

### Performance Requirements of a Battery for Commercial Applications

For all commercial applications, batteries are constructed for their particular service, so that the best performance may be obtained consistent with cost, weight, space and operational requirements. For example, batteries for automobiles and aircrafts are constructed by using thin anodes and cathodes having very small separation to conserve space and weight and to provide high rates of current discharge at low temperatures. But stand-by batteries use thick electrodes and thick separators to provide long life.

In addition to above, commercial batteries should have :

- High capacity, (very small variation of voltage during discharge),
- High energy efficiency,

$$(\% \text{ energy efficiency}) = \frac{\text{energy released on discharge}}{\text{energy required for charge}} \times 100,$$

- High cycle life, (cycle life means number of charging, discharge cycles before failure occurs),
- Long shelf life,
- Tolerance to different service conditions such as variation in temperature, vibration, shock etc and
- Reliability.

## 17 COMMERCIAL ELECTROCHEMICAL CELLS AND BATTERIES

### 17.1 Dry (or Leclanche) cell

It consists of a zinc anode which is shaped as a container for the electrolyte, a carbon cathode surrounded by  $\text{MnO}_2$  and a paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  as a cathode depolarizer. Cathode depolarizer facilitates the  $\text{H}^+$ -discharge reaction by removing the adsorbed hydrogen atoms.

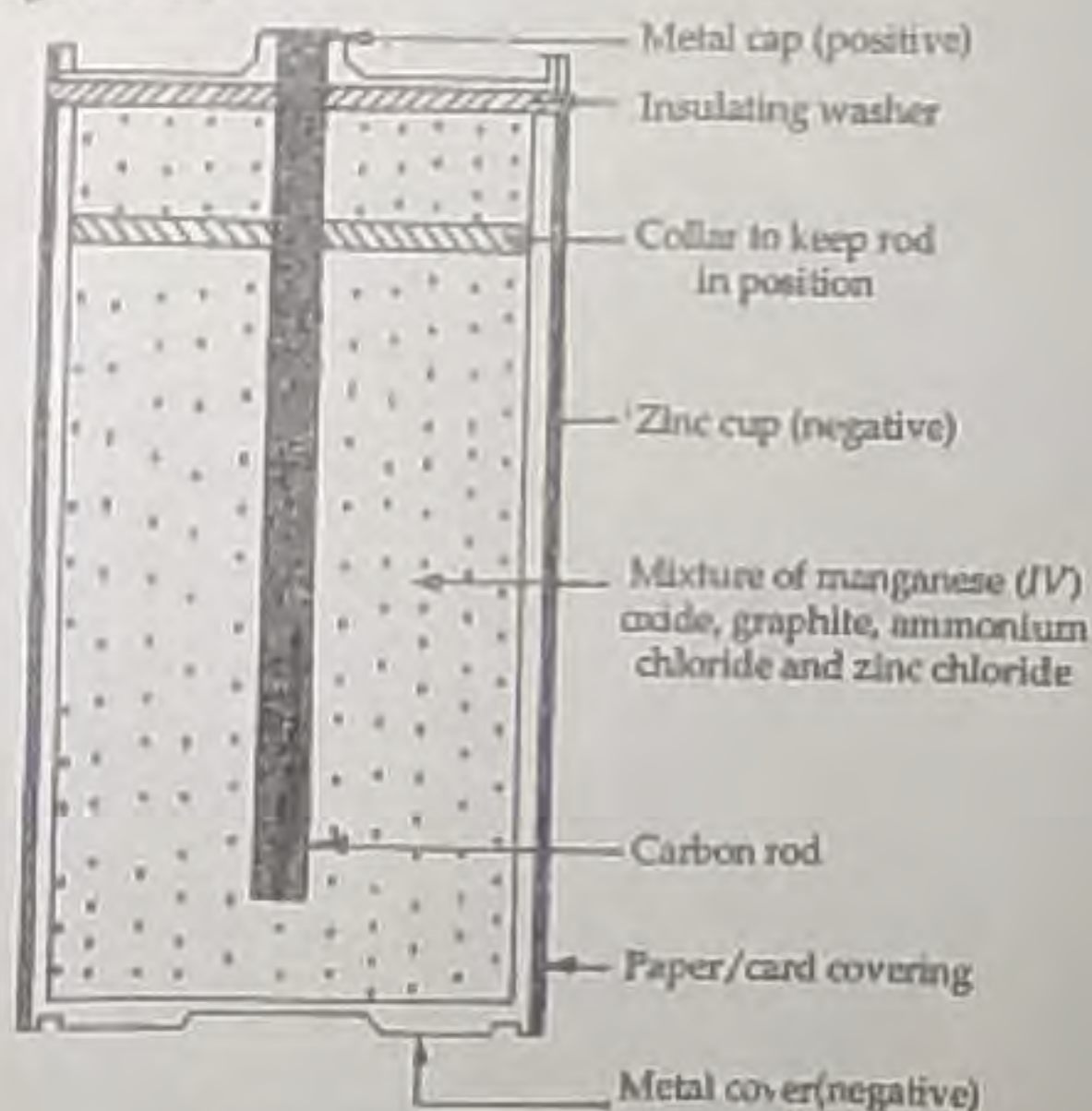


Fig. 10. Construction of a dry cell.



Such a cell is known as "dry cell" because of the absence of any mobile or liquid phase. Electrolyte consists of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$  and  $\text{MnO}_2$  to which starch is added to make it thick paste-like so that it is less likely to leak. The cell is encased in polypropylene cylinder and given a plastic coating to reduce leakage.

