CHAPTER 11

INORGANIC ENGINEERING MATERIALS

"Inorganic engineering materials play vital roles in civil and mechanical engineering fields, where very specific requirements are needed."

1 ABRASIVES

Abrasives *are the substances characterized by their hardness, and which are used to wear down softer surfaces by cutting, grinding or polishing".* For example, the housewife uses abrasive stone to keep her kitchen knives sharp ; the dentist uses an abrasive powder, when he cleans teeth, and tiny abrasive wheels to smooth down fillings. In industry, abrasives play important roles. Wood is ground into paper pulp, stone is cut, carved and surfaced, and cutting-tools sharpened on abrasives. The mass production of *interchangeable machine parts*, which not differ from each other by more than a fraction of a thousandth of a cm, is made possible by the use of precision grinding wheels.

Hardness of an abrasive is most important quality and is measured roughly on **Moh's** or **Vicker's scale.** Common abrasives (natural and artificial) in order of increasing hardness are : *talc*–1 ; *gypsum* (or NaCl)–2 ; *calcite* (or Cu)–3 ; *fluorite*–4 ; *apatite*–5 ; *feldspar*–6 ; *quartz*–7 ; *topaz* (or emery)–8 ; *corundum*–9 ; *diamond*–10. Artificial abrasives are, generally, *superior in uniormity* than natural abrasives and consequently, they are preferred to natural abrasives in industrial grinding, etc.

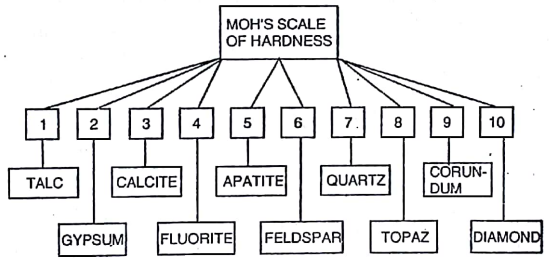

Fig. 1. Moh's scale of hardness.

2 NATURAL ABRASIVES

1. **Diamond,** which is crystallized carbon, *ranks first in hardness,* since it can cut into the surface of any other substance ; whereas only *another diamond can scratch a diamond.* It is chemically inactive and not attacked by acids, alkalis or fused potassium chlorate. *Diamonds that are off-colour or are otherwise faulty, are called* **borts.** The black diamond from Brazil, is called *carbanado* and has no value for jewellery. Borts and carbanado are used in drill-points, as saw-teeth for cutting rocks, stones or grinding wheels, dressers, and in operations, where *great hardness* is required.

2. **Corundum,** which is *crystallized aluminium oxide* (Al_2O_3), comes *next* to diamond in hardness. Corundum, which is not of gem quality, finds use as abrasives for grinding glasses, gems, lenses, metals, and metal-cutting.

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3. **Emery** *is fine-grained, opaque, massive mineral, dark-grey to black in colour.* It is found chiefly in Greek. *It is an aggregate of 55 to 75 percent crystalline alumina, 20 to 40 percent magnetite* (Fe_3O_4), *and about 12 percent other minerals, of which the chief is tourmaline.* Its hardness is about *8 on Moh's scale.* The grinding power of emery depends almost entirely *on the proportion of alumina it contains,* and on the effect of the other ingredients in determining true hardness of this mineral. Emery is used as tips of bits of cutting, and drilling tools, etc. Artificial emery (used for buffing and polishing) is a graded combination of alumina and magnetite.

4. **Garnets** *are trisilicates of alumina, magnesia and ferrous oxide.* The common garnet used as an abrasive is a complex calcium-aluminium- iron silicates with the approximate formula : $Ca_3Al_2(SiO_4)_3$. $Ca_3Fe_2(SiO_4)_3$. $Fe_3Al_2(SiO_4)_3$ Hardness of garnets ranges from *6 to 7.5 on Moh's scale.* Garnets are *too soft for grinding steel and iron,* but when glued to paper or cloth, they are used for *finishing hard woods.* They are also used for bearing pivots in watches, glass-grinding, and polishing metals.

5. **Quartz** *is composed of silica* (SiO_2). An impure grey, sometimes hydrated form of quartz, is the abrasive *flint* that is used on good quality *sand-paper.* It is almost a hard as garnet. Grinding and other sharpening stones are cut from *sandstone.* This rock consists of *quartz particles cemented together with feldspars, clays, carbonates and other minerals.* It is used for grinding floor, pigments, ores, etc.

3 ARTIFICIAL ABRASIVES

1. **Carborundum** or **silicon carbide** (SiC) is a bluish-black crystalline artificial mineral with hardness between corundum and diamond. *It is made by subjecting a mixture of silica and carbon (coke or coal) to high temperature (1,650–2,200°C) in an electric furnace.*

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO\uparrow$$

It is very hard (*Moh's scale = 9.3*), chemically unreactive, can withstand the action of high temperature without damage, but is not tough and is somewhat brittle. It is mainly used in cutting-wheels, abrasive papers, and clothes. It is extensively used for *grinding of materials of low tensile-strengths* like cast iron, brass, bronze, porcelain, marble, finishing of leather, glass and optical grinding of lenses.

2. **Alundum** (Al_2O_3) *is prepared by subjecting a mixture of calcined bauxite, coke, and iron to high-temeperature (about 4,000°C) in an electric arc furnace.* The iron, titanium, and silica impurities settle to the bottom of the furnace and after solidification, the hard crystalline alumina is separated, crushed, and graded. It is sold under a number of trade names, including *aloxite.* Alundum (or *artificial corundum*) is not as hard as carborundum, but is also less brittle, and tougher. It is, therefore, used in preference to carborundum, for grinding hard steels and other material of high tensile-strengths. On an abrasive paper and cloth, it is used for finishing woodworks.

3. **Boron carbide** or **norbide** (B_4C) *is inert and one of the hardest (about 9 Moh's) of all artificial abrasives, and made by heating boron oxide with coke in an electric furnace to approximately 2,700°C*

$$2\,B_2O_3 + 7\,C \longrightarrow B_4C + 6\,CO\uparrow$$

It is used on hard materials for making grinding dies, and for cutting and sharpening hard high-speed tools.

4 REFRACTORIES

Broadly speaking, *refractory is any material that can withstand high temperatures, without softening or suffering a deformation in shape.* Refractories are the essential materials of construction in metallurgy, engineering and chemical industries and without their use, it is impossible to maintain required high temperatures. The main objective of a refractory is to *confine heat* (*i.e.*, to resist loss of heat) and at the sametime to *resist the abrasive and corrosive action of molten metals, slags and gases* at high operating temperatures, without undergoing softening or distortion in shape.

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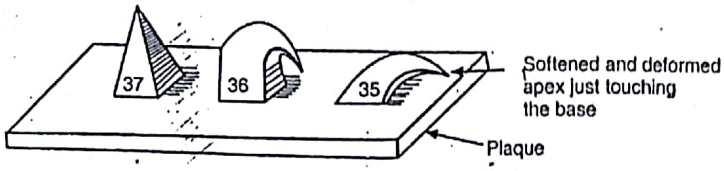

Fig. 2. Seger cone-test.

Table 1 : *Seger-cone number and fusion temperature.*

Seger-cone number	*Temperature °C*	*Seger-cone number*	*Temperature °C*	*Seger-cone number*	*Temperature °C*
1	1,110	12	1,350	27	1,610
2	1,120	13	1,380	28	1,630
3	1,140	14	1,410	29	1,650
4	1,160	15	1,435	30	1,670
5	1,180	16	1,460	31	1,690
6	1,200	17	1,480	32	1,710
7	1,230	18	1,500	33	1,730
8	1,250	19	1,520	34	1,760
9	1,280	20	1,530	35	1,770
10	1,300	23	1,550	36	1,790
11	1,320	26	1,580	37	1,825
				38	1,850

(2) **Strength or refractiorines-under-load :** Refractories in use, in industrial furnaces, have invariably to withstand varying loads of the products, being manufactured at high operating temperatures. *It is, therefore, essential that refractory materials must also possess high mechanical strengths, even at operating temperatures, to bear the maximum possible load, without breaking.* Some refractories, like fireclay and high-alumina bricks, soften gradually over a range of temperature, but under appreciable load, they collapse, far below their true fusion point, as determined by Seger cones. On the other hand, other refractories like silica bricks soften over a relatively narrow range of temperature and exert good load-bearing characteristics close to their fusion points.

R.U.L. test *is performed by applying a constant load (of 3.5 or 1.75 kg/cm^2) to the refractory specimen (of size 5 cm^2 and 75 cm high) and heating in a carbon-resistance furnace at a standard rate (of 10°C/minute).* The record of the height of the specimen *vs.* temperature is made by a plot, until the test-piece deforms or collapses by 10%. The R.U.L. is expressed as the temperature at which 10% deformation takes place. Under a load of 3.5 kg/cm^2 : (*i*) ***a high heat-duty brick should not deform a great deal (i.e., more than 10%) at 1,350°C*** ; (*ii*) ***an intermediate heat-duty brick at 1,300°C*** and (*iii*) ***a moderate heat-duty brick at 1,100°C.*** Most of the applications of refractories find use only under *compressive* load ; and in rare cases, they may be subjected to tension or shear alone.

