

TRADITIONAL AND MODERN USES OF CERAMICS, GLASS AND REFRACTORIES

Ceramics

8.1 INTRODUCTION

The word “ceramic” comes from the Greek word “keramikos”, “of pottery” or “for pottery.” A ceramic is an inorganic, non-metallic often crystalline oxide, nitride or carbide material made by the action of heat and subsequent cooling. During the heating and cooling non-crystalline ceramics also can be formed.

Table 8.1: Types of ceramics

<i>Crystalline ceramics</i>	<i>Non-crystalline ceramics</i>
Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories – Ceramic forming techniques include shaping by hand (sometimes including a rotation process called “throwing”), slip casting, injection moulding, dry pressing etc.	Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten or when in a state of toffee-like viscosity. If later, heat treatments cause this glass to become partly crystalline, the resulting material is known as a glass-ceramic.

Some elements such as carbon and silicon may be considered as ceramics. Traditional ceramic raw materials include clay minerals such as kaolinite, whereas more recent materials include aluminium oxide, known as alumina and also include silicon carbide and tungsten carbide. Ceramic materials are brittle, hard, and strong in compression, weak in shearing and tension. They

withstand chemical erosion that occurs in other materials subjected to acidic or caustic environments. Ceramics generally can withstand very high temperatures, such as temperatures that range from 1000 °C to 1600 °C. It may be crystalline or partly crystalline and also may be amorphous. Though most common ceramics are crystalline. Many different ceramic materials are now used in domestic, industrial and building products. Clay was one of the earliest materials used to produce ceramics. Pottery objects, made from clay, were the earliest ceramics and hardened in fire. Later ceramics were glazed and fired to create a coloured, smooth surface. Ceramics now include domestic, industrial and building products. In the 20th century, new ceramic materials were developed for use in advanced ceramic engineering.

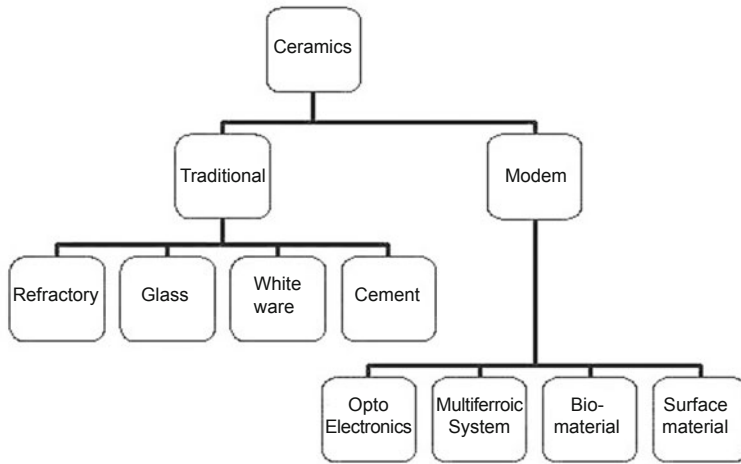


Fig. 8.1: Variation in ceramics.

8.2 PROPERTIES OF CERAMICS

The physical properties of any ceramic substance are a direct result of its crystalline structure and chemical composition. Density variations, grain-size distribution, type of porosity and second-phase content, can all be correlated with ceramic properties. Physical properties of chemical compounds include odour, colour, volume, density (mass/volume), melting point, boiling point, heat capacity, physical form at room temperature (solid, liquid or gas), hardness, porosity, and index of refraction. The microstructure includes most grains, secondary phases, grain boundaries, pores, micro-cracks, structural defects and hardness. Most bulk mechanical, optical, thermal, electrical and magnetic properties are significantly affected by the observed microstructure. The fabrication method is generally indicated by the microstructure.

8.3 MECHANICAL PROPERTIES

Mechanical properties include the many properties used to describe the strength of materials such as: elasticity, plasticity, tensile strength, compressive strength,

shear strength and hardness. Fracture mechanics is concerned with the study of the formation and subsequent propagation of micro cracks in materials. In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components. It applies the physics of stress and strain, in particular the theories of elasticity and plasticity. Thus, since cracks and other microstructural defects can lower the strength of a structure beyond that which might be predicted by the theory of crystalline objects, a different property of the material—above and beyond conventional strength—is needed to describe the fracture resistance of engineering materials. Fracture toughness is a property which describes the ability of a material containing a crack to resist fracture, and is one of the most important properties of any material for virtually all design applications. Fracture toughness is a quantitative way of expressing a material's resistance to brittle fracture when a crack is present. If a material has a large value of fracture toughness it will probably undergo ductile fracture. Brittle fracture is very characteristic of materials with a low fracture toughness value. Ceramic materials are usually ionic or covalent bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before any plastic deformation takes place, which results in poor toughness in these materials. These materials tend to be porous; the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength.

Table 8.2: Electrical properties of ceramics

<i>Electrical properties</i>	<i>Description</i>
Semiconductivity	Some ceramics are semiconductors. Most of these are transition metal oxides, such as zinc oxide. Ceramicists are most interested in the electrical properties that show grain boundary effects. Semiconducting ceramics are also employed as gas sensors. When various gases are passed over a polycrystalline ceramic, its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.
Superconductivity	The Meissner effect is demonstrated by levitating a magnet above a cuprate superconductor, which is cooled by liquid nitrogen. Under some conditions, such as extremely low temperature, some ceramics exhibit high temperature superconductivity. The exact reason for this is not known, but there are two major families of superconducting ceramics.
Piezoelectricity	A link between electrical and mechanical response is exhibited by a large number of ceramic materials, including the quartz used to measure time in watches and other electronics. The unit of time measured is the natural interval required for electricity to be converted into mechanical energy and back again.

(Contd.)

Table 8.2: (Contd.)

<i>Electrical properties</i>	<i>Description</i>
Pyroelectricity	The piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. These materials can be used to inter-convert between thermal, mechanical and electrical energy; for instance, after synthesis in a furnace, a pyroelectric crystal allowed to cool under no applied stress generally builds up a static charge of thousands of volts.
Ferroelectricity	In turn, pyroelectricity is seen most strongly in materials which also display the ferroelectricity, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. Pyroelectricity is also a necessary consequence of ferroelectricity.

8.4 UN-FIRED AND FIRED PROPERTIES

Many un-fired and fired properties are the result of interaction of two or more key characterizing features. Figure 8.2 identifies these features for a traditional ceramics and shows their relation to properties that can be evaluated before and after firing.

