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# CERAMICS
## INDUSTRIAL PROCESSING AND TESTING

J. T. JONES AND M. F. BERARD

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JOHN T. JONES, Associate Professor of Ceramic Engineering at Iowa State University, obtained the B.S. degree in Ceramic Engineering from the University of Utah in 1957. While a student he worked for Electroceramics, Incorporated, Salt Lake City, Utah, and Norton Company, Worcester, Massachusetts. From 1957 to 1962 he was employed as a development engineer and as a production superintendent by Coors Porcelain Company, Golden, Colorado. He received the Ph.D. degree in Ceramic Engineering with a minor in Metallurgy in 1965. Before joining the Ceramic Engineering staff at Iowa State University in 1966, he was assistant director of research at the Vesuvius Crucible Company in Pittsburgh. His research interests include crystal growing, diffusion in oxides, mechanical properties of oxides, and creep properties of ceramics. His publications include several articles in the *Journal of the American Ceramic Society* and the *American Ceramic Society Bulletin*.

MICHAEL F. BERARD received the B.S. degree in 1960 in Ceramic Engineering from Iowa State University and the M.S. degree from the same school in 1962. From 1962 to 1964 he was employed as a rocket nozzle materials engineer with the Aerojet-General Corporation, Sacramento, California. In 1964 he joined the staff of the Ceramic Engineering Department at Iowa State University where he earned the Ph.D. degree in 1968. He currently serves as an Associate Professor of Ceramic Engineering at Iowa State University and as Engineer at the Ames Laboratory of the U.S. Atomic Energy Commission. His research interests include diffusion in oxides and halides and properties of rare earth oxide ceramics. His publications include articles in the *Journal of the American Ceramic Society*.

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deposits of fireclays in the United States are found in central Missouri, although numerous other deposits are scattered over the country.

## FLUXING MINERALS

A flux is a material that appreciably lowers the required firing temperature of a ceramic by reacting with other materials present at low temperature to form glass. Many inorganic materials exhibit some fluxing tendency, but the most important fluxes for ceramics are those that contain alkalies (Li, Na, K, Rb, Cs), alkaline earths (Ca, Mg, Sr, Ba), boric oxide, and the lead oxides. Any mineral which contains appreciable amounts of these substances, usually as oxides, is therefore a fluxing mineral.

The feldspars are a group of minerals which form glass at moderate temperatures. All of the spars of importance to ceramics consist of aluminosilicates of sodium, potassium, or calcium. The pure spars are albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$). These minerals often occur in nature together. Specifically, the minerals albite and anorthite are found in solid solution in all proportions in the so-called plagioclase series. Very little solid solution is found between anorthite and orthocase. The most important feldspars for routine ceramic applications are mixtures of albite and orthoclase. These spars are often specified by their soda to potash ($Na_2O$:$K_2O$) ratio. Large deposits of feldspars are found in New England and North Carolina in the United States and also in Canada. Minor deposits of good quality spars are found in several other states.

Nepheline syenite is a fluxing material consisting of about 75 percent mixed soda and potash feldspars and about 25 percent of the mineral nepheline ($NaAlSi_2O_4$). The major deposits are in Ontario, Canada.

Talc is a hydrated magnesium silicate mineral with the chemical formula $Mg_3Si_4O_{10}(OH)_2$, similar in structure to pyrophyllite. This soft, almost soapy mineral is used as a major constituent in steatite porcelains, especially in wall tile, art pottery, and electrical insulators. Talc is also an important constituent in the cordierite porcelains which are known for their low thermal expansion. Important deposits of talc in the United States occur in the southern California–Nevada region, the North Carolina–Georgia region, and in Montana.

Soda ash is a hydrated sodium carbonate typically having the chemical formula $Na_2CO_3 \cdot xH_2O$ where $x = 1$, 7, or 10. This material is the primary source of soda ($Na_2O$) used in the production of flat and container glass. Some soda ash is taken from natural alkali deposits, but most of the material is produced by chemical processing of brine.