(3) **Dimensional stability** *is the resistance of a material to any volume changes, which may occur on its exposure to high temperature; over a prolonged time.* These dimensional changes may be *permanent (irreversible)* or *reversible.*

Irreversible changes *may result either in the* ***contraction*** *or* ***expansion*** *of a refractory. The* ***permanent contraction*** *is due to the formation of increasing amounts of liquid from the low fusible constituent of the refractory brick, when it is subjected to a long period of soaking at the high temperature.*

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Uses :

Refractories are mostly used for the construction of the linings of the furnaces, ba converters, kilns, crucibles, ladles, etc., employed for the manufacture of metals (ferrous as well non-ferrous), cement, glass, ceramics, paper, steel, etc.

Characteristics : A good refractory possesses the following characteristics : It should : (1) be *infusible* at the temperature to which it is liable to be exposed ; (2) be *chemically inerts* towards corrosive action of gases, metallic liquids and slags, produced in its immediate contact in furnaces ; (3) *resist the abrading action* of flue gases, flames, etc. ; (4) be able to *withstand the overlying load* of structure, at operating temperatures ; (5) *not crack and suffer loss in size*, at the operating temperatures ; (6) *expand and contract uniformly*, with temperature rise and fall respectively.

Classification of refractories : Refractories are classified into *three* main types, on basis of the *chemical properties* of their constituent substances ;

1. **Acid refractories** are those which consist of *acidic materials* like alumina (Al_2O_3) and silica (SiO_2). *They are not attacked by acidic materials, but easily attacked by basic materials.* Important members of this group are *alumina, silica* and *fireclay* refractories. examples

2. **Basic refractories** are those which consist of *basic materials* like CaO, MgO, etc. *These are not attacked by basic materials, but easily attacked by acidic materials.* Important members of this group are *magnesite* and *dolomite* refractories. examples

3. **Neutral refractories** are made from *weakly acid/basic materials* like carbon, chromite ($FeO . Cr_2O_3$), zirconia (ZrO_2), etc. Important members of this group are *graphite, chromite, zirconia,* and *carborundum* (SiC) refractories. examples

5 PROPERTIES OF REFRACTORIES

More important *characteristics* of refractories are :

(1) **Refractoriness** *is the ability of a material to withstand the heat, without appreciable deformation or softening under particular service conditions.* Refractoriness is, generally, measured as the *softening or melting temperature* of the material. As most of the common refractory materials are mixtures of several metallic oxides, so they *do not have a sharp fusion temperatures.* It is common practice to determine *softening temperature,* rather than fusion temperature. The softening temperatures of refractory materials are, generally, determined by using "**pyrometric cones** (also called *Seger cones*) test". *It is necessary that a material, to be used as refractory, should have a softening temperature much higher than the operating temperature of the furnace in which it is to be used.* It is, however, notworthy that the inner refractory lining in a furnace is at a much higher temperature than the outer ones. So, unless the refractory melts away completely, it can, usually, be employed to withstand a temperature higher than its softening temperature, since the outer end of refractory is at a lower temperature and still in solid state and it provides requisite strength.

Measurement : Refractoriness is, usually, determined by comparing the behaviour of heat on *cone of material to be tested* with that of a series of *Seger cones* of standard dimensions. The refractoriness is expressed in terms of *Pyrometric cone equivalent* (PCE). These cones are small pyramid-shaped, 38 mm high and have a triangular base, with 19 mm long sides. They melt or fuse at definite temperatures, when heated under standard condition of 10°C per minute. The temperature at which the fusion or softening of the test-cone occurs is indicated by its *apex touching the base* (*see* Fig. 1). The PCE value of the given refractory is taken as the number of the standard cone, *which fuses alongwith* the test-cone. If the test cone softens earlier than one standard cone, but latter than the next cone, the PCE value of the test sample is approximately measured as the average value of the two.

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(8) **Thermal spalling** *is breaking, cracking, peeling off or fracturing of a refractory brick or block, under high temperature*. So a good refractory must show a *good resistance to thermal spalling*. Spalling is, generally, due to *rapid changes in temperature*, which cause uneven expansion and contraction within the mass of refractory, thereby leading to development of internal stresses and strains. Spalling may also be due to *slag penetration* into the refractory brick, thereby causing *variation in the coefficient of expansion*. It has been found that ***spalling can be decreased by*** : (*a*) *using high porosity, low coefficient of expansion and good thermal conductivity refractory bricks*, since all these resist the development of internal stresses ; (*b*) *avoiding sudden temperature changes* ; (*c*) *by overfiring the refractories* (during manufacture) at high temperatures for a sufficiently long time, whereby *mineral inversion*, etc., takes place, making the material less susceptible to uneven expansion or contraction, when heated ; (*d*) *by modifying the furnace design* so that stresses are not set up, when the furnace is heated.

(9) **Resistance to abrasion or erosion :** *For a refractory to last longer, it is desirable that it is least abraded by descending hard charge, flue gases escaping at high speeds, particles of carbon or grit, etc.*, Resistance to erosion is very important for such constructions as by-product coke-oven walls, and linings of the discharge-ends of rotary cement kilns, etc.

(10) **Electrical conductivity :** Refractories to be used for lining *electric* furnaces should have *low electrical conductivity*. Except *graphite*, all other refractories are poor conductors of electricity. *However, electrical resistance of refractories decreases rapidly with temperature rise.*

(11) **Heat capacity** of furnace depends on : (*a*) *thermal conductivity* ; (*b*) *specific heat*, and (*c*) *specific gravity of refractory. In case of intermittently-operated furnaces, light-weight brickwork has an advantage*, since the working temperature can be achieved *in less time with less fuel*. Conversely, *the dense and heavy fire-bricks would be best* for regenerators, checker-works as in coke ovens, glass furnaces, and stoves for blast furnaces.

(12) **Texture :** *Coarse or light-textured bricks, because of their large porosity, are light in weight and hence, they are more resistant to sudden changes in temperatures*. However, their *crushing strength is low*. Such bricks are *more susceptible to the action of abrasion and corrosion*. On the other hand, *fine or dense-textured bricks* possess low porosity and hence, are heavier in weight. These are not so resistant to sudden changes in temperature. However, such bricks are less susceptible to action of abrasion and corrosion.

(13) **Permeability** *is a measure of rate of diffusion of gases, liquids and molten solids through a refractory*, Permeability depends upon the *size* and *number of connected pores*. With the rise of temperature, the permeability increases, since the viscosity of molten metals decreases with an increase of temperature. An increase in *bulk-density* (*i.e.*, ratio of weight to its volume) of a refractory increases the resistance to slag-penetration and spalling.

Conditions leading to failure of a refractory material : (*i*) Using a refractory of refractoriness *less* that of the operating temperature. (*ii*) Using *lower-duty* refractory bricks in a furnace than the actual load of raw materials and products. (*iii*) Using bricks of *higher* thermal expansion. (*iv*) *Rapid changes* in temperature of the furnace. (*v*) Using *heavy-weight* refractory bricks. (*vi*) Using refractory bricks which are *not properly fired*. (*vii*) Using bricks which *undergo considerable volume changes* during their use at high temperatures. (*viii*) Using *acidic/basic refractory* in a furnace in which *basic/acidic reactants* and/or products are being processed.

6 MANUFACTURE OF REFRACTORIES

Manufacture of refractories consists of the following *steps* :

1. Crushing : The raw materials in the form of big lumps are crushed to about 25 mm size.

2. Grinding : The crushed materials are ground, in suitable grinding machine, down to 200 mesh size.

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The liquid gradually fills the pores of the refractory body, causing a high degree of vitrification and sh
A typical example of such a behaviour as *fireclay brick*. The ***shrinkage*** of a refractory can a
caused by *the transformation of one crystalline form of material into another more dense form*. For exam
in a magnesite brick, amorphous MgO, which is relatively light (sp. gr = 3.05), is gradually converged
more dense crystalline form, periclase (sp. gr. = 3.54). With the increase in density, there is a natur
shrinkage of the material. On the other hand, *the transformation of quartz (sp. gr. = 2.65) in silica bricks*
to tridymite (sp. gr. = 2.26) and cristobalite (sp. gr. = 2.32) at high service temperature is accompanied by
a considerable increase in volume. This thus accounts for *permanent* expansion of silica bricks in service.

(4) Chemical inertness : A refractory should be selected that is *chemically inactive in use and does not easily form fusible products with slags, fuel ashes, furnace gases*, etc. Usually, the environment in most furnaces is either acidic or basic. *It is inadivisable to employ* ***an acid refractory in contact with an alkaline product or vice-versa.***

(5) Thermal expansion : In a furnace design, *allowance has to be made for thermal expansion, since practically all solids expand, when heated and contract, when cooled*. The expansion affects *all dimensions* (*i.e.*, length, area and volume) of a body. So, it is necessary that *a refractory material should have least possible thermal expansion*, because : (*i*) expansion of a refractory *decreases the capacity* of the furnace ; (*ii*) repeated expansion and contraction contribute much towards *rapid breakdown*, and wear and tear of the refractory material structure.

(6) Thermal conductivity : In industrial operations, refractory materials of both high thermal conductivity and low thermal conductivity are required, depending upon the type furnace. In most cases, furnace is lined with refractories of *low heat conductivities to reduce the heat losses to the outside by radiation* ; otherwise maintenance of high temperatures inside the furnace will become difficult. However, ***a good heat conductivity*** *of refractory is desirable for effective heat transmission in some furnace construction*, as in muffle-furnace walls, coke-oven batteries, in which *charge is separated from the flame*.

The densest and least porous brick have the ***highest*** *thermal conductivity, owing to the absence of air-voids*. On the other hand, *in* ***porous*** *bricks, the entrapped air in the pores, acts as a non-heat conducting material*. For making *porous* refractory bricks, the refractory material is mixed with a liberal amount of *carbonaceous* material, then moulded into bricks and burnt. The carbonaceous material burns off ; leaving behind *minute voids, which enhances the insulating quality*.