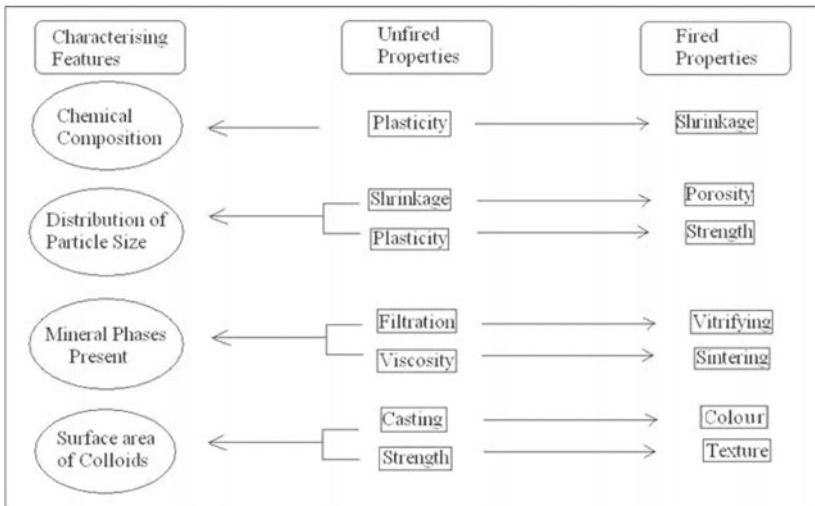


Fig. 8.2: Characteristic features of traditional ceramic and the properties that can be measured in un-fired and fired states.

8.5 OPTICAL PROPERTIES

Many ceramic substances, particularly the oxides, are optically transparent in single crystal or vitreous forms, e.g. the transparency of glass is perhaps its most useful and most characteristic feature. Optical properties are closely related

to structure and composition of ceramics since the degree of polarization is a function of ion size, bounding energy and crystallographic direction. The index of refraction is a sensitive quantitative measure of these materials, parameters. Optically transparent materials focus on the response of a material to incoming light waves of a range of wavelengths. Material is characterized by its transparency in certain wavelength regions (% transmission/mm thickness). Many ceramics and most glasses absorb highly in the infrared and ultraviolet regions of the spectrum. Frequency selective optical filters can be utilized to alter or enhance the brightness and contrast of a digital image. Guided lightwave transmission via frequency selective waveguides involves the emerging field of fibre optics and the ability of certain glassy compositions as a transmission medium for a range of frequencies simultaneously (multi-mode optical fibre) with little or no interference between competing wavelengths or frequencies.

Large ions in crystals or in glass compositions are more readily polarised than small ones and produce a high index of refraction. Most glasses are in the range 1.4-2.0; metals are usually >3.0.

Table 8.3: Refractive index of various crystal phase

<i>Crystal phase</i>	<i>Refractive index</i>	<i>Crystal phase</i>	<i>Refractive index</i>
<i>MgO</i>	1.74	<i>TiO₂</i>	2.71
<i>Al₂O₃</i>	1.76	<i>SiC</i>	2.68
<i>SiO₂</i>	1.55	<i>BaTiO₃</i>	2.40
<i>ZrSiO₄</i>	1.95	<i>LiF</i>	1.392

8.6 DEVELOPMENT OF ADVANCED CERAMICS USING MODERN TECHNIQUES

On the basis of atomic, electronic, grain boundary, microstructure, and macrostructure, advanced ceramics have been developed. The interactions of these structural levels result in materials which have properties suitable for specific application. The successors require an in-depth knowledge and use of thermodynamics, kinetics, phase equilibria and crystal structure.

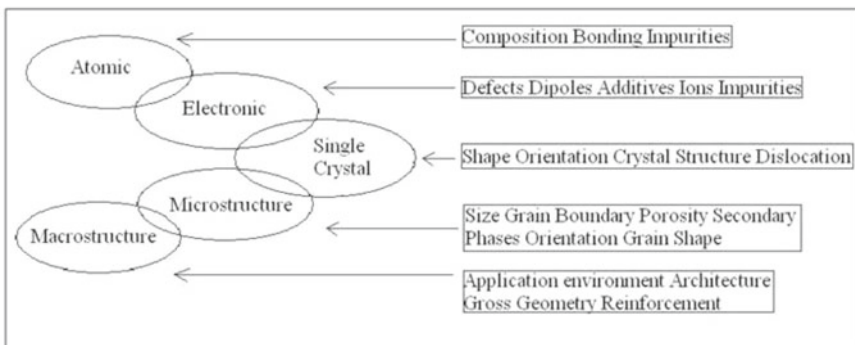


Fig. 8.3: Structural levels and interactions of ceramic materials.

8.7 USE OF CERAMICS

Ceramics differ from some other materials (viz. metals, plastics, wood products, textiles) in a number of individual properties, but perhaps the most distinctive difference to a designer or potential user of ceramic ware is the particularity of the individual ceramic piece. Actually ceramics are not readily shaped or worked after firing, except for some simple shapes of limited sizes. Many ceramics are manufactured as standard items: refractory bricks and shapes, crucibles, furnace tubes, insulators, thermocouple protection tube, fibre tubes etc.

Table 8.4a: Traditional use: Ceramic whiteware classes and their products

<i>Class</i>	<i>Types</i>	<i>Products</i>
Earthenware	Natural	Tableware, tiles
	Fine	Artware, kitchenware
	Talc	Artware, ovenware
Stoneware	Natural	Drain pipe, artware, kitchenware
	Fine	Tableware, cookware
	Basalt	Artware
	Jasper	Artware
Technical Ceramics	Electrical porcelains	Low-frequency insulators
	Steatite	High-frequency insulators
China	Cookware	Ovenware, stoveware
	Bone	Artware, tableware
Porcelain	High strength electrical	Low-frequency insulators
	Dental	Dentures
	Hard	Tableware, artware
	Technical vitreous	Ball mill ware, chemical ware

Table 8.4b: Use of ceramic products replacing metal items

<i>Ceramics for replacing metal items</i>	<i>Specific application</i>
Knife blades	The blade of a ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.
Vehicle ceramic Brake discs	These are resistant to abrasion at high temperatures.
Advanced composite ceramic	They have been designed for most modern armoured fighting vehicles.
Ceramic balls	These can be used to replace steel in ball bearings. They are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load. In very high speed applications, heat from friction during rolling can cause problems for metal bearings, which are <i>reduced</i> by the use of ceramics. Ceramics are also more chemically resistant and can be used in wet environments where steel bearings would rust.

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Table 8.4b: (Contd.)

High-tech ceramic	It is used in watch making for producing watch cases, due to its light weight, scratch resistance, durability and smooth touch.
Ceramic gas turbine engines	Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel (saves fuel).

8.8 BIOCERAMICS

Bioceramics, important subset of biomaterials, are ceramic materials that are biocompatible ranging from the ceramic oxides to the other extreme of resorbable materials. Bioceramics are used in many types of medical procedures. In primary medical procedures they are used as implants. Some rigid materials are commonly used as surgical implants though some bioceramics are flexible. Bioceramics are closely related to either the body's own materials, or are extremely durable metal oxides. In the medical fields as dental, and bone implants, ceramics are now commonly used. Artificial teeth and bones are relatively common place of its application. Surgical cements are used regularly. Joint replacements are commonly coated with bioceramic. Pacemakers, kidney dialysis machines, and respirators are the other examples of medical uses of bioceramics. Bioceramic materials are commonly subdivided by their bioactivity, viz. (i) Bioinert (ii) Bioactive. Bioinert includes oxide ceramics, silica ceramics, carbon fibre and synthetic diamond. Bioactive includes hydrogen apatite. Bioinert materials are non-toxic, non-inflammation causing. These materials must be long lasting, structural failure resistant, and corrosion resistant.

