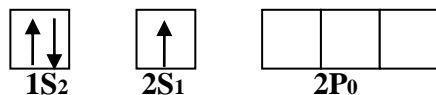


## BAND THEORY OF SOLIDS

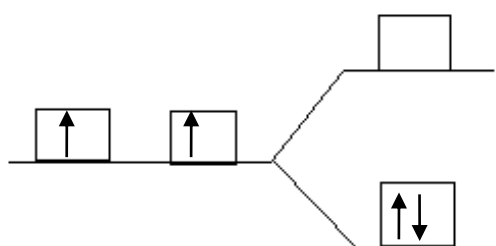
Band theory is extension of Molecular orbital theory of covalent bonds to solids.

### Salient features of Band theory:

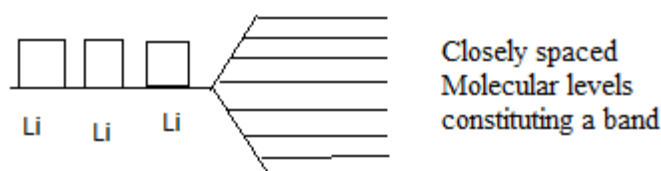
- Solids are made up of giant molecules in which a large number of spherical atoms are arranged in a regular close-packed pattern.
- When atoms are brought together in solids, the atomic orbitals of the valency shells interact forming molecular orbitals.
- During their interaction, their outer shells constitute one single system of electrons, common to entire array of atoms in a crystal.
- Let us take an example of lithium with electronic configuration



- In  $\text{Li}_2$  molecule-  $2S_1$  electrons from two Li atoms combine to form one Bonding,  $\sigma 2S_2$  and antibonding orbital,  $\sigma^* 2S_0$ .



- Similarly in  $\text{Li}_n$  molecule, n number of atomic orbital ( $2S$  of each lithium atom) combine to form a cluster of molecular orbital which are closely placed to each other. Each original energy level becomes a band of very closely spaced levels of small energy differences.



- Depending upon the composition of solids, bands are of two types-
  - a) **Overlapping bands**- Higher band overlap with empty lower band.  
Eg:- Valence  $2S$  band overlap with empty  $2P$  band in Beryllium.
  - b) **Non-overlapping bands**- Higher band do not overlap with lower band.  
Eg:- Valence  $3S$  band do not overlap with empty  $3P$  band in Sodium.

The band of energy levels occupied by valence electrons is called **Valence Band**.

It may be

- a) Partially filled with electrons. Eg:- Na, Cu
- b) Completely filled with electrons. Eg:- Be, Mg
  - The next higher permitted band above the valence band is called **Conduction band**. The conduction band may be empty or partially filled with electrons which are also called as free-electrons.
  - The gap between the valence band and conduction band is called **Forbidden gap**.

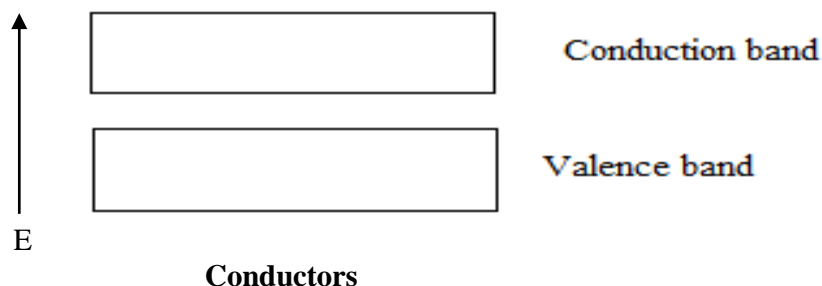
The width of the forbidden gap is called Energy gap ( $E_g$ ).

Depending on the  $E_g$ , solids are classified into three types.

- a) Conductors
- b) Insulators
- c) Semi-conductors

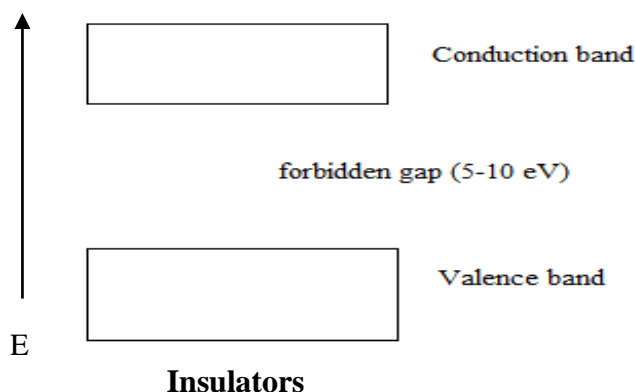
**Conductors**- In these materials, the energy gap is almost negligible.