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

$$P = \frac{W - D}{W - A} \times 100 \quad \text{where} \quad \begin{cases} W = \text{Wt. of saturated specimen.} \\ D = \text{Wt. of dry specimen.} \\ A = \text{Wt. of saturated specimen submerged in water.} \end{cases}$$

Porosity is an important property of refractory bricks, because it affects many other characteristics, *e.g.*, chemical stability, strength, abrasion-resistance and thermal conductivity. In a *porous* refractory, molten charge, slags, gases, etc., are likely to *enter more easily* to a greater depth and may react and *reduce the life* of refractory material. *Porosity* ***decreases*** *the strength, resistance to abrasion, resistance to corrosion/penetration by slags, gases etc., but* ***increases*** *resistance to thermal spalling (i.e., thermal shock-resistance)*. Moreover, *the* ***densest and least porous*** *bricks have the* ***highest thermal conductivity***, owing to the absence of air-voids. In *porous bricks, the entrapped air in the pores, acts as a non-heat conducting material*. A good refractory, in general, should have *low porosity*.

[A good refractory should have low porosity]

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3. Screening : It is employed to *purify* the refractory raw materials. For producing better refractories, it is essential to remove the *unwanted materials* from the raw materials and this done by : (*i*) settling, (*ii*) magnetic separation, and (*iii*) chemical methods.

5. Storage : After screening and mineral dressing, the pure materials are stored in storage bins with bucket elevators.

6. Mixing : It is done so that proper distribution of the plastic materials throughout the mass takes place. *This makes moulding easier.*

7. Moulding : Moulding may be done either manually or mechanically by the application of high pressure. *Hand-moulding* produces refractories of low density and low strength ; while *mechanical-moulding* produces refractories of high density and strength. In order to increase the density and strength of refractory by mechanical-moulding, the *de-airing* of refractory material is essential. De-airing is done : (*i*) by applying *vacuum* through vents in the moulds ; (*ii*) by allowing *air* inside the void space in the refractory to go out by decreasing the rate of pressure application and release of air ; (*iii*) by *double-pressing* : The material is first pressed and allowed to crack. Then, it is repressed again so as to close the voids.

8. Drying : Drying is carried out to remove the moisture from refractories, Generally, drying is carried out *very slowly* and under well-set conditions of humidity and temperature, depending upon the types of refractory. Drying is, usually, carried out in *tunnel driers*. Rack cars of bricks are placed in a long tunnel and heat is supplied by steam, which passes through the tunnel.

9. Firing : The refractories are fired to stabilize and strengthen their structures. The bricks are, generally, *fired at a temperature as high as or higher than their use temperature*. Firing of bricks is done in *tunnel kilns* or *shaft kilns* or *rotary kilns*. The firing temperature of different bricks are : 1,480°C for high-fired super duty bricks ; 1,700°C for kaolin bricks, and 1,870°C for some basic bricks.

7 COMMON REFRACTORY BRICKS

(1) **Silica bricks** *contain 90 to 95% SiO_2 and about 2% lime is added during grinding to* ***furnish the bond.*** Basic raw materials used for their manufacture are quartz, quartzite, ganister, sand, sandstone, etc. For their manufacture, the siliceous rock is crushed and ground with 2% lime and water. The thick paste is then made into bricks either by *hand moulding* or by *machine-pressing*. The bricks are dried in air or in heated rooms and then, burnt in kilns. During heating, temperature is *slowly* raised, in about 24 hours, to about 1,500°C and this is maintained for nearly 12 hours, so as to allow *quartzite* to be converted into *cristobalite*. Then, cooling is done carefully and it takes about 1 to 2 weeks. *During cooling, cristobalise is slowly changed into tridymite, so that a mixture of tridymite and cristobalite results in the final bricks.*

Properties : Silica bricks are yellowish in colours with brown specks throughout the body and contains about 25% pores. Silica bricks *do not contract* in use, but they have a *permanent expansion* of about 15%, when reheated. This effect is *reversible* and the brick returns to its original size. when cooled. This expansion is caused by *reversible allotropic transformation :*

$$\underset{\substack{\text{(Crystalline)}\\ \text{Sp. gr} = 2.65}}{\text{Quartzite}} \rightleftharpoons \underset{\substack{(\alpha\text{–form of silica})\\ \text{Sp. gr} = 2.26}}{\text{Tridymite}} \overset{117°C}{\rightleftharpoons} \underset{\substack{(\beta\text{–form of silica})\\ \text{Sp. gr} = 2.32}}{\text{Cristobalite}}$$

Thus, if during firing of silica bricks, quartzite is *not* converted into tridymite and crystobalite, the bricks will *expand* to the extent of about 17.2%, during use in the furnace and, consequently, the refractory structure will *fall. That is why heating at 1,500°C for about 12 hours in necessary, during the making of silica bricks.*

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Silica bricks have homogeneous texture, free from air-pockets and moulding defects. They can withstand a load of about 3.5 kg/cm^2 upto about 1,500–1,600°C. They are thus remarkable for their load-bearing capacity, especially at high temperatures. They possess low permeability to gases and are not susceptible to thermal spalling at temperatures below 800°C. *These properties make silica bricks very satisfactory for places subjected to uniform high temperatures, but fails badly otherwise.* Silica bricks are relatively light (sp. gr. = 2.3 to 2.4) and possess high rigidity and mechanical strength.

Uses : The main applications of silica bricks are roofs of open-hearth furnaces, open-hearth steel making furnaces, coke-oven walls, cowper stove domes, roofs of electric furnaces, linings of acid converters, glass furnaces, etc. Because of their high thermal conductivity, they are also used in by-products coke-ovens and gas retort settings.

(2) **Fireclay bricks** *are made from finely ground soft plastic material fireclay* ($Al_2O_3 . 2SiO_2 . 2H_2O$) *with* ***powdered calcined fireclay*** (*called 'grog'*). The exact proportions of the constituents depend on the type of bricks to be made. *Greater is the percentage of grog, the lesser will be the spalling tendency.* General composition of fireclay bricks ranges from 55% SiO_2 and 35% Al_2O_3 (*feebly acidic*) to 55% Al_2O_3 and 40% SiO_2 (*nearly neutral bricks*), the balance consists of accessory oxides in the clay like K_2O, FeO, CaO, MgO, etc.

Properties : Fireclay bricks are light-yellow to reddish-brown in colour, depending on the content of iron oxides. They are *slightly acidic* in character, the extent of acidic character depends upon the SiO_2 content. They possess low porosity and lower refractoriness than silica bricks. They, usually, fuse at 1,350°C under a load of 2 kg/cm^2. Their crushing-strength is *quite high* (about 200 kg/cm^2). A very useful property of the fireclay bricks is *better resistance to thermal spalling* than silica bricks and *this makes them very suitable for making a checker-works of regenerative furnaces and charging doors, etc., which are subjected to temperature fluctuations.* Fireclay bricks are much *cheaper* than silica bricks.

Uses : Fireclay bricks are *most widely used* of all the refractory bricks, since they are *very cheap and are well-suited for many applications.* They are used for the construction of blast furnaces, open-hearth furnaces, stoves, ovens, crucible furnaces, flues, kilns, boiler-settings, regenerators, charging doors, etc.

(3) **High-alumina bricks** *contain 50% or more of* Al_2O_3 and are, generally, made by mixing calcined bauxite (Al_2O_3) with clay bind.

Properties : They possess very low coefficient of expansion, high porosity, great resistance to slags, very little tendency to spall, high temperature load-bearing capacity, excellent wear-resistance and stability, both in oxidizing and reducing conditions, and are particularly inert to the action of gases like CO_2, H_2 and natural gas. They are thus very good refractories, but they are *very costly*, so not used much.

Uses : *'Medium-duty bricks'* (*i.e.*, containing 50 to 60% Al_2O_3) are used for zones of vertical shaft kilns for burning limes, linings of Portland cement rotary kilns, soaking pits, reheating furnaces, hearths and walls, etc., which are subjected to high abrasion. On the other hand, *'high-duty bricks'* (*i.e.*, containing 75% Al_2O_3) find applications specially in the sintering or hottest zones of cement rotary kilns, lower parts of soaking pits, brass melting reverberatories, lead-dressing reveberatory furnaces, aluminium melting furnaces, combustion zones of oil-fired furnaces, etc.

(4) **Magnesite bricks** are important and the *most widely used basic refractories. Calcined magnesite* (MgO) is powdered to a proper size, and then mixed with *caustic magnesia or sulphite lye* (a waste product of paper industries) or *iron oxide* as *binding material*, and then ground with water, and moulded into bricks. The bricks are then slowly heated to 1,500°C, and kept for about 8 hours at this temperature and then, *cooled slowly.*

Properties : Magnesite bricks can be used up to 2,000°C without load, and upto 1,500°C under a load of 3.5 kg/cm^2. They possess good crushing strength, good resistance to basic slags, very little shrinkage, but have *lot of spalling*, due to their sensitiveness to sudden changes of temperature. *Their resistance to abrasion is poor. Moreover, they show a tendency to combine with water and* CO_2.

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Uses : They are used where *high temperature* is required to be maintained, together with *great resistance to basic materials* like molten liquids of basic nature. Their chief use is in the steel industry for the lining of basic converters and open-hearth furnaces. Other applications are in hot mixer linings, copper converters, reverberatory furnaces for smelting lead, copper and antimony ores, hot zones of cement rotary kilns, refining furnaces for gold, silver and platinum, etc.