Table 8.4c: Advance ceramics: Applications of Bioceramics

<i>Materials used</i>	<i>Specific application</i>
Al ₂ O ₃	Orthopaedic loadbearing applications
Surface active glasses	Dental implants
Glass-ceramics	Coating for chemical bonding
Al ₂ O ₃ , HA-autogenous bone composite	Alveolar ridge augmentations
Trisodium phosphate, calcium and phosphate salts	Temporary bone space fillers
Al ₂ O ₃ , HA, glass-ceramics	Otolaryngological applications
Al ₂ O ₃ , HA, HA-PLA composites, surface active glasses	Maxillofacial reconstruction
Al ₂ O ₃	Coatings for tissues intergrowth
Bioactive glass-ceramics	Percutaneous access devices
PLA-carbon fibre composites	Artificial tendons and ligaments
Al ₂ O ₃ , HA-PLA composites	Periodontal pocket obliteration

Table 8.5: Products of clay-based ceramic materials

<i>Ceramic materials</i>	<i>Structural building materials</i>	<i>Refractory materials</i>	<i>Non-structural products</i>	<i>Structural products</i>	<i>Earthen ware</i>	<i>Stone ware</i>	<i>Porcelain</i>	<i>Technical ceramics</i>
Products	Bricks, terra cotta, roofing tiles	Flue lining, insulating bricks	Acid-resistant bricks, cement-clinker	Split bricks, quarry tiles	Pottery verified ware, table ware	Sanitary ware, tiles, insulators	Table ware	Chemical ware refractory ware

8.9 CLASSIFICATION OF CLAY-BASED CERAMICS

In modern science, ceramic is used in various aspects. Besides this ceramics developed on the basis of clay have some special uses such as structural building materials, refractory materials, non-structural products, structural products, earthen ware, stone ware, porcelain, and technical ceramics. The products of ceramic materials are known to us as bricks, terra cotta, flue lining, cement-clinker, chemical ware, refractory ware, table ware, tiles, sanitary ware, insulators, split bricks, quarry tiles, acid-resistant bricks etc.

The ceramics are classified into two types: coarse particles and fine particles. Again coarse particles are subdivided into porous and dense, on the basis of wt%, if weight % is greater than six then it will be defined as porous and if less than six it will be dense. Similarly fine particles are also subdivided into porous (weight % greater than 2) and (weight % less than 2) dense. The division porous again is classified in two types viz. structural building materials and refractory materials. Nonstructural products and structural products are the two subdivisions of dense or coarse particles. Earthenware is the example of the sub-division porous under fine particles. Dense is classified into three types, viz. stoneware, porcelain and technical ceramics.

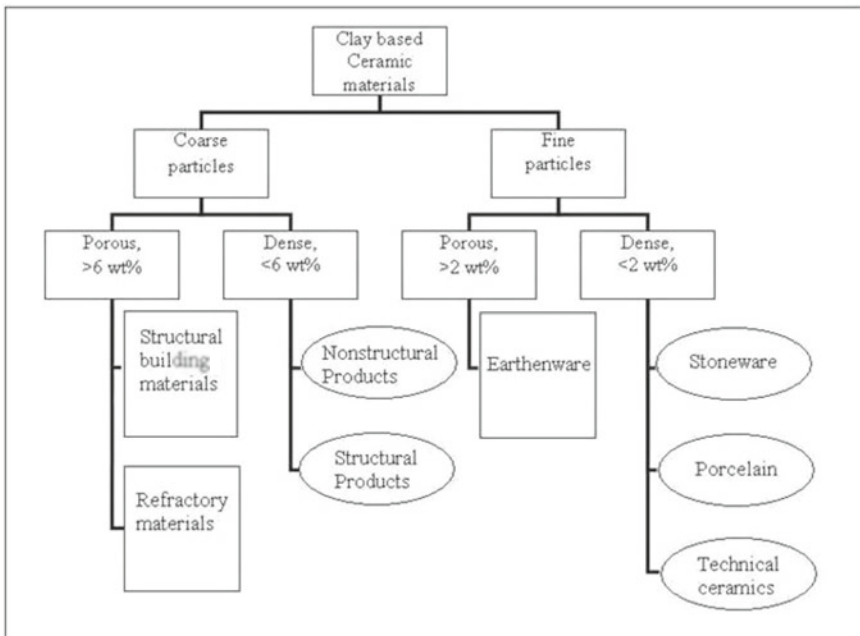


Fig. 8.4: Classification of clay-based ceramics.

8.10 CERAMIC PROCESSING METHOD

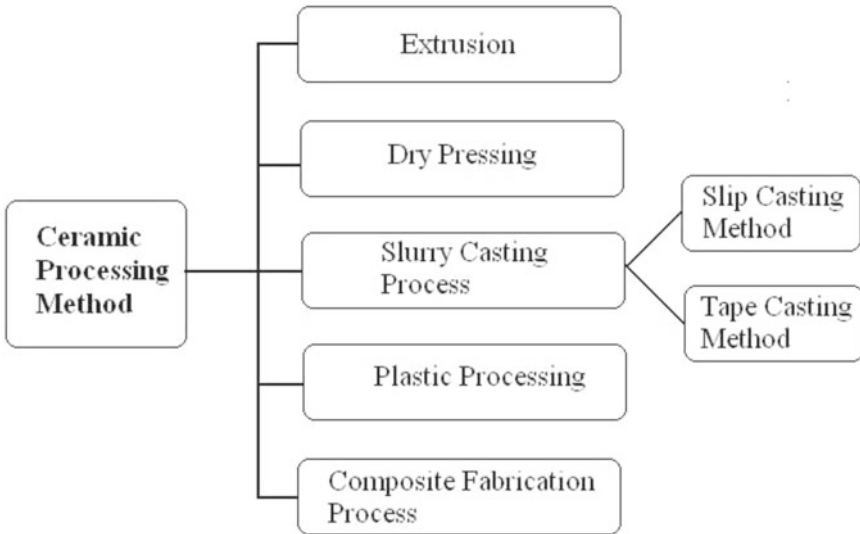


Fig. 8.5: Types of ceramic processing method.

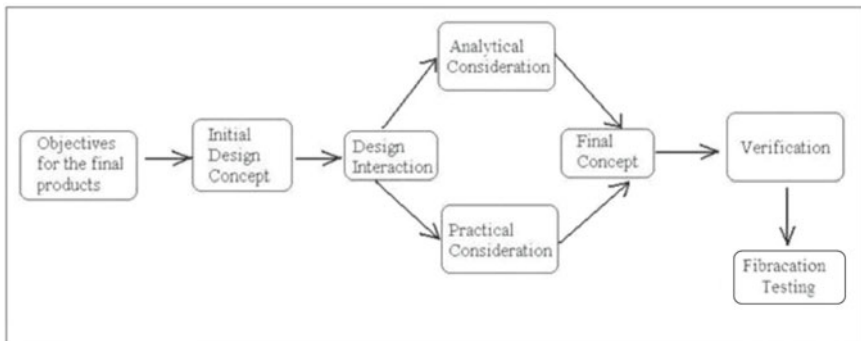


Fig. 8.6: Flow chart for ceramic design.