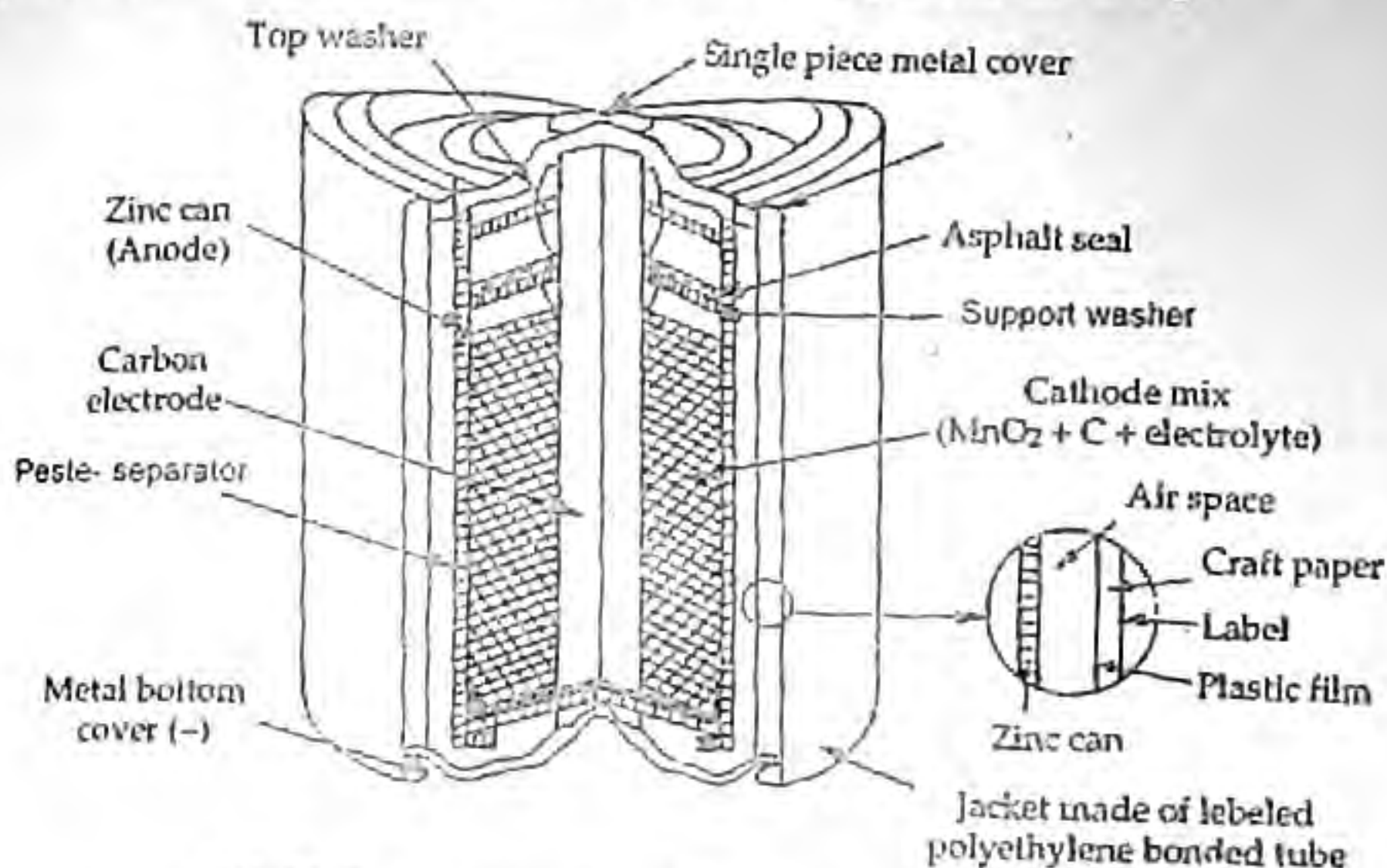
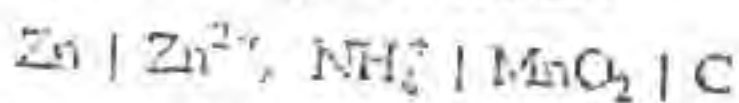
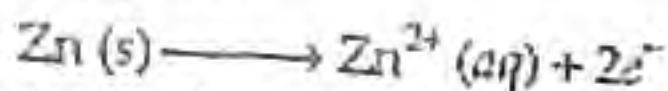


Fig. 11. Cutaway view of a typical pasted cylindrical dry cell.

The Zn -  $\text{MnO}_2$  (or dry) cell is represented as :



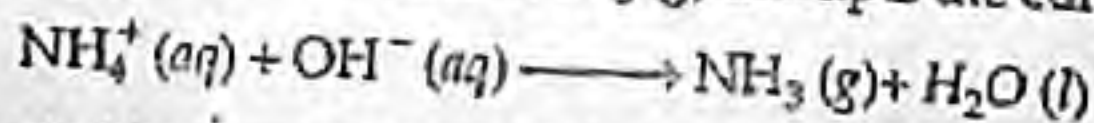
The oxidation reaction at anode is



The reduction reaction at cathode is

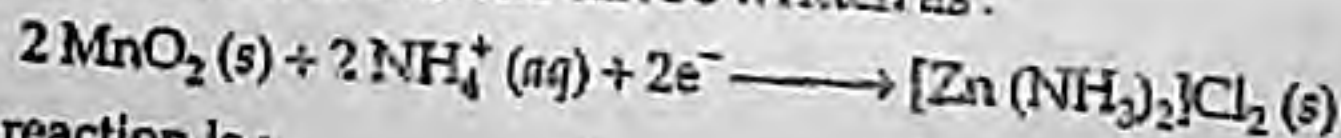


But, an reaction between  $\text{OH}^-$  thus formed at cathode and  $\text{NH}_4^+$  (derived from  $\text{NH}_4\text{Cl}$ ) evolves  $\text{NH}_3 (g)$ . This liberated  $\text{NH}_3 (g)$  disrupts the current flow.

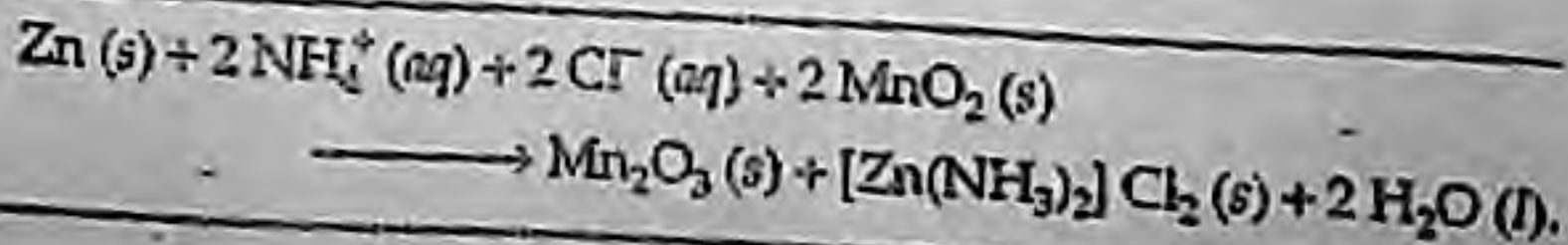


This is prevented by a reaction of  $\text{NH}_3 (g)$  with  $\text{Zn}^{2+}$  (from  $\text{ZnCl}_2$ ) to form the complex  $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2 (s)$ .

Thus, the reaction at cathode can be written as :



∴, the net reaction is ;



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

*Advantages :*

- (i) Low price, because cheap to make.
- (ii) Gives voltage of about 1.5 V.