- When a potential is applied to the half-filled valence band, the free electrons get excited to the empty conduction band and they begin to conduct. Eg:- Na, Al etc.
- In elements like Mg, conduction is mainly due to overlapping of filled valence band with higher empty band.
- Electrical conductivity of a metals decreases with rise in temperature because of the increased thermal vibrations of metal atoms which causes scattering of the electrons. Hence their flow is obstructed.



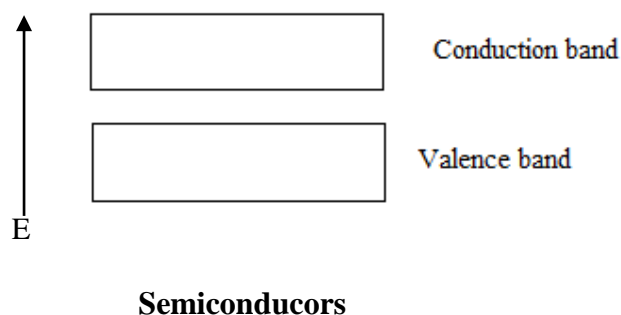
**Insulators**- In these materials, the energy gap is or order 5-10eV.

- In insulators, the valence band electrons are tightly bound to their parent nuclei and require large amount of electric fields to remove electrons to conduction band.
- They possess a complete valence band and completely empty conduction band.
- Eg:- Diamond, glass, solid NaCl, Plastics, ceramics etc.
- Electrical conductivity increases with increase in temperature. At room temperature, they act as best insulating materials. At higher temperatures, some of the valence electrons acquire sufficient energy to overcome the energy gap and enter the conduction band



**Semiconductors**- In these materials, the energy gap is of order of 1 eV.

- Solids having electrical conductivity in between those of insulators and conductors are called semiconductors.
- They have filled valence band, almost empty conduction band. Eg:- Si, Ge.
- Electrical conductivity increases with increase in temperature. The probability of promotion of electrons from valence band to conduction band decreases with the energy gap and increases with temperature



## CLASSIFICATION OF SEMICONDUCTORS

### SEMICONDUCTORS

- Semiconductors are materials with electrical conductivities that are intermediate between those of conductor's and insulators.
- They acts as insulators at very low temperature, but acts as sizable electrical conductors at room temperature.
- The width of band gap in semiconductors is intermediate to that of insulators and conductors.
- They are used for electronic purposes as they can carry an electric current by electron migration or hole propagation.
- The resistance of semiconductors decreases with increase in temperature- negative temperature coefficient of resistance.
- The resistibility is less than an insulator but more than a conductor.
- When a suitable metallic impurity e.g., arsenic, germanium, gallium, etc is added to a semiconductor, its current conducting properties change appreciably.

Semiconductors are classified into the following types-

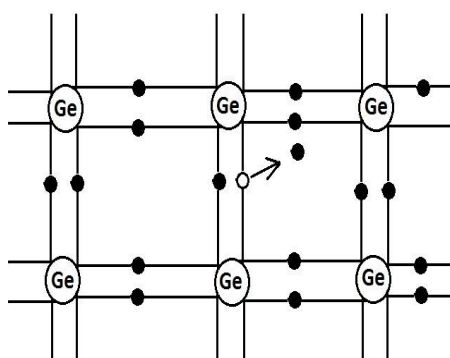
1. **Intrinsic semiconductors**
2. **Extrinsic semiconductors**
  - a) **n-type semiconductors**
  - b) **p-type semiconductors**
3. **Organic semiconductors**

#### 1. Intrinsic semiconductors

These semiconductors are pure enough that impurities do not appreciably affect its electrical behavior. Elements like Silicon, germanium, selenium acts as intrinsic semiconductors which have four valence electrons in their atoms and their band gap is about 1ev.

