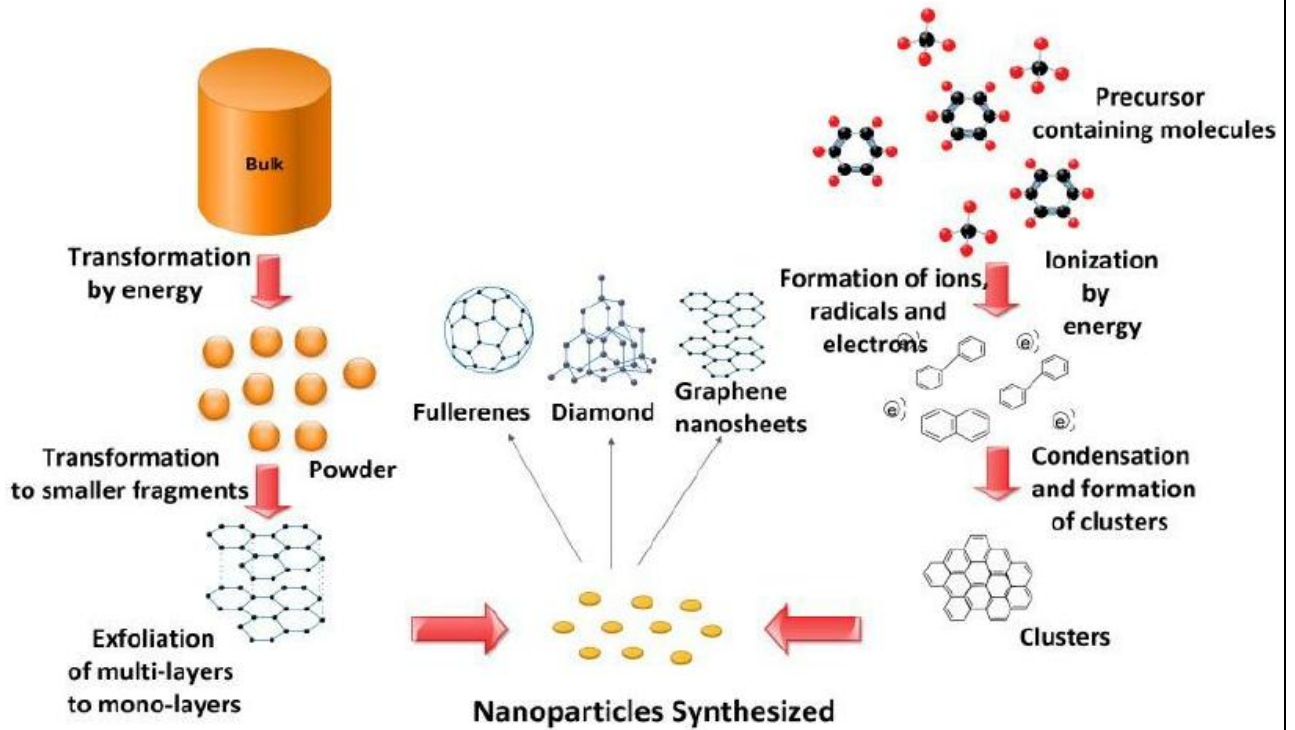
Isotropic nanomaterials	Anisotropic nanomaterials		
			
0D	1D	2D	3D
Spheres, Clusters	Nanorods, wires	Nanofilms, plates	Nanoparticles

- 0-D structures (3-D confinement):
 - Nanoparticles
 - Quantum dots
- 1-D structures (2-D confinement):
 - Nanowires
 - Quantum wires
 - Nanorods
 - Nanotubes
- 2-D structures (1-D confinement):
 - Thin films
 - Planar quantum wells
 - Superlattices
- Dimensionality, confinement depends on structure:
 - Bulk nanocrystalline films
 - Nanocomposites

❖ There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures.