Ceramic processing occurs through some sequential activities, which starts with raw materials, proceeds through batch preparation and forming and concludes with firing. The sequence of steps is illustrated by Fig. 8.7. Ceramics are formed from raw materials used for traditional ceramics which are different from those used for advanced ceramics. For traditional ceramics raw materials consist of silica, clay, fluxes and are refractory materials. Silica is obtained either from massive quartz deposit or pure quartz sands. The quartz is washed and ground. The most commonly used clay minerals are kaolin and talc. China clay is predominantly kaolin. Ball clays are finer particle size clays that contain

significant amounts of free silica and organic materials. Fluxes are materials, such as feldspars or nepheline syenite, which contain alkali oxides to promote the fusion of silica and alumina to form a glassy phase during firing. Refractory materials are a separate type of raw materials of ceramics and include oxides, carbides and other materials. It can easily withstand extremely high temperatures. Raw materials for advanced ceramics are usually chemically prepared powders of high purity. Powders of aluminum oxide, silicon nitride, zirconium oxide and silicon carbide are examples of highly processed raw materials for advanced ceramics. The optimum particle size distribution for ceramic powders is still a controversial issue. Fine spherical particles about 100 nm diameters is best for ordered packing into dense beds by highly dilute settling and are highly reactive.

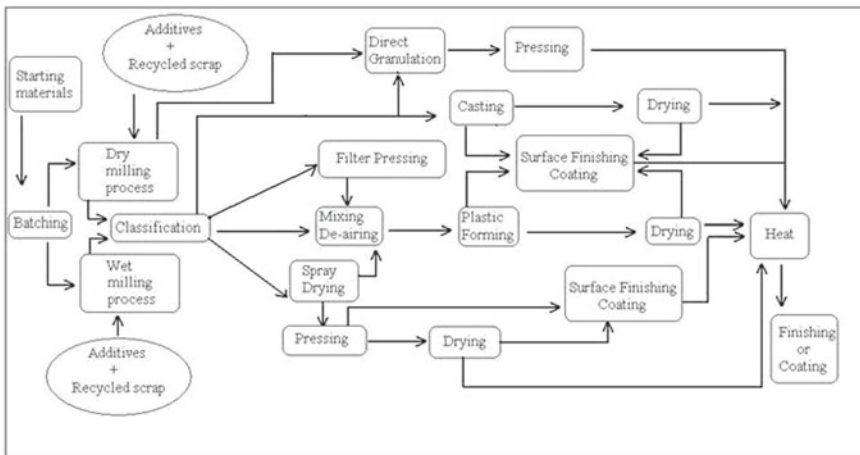


Fig. 8.7: General ceramic processing flow chart.

The powdered raw materials are prepared into various states that are compatible with the forming process. Powders used in dry processing methods are usually spray dried prior to pressing. The spray drying preparation permits the uniform incorporation of additives, such as binder and lubricants. Because spray drying is a granulation process, it combines many sub-micrometre sized powder particles into larger spherical particles that have excellent flow properties. Powders used in either slip casting or tape casting must be dispersed in aqueous or non-aqueous media to develop a fluid slurry. The proper dispersion of ceramic particles requires a thorough understanding of rheology and colloid chemistry. Dispersant type and amount, solids fraction, pH level and both powder particle size and distribution are important parameters. Ceramic powders used in either extrusion or injection moulding must be prepared.

Wide ranges of forming processes are used. Extrusion, dry processes and injection moulding are three processes that are widely used in polymer, metal and food technologies and therefore familiar to maximum engineers. Both slip

and tape casting of ceramic slurries are process developed for ceramic materials. Forming process of a particular component or structure depends on many parameters viz. size, shape and volume of component.

Extrusion

The extrusion process for forming ceramics is widely used in the structural clay products industry and is used to a lesser extent in the white ware and refractories industries. The principle advantage of this method is rapid and economic formation of dense ware. Extrusion can be used for ware of any shape that has an axis normal to a fixed cross section. The cross section may contain holes produced by pins in the die through which the material is extruded. Extrusion usually comprises three stages: pugging, deairing and extrusion through a die. The dry material is fed continuously into one end of a long trough, spread with water and cut and kneaded by rotating knives into a homogeneous plastic mass. The plastic material is forced by an auger through a shredding die and into the deairing chamber in which a vacuum is maintained. Removal of air from the material improves extrusion characteristics and permits formation of denser ware.

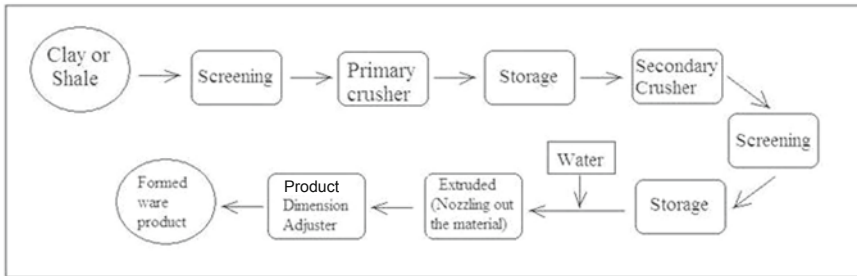


Fig. 8.8: Extrusion of structural clay bricks.

Table 8.6: Factors influencing forming process

<i>Forming process</i>	<i>Production value</i>	<i>Component shape</i>	<i>Component size</i>
Dry pressing	Small to medium	Simple	High
Injection moulding	Small	Complex	High
Slip casting	Large	Complex	Low
Tape casting	Thin sheets	Simple	High

Dry Pressing

It is a forming process in which nearly dry, free-flowing powders fill a metal die and are compacted under high pressure to the desired shape. Dry pressing process is more efficient. Shapes with a high aspect ratio, such as long, cylindrical bar are not prepared well by dry pressing because die well friction precludes the exertion of uniform pressure by the punches. The use of lubricant, both internal and external, to the ceramic powder reduces friction during the

pressing process, facilitating forming and further reducing undesirable density variations. When very low density is required in the passed component or when the component shape is too complex, isostatic pressing is used in place of dry pressing. Traditionally, ceramic powder is placed in a rubber mould of the proper shape and sealed. Due to pressure, powder is compacted and yields uniform density. Currently it is more common in production to use dry bag.

Plastic Processes

The forming of ceramic shapes by deformation of plastic mass has been popular due to the highly plastic nature of clay-based traditional plastic body. Presently many traditional ceramic shapes are made by various plastic processes. The principal processes used are extrusion, injection moulding, plastic pressing etc. extrusion and injection mouldings are similar processes. Both processes are capable of rapidly forming ceramic shapes by compressing plastic raw feed either into a desired shape (extrusion) or mould (injection moulding). Equipment of both processes are also similar.

Slurry Casting Process

Slip casting method: It is a fabrication method. In this process low-viscosity slurry of ceramic powder is poured into a porous plaster mould. The porous nature of the plaster mould draws water from the slurry that contacts the mould. This process continues as the capillary section of the mould continues to draw water through the increased ceramic solids at the mould wall. After establishing a sufficiently thick wall at the mould wall, the remaining liquid is drained, dried and when the cast is sufficiently dried, the mould is removed.