Borax is a hydrated sodium borate mineral having the chemical formula $Na_2B_4O_7 \cdot 10H_2O$. Since this mineral thermally decomposes to give two potent fluxes, soda and boric oxide ($B_2O_3$), it is a very powerful fluxing additive. The major uses of this mineral are in glasses, glazes,

and enamels. Dried lake beds in California often contain very pure deposits of borax and they serve as the chief sources of the mineral.

A number of lead oxides are used as fluxes in glazes and enamels and also as major constituents in the brilliant lead glasses used to produce glass crystal and optical glasses. The important lead oxides are litharge (PbO), red lead ($Pb_3O_4$), and white lead (also called basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$). These materials are products of the chemical processing industry and are not naturally occurring minerals.

## SILICA

Silica ($SiO_2$) in the form of quartz is the second most utilized ceramic raw material after the clays. It is the chief constituent in most glass batches and is a major ingredient in most glazes and porcelain bodies. Quartz is the most common mineral in the earth's crust, but is usually found mixed with other minerals in granite and other rocks. Very large deposits of sandstone of amazing purity occur in Illinois and West Virginia with numerous other deposits scattered through the Great Lakes states and California. These sandstones consist of loosely cemented quartz grains that are readily reduced to sand by hydraulic mining techniques.

The glass industry uses enormous quantities of silica in the form of glass sands resulting from the breakdown of sandstone. The silica used to impart strength and stability to porcelain bodies is a much finer-grained quartz called potter's flint which is produced by fine grinding of the more iron-free quartz sands. The same is true of the silica used as a glass-forming ingredient in glazes and enamels. Nearly pure silica is also molded into refractory shapes.

## REFRACTORY OXIDES

The high melting points and chemical corrosion resistance of several of the ceramic oxides make them useful as refractories where fireclays do not provide satisfactory service. These materials are often used as additives to increase the refractoriness of a ceramic mixture.

Alumina ($Al_2O_3$) is used extensively in the manufacture of technical ceramics. It is an excellent electrical resistor and abrasive, and its high melting point (2050° C) makes it an excellent refractory. There is a current trend to use alumina to replace part of the flint in porcelains to allow faster firing cycles. It is also used as an ingredient in certain heat resistant glasses. Alumina is produced from the minerals bauxite and diaspore which are mined in Arkansas and Missouri, but Dutch Guiana has become an important source for this material in recent years.

The so-called basic refractory oxides—magnesia (MgO), chromium oxide ($Cr_2O_3$), and lime (CaO)—have long been important furnace-lining materials for the steel industry. With the advent of the basic oxygen process in steelmaking, the need for these refractories has increased tre-

mendously. Magnesia can be produced by calcining, or "dead-burning," the mineral magnesite ($MgCO_3$), but the purer material is produced from seawater by precipitation as $Mg(OH)_2$. In either case, the mineral produced by high-temperature calcination is periclase (MgO), an extremely stable, high-melting-point material. Lime (CaO) is produced by calcination of limestone ($CaCO_3$). A mixture of lime and magnesia is produced by calcination of the mineral dolomite ($CaCO_3 \cdot MgCO_3$). Chrome-ore refractories are generally made from chromite which is a mineral consisting of chromium-iron spinel ($FeCr_2O_4$) but always containing some Mg and Al impurities. The refractoriness of chromite is often improved by the addition of MgO.

## MISCELLANEOUS CERAMIC RAW MATERIALS

In addition to those materials already described, several hundred other raw materials are used by the various ceramic industries. The tonnages of these materials used are considerably less than for the major materials already mentioned, but their dollar value is certainly not insignificant. Several of these minor materials are sufficiently common to warrant mention here.

Graphite is essentially pure carbon. It is a superrefractory material which will not melt even at the highest industrial temperature. Graphite is generally not wetted by melts and slags and therefore resists chemical attack. It must be protected from oxidation above red heat. Graphite can be found in nature, but the greatest quantity is produced synthetically from petroleum coke. Furnace liners, crucibles, casting molds, and electric furnace electrodes are the major ceramic uses of graphite. It is often mixed with fireclay to produce crucibles that are resistant to oxidation.