Top-Down Approach

Bottom-Up Approach



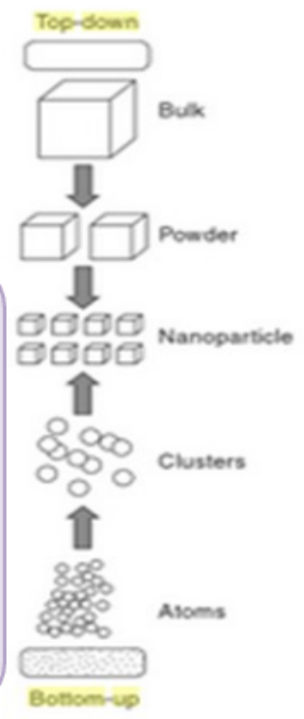
NANOMATERIALS SYNTHESIS

BOTTOM UP APPROACH

TOP DOWN APPROACH

- Nanomaterials are synthesized by assembling the atoms/molecules together.
- Instead of taking material away to make structures, the bottom-up approach selectively adds atoms to create structures.
- Eg) Plasma etching, Chemical vapour deposition

- Nanomaterials are synthesized by breaking down of bulk solids into nanosizes
- Top-down processing has been and will be the dominant process in semiconductor manufacturing.
- Eg) Ball Milling, Sol-Gel, lithography



Top-down vs. bottom-up

- **Top-down methods**

- begin with a pattern generated on a larger scale, then reduced to nanoscale.
- By nature, aren't cheap and quick to manufacture
- Slow and not suitable for large scale production.

- **Bottom-up methods**

- start with atoms or molecules and build up to nanostructures
- Fabrication is much less expensive
-

Application of Nano materials

- ✓ Nano materials are used in a variety of, manufacturing processes, products and healthcare including paints, filters, and insulation and lubricant additives.
- ✓ They are an emerging type of artificial enzyme, which have been used for wide applications in such as biosensing, bioimaging, tumor diagnosis.
- ✓ In paints nanomaterials are used to improve UV protection and improve ease of cleaning.

- ✓ Nanomaterials are being used in modern and human-safe insulation technologies, in the past they were found in Asbestos-based insulation
- ✓ **As a lubricant additive**, nano materials have the ability to reduce friction in moving parts. Worn and corroded parts can also be repaired with self-assembling anisotropic nanoparticles called TriboTEX.
- ✓ **Next-Generation Computer Chips** : The microelectronics industry has been emphasising miniaturisation, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling
- ✓ **Better Insulation Materials** : Nanocrystalline materials synthesised by the sol-gel technique result in foam like structures called "aerogels." These aerogels are porous and extremely lightweight; yet, they can loads equivalent to 100 times their weight. Aerogels are composed of three-dimensional, continuous networks of particles with air (or any other fluid, such as a gas) trapped at their interstices. Since they are porous and air is trapped at the interstices, aerogels are currently being used for insulation in offices, homes, etc. By using aerogels for insulation, heating and cooling bills are drastically reduced, thereby saving power and reducing the attendant environmental pollution.
- ✓ **Phosphors for High-Definition TV**: The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesised by the sol-gel techniques are candidates for improving the resolution of monitors.

Unit- III

Chapter- 2 - Cement & Ceramic Materials

❖ Introduction

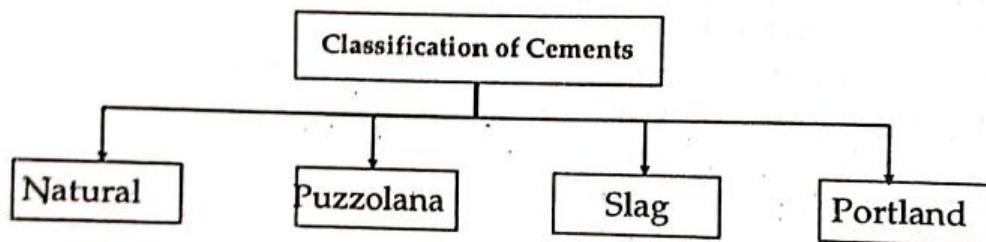
- The concrete is the most widely used non-metallic material of construction.
- In the most general sense of the word, cement is a binder, a substance that sets and hardens independently, and can bind other materials together.
- Finely ground powders and all have the important property that when mixed with water a chemical reaction (hydration) takes place.
- Hydration produces a very hard and strong binding medium for the aggregate particles.
- The cement to be used in a particular concrete or mortar will be selected on the basis of the particular properties required.