There are several factors in slip casting method. The porosity of the plaster mould is controlled by water content. The particle size of the powder should be relatively coarse to permit high level of vehicle permeability through the cast wall. Slip casting is widely used commercially because it enables the casting of complex shapes from an almost unlimited variety of ceramic composition, at a low cost. The most disadvantage of this process are low production rates and relatively short life of mould.

Tape casting method: Thin sheets of flexible ceramic tape are produced by the process of tape casting. These are prepared from ceramic slurries with binder and plasticizer that are cast into thin layers on either a glass plate or an impervious polymer film and allowed to dry. It is used in electronic industries.

There are several important differences between tape and slip casting; no porous mould is used in tape casting. Vehicle used in tape casting is usually a highly volatile organic liquid, whereas standard aqueous system is used in slip casting.

Composite Fabrication Processes

The challenge in the fabrication of ceramic-matrix fibre reinforced composites

is to uniformly incorporate the matrix phase around the fibres in a way that achieves full density without damaging the fibres. The most common process is slurry infiltration; this process is an extension of the polymer infiltration process used to make polymer-matrix composites. The slurry must be of sufficiently fine particle size to enable particles to penetrate the voids between the fibres.

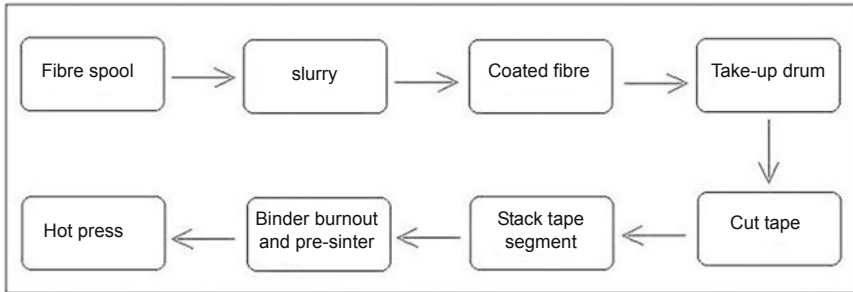


Fig. 8.9: Slurry infiltration process.

Two general processes are important in firing ceramics: vitrification and sintering. Vitrification occurs when constituent materials react at elevated temperatures to form a substantial amount of liquid phase, which acts to consolidate the ceramic body through the capillary forces. The sintering process has several stages that involve the following mass transport processes to varying degrees: evaporation/condensation, surface diffusion, and bulk diffusion.

Glass

8.11 INTRODUCTION

Glass, as a substance, plays an essential role in science and industry. It is an amorphous, solid material typically brittle and optically transparent. Its chemical, physical and, in particular, optical properties make it suitable for applications such as flat glass, container glass, optics and optoelectronics material, laboratory equipment, thermal insulator (glass wool), reinforcement materials (glass-reinforced plastic, glass fibre reinforced concrete), and glass art (art glass, studio glass). Silica is a common fundamental constituent of glass.

8.12 GLASS INGREDIENTS

Quartz sand (silica) is the main raw material in commercial glass production. While fused quartz (primarily composed of SiO_2) is used for some special applications, it is not very common due to its high glass transition temperature of over $1200\text{ }^\circ\text{C}$ ($2192\text{ }^\circ\text{F}$). Normally, other substances are added to simplify

processing. One is sodium carbonate (Na_2CO_3), which lowers the glass transition temperature. However, the Na_2CO_3 makes the glass water soluble, which is usually undesirable, so lime (calcium oxide (CaO), generally obtained from limestone), some magnesium oxide (MgO) and aluminium oxide (Al_2O_3) are added to provide for a better chemical durability. The resulting glass contains about 70 to 74% silica by weight and is called a soda-lime glass. Soda-lime glasses account for about 90% of manufactured glass.

Most common glass has other ingredients added to change its properties. Lead glass or flint glass is more 'brilliant' because the increased refractive index causes noticeably more specular reflection and increased optical dispersion. Adding barium also increases the refractive index. Thorium oxide gives glass a high refractive index and low dispersion and was formerly used in producing high-quality lenses, but due to its radioactivity has been replaced by lanthanum oxide in modern eye glasses. Iron can be incorporated into glass to absorb infrared energy, for example in heat absorbing filters for movie projectors, while cerium(IV) oxide can be used for glass that absorbs UV wavelengths. Borosilicate glasses (e.g. pyrex) have as main constituents silica and boron oxide. They have very low coefficients of thermal expansion (7740 Pyrex COE is $32.5 \times 10^{-7}/^\circ\text{C}$ as compared to $8.36 \times 10^{-5}/^\circ\text{C}$ for one type of soda-lime glass), making them more dimensionally stable. The lower COE also makes them less subject to stress caused by thermal expansion, thus less vulnerable to cracking from thermal shock. They are commonly used for reagent bottles, optical components and household cookware. Fining agents such as sodium sulphate, sodium chloride, or antimony oxide may be added to reduce the number of air bubbles in the glass mixture. Glass batch calculation is the method by which the correct raw material mixture is determined to achieve the desired glass composition.

8.13 MANUFACTURING OF GLASS

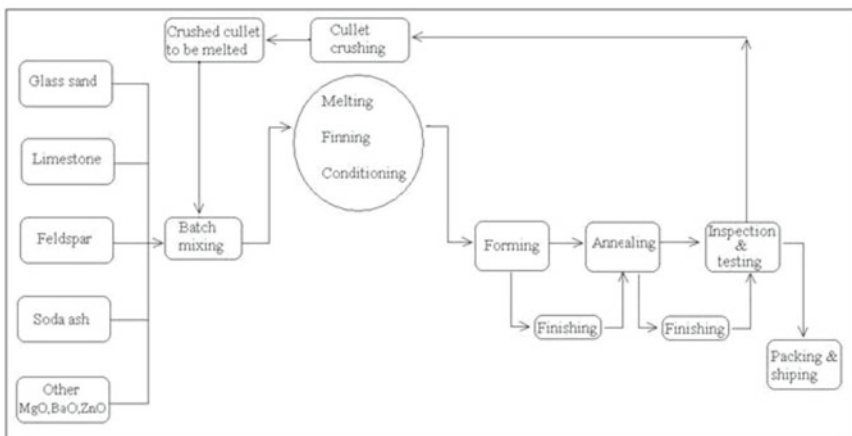


Fig. 8.10: Flow chart of glass processing.

Glass articles are manufactured by a process in which raw materials are converted at high temperatures to a homogeneous melt. Initial raw materials are selected according to purity, grain size, supply, easy melting and cost. Sand is most common ingredient. Container-glass manufacturers generally use sand between 20 and 30 mesh. Iron oxide and titanium are the primary contaminants. Limestone is the source of calcium and magnesium. It consists primarily of calcite (95%CaCO₃) or as a dolomitic limestone. High quality limestone contains less than 0.1% Fe₂O₃ and approximately 1% of silica and alumina. Feldspar is the common source of alumina. Boron is another raw material for manufacturing glass. Powdered anthracite coal is a common reducing agent in glass manufacture. Finning agents remove the bubbles in the molten glass and include sulphates, halides. They react by release of oxygen or sulphide trioxide.