Gypsum is a natural mineral having the formula $CaSO_4 \cdot 2H_2O$. When heated gently, part of the water of hydration is removed to produce plaster. When water is added, the plaster "sets" by rehydration back to gypsum. Plaster is a useful construction material, but it is also very important for use in ceramic forming molds (Ch. 4).

The sillimanite minerals all have the chemical formula $Al_2SiO_5$. Different crystalline forms are called kyanite, sillimanite, and andalusite. These natural minerals are used as sources of aluminum oxide to increase the refractoriness of ceramic compositions.

Silicon carbide (SiC) is an excellent refractory and abrasive material. It does not occur naturally, but is produced synthetically from sand and petroleum coke. When formed into refractory shapes it may either be used alone or in a mixture with fireclay.

Zirconia ($ZrO_2$) and zircon ($ZrSiO_3$) are important refractory materials and excellent thermal insulators. Zirconia is seldom used in the pure form, but rather is stabilized by the addition of lime or other oxides to eliminate destructive crystal structure changes during heating and cooling. Zircon is often used as an opacifier in glazes to increase their covering power.

CHAPTER THREE

# RAW MATERIALS PROCESSING

MOST CERAMIC RAW MATERIALS are located in large deposits in the earth's crust. The manufacture of ceramic products really begins with prospecting for these mineral deposits, and might be considered to include such operations as constructing roads and running utilities to the mine site. After mining, the minerals must be purified, crushed, sized, and transported to the manufacturing site. Here further crushing and sizing usually take place, followed by blending of various raw materials and conditioning with water or other additives. Only then can a useful product be formed from the raw mix. This chapter is concerned with the operations performed in ceramic manufacturing from the mining operation up to the forming step. A great variety of processing equipment is involved in these operations.

## MINING

Ceramic raw materials may be taken from the earth in several different ways. The most important method is called strip-mining or open-pit mining, and is useful when materials are located close to the surface in large, uniform deposits. The earth covering the deposit (called overburden) is removed with bulldozers and the raw material is then collected with standard earth-moving equipment or is occasionally washed out hydraulically. In a properly managed operation, the land is reclaimed and converted to pasture or other uses as the deposit is used up (*Fig. 3.1*).

When the mineral deposit is located far below the surface, vertical shafts or horizontal tunnels must be driven into the deposit. Material is often removed by drilling and blasting. The tunnels must usually be supported or shored up to prevent cave-ins. Miniature railroad systems can often be used to carry raw materials horizontally to the surface; at other times, the raw materials must be transported to the surface in vertical conveyors or elevators.

To minimize the cost of transportation of raw materials, ceramic plants are located close to the mining operation whenever possible. In such operations, the raw material is taken from the mine to the plant

**FIG. 3.1. Many *ceramic raw materials* including clays are *mined* by open-pit methods** (courtesy H. C. Spinks Co.): (a) After stripping away the overburden, heavy machinery is used to remove the clay.

(b) When the pit is exhausted, conservation-minded companies convert *the land to agricultural* or recreational uses.

with little or no treatment at the mine. In other cases, it is processed and refined (beneficiated) near the mine and then shipped to a distant ceramic market by railroad or truck. Feldspar, kaolin, and kyanite are good examples of materials which are beneficiated near the mine before shipment.

## CRUSHING AND GRINDING

Ceramic plants that use large quantities of bulk raw materials frequently have a sizeable investment in machinery designed to crush or pulverize raw materials and classify them according to particle size.