❖ Classification of Cement

Cement is a material which possesses adhesive and cohesive properties and capable of binding materials like bricks, stones, building-blocks etc.

Classification of Cements

There are four types of cements viz. Natural, Puzzolana, Slag and Portland cement. These are briefly discussed below :



(a) Natural Cement

Preparation. It is made by calcining a naturally occurring argillaceous limestone at a high temperature and subsequently, pulverizing the calcined mass. Calcium silicates and aluminates are formed by the combination of silica and alumina with calcium oxide during calcination.

Properties :

- It possesses hydraulic qualities,
- It is quite setting cement, and
- It possesses relatively low strength.

Applications :

- Mortars (combination of sand with natural cement) is used in laying bricks and setting stones.
- It is also used in large masses of concretes such as dams and foundations.

(b) **Puzzolana Cement.** It is oldest cement invented by Romans. It was used by them in making concrete for the construction of walls and domes.

Preparation : This is made by mixing and grinding of natural puzzolana and slaked lime. Natural puzzolana is deposit of volcanic ash produced by rapid cooling of lava. Lava in turn is a molten mixture of silicates of calcium, iron and aluminium.

Puzzolana cements form hydraulic cementing materials.

Properties. They also possess hydraulic properties.

Applications. They are first mixed with portland cements and then used for different applications.

(c) **Slag Cement**

Preparation. It is made from hydrated lime and blast furnace slag. A mixture of calcium and aluminium silicates (*i.e.*, blast furnace slag) is granulated by pouring it into a stream of cold water. Subsequently, it is dried and mixed with hydrated lime. Then the mixture is pulverized to fine powder. Sometimes, accelerator like clay, salt or caustic soda are added to hasten the hardening process.

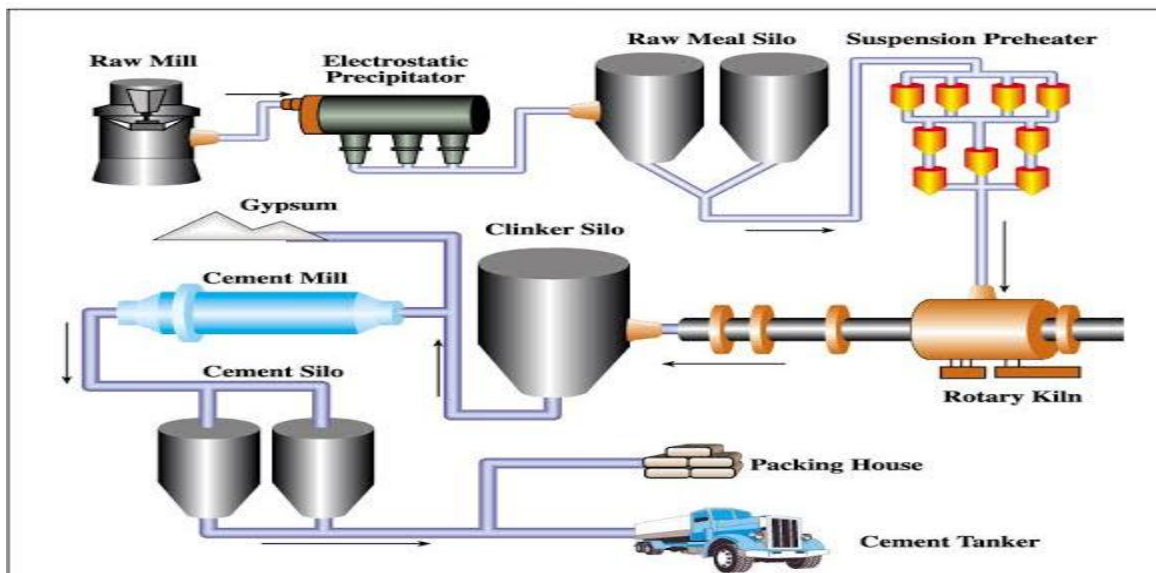
Properties :