#### Conduction Process:-

- When an electron from the valence band is ejected, a covalent bond is broken and a positively charged hole is left in the valence band.
- The hole travels to an adjacent atom by accepting an electron from the latter one.
- This forms a new covalent bond and breaks an existing covalent bond by filling up the previous hole and creating a new hole.
- When electric field is applied, electrons in the conduction band move to the anode and positively charged hole moves to cathode.
- Hence current is produced due to **simultaneous movement of conduction band electrons and valence bond holes** in opposite directions.

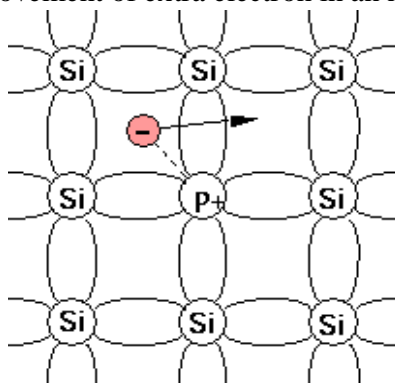


#### 2. Extrinsic semiconductors-

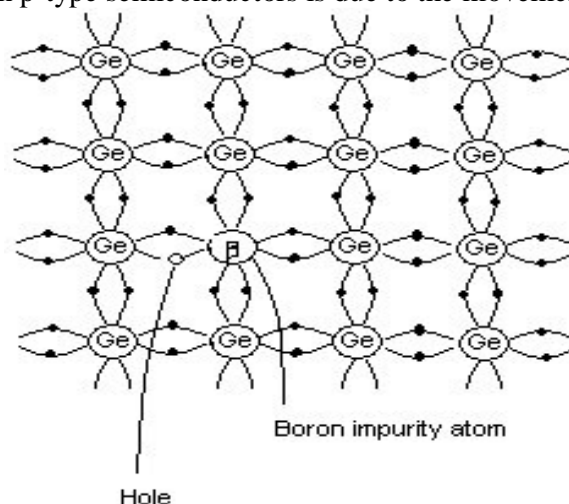
Intrinsic semiconductors when added with extremely small amount of substitutional impurities (doping) are called extrinsic semiconductors. On adding a doping agent, the energy gap gets reduced and makes the electron flow easy from valence band to conduction band. The conductivity increases by 10,000 times. Based on the doping agent added, extrinsic semiconductors are classified into two types:-

i) **n-type semiconductors-**

- These semiconductors contain a small quantity of a penta valent element impurity (like phosphorous, arsenic or antimony).
- The doping atom forms four covalent bonds with the surrounding four atoms of intrinsic semiconductor (Germanium, Silicon etc) with the help of its four valence electrons.
- The fifth excess electron remains loosely bound to the donor atom itself. It is easily excited from the valence band to conduction band on applying electric field.
- Thus conduction is due to movement of extra electron in an n-type semiconductor.

ii) **p-type semiconductors**

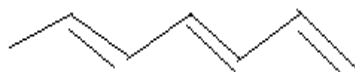
- They contain a small quantity of a trivalent element (like boron, aluminium).
- The three valence electrons present in the trivalent impurity forms three covalent bonds with the surrounding three of the four atoms. So that one bond in one of the four surrounding atom is left incomplete.
- This gives rise to a positive hole.
- On applying an electric field, a hole travels to an adjacent atom by acquiring an electron and establishes a new covalent bond, by breaking an existing covalent bond in the adjacent atom.
- Hence conductivity in p-type semiconductors is due to the movement of positive holes.



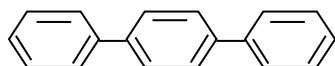
### 3. ORGANIC SEMICONDUCTORS

Organic semiconductors are conjugated organic polymer materials having very high conductivity. These materials have intrinsic semi-conductivity with an energy gap of 1.0- 2.0 eV.

Conjugated Organic Polymers-



Polyacetylene.



Polyphenylene.