Jaw crushers and gyratory crushers are frequently used as primary crushers to reduce the size of lumps of raw material from as large as a yard in diameter down to a few inches. The jaw crusher uses a horizontal squeezing motion to crush the raw material between vertical plates of hardened steel (Fig. 3.2). The gyratory crusher uses eccentric

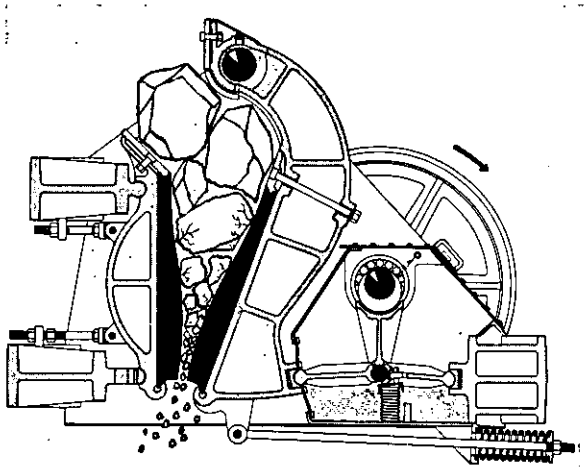


**FIG. 3.2. The jaw crusher breaks up rock by applying pressure between swinging metal jaws** (courtesy Pennsylvania Crusher Corp.).

rotating motion to crush the material between concentric steel cones (Fig. 3.3).

Secondary crushing refers to reduction in size from lumps a few inches in diameter down to particles 0.1 inch or less in diameter. Clay materials frequently undergo secondary size reduction by crushing under steel-tired wheels (mullers) in a shallow rotating pan. Plows force the clay under the heavy mullers, and perforations in the bottom of the pan allow material of sufficiently small size to drop through (Fig. 3.4).

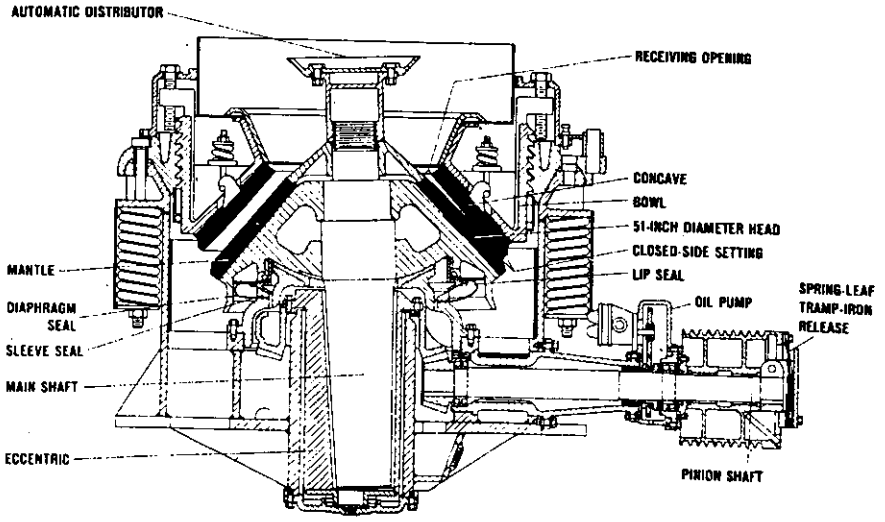



**FIG. 3.3. The gyratory crusher is similar in principle to a jaw crusher, but a stationary bowl and eccentrically gyrating cone are used to apply pressure to the rock** (courtesy Pennsylvania Crusher Corp.).

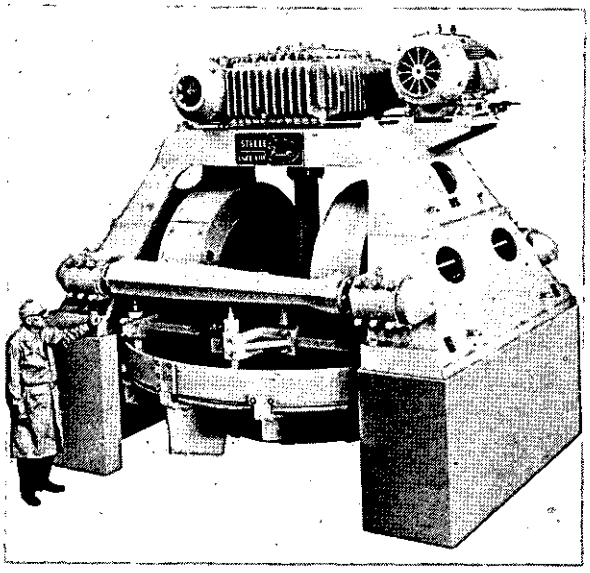


**FIG. 3.4. A dry pan showing the heavy mullers and plows** (courtesy J. C. Steele & Sons, Inc.).

This crushing device is called a dry pan. After dry panning, most clay materials need no further crushing.