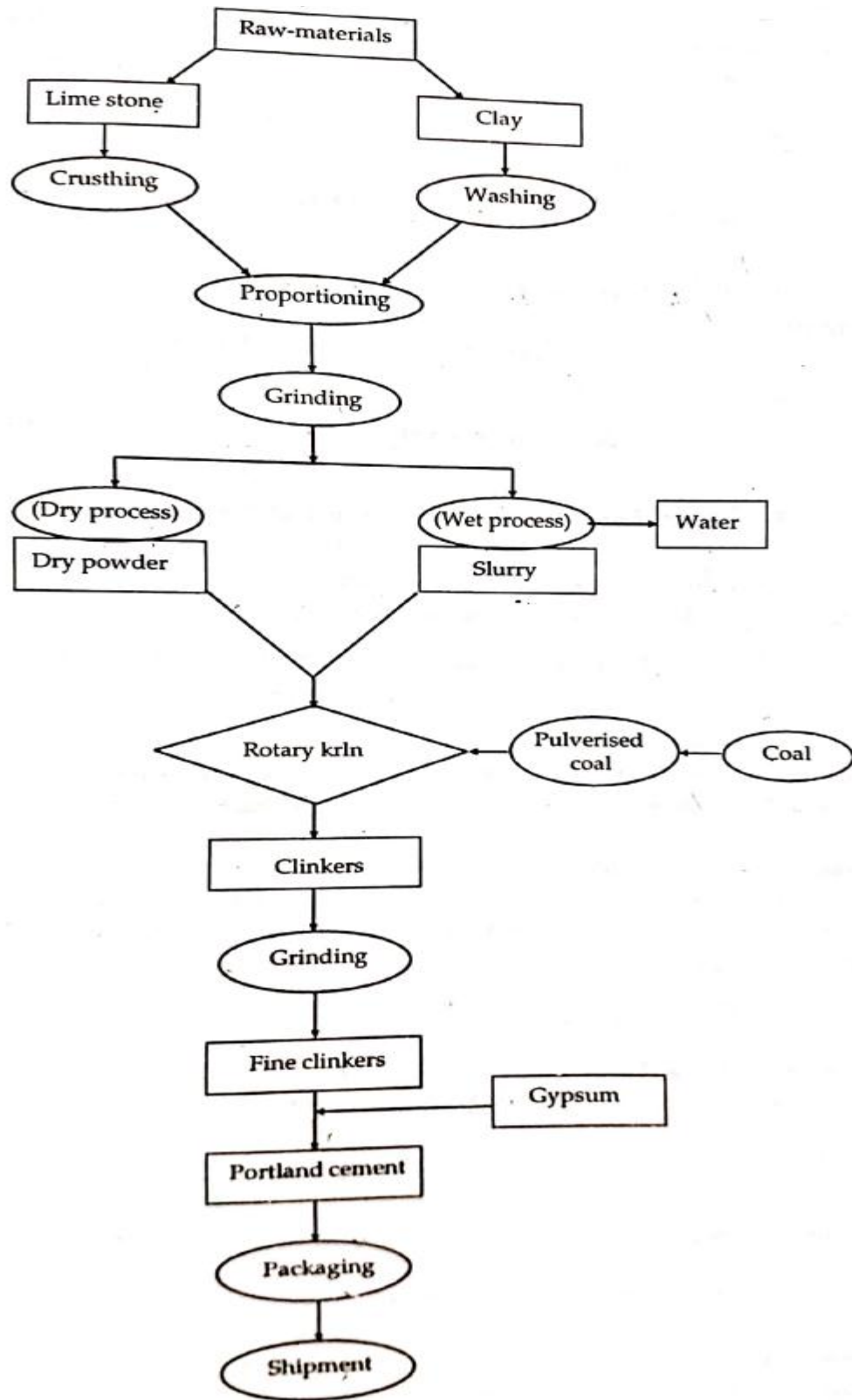
- (i) Slag cements are slow setting,
- (ii) They are poor in abrasion-resistance and
- (iii) They have lower strength.

Applications. Because of the above shortcomings, slag cements have very limited applications. It is used for making concrete in bulk construction.