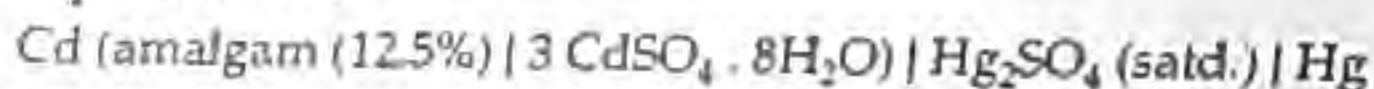
*Disadvantages :*

- (i) If current is rapidly drawn from it, products build up on the electrodes thereby causing drop in voltage.
- (ii) The cell run down slowly, even if it is not in use. (This is due to the fact that electrolytic medium is acidic so that Zn metal slowly dissolves).

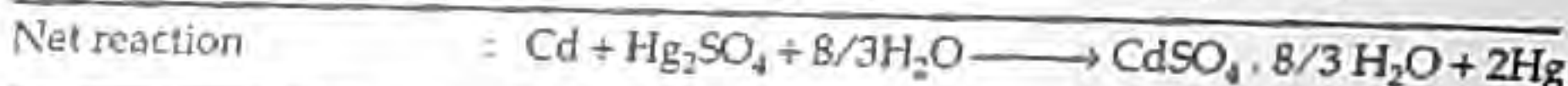
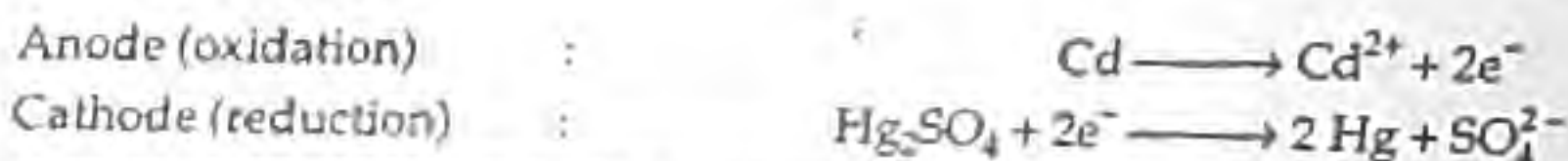
*Uses :* It finds uses in calculators, transistor radios, flash-lights etc. (i.e., the small (but not miniature) portable power sources).

### 17.2 The Weston-Cadmium Cell

- (i) It is also a primary cell.
- (ii) It is represented as :



Reactions at



The emf of the cell is 1.0183 volts.

### 17.3 The Lead-Acid Storage Cell

A storage cell can operate both as a voltaic cell and as an electrical cell. It has the ability to work both ways, to receive electrical energy and also to supply it. When it operates as a *voltaic cell*, it supplies electrical energy and as a result it eventually becomes 'run-down'. It then needs to be recharged. When being recharged, the cell operates as an *electrolytic cell*.

*Lead-acid storage cell* is the common example of storage cell. It is so classified because the electrolyte is an acid and the plates are largely leads. It consists of a lead-antimony alloy coated with lead dioxide as cathode and spongy lead as anode. The electrolyte is a 20% solution of  $\text{H}_2\text{SO}_4$  (specific gravity 1.15 at

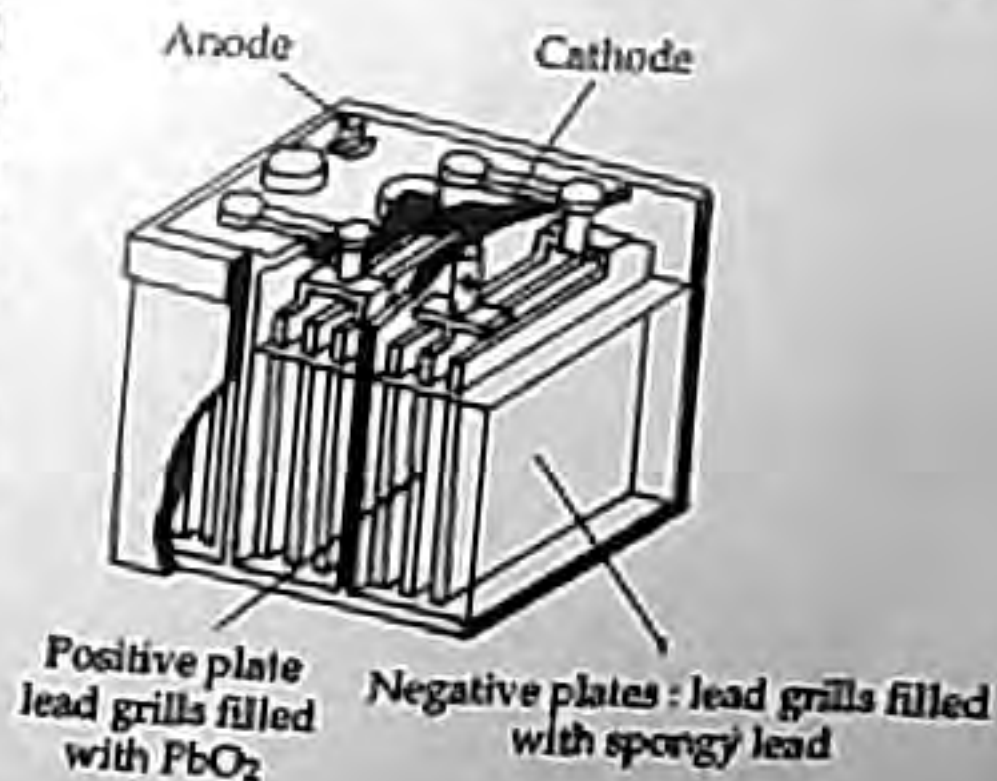


Fig. 12. A lead accumulator for car consists of six lead-acid storage cells in series and it is capable of delivering 12 V.



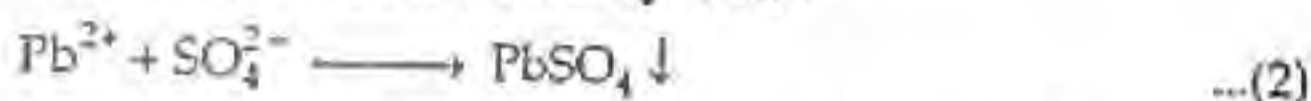
25°C). In fact, a lead accumulator for car consists of six lead-acid storage cells in series *i.e.*, in electrolyte ( $\text{H}_2\text{SO}_4$ ), six electrode pairs, with inert porous partitions in between, are dipped.

**Discharging.** When the lead accumulator is used for supplying electrical energy, it is said to be discharging. The lead electrode loses electrons, which flow through the wire.