(5) **Dolomite bricks** *are made by mixing calcined dolomite (CaO + MgO mixture in equimolecular proportions) with* ***silicate binder.*** *They are fired at 1,500°C of about 24 hours.*

Properties : Dolomite bricks possess less strength, more softness and porosity, greater shrinkage and high hygroscopicity than magnesite bricks. However, they can withstand a load of 3.5 kg/cm^2 at 1,650°C. They are also not very resistant to thermal-shocks. *Properties of dolomite bricks can be modified by "stabilization", in which dolomite is mixed with serpentine* ($MgO.SiO_2$) *and the mixture is calcined, resulting in the formation of di-and tri-calcium silicates, which do not absorb water and carbon dioxide.* After calcination, it is mixed with a *silicate binder* and made into bricks, which on firing at 1,500°C for a day or so give *stabilized bricks.* Stabilized dolomite bricks are quite stable towards basic slags.

Uses : Dolomite is rarly used as a direct refractory, but is useful as *repair* material. Stabilized dolomite bricks are, however, used for basic electric furnace linings, Bessemer converters, open-hearth furnaces, ladle-linings, etc., and as a cheap substitute for magnesite bricks.

(6) **Carbon bricks** *are made by firing crushed coke with* ***pitch or tar*** *(**binding** material) or graphite mixed with* ***clay*** *at about 1,300–1,400°C.* During firing, *contact of the bricks with air is minimized* by filling the space in-between the bricks with a mixture of sand and powdered coke.

Properties : Graphite and carbon refractories are excellent refractory materials, but *they can only be used under neutral or reducing conditions,* because they are oxidized readily in air at elevated temperatures. They are practically infusible, insensitive to spalling, highly thermal conductive, close-textured and can withstand temperature fluctuations and chemical attack of acids, alkalis and all solvents, except the oxidizing ones.

Uses : Carbon and graphite bricks are widely used as materials of construction for electrodes, linings of highly chemically-resistant equipments, atomic reactors, electric furnaces, heat-transfer systems, and in copper, aluminium and lead smelting furnaces.

(7) **Chromite bricks** *are made by firing at 1,500–1,700°C crushed chromite are* ($FeO \cdot Cr_2O_3$) *mixed with a little* ***clay*** *as binding material.*

Properties : Chromite bricks are *neutral* in character. They possess high density, *resistance to acidic as well as basic slags* and moderate resistance to spalling. They can be used upto 1,800°C and their refractoriness under a load of 3.5 kg/cm^2 is 1,430°C. They possess good crushing strength (350 to 550 kg/cm^2). They have moderate thermal conductivities.

Uses : Their most important use is *in separating acidic and basic refractory lining,* so as to prevent their interaction, even at high temperatures, *e.g.,* between acid-roofs of basic open-hearth furnace and the basic bricks of side walls. Other applications are in bottoms of soaking pits, sodium carbonate recovery furnaces. etc.

(8) **Carborundom (SiC) bricks :** *Silicon carbide (SiC) is made in an electric furnace at a temperature of 1,500°C from sand (60%) and coke (40%) with the addition of some saw-dust and a little salt.* When burned, saw-dust evolves gases, which by circulation, increases the porosity of the charge. Salt reacts with iron and similar impurities, present in the raw materials, forming volatile chlorides. *This increases the porosity of the final product.* The silicon carbide, removed from the furnace, is a mass of inter-locking iridescent crystals. The product is then mixed with *bonding agent* (like clay, silicon nitride, etc.), and then shaped, dried and fired. Recently, *self-bond type silicon carbide bricks* have been prepared. The silicon carbide particles are mixed with a *temporary binding agent* (such as glue) and then pressed and dried at 2,000°C, when *inter-crystalline bonds* of silicon carbide develop.

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Properties : *"Clay-bonded"* silicon carbide bricks can be used upto 1,750°C, as this product softens near this temperature, *'Silicon nitride bonded "*bricks have a high strength and superior thermal-shock resistance than clay-bonded products. *"Self-bonded"* product has high refractoriness, superior strength, high density, high abrasion-resistance and high chemical-resistance. Silicon carbide refractories, in general, are characterized by *high thermal conductivity and low thermal expansion. However, they tend to oxidise to silica, when heated in air at a temperature range of 900 to 1,000°C.* But this drawback in overcome by *coating* them with a thin layer of *zirconium.*

Uses : They are used for *partition walls* of chamber kilns, coke ovens, muffle furnaces, recuperators and floors of heat-treatment furnaces. Moreover, due to their high electrical conductivity, they are used as *heating elements* in furnaces in the form of rods and bars (*globars*).

(9) Zirconia brick *is obtained by heating zirconite mineral* (ZrO_2) *and using colloidal zirconia (prepared by drying zirconium nitrate solution and making the residue into solution and again drying) or alumina as binding material at 1,700°C.* Since mineral zirconite undergoes volume changes on heating and cooling, so it is *stabilized* by adding MgO or CaO.

Properties : Zirconia refractories are, usually, classed as neutral refractories, but *they are not quite resistant to acidic slags* and hence, they are actually on the border-line between neutral and basic refractories. They can be used upto 2,000°C, but specially prepared bricks can be used even up to 2,600°C. Their refractoriness under a load to 3.5 kg/cm^2 is about 1,900°C. They are also quite resistant to thermal-shocks.

Uses : Zirconia bricks are *very costly* and hence, used only where *very high temperature* is maintained, *e.g.*, high-frequency electric furnaces.

(10) Beryllia bricks *are made by firing moulded articles from powdered pure beryllia mineral at 1,900–2,000°C.*

Properties : They possess high melting point (2,550° C), *low electrical conductivity, high thermal conductivity, good resistance to thermal-shocks, and inertness to carbon dioxide and carbon monoxide* upto 2,000°C. They have considerable *hot-strength*

Uses : In jet propulation fields (due to hot strength), making crucibles (to melt uranium and thorium), in nuclear engineering as *moderator* (in view of its low neutron absorption capacity), and *radiation shields* in carbon resistance furnaces. However, its only drawback is that beryllia is capable of volatilizing, even at, 1,000°C, especially in the presence of water vapour ; and beryllia dust, if inhaled even in small quantities, cause series health hazards. Hence, *greater precautions* must be taken to have correct ventilation, etc.

(11) Chrome-magnesite refractory *is obtained by blending chrome ore with magnesite, followed by moulding and firing.* During firing, the serpentine ($3\,MgO\,.\,2\,SiO_2\,.\,H_2O$) present in the chrome ore decomposes to yield *forsterite* ($2\,MgO\,.\,SiO_2$) and *magnesium silicate* ($MgSiO_3$). The latter then combines with MgO (of magnesite) to form forsterite.

$$\underset{\text{Serpentine}}{3\,MgO\,.\,2\,SiO_2\,.\,H_2O} \xrightarrow{\Delta} \underset{\text{Forsterite}}{2\,MgO\,.\,SiO_2} + \underset{\text{Mag. silicate}}{MgSiO_3} + H_2O$$

$$MgSiO_3 + MgO \longrightarrow \underset{\text{Forsterite}}{2\,MgO\,.\,SiO_2}$$

Depending upon the *relative proportions* of chromite and magnesite blended before firing, the chrome-magnesite refractories are mainly of *two* types :

(*i*) ***Magnesite-chrome refractories** contains about 60% MgO and 8-18%* Cr_2O_3. These refractories are used in place of comparatively costlier 'silica bricks', due to their : (*a*) higher refractoriness (about 2,300°C), (*b*) higher thermal spalling, (*c*) higher thermal conductivity, and (*d*) higher resistance to erosion and consequent corrosion by high-speed flowing gases, slags and molten metals.

(*ii*) ***Chrome-magnesite refractories** contains about 40-50% Mg and 15-35%* Cr_2O_3. These possess properties similar to those of (*i*), but they are more prone to undergo *structural spalling.*

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8 CERMETS

Cermets *are hot-pressed or sintered materials, consisting of combinations of* ***ceramics*** *and* ***metals.*** They possess : (*i*) *high refractoriness of ceramics,* (*ii*) *high thermal conductivity of metals,* (*iii*) *high thermal-shock resistance of metals, and* (*iv*) *high shapeability.* The *metal* serves as a *binder* for high refractory *ceramics particles.*

Refractory ceramics used in cermets manufacture are ***highly refractory carbides*** (such as zirconium carbide, molybdenum carbide, tungsten carbide, titanium carbide, chromium carbide, etc.), *borides* (such as of molybdenum, titanium, tungsten, and zirconium), *oxides* (such as of magnesium and aluminium) as well as certain *silicides* and *sulphides.* The *metals* used are iron, aluminium, chromium, cobalt, nickel and molybdedum. *Most cermets contain about 80% of ceramic materials, and 20% of the metal.* They are, usually, fabricated by *powder metallurgy* techniques.

Uses : Cermets are used as high refractories in various applications in which high temperature and high shock-resistance are required, as in rocket and jet engine parts, spinning tools for hot metals, hot-forging dies, and similar applications.

9 INSULATING REFRACTORIES

In order to minimize, either externally or internally, heat losses from a furnace (due to conduction), *refractories of low thermal conductivities* are used as *heat-insulators.* For low operating temperatures (below 900°C), ***diatomaceous-earths*** (*hydrated silicates of iron, containing magnesia*) like *kieselguhr, vermiculite, asebesos* are, usually, employed as heat-insulators. However, these are not suitable for high temperature operations, because kieselguhr undergoes a large contraction ; while vermiculite expands to a large extent on heating. Consequently, *porous refractories* are employed under such circumstances. *The air inside the voids acts as poor conductor of heat. Porous refractories* are made by incorporating *combustibles* like saw-dust, cork, husks, etc., to the usual refractory materials, before firing. Alternatively, a *slip* made up of clay, grog and water is mixed with chemically prepared *foam* [made by of rosin (45%), caustic soda (7%) and rest water and *stabilized* [with glue and alum]. The mixture is poured into moulds and fired.