Hammer or impact mills may be used for the secondary crushing of hard, brittle materials. These mills break down material by impact with rapidly moving steel hammers. The hammer mill uses a screen to control the maximum size of particle leaving the mill; the impact mill has no screen and produces a less uniform product. Cone crushers, which operate on the same principle as gyratory crushers, may also be used for hard materials. Other secondary crushers in common use are the smooth roll crushers, which crush the material by pinching between two narrowly spaced rollers, and the toothed roll crushers, which crush material between a toothed roller and a curved steel plate (Fig. 3.5.

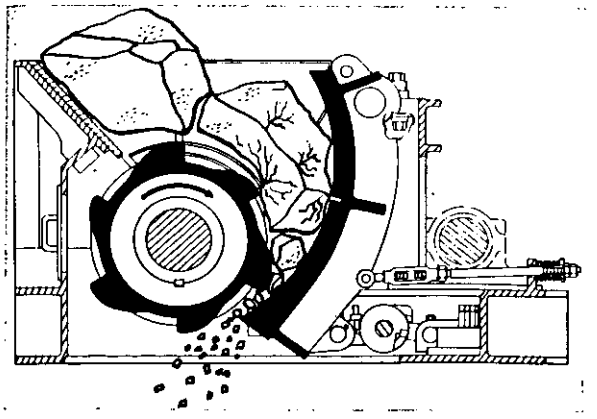


**FIG. 3.5. A toothed-roll crusher pinches rock between a plate and a rotating toothed-roll to give a combination of shear, impact, and compression** (courtesy Pennsylvania Crusher Corp.).

When a very fine particle size product is required, as for example in the cement industry and in preparing casting slips, a tertiary size reduction is necessary. This operation is termed fine grinding and is often accomplished in some kind of a tumbling mill. These mills consist of large rotating cylinders partially filled with heavy steel or dense ceramic grinding media of spherical shape (ball mill), or in the form of heavy rods of the same length as the cylinder (rod mill). Occasionally flint pebbles will be used as the grinding media (pebble mill). Raw material smaller than an inch in diameter is fed to these mills, and the resulting product can be 50$\mu$m or less in diameter depending on grinding time. This tremendous size reduction takes place by impact of the material with the tumbling grinding media and by abrasion between the media and with the mill wall. If no iron contamination of the product can be tolerated, all-ceramic-lined mills and ceramic grinding media must be used. Milling can be done dry, but it is much more efficient when the raw material is in slurry form (Fig. 3.6). In dry grinding, an air separator (whizzer) can be used to carry away the light, fine product while the heavier, coarse material remains behind for further grinding.

Considerable amounts of tramp iron may be present in raw materials after mining, transporting, and crushing, and magnetic separators can be used to remove most of this iron. The type of separator used depends on whether the material is being processed dry or as a slurry. Permanent bar magnet grids or magnetized conveyor pulley terminals are useful for dry processing, while electromagnetic "filters" may be used for slurries.

## SCREENING

Screens are used by the ceramic industries to separate out particles in a specific size range from a mixture of particle sizes. Screens may be