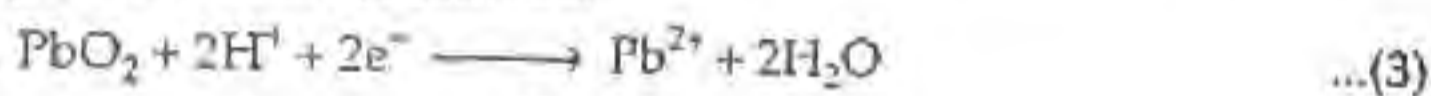
*i.e.*, at anode, oxidation takes place



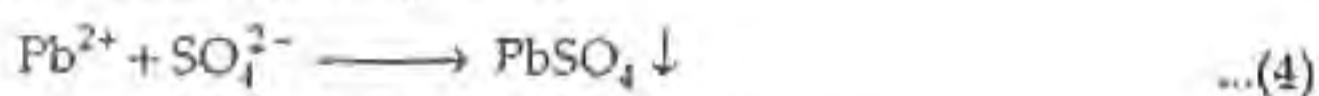
The so formed  $\text{Pb}^{2+}$  ions then combine with  $\text{SO}_4^{2-}$  ions.



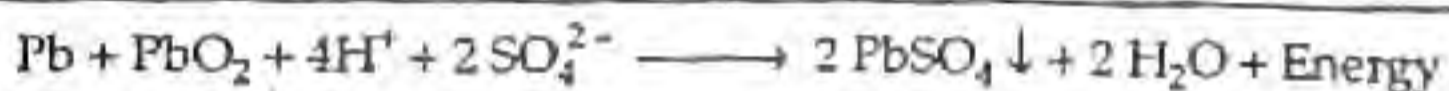
The released electrons flow to the cathode, where  $\text{PbO}_2$  forms  $\text{Pb}^{2+}$ . In other words, lead undergoes reduction at cathode.



The  $\text{Pb}^{2+}$  ions then combine with  $\text{SO}_4^{2-}$  ions.



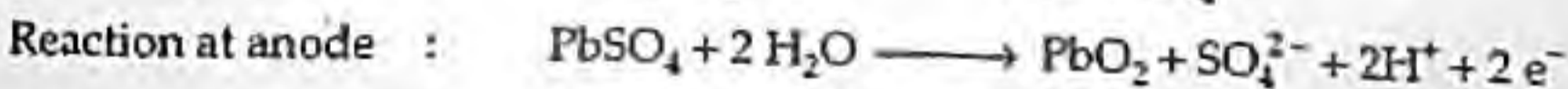
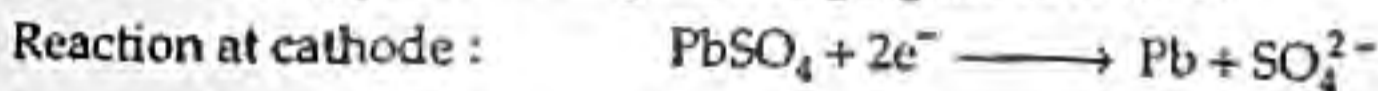
Thus, the net reaction during use (or discharging) is :



The voltage of each cell is about 2.0 volts at a concentration of 21.4%  $\text{H}_2\text{SO}_4$  at 25°C. That's why, a lead accumulator for car (consisting of six lead-acid storage cells in series) is capable of delivering 12 volts.

**Charging.** During the discharging,  $\text{PbSO}_4$  is precipitated at both the electrodes. When  $\text{PbSO}_4$  covers completely both anode and cathode, the cell stops functioning as a voltaic cell. For further use, it needs to be re-charged.

Recharging is done by passing an external e.m.f. greater than 2 volts so that the reactions taking place during discharging are reversed.



$\therefore$  Net reaction during charging is :



Obviously, during the charging cycle, the cell electrodes are restored to their original conditions (*i.e.*, Pb and  $\text{PbO}_2$  respectively.)

Generally, overcharging does not cause any damage because continued electrolysis liberates  $\text{H}_2$  and  $\text{O}_2$  at the electrodes. But excessive charging may reduce the acid level and may damage the exposed electrodes. It sometimes results in a high pressure build up due to gas evolution and might lead to explosion. Now a days, a catalyst is incorporated which enables the combination of  $\text{H}_2$  and  $\text{O}_2$  into water thus minimizing a high pressure build up.



As is apparent from the net reactions for discharging and charging, concentration of  $H_2SO_4$  decreases during discharging and the conc. of  $H_2SO_4$  increases during charging operation. As the electrochemical reaction during charge consumes  $H_2SO_4$ , the extent to which the battery has been discharged can be checked by measuring the density of  $H_2SO_4$  in it with a hydrometer.

With  $1^\circ C$  decrease in temperature, there is a decrease of  $1.5 \times 10^{-4} V$  in emf of lead storage battery. In hilly areas, in cold weather, suppose the temperature falls to  $-10^\circ C$ . For this  $40^\circ C$  fall in temperature (from  $30^\circ C$  to  $-10^\circ C$ ), the decrease in voltage is  $6 \times 10^{-3} V$ . This is only about 0.05% of operating voltage (12 V) of lead acid storage cell. But the peoples living in cold climates sometimes have trouble starting their cars. The real cause of apparent breakdown of battery is an increase in the viscosity of the fluid as the temperature decreases. Consequently, an apparently 'dead battery' recovers its ability to deliver normal power, if it is warmed up to room temperature.

Generally cell containers are made of hard rubber and plastic. For Railway automobile and motive power batteries the cell containers are made of highly shock resistant materials such as semi hard rubber, modified PS or PP. Stationary batteries use jars made of clear modified PS. For submarine service which requires extreme shock resistance, rubber-lined polyester fiber-glass jars are used.

#### *Applications of lead acid storage cells*

These cells are used for supplying current to electrical vehicles, railway mines, laboratories, hospitals, automobiles, power stations, broadcasting stations in telephone exchanges, gas engine ignition, automobiles, stand-by supplies (UPS) etc.

#### **Gel Lead Accumulator Battery**

In these gel batteries, sulphuric acid and other electrolytes are converted into a gel by suitably mixing the acid with sodium silicate. This gel is then carefully introduced into a modified polypropylene or polystyrene container in such a way that there are no air bubbles.

These gel batteries need less maintenance. They have no problems of acid spillage and other hazards encountered in lead-acid storage batteries.

These gel batteries are specially used in motor cycles and air crafts.