(d) **Portland Cement.** It is made by calcining (at about 1500°C) an intimate and properly proportioned mixture of clay and lime containing raw materials. After calcination, retarder like gypsum is added.

❖ Manufacturing of Portland Cement





Flow diagram for manufacture of Portland cement.

❖ Manufacturing Process:

- **Raw Materials : Lime (CaO), Silica (SiO₂), Alumina (Al₂O₃), Fe₂O₃, clay minerals**
- The manufacturing involves the following operations.
- **(A) Crushing:** It is done in a primary crusher (which reduce the size of lime stone to an approximately 5 inch in size.) and in secondary crusher (it further reduce the size to 3-4 inch in size)
- **(B) Mixing:** It begins with the acquirement of raw materials such as limestone, sand and clay.
- These are mixed either by a dry process or by the wet process. The raw materials which are stored in the bins are first proportioned and then delivered to grinding mill.
- The dry process produces the fine powder. It is stored in the bins. The Wet process result in slurry, which is mixed and pumped to a storage basins.
- **(C) Burning :** Both dry and wet process feed rotary kilns where burning results in actual chemical changes.
- The rotary kiln is long steel cylindrical with length 30-160 meters and diameter 2-4 meters.
- Its inside surface is lined with fire brick refractory.
- It is slightly inclined downwards towards the exit end.
- It can be rotated at desire speed as it is mounted on rollers. The material is fed in the rotary kiln from the upper end.
- As the kiln rotates, the material passes slowly from the upper to the lower end at a rate controlled by the slope and speed of rotation of the kiln.
- The kiln is heated from the lower end. The upper end is cooler.
- As the material passes through the kiln, its temperature is raised to the point of clinkering temperature where the actual chemical reaction take place.
- In fact there are different zones in rotary kiln...
- **(1) Drying Zone :** Here the temperature is moderate (100-500 °C) and this zone is located at upper one-fourth of the length of the kiln.
- This zone is known as drying zone, because the moisture is given out and material get heated.

- (2) **Calcination Zone**: Its temperature is about 1000 °C and it is the middle portion of the kiln. In this zone, CO₂ is ejected from the limestone, quick lime is formed in the form of small lumps, called nodules.



- (3) **Burning Zone** : Its temperature is about 1400-1500 °C and is the bottom and hottest portion of kiln. In this zone, mixture melts and forms little rounded pasty masses of about the size of the peas which are called **clinkers**.
- The clinker produced is greenish black or black in color and has rough textured. In this zone, lime and clay undergo fusion yielding calcium aluminates and silicates.



- (4) **Grinding**: From clinker storage the material is transported to final grinding where it is ground to the requisite fineness according to the class of the product. \
- Finely ground clinkers sets very fast by absorption of moisture from the atmosphere. To control the setting time of the Portland cement approximately 2 to 3 % gypsum is added.
- The mixture of clinker and gypsum is known as Portland cement. It is stored in silos from which it is bagged or loaded for shipment.

Mixing and crushing of raw materials: Actually the purpose of both processes is to change the raw materials to fine powder.

Dry process	Wet process
<ul style="list-style-type: none"> <input type="checkbox"/> This process is usually used when raw materials are very strong and hard. 	<ul style="list-style-type: none"> <input type="checkbox"/> This process is generally used when raw materials are soft because complete mixing is not possible unless water is added.
<ul style="list-style-type: none"> <input type="checkbox"/> In this process, the raw materials are changed to powdered form in the absence of water. 	<ul style="list-style-type: none"> <input type="checkbox"/> In this process, the raw materials are changed to powdered form in the presence of water
<ul style="list-style-type: none"> <input type="checkbox"/> Dehydration zone requires a somewhat shorter distance than wet process. 	<ul style="list-style-type: none"> <input type="checkbox"/> Dehydration zone would require up to half the length of the kiln easiest to control chemistry & better for moist raw materials
<ul style="list-style-type: none"> <input type="checkbox"/> 74% of cement produced. 	<ul style="list-style-type: none"> <input type="checkbox"/> 26% of cement produced
<ul style="list-style-type: none"> <input type="checkbox"/> kilns less fuel requirements 	<ul style="list-style-type: none"> <input type="checkbox"/> High fuel requirements - fuel needed to evaporate 30+% slurry water- The kiln is a continuous stream process vessel in which feed and fuel are held in dynamic balance
<ul style="list-style-type: none"> <input type="checkbox"/> In this process calcareous material such as lime stone (calcium carbonate) and argillaceous material such as clay are ground separately to fine powder in the absence of water and then are mixed together in the desired proportions. <input type="checkbox"/> Water is then added to it for getting thick paste and then its cakes are formed, dried and burnt in kilns. 	<ul style="list-style-type: none"> <input type="checkbox"/> In this process, raw materials are pulverized by using a Ball mill, which is a rotary steel cylinder with hardened steel balls. When the mill rotates, steel balls pulverize the raw materials which form slurry (liquid mixture). The slurry is then passed into storage tanks, where correct proportioning is done. Proper composition of raw materials can be ensured by using wet process than dry process. Corrected slurry is then fed into rotary kiln for burning.