Table 2 : *Properties of common refractories.*

Refractory	*Major component (% by wt.)*	*Refractoriness (°C)*	*Porosity (%)*	*Thermal resistance*	*Abrasion resistance*	*Acidic slags & fluxes*	*Basic slags & fluxes*
1. Silica	$SiO_2 = 93 - 96$	1,700	16 – 18	Good (1,600°C)	Good	Fair	Poor
2. Fireclay	$SiO_2 = 40 - 55$; $Al_2O_3 = 35 - 55$	1,700 – 1,830	20 – 23	Good	Good	Good	Medium
3. High alumina	$Al_2O_3 = 50 - 60$; $SiO_2 = 40 - 45$	1,750	20 – 29	Good	Good	Good	Poor
4. Magnesite	$MgO = 80 - 95$; $Fe_2O_3 = 2 - 7$ $Al_2O_3 = < 4$	< 2,000	20 – 23	Poor	Medium	Poor	Good
5. Dolomite	$CaO = 58$; $MgO = 40$	1,650	= 20	Poor	Medium	Poor	Good
6. Carbon	$C = 85 - 90$	< 2,000	22 – 32	Good	Poor	Good	Fair
7. Chromite	$Al_2O_3 = 15 - 23$; $Cr_2O_3 = 30 - 15$ $Fe_2O_3 = 10 - 17$; $MgO = 14 - 20$	1,800 – 1,900	18 – 25	Fair	Medium	Fair	Good
8. Carbo-rundum	$SiC = 89 - 91$	< 2,100	17 – 20	Good	Good	Good	Poor
9. Zirconia	$ZrO_2 = 67$	= 2,500	–	Good	Good	Good	Poor
10. Beryllia	$BeO = 99$	= 2,500	= 30	Good	–	Poor	Good

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10 INORGANIC CEMENTING MATERIALS

Inorganic cements *are materials that exhibit characteristic properties of setting and hardening, when mixed to a paste with water.* This makes them capable of joining rigid masses (like bricks, stones, tiles, etc.) into coherent structures. Inorganic cements can be divided into *hydraulic* and *non-hydraulic* types, according to the way in which they set and harden. **Hydraulic cementing materials** (like *Portland cement*) *are capable of setting and hardening under water ; while* **non-hydraulic cements** (like *ordinary lime*) *harden in air and hence, cannot be used under water.*

11 GYPSUM PLASTER

The mineral **gypsum** [which consists essentially of hydrated calcium sulphate, $CaSO_4 . 2 H_2O$] *is extensively used as raw material for the manufacture of plasters,* which are almost universally used for coating the inner walls of dwellings. As mined, however, it usually contains a considerable percentage of impurities, the chief of which are clay, calcium and magnesium carbonates, and iron oxide.

Plaster of Paris [$CaSO_4 . \frac{1}{2} H_2O$] *is produced by heating fairly pure gypsum to a temperature of about 120–160°C.* If the gypsum by heated above 200°C, the anhydrous sulphate is produced, which loses the power of readily combining with water. The various changes may be depicted as follows :

$$\underset{\text{(Gypsum)}}{CaSO_4 . 2 H_2O} \rightleftharpoons \underset{\text{(Orthorhombic dihydrate)}}{CaSO_4 . 2 H_2O} \overset{120°}{\rightleftharpoons} \underset{\text{(Plaster of Paris)}}{CaSO_4 . 1/2 H_2O} \xrightarrow{200°C} CaSO_4$$

The operation of manufacturing plaster of Paris from gypsum consists in first crushing and grinding of gypsum, and then calcining the ground product in kilns (heated to about 150°C) and finally, pulverizing the calcined product.

Setting and hardening : *When plaster of Paris is mixed with water, the powder forms a plastic mass, which quickly hardens or sets, expanding slightly in the process and regains the closely-packed crystalline structure of gypsum* ($CaSO_4 . 2 H_2O$). Setting of plaster of Paris can be *accelerated* by admixing it with alkali sulphates like K_2SO_4, Na_2SO_4 (or alums), which initiate as well as hasten the crystallization process.

Uses : (1) Its *slight expansion on setting,* renders plaster of Paris suitable for making moulds, since details are thereby accurately reproduced. (2) It is used in making castings structural tiles and in *surgical bandages.* (3) Its chief uses are as *plaster for walls* and in *plaster-board,* which is made up of alternate layers of a fibrous material such as felt or paper and gypsum plaster.

12 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* (calcarious) and *Al + Si* (argillaceous). *The cements have property of setting and hardening under water, by virtue of certain chemical reactions with it and are, therefore, called* **'hydraulic cements'**.

CLASSIFICATION : (1) Natural cement *is made by calcining a naturally occurring argillaceous limestone (i.e., 20-40% clay-containing limestone) at a high temperature and subsequently, pulverizing the calcined mass.* During calcination, silica and alumina, present in sufficient quantities, combine with the calcium oxide to form the corresponding calcium silicates and aluminates.

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* ASPDIN Joseph (1788-20 March 1855) was an English mason, bricklayer and inventor who patented Portland cement on 21 October 1824. The eldest son of a Leeds bricklayer, he began using artificial cements made by burning ground limestone and clay together. He named it 'Portland' as he thought its colour resembled Portland Stone. This first true artificial cement was the first real improvement on cement since John Smeaton had made the first modern concrete by mixing powdered brick and adding pebbles as aggregate back in 1756.

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Sequence of chemical reactions during setting and hardening of cement : When water is added to cement, its various constituents undergo hydration and crystallization at different rates. (*i*) At first, hydration of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) takes place. (*ii*) Next, the hydration of tricalcium silicate (C_3S) begins within 24 hours and gets completed in 7 days. (*iii*) The gel of aluminate begins to crystallize and at the same time, dicalcium silicate (C_2S) begins to hydrate in 7 to 28 days. Thus, the *initial set* of cement is due to the *hydration of aluminate*. The development of *early-strength*, between 1 to 7 days, is due to the *hydration of tricalcium silicate* and the further hydration of aluminate. The *increase of strength*, between 7 to 28 days, is due to *hydration of dicalcium silicate and continued hydration of tricalcium silicate.*

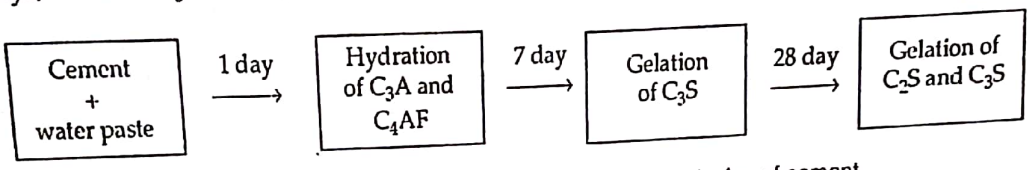

Fig. 6. Sequence of changes during setting and hardening of cement.

Function of gypsum in cement : Tricalcium aluminate (C_3A) combines with water very rapidly with the evolution of a large amount of heat.

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

After the initial-set, the paste becomes somewhat stiff. However, the added gypsum retards the dissolution of C_3A by forming *insoluble calcium sulpho-aluminate* :

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

This reaction prevents a high concentrations of alumina in the cement solution, thereby *retarding the early initial-set of the cement.*

17 HEAT OF HYDRATION OF CEMENT

When water is mixed with cement, hydration, hydrolysis and gelation reactions start and some heat is liberate simultaneously. On an average, 500 kJ/kg of heat is evolved during complete hydration of cement. The heats of hydrations of various constituents of cement are as follows :

Constituent of cement	C_3A	C_3S	C_4AF	C_2S
Heat of hydration (kJ/kg)	880	500	420	250

Consequently, in order to avoid the shrinkage cracks on setting and hardening, it is quite necessary to pour concrete in position in such amounts that the *heat liberated during hydration is dissipated as quickly as possible.*

18 SPECIAL CEMENTS

(1) **Aluminous or high-alumina cements** *are made by fusing a mixture of bauxite and limestone at 1,500 to 1,600°C in rotary kiln and then grinding the resulting mass to the same fineness as that of Portland cement.*

Typical composition of such a cement is : 35 to 40% CaO : 35 to 55% Al_2O_3 ; 5 to 15% FeO + Fe_2O_3, and 5 to 10% SiO_2. The most important constituents of such cements are *monocalcium aluminate* (CA) and *tricalcium pentaluminate* (C_3A_5), besides some dicalcium silicate (C_2S) and tetracalcium aluminoferrite (C_4AF). Both CA and C_3A_5 hydrate initially to a gel, $CaAl(OH)_5\,.\,3H_2O$, which gradually changes to a very stable crystalline complex, $Ca_3Al_2(OH)_{12}\,.\,3H_2O$ and a gel of aluminium hydroxide, $Al(OH)_3$. The setting time of high-alumina cement is similar to that of Portland cement, but its *rate of hardening is very rapid and full-strength is attained in 24 hours.* Since the crystalline complexes formed from high-alumina cements are stable, even on heating, so the *aluminous cement retains its strength at high temperatures.* Another advantage of high-alumina cement, as compared to Portland cement, is its *superior chemical-resistance to sea-water and sulphate-bearing ground water.*

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Moreover, such a cement *is resistant to very dilute acid solutions* (frequently occurring in industrial wa *dilute sulphourous acid solutions* (resulting from the combustion of sulphur-containing fuels) and to hydr sulphide solutions.