Materials of optimum grain size are weighed carefully, and mixed together intimately. The efficiency of the melting operation and the uniformity and quality of the glass product are very often determined in the mix house. Batch handling systems vary widely throughout the industry, from manual to fully automatic. The method by which the batch is mixed depends more on the type of glass than on the size of the tank. High SiO₂ glasses tend to be batch-mixed in pan-type mixers. The batch is first dry-blended and then small amounts of liquids are sometimes added or wet-blended. The whole operation takes 3 to 8 mins; longer treatment may unmix or segregate the batch.

Table 8.7: Examples of batch homogenization

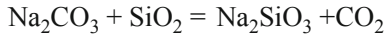
<i>Batch materials</i>	<i>Weight kg</i>	<i>Oxides supplied, kg</i>							
		<i>SiO₂</i>	<i>Al₂O₃</i>	<i>FeO</i>	<i>CaO</i>	<i>MgO</i>	<i>K₂O</i>	<i>Na₂O</i>	<i>LOI</i>
Sand	300	299.3	0.2	0.03	-	-	-	-	0.5
Soda ash	100	100	-	-	-	-	-	58.3	41.7
Feldspar	40	26.4	7.6	0.03	0.4	-	4.1	1.3	0.1
Aragonite	90	90	-	0.02	49.0	0.2	-	-	40.7
Powdered coal	9	-	-	-	-	-	-	-	9
Iron pyrites	1.4	-	-	0.84	-	-	-	-	0.6
Cullet (crushed glass)	460	333.7	9.2	1.03	48.8	-	-	67.2	-
Salt cake	4	-	-	-	-	-	-	2.1	1.9

Table 8.7 shows by example the problem of batch homogenization, where 1 kg pyrites and 4 kg salt must be uniformly dispersed throughout a 1000 kg batch, nearly one third of which is 50 mesh sand and nearly half of which is cullet (1-2 cm) glass.

Melting

When the intimately mixed batch is charged into the hot furnace, a series of melting, dissolution, volatilization and redox reactions take place between the materials in a particular order and at the appropriate temperature.

Dissolution of the more refractory grains, such as sand, is created by fluxes, e.g. sodium carbonate.



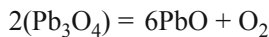
As the reaction continues,



Finally at about 780 °C, a mixture approaching an eutectic liquid is formed. $3 \text{Na}_2\text{Si}_2\text{O}_5 + \text{SiO}_2$ forms a mixture approaching.

The decomposition of alkali carbonates proceeds in a similar manner, as does their fluxing action on sand and other minerals, notably alumina-containing ones such as nepheline syenite and feldspars. Finning is the physical and chemical process of removing gas bubbles from the molten glass melt. Gas is evolved during the 1st stages of melting because of:

- decomposition of carbonates and sulphates
- air trapped between the grains of the fine grained batch materials and water evolved from the hydrated batch materials
- change in oxidation state of some of the batch materials, e.g. red lead:



Melting units range from small pot furnaces for manual production to large, continuous tanks for rapid machine forming. After mixing, the raw materials are charged into a furnace for melting. Pot furnaces are used for melting smaller quantities of glasses below 1400 °C. The largest furnaces are continuous regeneration furnaces that recover waste heat from burned gases. They produce large quantities of quality glass and are either cross or end-fired. Small, continuous melting tanks, filled automatically or by hand, produce high quality glass, such as optical ophthalmic glasses, at low volume. The largest furnaces are continuous regenerative furnaces that recover waste heat from burned gases. They produce large quantities of quality glass.

8.14 MECHANICAL FINISHING

Glass can be cut by the following methods:

- Sawing is done with wire or circular blades used in conjunction with loose bonded abrasive.
- In score-break glass method, the piece of glass is scored with a tool such as diamond, steel and then bent to apply tension.

- Flame cut-off is accomplished with pinpointed flames which heat the glass until it is soft enough to separate.
- Score-thermal crack-off is done by applying heat opposite a mechanically produced score on the glass surface.

Process of Mechanical Finishing

Drilling: Glass is drilled with carbide or bonded diamond drills under a suitable coolant such as water or kerosene. Other drilling processes include a metal tube rotating about its axis, an ultrasonic tool in combination with abrasive slurry, or an electron beam.

Grinding: Glass is ground with diamond, silicon carbide, garnet and sand. These materials are used loose, as in the grinding process employed for plate glass. They are bonded in grinding wheels or coated on fabric belts.

Mechanical polishing: It is more or less similar to grinding, but the polishing compound (cerium oxide, ferric oxide) is finer. The polishing tool may be plastic, cellulose and pitch. A mixture of hydrofluoric and sulphuric acids is used for acid-polishing.

8.15 CHEMICAL FINISHING

Treatment of glass surface with use of chemicals may alter its appearance and durability e.g. ion exchange helps to alter strength of glass articles. A glass, e.g., a sodium aluminosilicate, is immersed in a bath of potassium nitrate at a temperature about 50 °C below its strain point. The sodium ion is replaced by potassium ion and thus diffused from glass. Stress release is minimized because of the low process temperature. Chemical strengthening produces higher strength in thinner glass than does thermal tempering, but it is more susceptible to weakening by abrasion. Silver and copper containing mixtures can be applied to produce colours through ion exchange in glass. Sometimes acid etching or frosting with dilute hydrofluoric acid produces articles on glass surface.

Cleaning

Methods of cleaning glass are closely related with the types of glass and its uses. Cleaning requires some considerations like: the soil to be removed, the interaction between soil and glass and the effects of cleaning glass surface. Aqueous solvents are frequently used for cleaning. Organic solvents usually have no harmful effect on most glasses. Some organic solvents may be used alone or as aqueous mixtures in commercial cleansers.

8.16 GLASSMAKING IN THE LABORATORY

New chemical glass compositions techniques can be initially investigated in small-scale laboratory experiments. In the laboratory mostly pure chemicals

are used. Care must be taken that the raw materials have not reacted with moisture or other chemicals in the environment (such as alkali oxides and hydroxides, alkaline earth oxides and hydroxides, or boron oxide). Evaporation losses during glass melting should be considered during the selection of the raw materials, e.g., sodium selenite may be preferred over easily evaporating SeO_2 . Also, more readily reacting raw materials may be preferred over relatively inert ones, such as $\text{Al}(\text{OH})_3$ over Al_2O_3 . Usually, the melts are carried out in platinum crucibles to reduce contamination from the crucible material. Glass homogeneity is achieved by homogenizing the raw materials mixture (glass batch), by stirring the melt, and by crushing and re-melting the first melt. The obtained glass is usually annealed to prevent breakage during processing. In order to make glass from materials with poor glass forming tendencies, novel techniques are used to increase cooling rate, or reduce crystal nucleation triggers.

8.17 PROPERTIES

Thermal Properties

Thermal expansion: The thermal expansion properties, particularly the low expansions, are the primary properties that have been exploited commercially. The low expansion materials have been used for applications where thermal shock resistance is important such as cookware, stove tops, heat exchangers etc. They have also been used in applications such as mirror substrates where minimal thermally induced distortions are important. Higher expansion materials have been used for sealing various metals and alloys.