#### **The Performance Requirement of Lead-Acid Batteries**

Application	Requirements
(i) Industrial and military applications	High reliability, Long life (more than 600 times cycle life), Efficiency (more than 60%), Voltage of 90 - 400 V with a capacity of 10 - 20 kAh.
(ii) In motor cars for starting	A high-pulse (typically 400 - 450 A for 30 seconds without the voltage dropping below 7.2 V) to permit engine starting, High cycle life, Ability to provide 25 A for 3 hours without the voltage dropping below 10.5 V and A capacity of 100 A h.



(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  $1500^{\circ}\text{C}$ ) an intimate and properly proportioned mixture of clay and lime containing raw materials. After calcination, retarder like gypsum is added.

It is discussed in detail in the following sections.

## 3 PORTLAND CEMENT

Portland cement is also known as "magic powder". It consists primarily of compounds of lime, silica, alumina and iron. It forms a paste when mixed with water. This paste subsequently hardens and binds the aggregates (crushed rock, sand, gravel, etc.) together to form a hard durable mass called concrete. Thus, cement is one ingredient of concrete.

William Aspdin is generally recognized as the father of the modern portland cement industry. Because in 1824, he produced an improved cement by heating a mixture of limestone and clay and crushing the resulting product to a fine powder. The name portland cement was used because this powder, on mixing with water, set to give a hard, stone-like mass which resembled stone quarried on the Isle of Portland, England.

Portland cement is a type of cement, not a brand name. Each cement manufacturer makes portland cement. All portland cements are *hydraulic cements* because they set and harden under water.

### 3.1 Manufacture of Portland Cement

*Raw Materials*. Raw materials required for the manufacture of Portland cement may be divided into those supplying



(a) The lime (CaO) component (i.e. calcareous materials such as Aragonite, Calcite, Marl, Shale and limestone); (b) The silica (SiO<sub>2</sub>) component (i.e., siliceous materials such as clay, marl, shale and sand); (c) The alumina (Al<sub>2</sub>O<sub>3</sub>) component (i.e., Argillaceous materials such as alumina-ore refuse, caly, fly ash and shale); (d) The iron (Fe<sub>2</sub>O<sub>3</sub>) component (i.e. Ferriferous materials such as clay, iron ore, mill scale etc.)

**Manufacturing process.** The manufacture of portland cement involves the use of skills of engineers, chemists and technicians to ensure a uniform product. The actual manufacturing involves the following operations:

(i) **Crushing.** It is done in primary crusher (which reduces the size of limestone to an approximately 5-in) and in secondary crusher (it further reduces the size to 3/4-in).

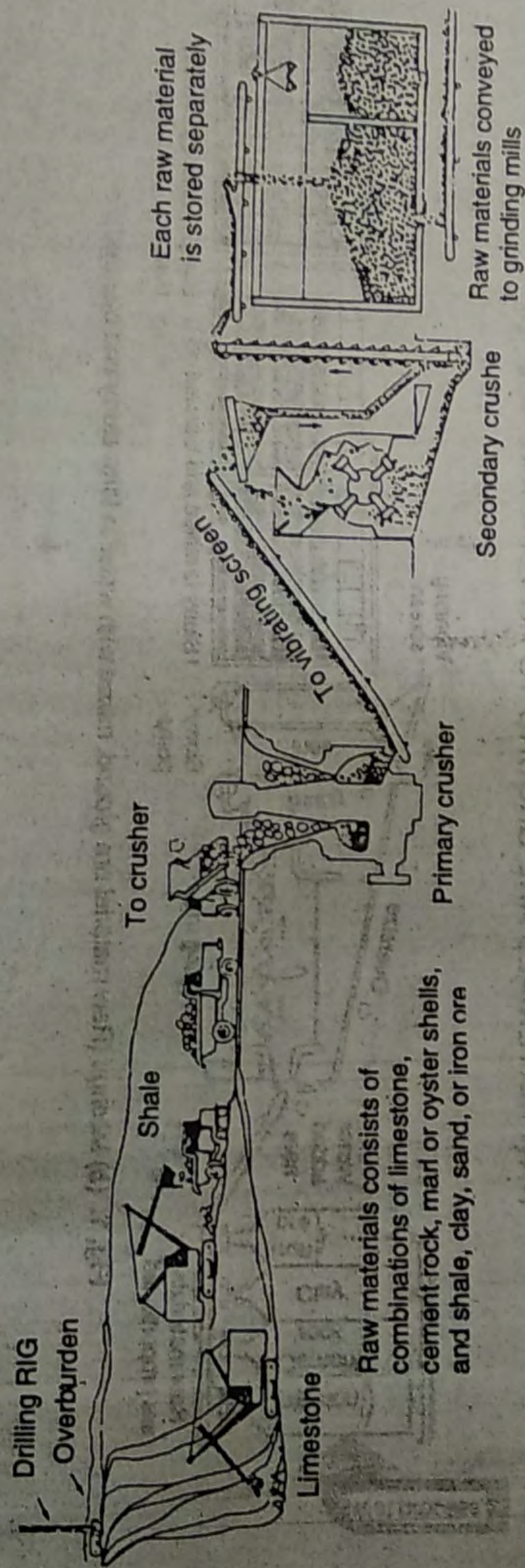
(ii) **Mixing.** It begins with the acquisition of raw materials such as limestone, sand and clay. These are mixed either by the dry process or by the wet process. The raw materials which are stored in the bins are first proportioned and then delivered to the grinding mill. The *dry process* produces a fine ground powder. It is stored in bins. The *wet process* (in the presence of water) results in a slurry, which is mixed and pumped to storage basins.

(iii) **Burning.** Both dry and wet processes feed rotary kilns where burning results in actual chemical changes. The rotary kiln is a long steel cylinder with length 30-160 metres and diameter 2-4 metres. Its inside surface is lined with fire brick refractory. It is slightly inclined downwards towards the exist end. It can be rotated at desired speeds 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 (using solid, liquid or gaseous fuel) 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 reactions take place. In fact, there are different zones in the rotary kiln, viz.

Table 1. Pros and Cons of dry and wet Processes

Dry Process	Wet Process
1. It is a slow and costly process.	It is comparatively faster and cheaper process.
2. Cost of production of cement is less, as the fuel consumption is low. Shorter kiln is sufficient.	Cost of production is somewhat higher because of the higher fuel consumption. As longer kiln is needed to drive off the excess water.
3. The quality of cement produced is inferior.	The quality of cement produced is somewhat superior, as more accurate control of composition can be attained.
4. This process is adopted when the raw materials are quite hard.	This process is preferred when the raw materials are soft.
5. This process is not suitable when the principal raw material has an inherent moisture content of 15% or more, as it is uneconomical to drive away the excessive quantity of moisture.	This process has to be adopted in this case.