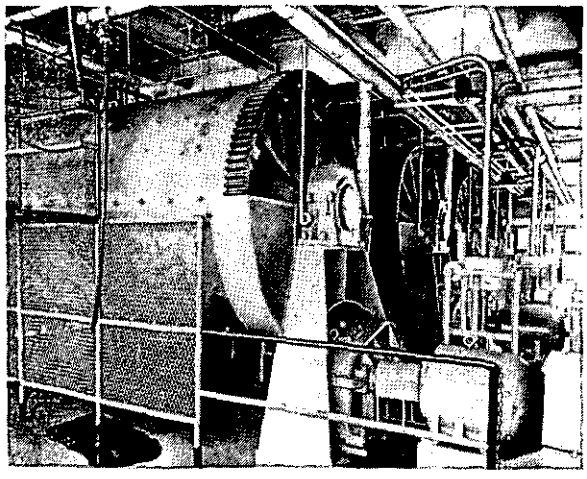
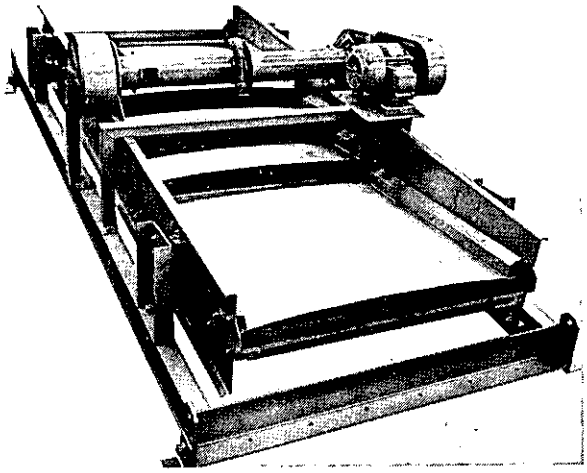


**FIG. 3.6. Large ball mills used in the preparation of materials for porcelain sparkplug insulators** (courtesy Abbe Engineering Co., Brooklyn, N.Y.).



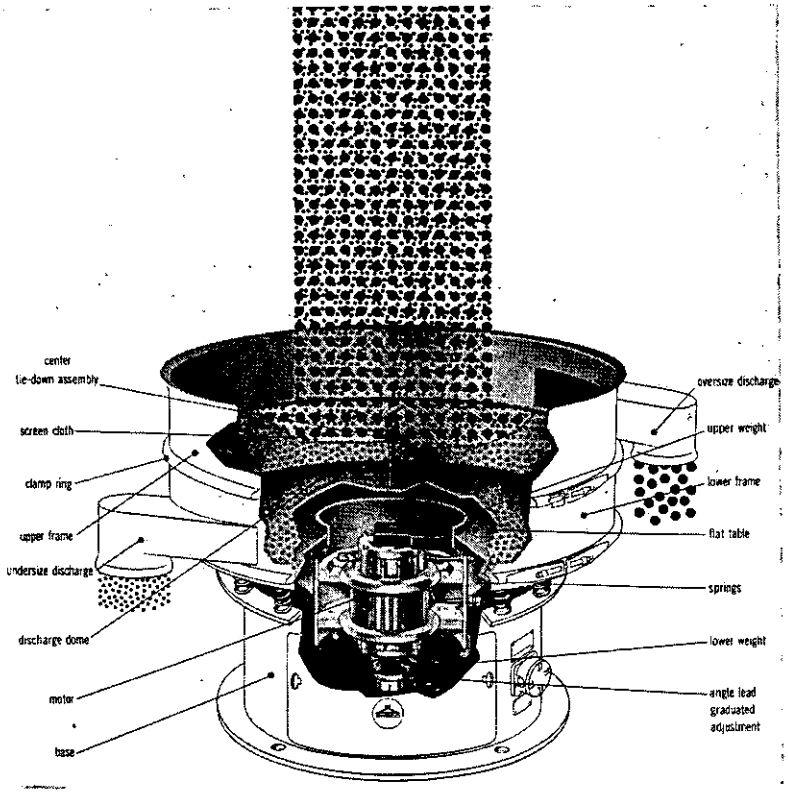



**FIG. 3.7. Vibrating screens:**
(a) Inclined rectangular deck (courtesy W. S. Tyler Inc.).

(b) Horizontal deck, vibro-energy separator (courtesy SWECO, Inc.).

used either to eliminate coarse material (oversize) or to eliminate fines (undersize). For example, a screen operating on the output of a crusher can separate insufficiently crushed particles from properly crushed material. When the oversize is returned to the crusher, the operation is called closed circuit crushing. Screens can also be nested one above the other to produce narrow size fractions that can be stored separately and later reblended in the correct proportions to insure a uniform product. Small, specially constructed screens called testing sieves are used to measure the particle size distribution of ceramic powders. (See Ch. 10.)