The advantages of *rapid-hardening* of aluminous cement is, however, offset to some extent by a *evolution of heat of hydration*, which cannot be easily dissipated in a short time. This causes a considerable in the temperature of the concrete mass, if in a layer of more than 5 cm thickness, but it is an asset w *concreting is done under freezing conditions*. High-alumina cement should not be mixed with Portland cem when fresh, because a *flash set occurs*, resulting in a *very weak bond*. However, hardened Portland cement be bonded to high-alumina cement to get a strong bond.

(2) **High early-strength (H.E.S.) cements** *are made from materials with a high lime to silica ratio.* Th contain a *higher proportion of tricalcium silicate* than regular Portland cements and hence, *harden more quick and with greater evolution of heat*. During the manufacture of such rapid hardening cements, addition of gypsu during the final grinding, is usually *avoided* and also such cements are *grinded much finer* than ordina cements. Such cements have only 5 minutes and 30 minutes initial and final setting times respectively.

(3) **White Portland cement** *is white in colour, owing to the absence of iron compounds.* Such cements ar made from raw materials which are *free from iron oxide.* It is very expensive and finds useful applications, *e.g.*, repairing and joining marble pillars and blocks, manufacture of tiles and for mosaic works. For the latter purpose, the cements may be coloured by means of colouring matters like yellow ochre, venetain red, etc.

(4) **Sorel cement** *is made by the addition of a strong solution of magnesium chloride to finely ground calcined magnesia.* The material, sometimes known a *magnesium oxychloride cement* [$3MgO . MgCl_2 . 11H_2O$], *sets hard in three to four hours.* This material is principally used in composite flooring. Such floorings have the advantage of being non-slip, fire-proof, not easily scratchable, durable and capable of taking a good wax or oil polish.

The rate of hardening of cement is still increased by addition of *calcium chloride or formate.* The accelerated rate of setting is especially useful during cold weather. It is believed that $CaCl_2$ accelerates the hydration of C_2S and C_3S, the strength-contributing components of the cement. On the other hand, the hydration of C_3A is retarded. The optimum quantity of $CaCl_2$ to be used for such purposes is 1.5% by weight of the total weight of cement. However, if this is exceeded, the corrosion of the steel embedded in the concrete is promoted, especially if the concrete is less compact or porous.

(5) **Barium and strontium cements** *are obtained by replacing calcium by barium or stronium.* So, such as a cement contains tribarium and dibarium silicates, instead of calcium silicates. Such cements show increased resistance to penetrations by radioactive radiations. Hence, they find extensive applications in *concrete shields for atomic piles.*

(6) **Silicate cements or acid-resistant cements** *are produced by mixing an inert acid-resisting aggregate (such as finely ground quartzite) with sodium or potassium or silicon ester, in suitable proportions.* Their cementing propety is due to the precipitation of the silica gel, caused by adding suitable setting agents such as sodium silicon fluoride or ethyl acetate or by evaporation of water. The bond developed by silicate cement is hard, but also brittle. On drying, this cement becomes very porous and permeable to liquids. For this reason, it should always be kept wet or immersed in a liquid to prevent shrinking of the gel.

(7) **Water-proof cement :** Such a cement is obtained by adding *water-proofining substances* (like calcium stearate, aluminium stearate and gypsum with tannic acid) to ordinary Portland cement, during grinding. The characteristics of such cements depend on the type and quantity of admixture added. A water-proof cement has to do *two* distinct functions, *viz.*, (*i*) *to make concrete impervious to water under pressure, and* (*ii*) *to resist the absorption of water.* Chemically inactive substances added are like calcium soaps, aluminium soaps, resins, vegetable oils, waxes, coal-tar residues and bitumen, which acts as *pore-blocking agents.* These act as *water-repelling agents.* Moreover, they increase appreciably the *resistance to the penetration of moisture.*

19 CONCRETE AND RCC

Concrete *is a building and structural material, obtained by mixing a binding material (cement or lime), inert mineral aggregates (sand, crushed stone, gravel, broken brick, slag, etc.) and water in a suitable proportion and which can be readily worked or moulded into almost any desired shape and when set, it is compact, rigid, strong and durable.*

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When *lime* is the binding material, the concrete is known as *lime concrete* and when *cement* forms the binding material, the concrete is called as *cement concrete.* The proportions of cement and aggregates in concrete vary with the use to which it is to be put. For *water-tight works,* concrete is made up of 1 part cement, 1 part sand and 2 parts gravels. If not required to be water-tight, the mixture can be changed to 1 part cement, 3 parts sand, and 5 parts gravels. *The more the cement, within limits, the more water-proof the concrete will be.*

Uses of concrete : Concrete is by far the most important of all non-metallic materials of construction. It ranks *second* only to steel in its wide and varied constructional importance. Its typical uses are in roads, buildings, floors, roofs, columns, arches, tanks, sewers, foundations, abutments, piers, reinforce-works, water-proof structures and other purposes where compressive strength is required.

Curing of concrete : *The hardening of concrete is due to hydration reaction of the constituent cement compounds.* These processes continue indefinitely, but the greatest amount of strength and hardness is developed during the first few days, immediately following placement, *So it is essential to keep the concrete damp for at least a week, to enable the hydration reactions to occur completely.* Moreover, the chemical reactions of the cement and water progresses only under favorable temperature conditions. *Reactions are slowed down in concrete at low temperature and completely stops, when the water in the concrete is frozen. Curing is the process of maintaining a satisfactory moisture content and favorable temperature in concrete during the period immediately following placement, so that hydration of the cement may continue, until the desired properties are developed to a sufficient degree to meet the requirement of service.* During hydration of cement, lot of heat is evolved. So special care has to be taken to dissipate this heat ; otherwise cement work is likely to develop *cracks. Thus, curing also helps in dissipation of heat.*

Reinforced concrete construction (R.C.C.) : *Plain concrete has a great compressive strength, but little ability to withstand tension.* Consequently, structures which are required to bear tensile stresses are *reinforced* (or strengthened) by embedding steel bars or rods and metal meshes in such a way that the tension is taken up by the steel ; while the concrete carries the compression. *This combination of steel and concrete produces structure, called reinforced concrete construction (R.C.C.), which can bear all types of loads.* Reinforced concrete work is mostly used in floor-beams, piers, lintels, girders, arches, slabs, bridges, etc.

Advantage of R.C.C. over plain concrete : (1) R.C.C. is easier to make and cast into any desired shapes, which can bear *all types of loads.* (2) It possesses *greater* rigidity, moisture and fire-resistances. (3) Steel reinforcement also tends to *distribute the shrinkage cracks,* thus preventing the formation of large cracks. (4) Its maintenance cost is *practically negligible.*

20 DECAY OF CONCRETE

Although cement concrete is mechanically quite strong, yet it highly susceptible to chemical attack, because concrete contains some free lime (CaO). In acidic water (*viz.*, pH < 7), lime of concrete dissolves, thereby making it *weak,* pH of most natural waters is slightly greater than 7 (*i.e.* they are slightly alkaline), consequently, such waters do not have any marked effect on the strength of concrete. However, as the acidity increases (or pH decreases), the deterioration of concrete enhances. It may be pointed here that *lime is more soluble in soft water than hard water.* Consequently, deterioration of concrete is more quick, when in contact with soft water. Lime of concrete is also removed by sulphates and chlorides, present in water. If concrete is soaked in mineral oil for sometime, its resistance to abrasin decreases. Sugar also causes concrete failure. If even as low as 0.1% sugar is added to cement, the setting time is delayed and its strength is greatly reduced, during the first four weeks. The cause of concrete failure, due to presence of sugar has been traced in the use of old sugar sacks for carrying sand or for covering the freshly concrete used during curing.

The most serious type of damage to concrete takes place in the presence of *sulphates.* The sulphates combine with tricalcium aluminate to form sulpho-aluminates, which occupies *more volume.* This causes expansion, thereby the life of concrete is greatly reduced. Such a danger can be avoided by eliminating tricalcium aluminate from the cement composition and manufacturing cement containing tetracalcium aluminoferrite, instead of aluminate.

Protection of concrete : (1) *By giving a coating of bituminous material.* This prevents direct contact between concrete and water. This is a very cheap method.

(2) *By coating the surface with silicon fluoride* in a soluble form together with oxides of Zn, Mg or Al. The precipitate of calcium fluoride so-formed in the capillaries prevents dissolution of lime.

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21 GLASSES AND CERAMICS

Glass *is an amorphous, hard, brittle, transparent or tranlucent, super-cooled liquid of infinite viscosity, obtained by fusing a mixture of a number of metallic silicates, most commonly of Na, K, Ca and Pb. It possesses no sharp melting-point, definite formula or crystalline structure.* Within certain limits, it may be represented as $x\ R_2O\ .\ y\ MO\ .\ 6\ SiO_2$, where R is an atom of *monovalent* alkali metal like Na, K, etc., M is an atom of a *bivalent* metal like Ca, Pb, Zn, etc., *x* and *y* are *whole numbers*. Thus, approximate composition of ordinary glass (called *soda-lime glass*) is $N_2O\ .\ CaO\ .\ 6\ SiO_2$. In some glasses, SiO_2 may be replaced by $Al_2O_3\ .\ B_2O_3\ .\ P_2O_5$, etc.