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Fig. 1. (a) Crushing : stone is first reduced to 5-in. size, then 3/4-in, and stored.



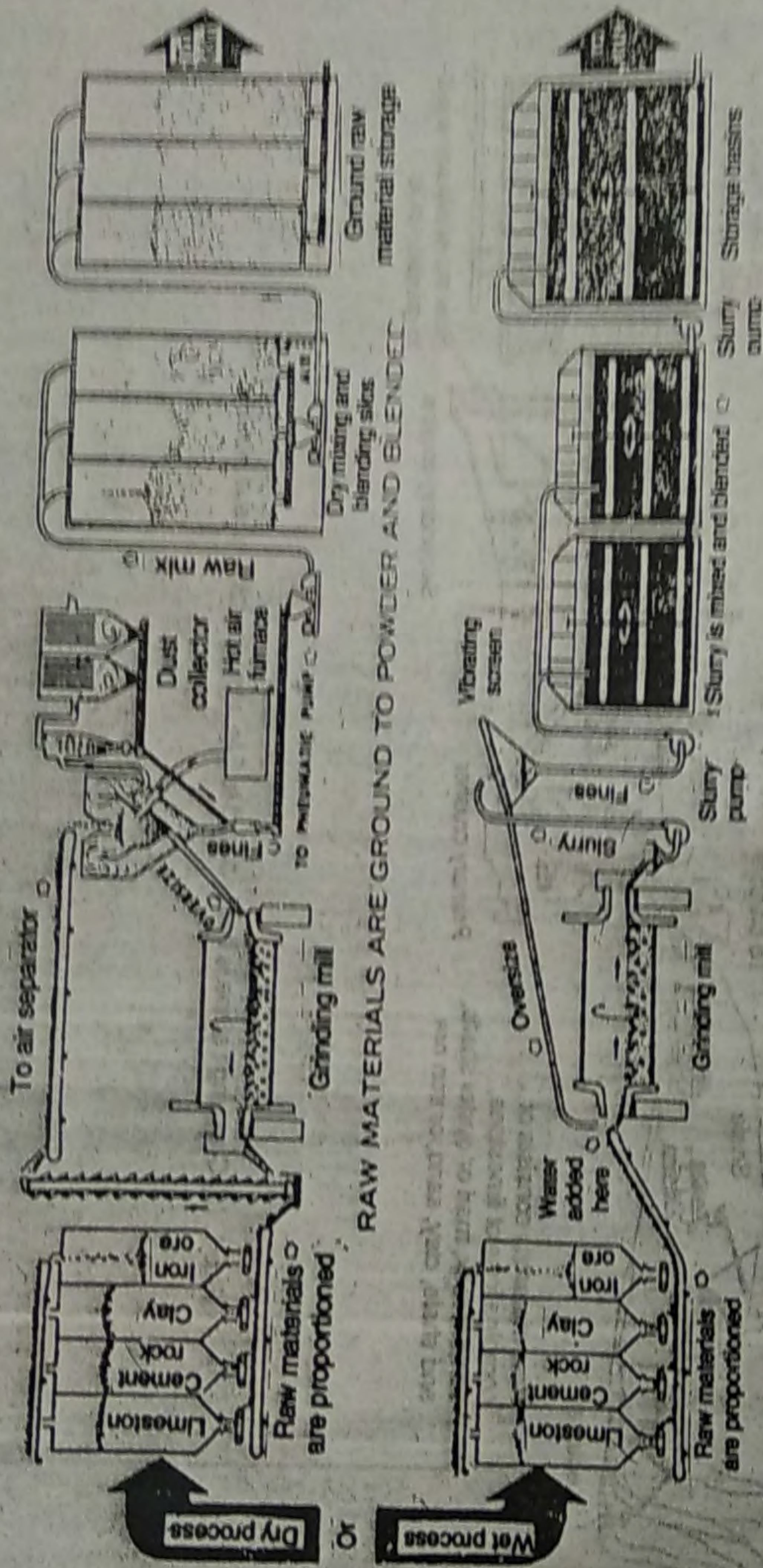


Fig. 1. (b) Mixing : (Raw material are ground, mixed with water to form slurry and blended).



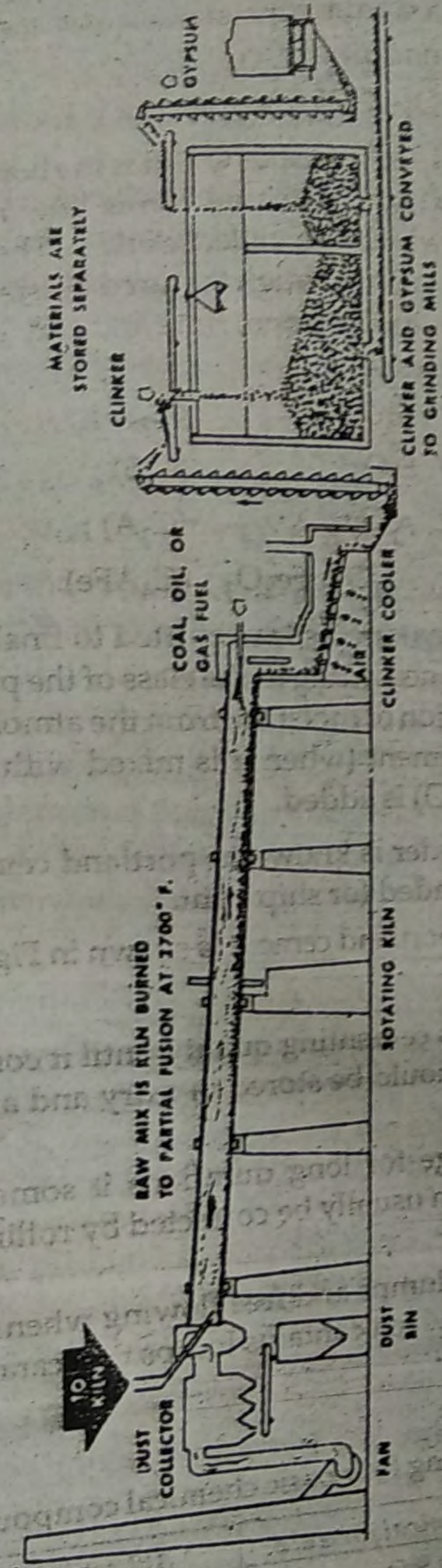


Fig. 1. (c) Burning: Burning changes raw mix chemically into cement clinker.