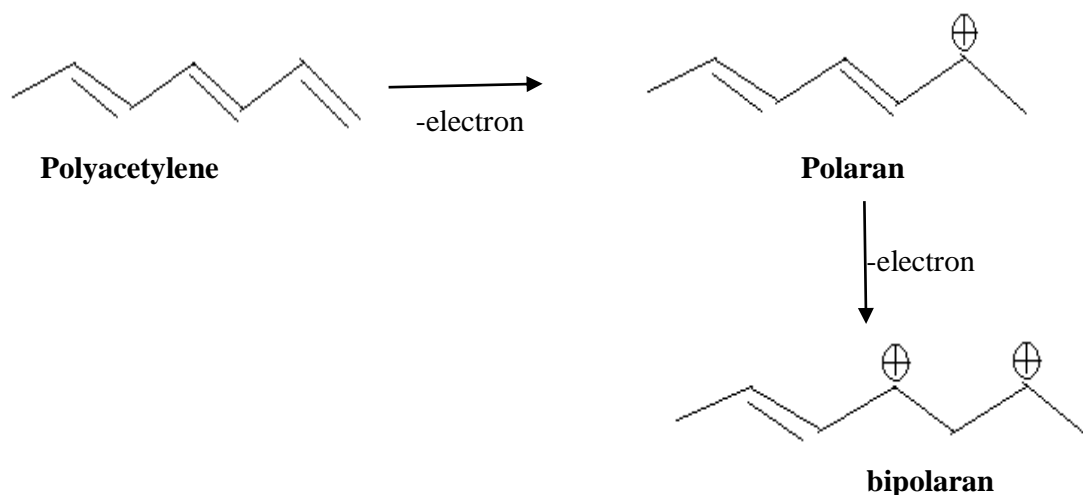
They become more conducting on doping with oxidizing or reducing agents.

If the dopant used is a Lewis acid like  $AlCl_3$ ,  $I_2$ ,  $FeCl_3$  or oxidizing agent or electron withdrawing group etc. then obtained semiconductor is called **p- type semiconductor**.

If the dopant used is a Lewis base like  $NH_3$ ,  $H_2O$  or reducing agent or electron donating group etc. then obtained semiconductor is called **n- type semiconductor**.

**Conducting process-**

- Electron is removed from the valence band by oxidation of the conjugated polymer due to which a vacancy (cation radical) equivalent to hole is formed.
- This partially delocalized cation radical, delocalized over a few monomer units, is called **Polaran**. Breaking of two conjugated bonds and formation of a dispositive radical leads to **bipolaran**.
- Low doping gives a polaron and high doping gives a bipolaran.



The polarans and bipolarans are mobile under the influence of electric field.

They can move along the polymer chain as like electrons and holes move in inorganic semiconductors.

**Advantages of organic semiconductors-**

- They are used in photovoltaic cells, electrode photo cells, electro-chromic and memory devices.
- They are also used in communication devices.

## Building Materials

### CEMENT

Cement may be broadly be described as a material possessing adhesive and cohesive properties, and capable of bonding materials like stones, bricks, building, blocks etc.

The principal constituents of cement used for constructional purposes are compounds of Ca (calcareous) and Al & Si (argillaceous). The cements have property of setting and hardening under water.

### **Manufacture of Portland cement:**

Raw materials required for the manufacture of the Portland cement are

- 1) Calcareous materials, Cao(such as lime stone, chalk, marl etc)
- 2) Argillaceous materials, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (such as clay, shale, slate etc.)
- 3) Powdered coal or fuel oil
- 4) Gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O)

### **Manufacturing of Portland cement involves the following steps:**

1. Mixing
2. Burning
3. Grinding
4. Packing

1) Mixing of raw materials can be done either by

- a) Dry process
- b) Wet process

#### **a) Dry process**

- The raw materials (lime stone and clay) are crushed in to roughly 2-5 cm size pieces, dried, ground and mixed in proper proportions.
- The mixture is then finely powdered and fed on to a rotary kiln of 50 to 80 m long and 3 m in diameter.
- The kiln kept inclined and is rotated at the rate of about one revolution per minute.

#### **b) Wet process**

- The calcareous materials are crushed, powdered and stored in big storage tanks.
- The argillaceous material is thoroughly mixed with water in wash mills to remove any adhering organic matter and clay is also stored in a storage tank.
- Powdered lime stone and washed wet clay are allowed to flow in a channel in the required proportions from the channel, the two raw materials are led to grinding mills, where they are mixed to form a paste called slurry.
- The slurry contains 38-40% water. The slurry is kept ready for feeding in to a rotary kiln.