General properties of glass : Glass : (1) is amorphous, (2) has no definite melting-point. (3) can absorb, reflect or transmit light, (4) can take high polish, (5) is a good electrical insulator, (6) is affected by alkalis, (7) is not affected by air, water or acids or chemical reagents, except HF, which converts its silica into SiF_4, (8) can be formed into articles, even of intricate shapes, (9) is very brittle, (10) softens on heating, (14) is light, because it has homogeneous internal structure similar to liquids, (15) has no crystal structural and hence, no slippage between planes can occur. Hence, glass has a high compressive strength.

Ceramics (from Greek *keramos* meaning burnt stuff) *are inorganic, non-metallic materials that are processed and/or used at high temperatures.* They include silicates, metallic oxides, and their combination. Ceramics can be grouped into *three* broad divisions–clay products, refractories and glasses, according to their common characteristic features. Clay products can be sub-divided into *three* main types, namely :

1. **The structural clay products,** all of which contain *iron oxides*. They are used for *bricks, tiles* and similar products.

2. **The whitewares,** which are *paler substances* such as *Porcelain*, and *China*, and

3. **Chemical stonewares,** which have been *specially-treated* to be hard, resilient and non-porous.

Closely related to ceramics, in chemical composition, are natural rocks and their disintegration products such as clay, sand and gravels.

Clay : The term **clay** *denotes certain earths, which are highly plastic, when wet and which, when heated to redness, loses their plasticity and are converted into a hard mass, which is unaffected by water. Clays are formed by the weathering of igneous,* (*e.g.*, granite), *and felspathic rocks by various agencies through time and are composed essentially of hydrated* ***aluminium silicates*** (such as $Al_2Si_2O_7\ .\ 2H_2O$), together with other substances such as *mica* and *quartz*, which were present with the feldspar in the original rocks (*e.g.*, granite).

$$\underset{\text{Potash feldspar}}{2\ KAlSiO_8} + 2\ H_2O + CO_2 \longrightarrow K_2CO_3 + \underset{\text{Clay}}{Al_2O_3\ .\ 2\ SiO_2\ .\ 2H_2O} + 4SiO_2$$

The alkali is *leached-out* by water.

If the clay remains at the original location, it is a **primary clay,** *usually white with a low content of iron, so that it 'burns' white : and it is called 'Kaolin' or 'China clay'.* If in the course of geological changes, the clay has been *transported* (by water, glacier or wind) to *another location,* it is a **secondary clay ;** it now contains limestone powder, hydrated oxides, mud and organic impurities in varying amounts.

22 MANUFACTURE OF GLASS

Raw materials : Chief *source* of incorporating :

(*a*) *Sodium* is soda, Na_2CO_3. (*Soft glass*)

(*b*) *Potassium* is potash, K_2CO_3. (*Hard glass*)

(*c*) *Calcium* are limestone, chalk and lime.

(*d*) *Lead* are litharge, and red lead. (*Flint glass*)

(*e*) *Silica* are quartz, white sand, and ignited flint.

(*f*) *Zinc* is zinc oxide. (*Heat and shock-proof glass*)

(*g*) *Borate* are borax, and boric acid, (*Heat and shock-proof glass*)

(*h*) *Cullets* or pieces of broken glass to *increase the fusibility.*

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(*i*) ***Colours*** : *Yellow*–ferric salt ; *Green*–ferrous and chromium salts ; *Blue*–cobalt salts ; *Purple*–manganese dioxide ; *Red*–nickel salts or Cu_2O; *Lemon-yellow*–CdS. ; *Fluroescent greenish-yellow*–uranium oxide ; *Opaque milky-white*–cryolite (Na_3AlF_6) or calcium phosphate.

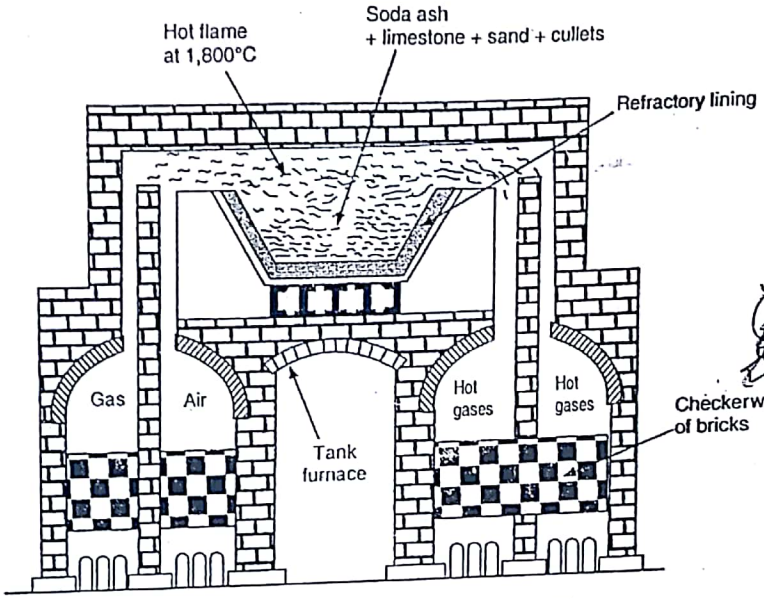

Fig. 7. Manufacture of glass.

Manufacturing steps : (*i*) ***Melting*** : Raw materials, in proper proportions (*e.g.*, sand, soda ash and limestone for *common glass*) mixed with cullets, are finely powdered and intimate mixture (called *'batch'*) is fused in either *fireclay pots* (in case of *high-grade glass*) or *tanks* that form part of an open-hearth furnace, in which heating is done by burning *producer gas* and *air* mixture over the charge. At high prevailing temperature (about 1,800°C), the charge melts and fuses. The melting process in case of ordinary *soda-glass* involves the following series of reactions :

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

When all the carbon dioxide has escaped out of the moten mass, *decolorizers* (such as MnO_2 or nitre) are added to do away with ferrous compounds and carbon, if present. *If a coloured glass is desired, the colouring salts are added at this stage.* Heating is continued, till the moten mass is free from bubbles and glass-balls ; and then cooled to about 800°C.

(*ii*) ***Forming and shaping*** : Molten glass is then worked into articles of *desired shapes* by either blowing or moulding or pressing between rollers.

(*iii*) ***Annealing*** : Glass articles are then allowed to *cool gradually* to room temperature by passing through different chambers with *descending* temperatures. *If allowed to cool rapidly, glass being bad conductor of heat, the superficial layer cools down first ; leaving the interior portion in a state of strain. Owing to this unequal expansion, the articles are likely to crack to pieces.* The *longer* the annealing period, the *better* the quality of the glass.

(*iv*) ***Finishing*** : All glass articles, after annealing, are subjected to finishing processes such as cleaning, grinding, polishing, cutting, sand-blasting, etc.

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23 TYPES OF GLASSES

Commercial glasses can be *classified* as follows :

(1) Soda-lime or soft glass : The raw materials are *silica* (sand), *calcium carbonate* and *soda ash*. Their approximate composition is $Na_2O . CaO . 6 SiO_2$. They are low in cost, resistant to devitrification and relatively resistant to water. They *melt easily* and hence, can be hot-worked easily. Such glasses are, however, *attacked by common reagents like acids.*

Uses : They are widely used as *window glasses, electric bulbs, plate-glasses, bottles, jars, building blocks, and cheaper tablewares*, where high temperature-resistance and chemical-stability are not required.

(2) Potash-lime or hard glass *is obtained from silica (sand), calcium carbonate, and potassium carbonate.* Their approximate composition is $K_2O . CaO . 6 SiO_2$. They possess *high melting-point, fuse with difficulty* and are *less acted upon by acids, alkalis and other solvents than ordinary glasses.*

Uses : These glasses (*costlier* than soda-lime glasses) are used for *chemical apparatus, combustion tubes,* etc., which are to be used for heating operations.

(3) Lead glass or flint glass *is made by using lead oxide, instead of calcium oxide, for fusing together with silica.* For *dense optical glasses,* as much as 80% of PbO is incorporated. In addition, K_2O is used, instead of sodium oxide. So, its approximate composition is $K_2O . PbO . 6 SiO_2$.

Lead glass is a good deal *more expensive* to make than ordinary lime-soda glass, but much *easier to shape and work with.* Lead glass has a lower softening temperature than soda-glass and also a *higher refractive–index.* It has excellent electrical properties. It is bright, lustrous and possesses high specific gravity (3 to 3.3).

Uses : Lead glasses are used widely for *high-quality tablewares, optical purposes* (like lenses, etc.) ; *neon sign tubings, cathode-ray tubes, electrical insulators* and *in art objects,* because of their high lustre. High lead-content glasses are used for *extra-dense optical glasses* for windows and shields to protect personnel from X-rays and gamma-rays in medical and atomic energy fields respectively.

(4) Borosilicate glass or pyrex glass or jena glass *is the most common of the hard glasses of commerce.* Such glasses contain virtually *only silica and boron,* with a small amount of alumina and some alkali oxides. A typical formula for such a glass would be following :

Percentage	80.5	13	3	3	0.5
Component	SiO_2	B_2O_3	Al_2O_3	K_2O	Na_2O

The substitution for alkali (Na_2O) and basic alkaline-earth oxides (CaO) of the soda-lime glasses by boron and aluminium oxides, results in a glass of *low thermal coefficient of expansion, and high chemical-resistance.* Borosilicate glasses have *very high softening points* and excellent resistivity (*i.e., shock-proof*).