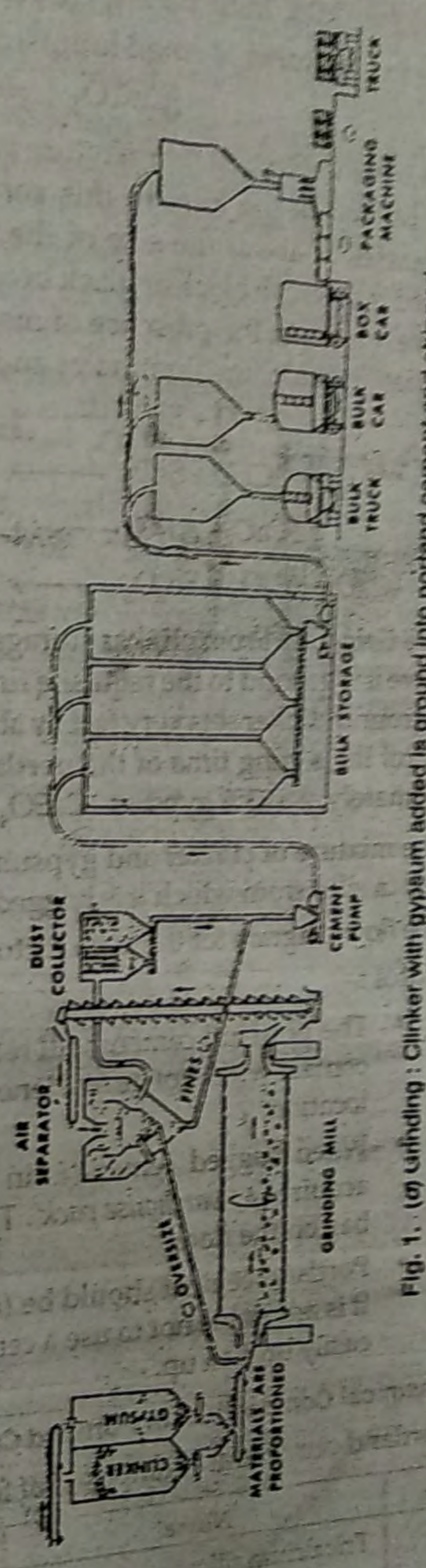
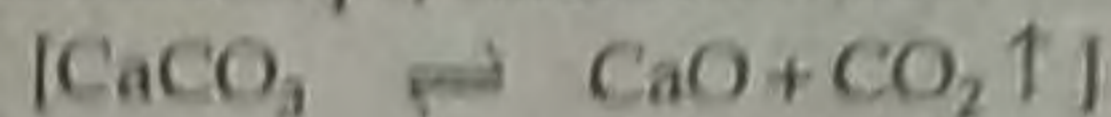


Fig. 1. (a) Grinding: Clinker with gypsum added is ground into portland cement and shipped. Manufacture of portland cement.

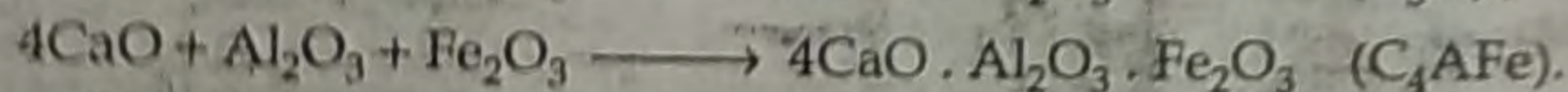
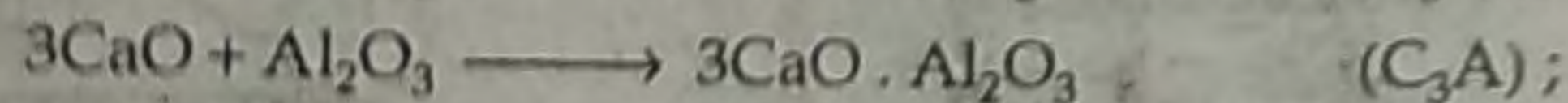
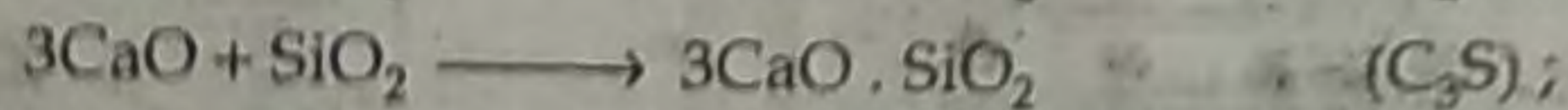
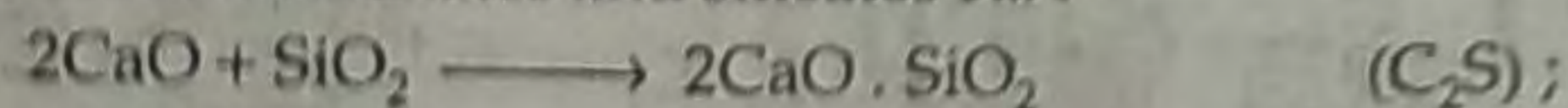


(a) *The drying zone.* Here the temperature is moderate (100-500 °C) and this zone is located at upper one-fourth of the length of the kiln. This zone is known as drying zone, because the moisture is driven out and the materials get heated.

(b) *Calcination zone.* Its temperature is about 1000 °C and it is the middle portion of the kiln. In this zone, CO<sub>2</sub> is expelled from lime-stone, quick-lime (CaO) is formed in the form of small lumps, called nodules.



(c) *Burning Zone.* Its temperature is about 1400 - 1500 °C and is the bottom and hottest portion of the 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 colour and has rough textured. Its size makes it relatively inert in the presence of moisture. In this zone, lime and clay undergo fusion yielding calcium aluminates and silicates *via* :



(iv) *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 clinker sets very fast by absorption of moisture from the atmosphere. To control the setting time of the portland cement (when it is mixed with water) approximately, 2 to 3% gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) is added.

The mixture of clinker and gypsum powder is known as portland cement. It is stored in silos from which it is bagged or loaded for shipment.

The flow diagram for the manufacture of portland cement is shown in Fig. 2.

#### Notes :

- The portland cement will retain its cementing quality until it comes in contact with moisture. Hence, it should be stored in a dry and airtight location.
- When bagged cement is in storage for long durations it sometimes acquires a 'warehouse pack'. This can usually be corrected by rolling the bag on the floor.
- Portland cement should be free of lumps and free flowing when used. It is advisable not to use a cement which contains lumps that cannot be easily broken up.