Thermal stability: The maximum use temperature must be defined in terms of a time factor and degree of loading. The crystalline phase plays an important role, but the maximum use temperature is limited by the residual glass which may crystallize further or it may enhance deformation by viscous flow. The glass ceramic materials are generally more refractory than the common glasses but less refractory than the common oxide refractories.

Optical Properties

Glass is in widespread use largely due to the production of glass compositions that are transparent to visible wavelengths of light. In contrast, polycrystalline materials do not in general transmit visible light. The individual crystallites may be transparent, but their facets (grain boundaries) reflect or scatter light resulting in diffused reflection. The surface of a glass is often smooth since during glass formation the molecules of the super cooled liquid are not forced to dispose in rigid crystal geometries and can follow surface tension, which imposes a microscopically smooth surface. These properties, which give glass

its clearness, can be retained even if glass is partially light-absorbing i.e. coloured. Glass has the ability to refract, reflect and transmit light following geometrical optics, without scattering it. It is used in the manufacture of lenses and windows. Common glass has a refraction index around 1.5.

Colour

Common soda-lime float glass appears green in thick sections because of Fe^{2+} impurities. Colour in glass may be obtained by addition of electrically charged ions that are homogeneously distributed (such as in photochromic glasses). Ordinary soda-lime appears colourless to the naked eyes when it is thin, although iron (II) (FeO) impurities produce a green tint which can be viewed in thick pieces. Further FeO and additions may be used for the production of green bottles.

Soda-lime glass for containers is slightly different from soda-lime glass for windows (also called flat glass or float glass). Float glass has a higher magnesium oxide content as compared to container glass, and a lower silica and content.

Transmission

The spectral transmission of glass is determined by reflection at the glass surfaces and the optical absorption within the glass. Transmission may be controlled by the types of glass used, e.g., silicate, phosphate, borate, etc., or by the control or addition of colouring additives, melting atmosphere, melting temperatures and cooling schedules. In glasses containing suspended particles, transmissions diffuse. Oxides that are frequently used to control colour in glass are listed in Table 8.8.

Table 8.8: Colouration of glass

<i>Effect</i>	<i>Oxide</i>
Colourless, uv transmitting	SiO_2 , P_2O_5
Colourless, uv absorbing	CeO_2 , TiO_2 , Fe_2O_3
Blue	CO_3O_4 , S, $\text{Cu}_2\text{O}+\text{CuO}$
Purple	MnO_2
Brown	MnO , $\text{MnO}+\text{Fe}_2\text{O}_3$, NiO , TiO_2
Yellow	CdS , $\text{CeO}_2+\text{TiO}_2$, UO_3
Orange	$\text{CdS}+\text{Se}$
Green	Cr_2O_3 , V_2O_3 , CuO , MoO_3
Red	$\text{CdS}+\text{Se}$
Amber	Na_2S
Black	CO_3O_4

8.18 ECONOMIC ASPECTS

Glass manufacture is classified according to the product into flat, container, fibre, or specialty glass. The flat and container companies produce over 14×10^6 soda-lime glass per year. The specialty glass manufactured of pressed and blown ware, television bulbs, and lighting and optical glasses melt hundreds of glass compositions to fulfill the need for a large variety of products.

Various Glass Types

Flat glass: In United States, 31 flat-glass plants are operated by PPG Industries, Libbey-Owens-Ford (LOF), Food Motor Company, AFG Industries, Combustion Engineering, The West Virginia Flat Glass Company. Growth of this industry depends upon the construction and automotive markets. The float process produces 85% of all the flat glass. The remainder is thin sheet for picture glass or rolled and patterned glass. Production of the flat glass is cyclical but increases in volume by approximately 4% per year. Less than 10% of the total used is imported.

Container glass: Statistics for food, beverage, drug and cosmetic, and household and industrial containers are compiled and published by the glass packing institute (GPI). Beverage containers, including soft drink, beer, wine and liquor, constitute the largest segment followed by food, drug and cosmetic, and household. Imports are of very minute importance because of high transportation costs. Export of container glass is only about 1% of the total amount manufactured for the same reason.

Fibre glass: This glass is classified as either wool or textile. More than a dozen companies produce textile fibers for draperies, tyres, paper, etc. More than 80% of production is used for building insulation, the remainder for industrial equipment and pipe insulation. Growth of the insulation market has been faster than the textile area because of the demand for additional insulation in both new and existing building.

Specialty glass: The pressed-and-blown or hollow-ware industry is comprised of over one hundred companies in United States. The wide variety of products is divided into categories of pressed-and-blown glass for table, kitchen, art and novelty applications and products of purchased glass.

Refractory

8.19 INTRODUCTION

Refractory materials can withstand high temperature and do not fuse as these are chemically and physically stable even at a very high temperature. The oxides

of aluminium, silicon, magnesium and calcium are the mostly used materials for manufacturing of refractories. Fire clays are also widely used for this purpose. Refractory materials are used in linings for furnaces, kilns and used for making other high temperature items like crucibles etc.

8.20 CLASSIFICATION OF REFRACTORY MATERIALS

Refractories are classified on the basis of (i) physical form, (ii) refractoriness (temperature stability range), (iii) chemical composition and (iv) method of manufacture.

Table 8.9: Various forms of refractories

<i>Based on physical form</i>				
Shaped	These have fixed size and shapes and further divided into (a) standard shapes and (b) special shapes.			
	(a) Standard shapes have dimensions that are conformed by most refractory manufacturers and are generally applicable to kilns or furnaces of the same types.			
	(b) Special shapes are specifically made for particular kilns or furnaces.			
Unshaped	These are without definite form and are only given shape upon application. These types are better known as monolithic refractories. The common examples are ramming masses, castables, gunning masses, mortars etc.			
<i>Based on refractoriness</i>				
Type of refractory	Low heat duty refractories (LHD)	Medium heat duty refractories (MHD)	High heat duty refractories (HHD)	Super duty refractories (SD)
Refractoriness, °C	1520-1630	1630-1670	1630-1730	>1730

Based on Method of Manufacture

- Dry press process
- Fused cast
- Hand moulded
- Formed (normal, fired or chemically bonded)
- Un-formed (monolithics-plastics, gunning, castables. spraying)

Table 8.10: Types of refractories based on chemical composition

<i>Type of refractory material</i>	<i>Use</i>	<i>Description</i>
Acidic refractories (e.g. silica, fire, clay etc.)	These are used in areas where slag and atmosphere are acidic. They are stable to acids but attacked by alkalis.	Aluminium-silicate refractories These refractories vary widely in their physical, chemical and mineralogical characteristics depending on the nature and proportion of silica and alumina present on them.
Basic refractories (e.g. chromite, graphite, carbide etc.)	These are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases.	Silica refractories These refractories consist mainly of silica. Raw materials various refractories are (97%), alkalis (<0.3%) and alumina (<10%). Alumina Manufactured from burnt bauxite, electro cast bauxite.
Neutral refractories (e.g. bauxite, lime, dolomite etc.)	These are used on areas where slags and atmosphere are basic; they are stable to alkaline materials but react with acids.	Dolomite refractories Produced by calcining natural dolomite which is mainly a mixture of lime and magnesia. Chrome magnesite refractories These are mixture of calcined magnesite and chromium oxide in various proportion necessary to develop required properties in them. Magnesite refractories Produced from dead burnt magnesia (MgO).