Uses : They are used extensively in industry for pipelines for corrosive liquids, gauge glasses, superior laboratory apparatus, kitchenwares, chemical plants, television tubes, electrical insulators, etc.

(5) Aluminosilicate glass : A typical analysis of such a glass would be following :

Percentage	55	23	7	9	5	1
Component	SiO_2	Al_2O_3	B_2O_3	MgO	CaO	$Na_2O + K_2O$

This type of glasses possess *exceptionally high softening temperatures.*

Uses : For high-pressure *mercury discharge tubes, chemical combustion tubes, certain domestic equipments, etc.*

(6) 99.5% silica glass or vitreosil *is produced by heating pure sand (SiO_2) to its melting point (or about 1,750°C).* Because of absence of fluxing agents, it is extremely difficult to get rid of all air-bubbles. Moreover, owing to the *high viscosity of this glass at its working temperature, shaping is rather difficult.* The final product is *translucent.* Its softening-temperature is about 1,650°C. Its thermal expansion is *lowest,* namely, only 0.55×10^{-6} cm cm^{-1} °C^{-1}.

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If vitreosil glass is heated for long periods, above its melting point, it finally becomes ***transparent*** *and is then known as "****clear silica glass****", i.e.,* glass of considerable *light transmission properties, e.g.,* 1 m thick of this material allows no less than 93% of light to pass.

Uses : It is used mainly for *chemical plants, chemical laboratory wares, electrical insulating materials in electrical heaters, furnaces, etc.*

(7) Safety glass* *is made by taking two or three flat sheets of glass and in-between them* ***alternate thin layer of vinyl plastic*** *is introduced and the whole is subjected to slight pressure. It is then heated, till the glass layers and plastic layers merge into one another to give a sandwich.* On cooling, the glass becomes quite *tough.* When such a glass breaks, it *does not fly into pieces,* since the inner plastic layer tends to hold back the broken pieces of the glass.

Uses : It is mostly used in *automobile* and *aeroplane* industries as *wind shields,* etc.

(8) Optical or crookes glasses *contain phosphorus and lead silicate, together with a little* ***cerium oxide.*** The latter is capable of *absorbing ultra-violent light* (which is injurious to eyes). Moreover, they are given *thorough homogeneity.* This is secured by a very careful manufacturing process and by careful heating the molten mass for a *prolonged time.* In general, optical glasses have low melting-points and are relatively soft. Their chemical-resistance and durability are appreciably lower than those of ordinary glass.

Uses : They are used for making *lenses.*

(9) Polycrystalline glass or pyroceram *is produced by adding one or more nucleating agents to a special or conventional glass batch, which is then shaped into a desired forms. The material is then subjected to a controlled heat-treatment.* The *nucleating agents* induce the formation of a large number of sub-microscopic crystallites, which act as centres for further crystal growth. Crystalline glass is *not* ductile, but has much greater impact-strength than ordinary glass. It exhibits high strength and considerable hardness and can be formed and shaped into articles by any methods of moulding.

(10) Toughened glass *is made by dipping articles, still hot, in an oil-bath, so that same chilling takes place.* By doing so, *the outer layers of the articles shink and acquire a state of compression ; while the inner layers are in a state of tension.* Such a glass is more elastic and capable of withstanding mechanical and thermal-shocks. When such a glass breaks, it *does not fly, but is reduced to fine powder.*

Uses : It is used for *window shields of fast moving vehicles* (like cars, trucks, aeroplanes), *window shields of furnaces, automatic opening doors and large show-cases,* etc.

(11) Insulating glass *is a transparent unit, prepared by using two more plates of glass separated by 6 to 13 mm thick gap, filled up with dehydrated air and then, hermetically sealing around the edges.* This provides a *high insulation against heat.* Thus, if such glass is used for separating apartments, it *does not transmit heat* and consequently, the apartments will remain cool, during summer and warm, during winter.

(12) Wired glass *is formed by embedding a wire mesh at the centre of the glass sheet, during casting.* The main advantage of this glass is that when it breaks, it *does not fall apart into splinters.* Moreover, it is more *fire-resistant* than ordinary glass.

Uses : For making *fire-resisting doors, windows, skylights, roofs,* etc.

(13) Laminated glass *is made by pressing (or bonding) together two or more sheets/plates of glass with one or more alternating layer of bonding material like plastic resin, asphalt or synthetic rubber.* The laminated glass is : (*i*) *shatter-proof* (*i.e.,* its pieces do not fly off, when suddenly broken) ; (*ii*) *shock-proof* (*i.e.,* it can withstand sudden changes of temperature and even some pressure, without breaking).

A ***bullet-resistant laminated glass*** *is obtained by pressing together several layers of glass with vinyl resins in alternate layers.* Ordinarily, thickness of such glass varies from 12.7 mm to 76.5 mm. Even thicker types are made for *specific uses.*

Uses : As an ideal material for use as *safety glass in aircrafts, automobiles, helicopters, submarines,* etc. *Bullet-resistant laminated glass* finds application in *making automobile wind-screens, looking windows,* etc.

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* **Edouard Benedictus** (a French painter, composer, writer and chemist) is the man who discovered safety glass in 1903. He prepared "Triplex" two planes of glass sandwiching a layer of Collodion.

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(14) **Glass wool** *is a fibrous wool-like material, composed of intermingled fine threads or filaments of glass.* Glass used for this purpose should be completely *alkali-free.* Glass filaments are obtained by forcing molten mass of glass through small orifices (or holes), of average diameter of 0.0005 to 0.007 mm. continuously. The filaments of glass so-obtained are thrown over a rapidly revolving drum to get the material in wool-like form.

Properties : (1) It is non-combustible and fire-proof. (2) Its electrical conductivity is low. (3) It is completely heat-proof *i.e.*, heat has no effect on it size and volume. (4) It does not absorb moisture or water. (5) It resists actin of most chemicals. (6) Its density is low (about 65 kg/m^3). (7) Its *thermal conductivity is low* (about 0.033–0.034 kcal/m^2/°C/hr. (8) its tensile strength is about *eight times* that of steel.

Uses : (1) It is employed for *heat-insulation purposes, e.g.*, in domestic and industrial appliances like oven, insulation of metal pipelines, motors, vacuum-cleaners, walls and roofs of houses. (2) Being resistant to chemicals, glass wool is used for *filtration of corrosive liquids* like acid and acidic solutions. (3) It is used for *elctrical insulation.* (4) It is also used for *sound insulation.* (5) It is also employed in air-filters as dust-filtering materials. (6) It is also used for manufacturing *fibre-glass*, by blending with plastic resins.

24 PLASTICITY OF CLAYS

The ***plasticity of clay*** can be defined as *its ability to form a plastic mass (dough) with water. The mass can be easily moulded to any shape, but retains sufficient rigidity to prevent deformation on standing.* Dry clay is *not plastic*, and a certain amount of *water* has necessarily to be added to produce the required plasticity. *The function of water is to form a film around the flaky clay particles, so that their parallel orientation and movement under pressure is facilitated. The amount of water required to make a clay plastic, depends on the size and shape of the clay particles, their surface characteristics, and presence of electrolytes (salts).* For every clay, there is a certain minimum water-content, below which it ceases to behave as plastic material and becomes crumbly. This is called, the ***plastic-limit*** of a clay. *As the proportion of water increases, the clay becomes more and more plastic, until the point is reached at which it starts flowing and becomes wet and sticky.* This point, is called the ***liquid-limit.*** The difference in the water-content between the liquid limit and the plastic-limit, is called the ***plasticity index,*** which represents the *plasticity-range* of the clay.

Plasticity of clay and its effect on moulding : Depending on the methods employed, *different plasticities* of raw mixes are required to produce a product of desired size and properties. Thus :

(*i*) ***Hand-moulding and machine-extrusion*** require a mass of *plastic* consistency, classified as *'stiff mud'*.

(*ii*) ***Machine-pressing*** is best accomplished on *'stiff plastic'*, and *semi-dry mixes.*

(*iii*) ***Slip-casting*** requires a mix of *semi-liquid consistency*, so that it can be easily poured in a mould.

The *required plasticity* can be secured by :

(*i*) ***Weathering and grinding*** produces a *uniform clay-water paste*, in which clay particles are well dispersed and surrounded by water-films. This treatment *greatly improves the plasticity and homogeneity of the mass.*

(*ii*) ***Blending***, *i.e., mixing two or more ingredients in such proportions that a mass of required composition and plasticity is obtained.* The usual ingredients are *clay, non-plastic materials* (like finely ground quartz or flint), and *fluxes.* This is particularly used in the manufacture of *high-grade products* such as whitewares, chemicalwares and porcelain. *Blending of clay with* ***non-plastic materials*** *reduces the proportion of water required in the clay to get mass of a* ***desirable plasticity,*** *thereby preventing an excessive drying shrinkage.* ***Fluxes*** *are substances added to a mix to* ***lower its fusion-point,*** *thereby making possible more complete vitrification, even at not too high temperature.*

25 WHITEWARES OR WHITE-POTTERY

The genetic name is given to materials that give products, after firing, which are ***white*** *or* ***pale-cream*** *in colour.* The raw materials used for the manufacture of whitewares contain *little or no compounds of iron.* Whitewares are made by mixing *China clay, feldspar* ($KAlSiO_8$) and *flint* (SiO_2). The proportions of these components are adjusted according to the properties desired in the finished article. Whitewares possess *good strength, translucency* and *very low porosity.* This is attained by firing the products at high temperatures (*viz.*, 1,450–1,500°C), when *partial vitrification* of the ceramic constituents takes places.

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