### 3.2 Chemical Composition of Portland Cement

Portland cements are composed of following four basic chemical compounds :

S. No.	Name	Chemical formula	Abbreviation
1.	Tricalcium silicate	3 CaO SiO <sub>2</sub>	C <sub>3</sub> S
2.	Dicalcium silicate	2 CaO SiO <sub>2</sub>	C <sub>2</sub> S
3.	Tricalcium aluminate	3 CaO Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A
4.	Tetracalcium aluminoferrite	4 CaO Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AFe



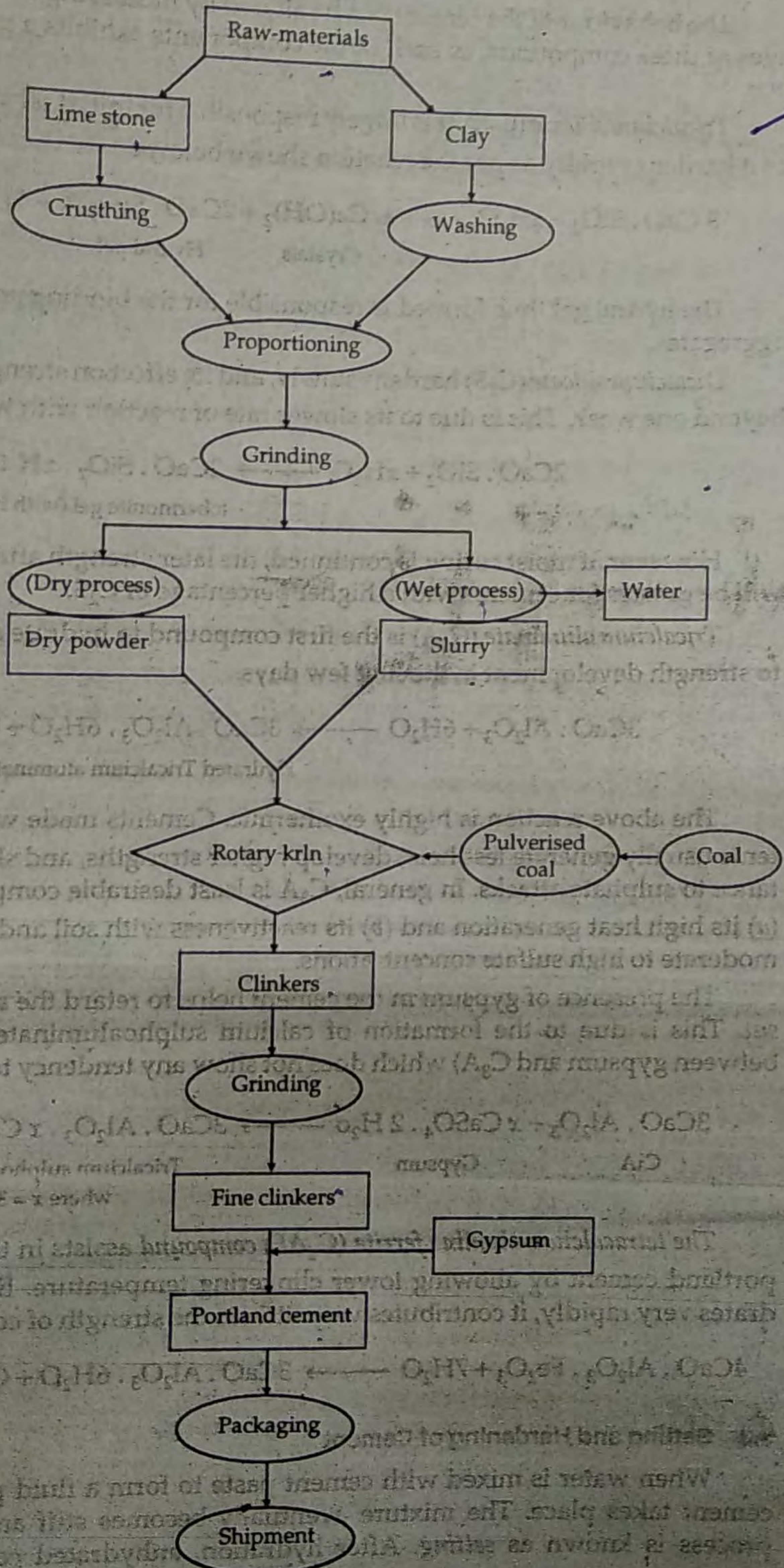


Fig. 2. Flow diagram for the manufacture of portland cement



## CEMENTS

The hardening process is very slow, it takes months or even years. In this process, a hard coherent mass is formed as the  $\text{CaCO}_3$  crystals interlock the sand particles. In the matrix of the set mortar, the dispersed sand minimizes the development and propagation of cracks by presenting the heterogeneous phase during the hardening process.

*Setting of hydraulic lime* is mainly caused by the decomposition of complex silicates of calcium and aluminium into simpler compounds such as silicate aluminate and hydroxide of calcium. This decomposition takes place in presence of water. The so formed simple compounds crystallise to form a hard mass in the interior; while calcium hydroxide  $\{\text{Ca}(\text{OH})_2\}$ , which is soluble in water, comes to the surface. There it crystallizes to form calcium carbonate, under the action of atmospheric carbon dioxide. Due to this fact, hydraulic limes can set and harden under water also. A free circulation of air is beneficial for hardening, since it provides necessary  $\text{CO}_2$  and also removes the water formed in the hardening reaction by evaporation.

## 5 PLASTER OF PARIS

It is formulated as hemihydrate of calcium sulphate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  (or  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and is believed to consist of a series of hydrates ranging from  $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to anhydrous  $\text{CaSO}_4$ .

The commercially available plaster of paris is a mixture of the hemihydrate of calcium sulphate ( $\text{CaSO}_4$ ) and some unchanged gypsum.

*Preparation.* It can be prepared from gypsum (hydrated calcium sulphate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) by following unit operations:

- (i) crushing and grinding of gypsum;
- (ii) calcination of ground gypsum in kilns by heating to about  $150^\circ\text{C}$ ; and
- (iii) pulverizing the calcined product.

### Setting and hardening

Plaster of Paris forms a plastic mass when it is mixed with water. This plastic mass quickly sets or hardens. During this process, it slightly expands and regains the closely-packed crystalline structure of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

Alums or alkali sulphates ( $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  etc.) can initiate as well as hasten the crystallization process. Hence, they are used for accelerating the setting of plaster of paris.

### Applications of plaster of Paris

- (i) It is used for making moulds as it expands slightly on setting, details are thereby accurately reproduced.
- (ii) It is used in making surgical bandages, structural tiles and castings.
- (iii) It is also used for making plaster-board, which is made up of alternate layers of gypsum plaster and a fibrous material such as felt or paper.