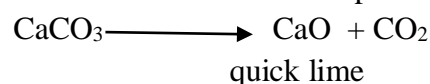
### **Process:**

- The raw mixture or corrected slurry is injected in to the kiln at its upper end.
- While hot flames are forced in to the kiln from the lower end.
- Due to slope and slow rotation of the kiln, the materials fed in move continuously towards the hottest end at a speed of about 15m per hour.
- As the mixture of or slurry gradually descends the temperature rises.

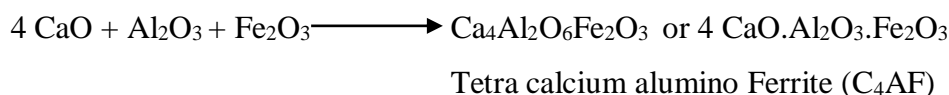
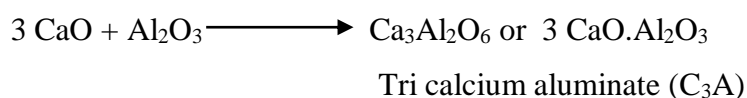
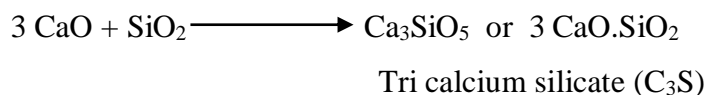
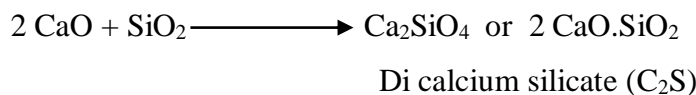
### **2. Burning**

- 1) **Drying zone:** In the upper part of kiln, where the temperature is around 400<sup>0</sup>c, most of the water in the slurry gets evaporated.

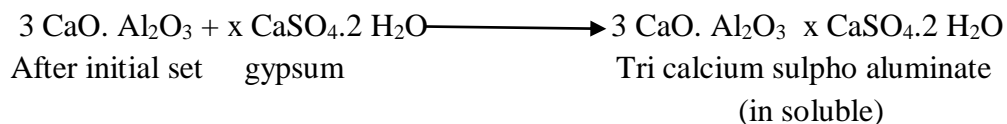
- 2) **Calcination zone:** In the central part of kiln, where the temperature is around  $1000^{\circ}\text{C}$ , lime stone of dry mixture or slurry under goes decomposition to form quick lime and  $\text{CO}_2$  and later escapes out. The material forms small lumps called nodules.



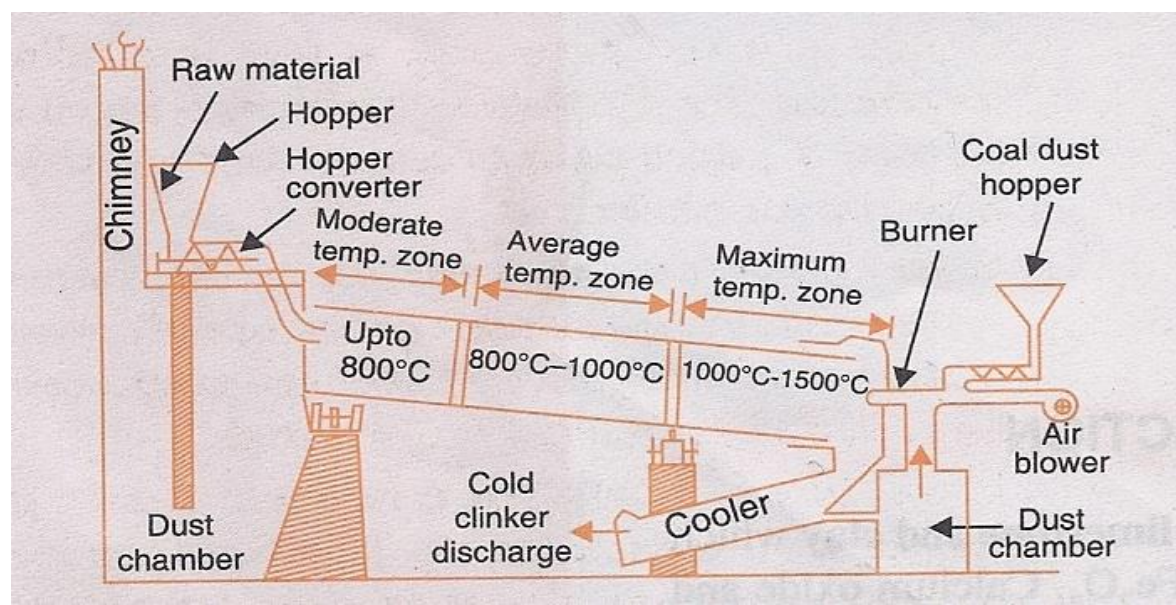
- 3) **Clinkering zone:** In the lower part of the kiln, the temperature is between  $1,500$  to  $1,700^{\circ}\text{C}$ . Here lime and clay undergo chemical interaction or fusion yielding calcium aluminates and silicates. The aluminates and silicates of calcium then fuse together to form small hard, grayish stones called clinkers.