Chemical Composition of Portland Cement

Table 1.4. Approximate Oxide Composition Limits of Ordinary Portland Cement

Oxide	Per cent content
CaO	60-67
SiO ₂	17-25
Al ₂ O ₃	3.0-8.0
Fe ₂ O ₃	0.5-6.0
MgO	0.1-4.0
Alkalies (K ₂ O, Na ₂ O)	0.4-1.3
SO ₃	1.3-3.0

❖ Setting and Hardening of cement

- **Setting** : When water is mixed with cement paste to form a fluid paste, hydration of cement take place. The mixture eventually becomes stiff and then hard. This process is known as setting.
- **Hardening**: After hydration, anhydrated compound become hydrated which have less solubility. Hence they are precipitated as insoluble gels or crystal. This process of crystallization is known as Hardening.

❖ I.S.I. Specification of Portland cement.

- (i) Lime saturation factor $\left[\frac{\text{CaO} - 0.7 \text{SO}_3}{2.8 \text{SiO}_2 + 1.2 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3} \right]$
= 0.66 to 1.02
- (ii) The ratio $\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$ shall not be less than 0.66
- (iii) Insoluble residue should not exceed 2%
- (iv) The weight of magnesia (MgO) : should not exceed 6%
- (v) Total sulphur contents, calculated as sulphuric anhydride (SO₃) shall not be more than 2.75%
- (vi) Loss on ignition shall not exceed 4%
- (vii) Fineness not to exceed 10%, after sieving the residue (by weight) on B.S. 170-mesh test sieve.
- (viii) Setting times : Initial = 30 minutes
Final = 10 hrs.
- (ix) Heat of hydration :
After seven days : ≤ 65 cal/gm
After twenty Eight days : ≤ 75 cal/gm
- (x) Compressive strength :
After three days : ≥ 1600 lb/sq. inch
After seven days : ≥ 2500 lb/sq. inch
- (xi) Tensile strength :
After three days : ≥ 300 lb/sq. inch
After seven days : ≥ 375 lb/sq. inch

❖ Physical properties of Portland cement

Fineness: The fineness of cement means the particles size of cement. It affects the hydration process of cement. That means it affects the rate of strength gain of cement.

Soundness : It is the ability of a cement to maintain a stable volume after setting. Good soundness cement doesn't shrink after hardening.

Consistency: Consistency means the required water to produce plastic cement paste for particular cement. Thus one can know the water-cement ratio for better workability of the mix.

Setting Time: As soon as the water is mixed with Portland cement, the hydration process starts and it begins to set. Cement has two setting time, initial-setting time and final-setting time. In construction, initial-setting time shouldn't be too early and final-setting time shouldn't be too late. Normally, initial-setting time is 30 to 45 minutes and final-setting time is below 10 hours.

Compressive Strength : Minimum compressive strength result for 3 days mortar cube should be 16 N/mm^2 and for 7 days cube should be 22 N/mm^2 .

Heat of Hydration: The cement reacts as soon as the water is added. It is called hydration. During hydration, cement generates heat. This is the Heat of Hydration.