Table 8.11: Firing temperature of refractories

<i>Refractory Type</i>	<i>Fireclay bricks</i>	<i>Silicon carbide bricks</i>	<i>High alumina bricks</i>	<i>Silica bricks</i>	<i>Chrome bricks</i>	<i>Direct bonded bricks</i>	<i>Magnesite bricks</i>
Firing temperature, °C	1250-1400	1370-1510	1450-1550	1450-1510	1450-1650	1650-1760	1450-1650

8.21 PROPERTIES OF REFRACTORY

Resistant to high temperature, heavy load, fluxes and corrosive fluids like slag are the important properties of refractories. Strength and specific gravity are some other important properties.

Refractoriness: It is the temperature at which the refractories fuse. It should be much higher than the operating temperature of the refractory.

Specific gravity: It should be low to produce more number of bricks per unit width.

Thermal conductivity: Thermal conductivity is increased when the porosity of refractory bricks decreases and the air is entrapped in refractory decreases.

Electrical conductivity: The electrical resistivity of the refractory drops rapidly with increase in temperature. For electrical furnaces, the electrical conductivity of refractory material should be low.

Strength: It is the resistance of the refractory against load shear stresses etc. In refractoriness, under load is important as some refractories fail at a lower temperature when subjected to load.

Chemical composition: Chemical composition of the refractory should be such that the surroundings do not react with refractory and corrode it.

Resistance: Erosion occurs when refractory comes in contact with metal and gas carrying dust and slag particles. Abrasion resistance of refractory is increased by using denser (low porosity), fine grained and wear resistant refractory materials.

8.22 GENERAL MODE OF MANUFACTURE

Manufacture of refractory consists of the following processes:

Grinding: It is an initial important method to ground the raw materials for obtaining proper size which is required. The ratio of coarse and fine is normally maintained at 55:45. Equipments used for this purpose are various types of crushers, hammer mills, ball mills etc.

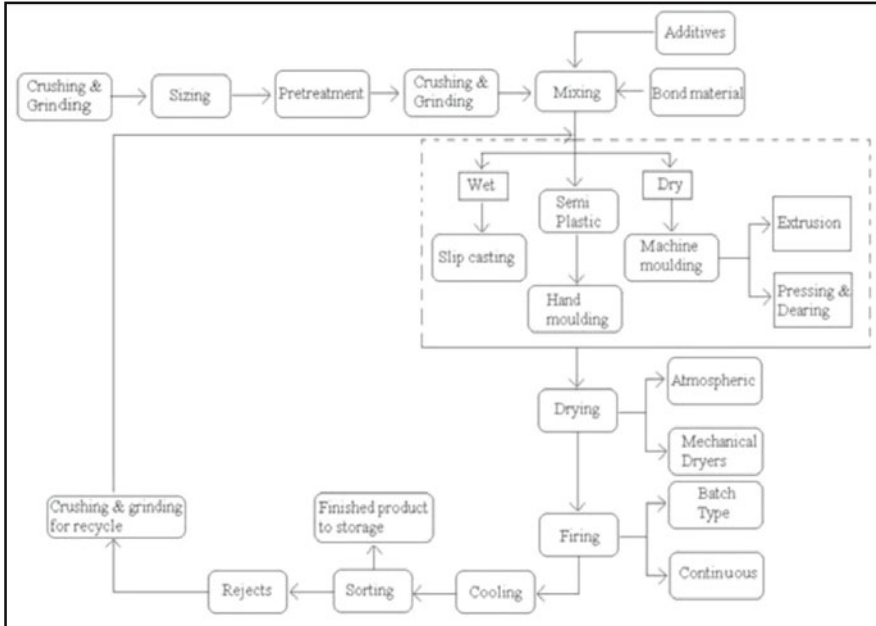


Fig. 8.11: General mode of manufacture.

Pre-Treatment: Pretreatment methods include firing at high temperature which bring about the complete mineral conversion and thus stabilize the mineral. The constituents of the finished refractory produced by reaction between the solid particles of raw materials and these refractory materials will be in equilibrium condition. Silica contains quartz which is not stable at high temperatures but undergoes transformation to its allotropic forms—tridymite and cristobalite—involving high volume changes. Tridymite, with higher symmetry, a more open structure and cristobalite with highest symmetry and the most expanded structure are two forms of polymorphs of quartz. These polymorphs are related to each other by reconstructive transformation, a process that requires considerable energy. Quartz is transformed into tridymite on very prolonged heating at 870 °C. On heating above 1470°C, this is transformed into cristobalite. Conversion of quartz into tridymite involves 16% increase in volume whereas conversion of tridymite into cristobalite involves a little contraction in volume. Similarly fireclay which consists of numerous hydrous alumina silicate minerals, breakdown to several constituents on heating and these constituent tend to form stable mullite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Magnesite is dead burnt to eliminate all the CO_2 from it and to convert it into stable crystalline magnesia (MgO) known as ‘Periclase’ and involves least shrinkage in refractory materials on firing. Dolomite also is dead burnt to calcium and periclase.

Mixing: The grinded refractory materials are mixed homogeneously with the binding material (having plasticity) to facilitate easy moulding. Pugmills are used to ensure even distribution of fine and coarse particles in the whole mass. Water, additives, binding materials and mineralizers are added and the mass is mixed thoroughly to ensure homogeneity of the product (i.e. of uniform composition and uniform distribution of fine and coarse grains etc.) for easy moulding and development of useful properties of the fired refractories.

Moulding: It is done mechanically by applying high pressure or normal as suitable to increase density and strength of refractory. Moulding which follows mixing of refractory materials is done through two processes.

Hand moulding: It is carried out in wooden boxes and is cheaper than machine on a jobbing basis.

Machine moulding: Machine-moulded refractories have higher strength and density than hand-moulded refractories. Machine moulding can be used for semi-plastic mixture using moderate moulding pressures.

Drying: Drying of moulded refractories increases its green strength by removing moisture and thus making them safe for subsequent handling. It is done at slow rate to avoid voids and high shrinkage and crack formation.

Firing: Bricks are burnt into kiln to remove water of hydration, vitrification and development of stable mineral forms. Shrinkage in volume upto 3% occurs during burning. Degree of firing of silica brick is indicated by its specific gravity. High specific gravity of 2.5 indicates the presence of considerable amount of unconverted quartz in the refractory whereas a specific gravity of 2.32 to 2.37 indicates adequate firing and transformation of quartz to tridymite or cristobalite.

QUESTIONS

1. Explain how various properties of ceramics are related with their products.
2. Give a schematic diagram to focus how ceramic is made.
3. What is the relation between traditional use and modern application of ceramics.
4. Give a schematic diagram to highlight the flow chart of glass processing method.
5. Briefly describe the mechanical finishing process of glass.
6. Explain the following terms: Flat glass, Fibre glass, Specialty glass, Container glass.
7. Based on physical form, how do you classify refractory materials.
8. Give a brief description about the general mode of manufacture.

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