3) **Grinding:** The cooled clinkers are ground to a fine powder in ball mills or tube mills. During final grindings, a small quantity of powdered gypsum is added, so that the resulting cement does not set very quickly, when it comes in contact with water. Gypsum thus acts as a retarding agent for early setting of cement.



4) **Packing:** The ground cement is stored in silos, from which it is fed to automatic packing machines. The cement coming out of the grinding mill is packed and marketed.

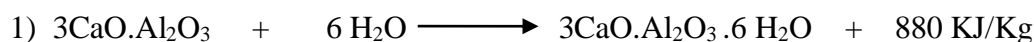


### Functions of ingredients of cement

- 1) **Lime (CaO)** principal constituent of cement. Its proportion must be properly regulated. However, excess of lime reduces the strength of cement, because it makes the cement to expand and disintegrate (60-69%)
- 2) **Silica (SiO<sub>2</sub>)** imparts strength to cement (17-25%)
- 3) **Alumina (Al<sub>2</sub>O<sub>3</sub>)** makes the cement quick setting. Excess of alumina however weakens the cement (3-8%)
- 4) **Calcium Sulphate** (Gypsum) helps to retard the setting action of cement.
- 5) **Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>)** provides: Colour, Strength, Hardness to the cement (2-4%)
- 6) **Sulphur trioxide (SO<sub>3</sub>)** in small proportion, is desirable. When present in small amount, it imparts soundness to cement. However, its excess reduces the soundness of cement (1-3%)
- 7) **Alkalis (Na<sub>2</sub>O+K<sub>2</sub>O)** if present in excess cause the cement efflorescent (0.3-1.5%)

### ❖ Setting and Hardening of Portland Cement

- Port land cement on mixing with water is converted into a plastic mass called cement paste. It slowly loses its plasticity and become stiff. This is called setting and it is tested with a standard needle.
- **Setting is defined as stiffening of the original plastic mass due to initial gel formation.**
- **Hardening is development of strength due to crystallization setting takes place few hours but hardening takes several years to complete.**
- The setting and hardening are mainly due to hydration and hydrolysis reactions.
- When cement is mixed with water, the paste become quite rigid within short time which is known as **initial set or flash set**. This is due to C<sub>3</sub>A which hydrates rapidly as follows.



Or



Tri calcium aluminate

Hydrate Tri calcium aluminate



Or



Tetra calcium aluminoferrite

Hydrate Tri calcium aluminate

Also Di calcium silicate starts hydrolyzing **Tobermonite gel** ( which possesses a very high surface area and adhesive property ), which also contributes to **initial setting**.



Or



Di calcium Silicate

Tobermonite gel



Final setting and hardening of cement paste is due to the formation of tobermonite gel plus crystallization of  $\text{Ca(OH)}_2$  and hydrated tri calcium aluminate