Specific Gravity : Specific Gravity of cement is necessary for calculating the mass for the desired volume of cement. The Specific Gravity of normal type of cement is 3.15

❖ Plaster of Paris (POP)

→ Calcium sulphate with half a molecule of water per molecule of the salt (hemi-hydrate) is called plaster of paris (plaster of paris).

Preparation

→ plaster of paris is prepared by heating gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at 120°C in rotary kilns, where it gets partially dehydrated.

→ The temperature should be kept below 140°C otherwise further dehydration will take place and the setting property of the plaster will be partially reduced.

Properties

→ It is a white powder. When mixed with water (1/3 of its mass), it evolves heat and quickly sets to a hard porous mass within 5 to 15 minutes. During setting, a slight expansion (about 1%) in volume occurs so that it fills the mould completely and takes a sharp impression. The process of setting occurs as follows:

Uses

- In surgery for setting broken or fractured bones
- For making casts for statues, in dentistry, for surgical instruments, and toys etc
- In making black board chalks, and statues
- In construction industry

❖ Refractory Materials

→ A **refractory material** or **refractory** is a heat-resistant material: that is, a mineral that is resistant to decomposition by heat, pressure, or chemical attack, most commonly applied to a mineral that retains strength and form at high temperatures.

→ Refractories are inorganic non-metallic material which can withstand high temperature without undergoing physico – chemical changes while remaining in contact with molten slag, metal and gases. They are exposed to environments above 1,000 °F

→ Refractory materials must be chemically and physically stable at high temperatures. Depending on the operating environment, they must be resistant to thermal shock, be chemically inert, and/or have specific ranges of thermal conductivity and of the coefficient of thermal expansion.

→ It is classified as below:

→ 1. **Acidic refractories** consist of acidic materials like alumina (Al_2O_3), and silica (SiO_2). They are impervious to acidic materials, but easily attacked by basic materials. Important members of this group are alumina, silica, and fireclay refractories.

→ 2. **Basic refractories** consist of basic materials such as CaO , MgO , etc. These are impervious to basic materials, but easily attacked by acidic materials. Important members of this group are magnesite and dolomite refractories.

→ **3. Neutral refractories** are made from weakly acid/basic materials such as carbon, silicon carbide (SiC), chromite (FeCr_2O_4) and zirconia (ZrO_2).

❖ **A good refractory material should have the following properties:**

- It should be able to withstand high temperatures generated in the furnace.
- It should be able to withstand sudden alternating heating and cooling, i.e., thermal shocks.
- It should be able to withstand abrasion and rough usage.
- Its contraction and expansion due to the inevitable temperature variation should be minimum possible.
- It should be able to withstand fluxing action of the slags and the corrosive action of gases.
- It should have good heat insulating properties.
- It should be chemically inactive at elevated temperatures.
- It should be impermeable to gases and liquids as far as possible.
- If used in electric furnaces, it must have low electrical conductivity.

❖ Some important refractories

Fireclays

Common fire clays contain 25 to 45% Al_2O_3 and 50- 80% SiO_2 . Clays with higher Al_2O_3 are higher alumina refractories.

Properties

- Porosity varies from 8 to 24% depending on the firing temperature.
- At high temperatures fire clay refractory combine with alkalis such as soda and potash.
- Cold crushing strength is 950 kg/cm^2 at 20°C and decreases drastically at 800°C to 555°C .

	Al_2O_3 (%)	Refractoriness
Medium duty	30 - 32	1665°C
High duty	38 - 40	$1700 - 1717^\circ\text{C}$
Super duty	42 - 45	$1743 - 1763^\circ\text{C}$

Uses: Furnaces, regenerators, ovens, and kilns.

High alumina refractories:

Al_2O_3 varies from 45 to 95%. Commonly used refractory are sillimanite (Al_2O_3 61%) and mullite (70 – 85% Al_2O_3). Some of the properties are

- High refractoriness
- Better resistance to slag and spalling
- Higher load bearing capacity.
- Fusion point $>1850^\circ\text{C}$.

Uses: B F stoves, cement and lime rotary kilns, electric arc furnace roofs, ladle, glass making furnaces, etc.