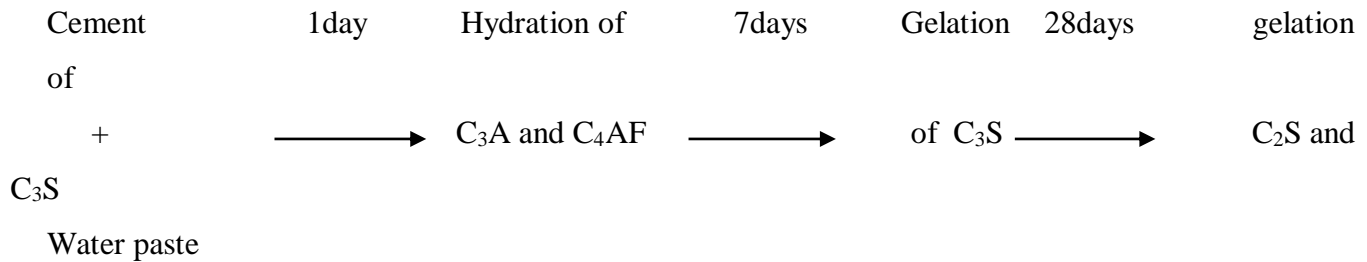
Or



Di calcium Silicate

Tobermonite gel

### Sequence of chemical reactions during setting and hardening of cement.



### ❖ Refractories

- The word refractory implies resistant to melting or fusion.
- In technology refractory is **inorganic material that can with stand high temperature without softening or suffering any deformation in shape.**
- Thus, refractories are used for the construction of linings of furnaces, kilns, ovens, converts, crucibles and retorts.

### Classification of Refractories

#### Acidic refractories :-

These are the refractories, which consist of acidic materials like alumina, silica. These are not attacked by acidic materials, but severely attacked by basic materials.

Examples- Alumina (50%  $\text{Al}_2\text{O}_3$ ), Silica and fire clay refractories.

**Silica Refractories:** Silica refractories contain more than 90% silica. Fine grained quartzite is the principal raw material for this brick.

**Manufacture:** In this silica rock is crushed and ground with lime and water. This mixture is made into bricks by hand moulding or machine pressing. The bricks are dried and fired in kiln. Now quartz convert in to cristobalite and tridymite. Which are the more stable allotropes of silica. If this change does not takes place then temp. is slowly raised to  $1500^\circ\text{C}$  for longer period.

**Properties:** silica bricks are slightly yellowish in colour with brown specks distributed throughout the mass.

**Uses:** They are used in steel making furnaces and coke ovens. They are also used in glass furnaces.

**Basic refractories:-**

These are the refractories which consist of basic materials like CaO, MgO etc. These are not attacked by basic materials, but easily attacked by acidic materials.

Examples: magnesite and dolomite refractories.

Magnesite bricks:- These are the basic refractories composed of MgO, which is one of the most basic refractory oxides.

The dead burnt magnesite is ground, mixed with water, moulded under pressure, dried and fired to give fire bonded bricks. To obtain the chemically bonded ones, the dead burnt magnesite is mixed with small amount of chromite ore. The mixture is then ground with water and moulded under pressure.

**Uses:** Pea magnesite (about 1cm diameter) is used to make bottoms of the basic furnaces.

**Neutral refractories:-**

These are made from weakly acidic or weakly basic materials like carbon, chromites and zirconia etc. these are not attacked by either acids or bases.

Examples: graphite, zirconia, carborundum and chromites

**Carborundum :** silicon carbide brick is known as carborundum refractory. It is prepared by fusing together silica (60%) and coke (40%) with small amount of sawdust and salt in an electric furnace.

Saw dust burns off and leaves pores in the brick. To obtain bonded refractory is mixed with clay dried and fired and then mixed with bonding agent glue. So self bonded bricks are obtained.

**Properties :** these are having high conductivity and mechanical strength.

**Uses :** they are used in ceramic industries, coke ovens, muffle furnaces.

## Ceramics

The word ceramic is derived from the Greek Keramos means burnt stuff. In modern usage ceramics are polycrystalline inorganic metallic or non metallic materials that are processed and used at high temp. Ceramic materials include a wide range of silicates, metallic oxides and combination of silicates and metal oxides.

### Engineering Applications

1. The older ceramics refer to white wares and are widely used in tiles, sanitary ware, insulators and high frequency applications.
2. White wares also used in chemical industries as crucibles, jars and compounds of chemical reactors.
3. Pyrometer tube, burner, burner tips and radiant heater supports are somewhat heat resistant items, which are also used as white wares.

4. The newer ceramics have high hardness and high resistant to heat and oxidation. Therefore they are used in applications such as refractories for industrial furnaces
5. Ceramics are now being used in electrical and electronic industries for insulators, semi conductors, super conductors, glass, porcelain, alumina, quartz, mica etc.,
6. Yattrlox is a type of ceramic. It is useful in optical applications, because it is transparent as window glass and can resist very high temp.
7. Ceramic materials are also used as cutting tools.