Chromite – Magnesite: Amount of chrome ore is > magnesite. Some properties are

- Used up to 1700°C
- Resistant to thermal shocks
- Basic in nature

Uses in: Inner lining of basic oxygen steelmaking vessel, Side walls of soaking pits etc

Magnesite: These refractory are basic in nature. Some properties are

- High refractoriness and thermal conductivity
- Great resistance to basic slag

Silicon carbide

SiC content exceeds 85% in these type of refractories. Some of the important properties are

Properties:

- High thermal conductivity and high refractoriness
- Resistance to thermal spalling and temperature load bearing capacity is high
- Inert to acid slags and
- Light weight

SIALON:

This class of refractory is prepared by using alumina and silicon nitride. Powdered mixture of alumina and silicon nitride is hot pressed at 18 – 30 M Pa and 1700 – 1760°C in graphite moulds in order to produce a low porosity dense product. SIALON refractory shows

- good resistance to oxidation, and action of molten metals like Al, Zn, Cd, Fe and steel and
- resistance to H₂SO₄, HCl, borax and alkalis.

❖ Glass

- Glass is an inorganic product of fusion, which has been cooled to a solid state condition without crystallizing
- Glass is a non-crystalline solid that exhibits a glass transition temperature.

→ TYPES OF GLASSES

- Based on the composition of glasses (or sometimes based on their applications) they are classified broadly into two categories as oxide glasses and non-oxide glasses. The constituents in the glass composition play major role in the application and classification of glasses.
- **Oxide glasses** may be single component glasses (SiO₂, GeO₂etc) binary systems (SiO₂-Na₂O, PbO-GeO₂, B₂O₃-Na₂O, B₂O₃-K₂O), ternary systems(B₂O₃-Na₂O-K₂O, Na₂O-CaO-SiO₂, K₂O-MgO-SiO₂etc) quaternary glass systems (LiF-Li₂O-P₂O₅-Nb₂O₅, Li₂SO₄-ZnSO₄-B₂O₃-VOSO₄, AgI-Ag₂O-B₂O₃-AS₂O₃etc or multi component glass systems like SiO₂-Al₂O₃-CaO-MgO-Na₂O, SiO₂-Al₂O₃-CaO-MgO-K₂O).

→ **Non-oxide glasses** are also prepared in many compositions. Some important non-oxide glasses are chalcogenide glasses. Non-oxide glasses such as Fluorozirconate and Fluoroaluminate groups are popular for making glass fibers. These glasses are used in electrical and optical memories.

→ Oxide glasses depending on composition may be further classified and some of these oxide glass systems are discussed briefly here.

→ **Soda-Lime Glasses**

→ The less expensive commercial glass is soda–lime glass.

→ These are used as window glasses because of their good light transmission.

→ Soda–lime glasses are also used as glass containers, jars etc.

→ The chief constituents in soda-lime glass are silica (SiO_2 -60-75%), soda(Na_2CO_3 -12-18%) and lime (CaCO_3 or MgCO_3 -5-12%).

→ Other materials are also added to these constituents to get required properties.

→ The main disadvantage of these glasses is they are not resistant to high temperatures and sudden thermal changes.

→ **Borosilicate Glasses**

→ Borosilicate glass is widely used in the manufacture of laboratory glassware, pharmaceutical containers, high-power electric bulbs etc.

→ Because of their good heat resistant properties and thermal shock resistance they are used in chemical industry, domestic kitchen cooking utensils (microwave or oven ware).

→ The main ingredients of borosilicate glass are silica (SiO_2 -70-80%) and boric acid (7-13%). Oxides of sodium, potassium and aluminum are added to borosilicate composition to get good chemical durability.

→ Lead Glasses

- Lead glasses are widely used for decorative purposes because of their bright brilliance due to high refractive index.
- Generally lead glasses contain SiO_2 (54-65%), PbO (18-38%) Na_2O (13-15%) and other oxides in small proportions. If the PbO content is less than 18% in the glass it is called as crystal glass.
- If the lead content is high (65%), the glass can be used for radiation shield glass as lead absorb rays.