Screens are normally operated in a sloped position to insure a "pouring" action of material over the screen deck. The screen is usually vibrated mechanically or electromechanically to aid in material flow and improve efficiency. Figure 3.7 illustrates vibrating screens.

The size of screened material is normally specified by mesh numbers. The mesh number of a screen is the number of openings per lineal inch of screen surface. The higher the mesh number, the smaller the opening size. The size openings of the various mesh screens are given in Table 10.1. If material has been passed through an 8-mesh screen, it may be referred to as "minus 8-mesh," "through 8-mesh," or simply "8-mesh." If the material has passed through an 8-mesh screen, but would not pass through a 10-mesh screen, it is referred to as "—8 +10," "through 8-on-10-mesh" or simply as "8/10" material.

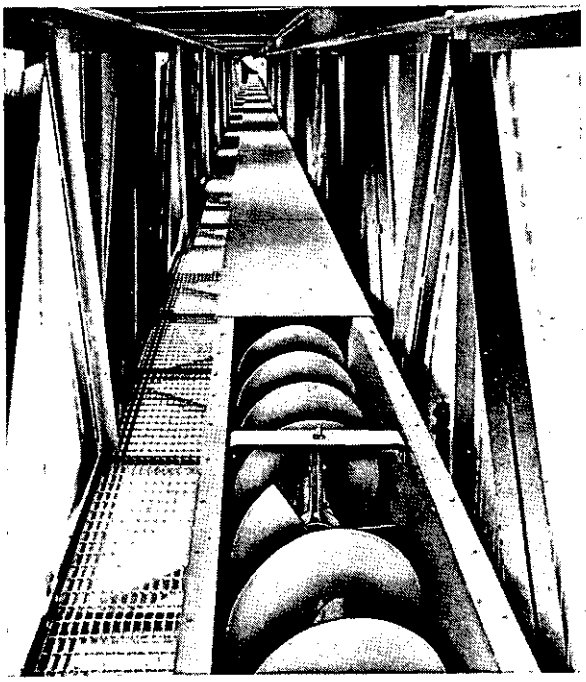
The efficiency of a screen is a measure of its ability to perform the separation or "cut" between coarse and fine material. An inefficiently operating screen will usually produce an oversize stream that actually contains an appreciable amount of fines that should have fallen through the screen. This will occur whenever a sizeable fraction of the screen openings are covered over or plugged by material. If the screen is fed too rapidly, much of the material will never contact the screen surface and can thus never be sized. Plugging of the screen openings (binding) can be caused by particles only slightly larger than the opening (near mesh particles) or by sticky materials such as damp clays. The latter problem can be eliminated by electrically heating the screen surface to dry out damp material. Wear of the screen by abrasive materials can enlarge the openings so that coarse material enters the undersize stream. This will also constitute a loss in efficiency.

## MATERIALS HANDLING

Many ceramic industries purchase large quantities of raw materials already crushed, screened, and purified. These materials are received either as bulk shipments in railroad hopper cars or in bags by railroad car or truck. Bagged materials may be stacked under cover in an ordinary warehouse facility, but bulk materials must be stored in bins and silos. The lack of uniform flow of powdered materials in a bin is a cause of many production problems, especially when nonfree flowing materials like clays are involved. The removal of material from the

bottom of a bin is often hampered by packing (bridging or arching) due to the weight of material above. Careful design of the bins, including consideration of bin wall slope angles and surface finish, can sometimes alleviate flow problems. The most common solution to flow problems in bins however is to incorporate some kind of bin vibrator or internal stirring device to improve flow.

Bagged materials are generally transported around a plant by means of forklift trucks, but bulk materials must be transported by means of conveyors (Fig. 3.8, a–e). A screw conveyor has an auger turning in-



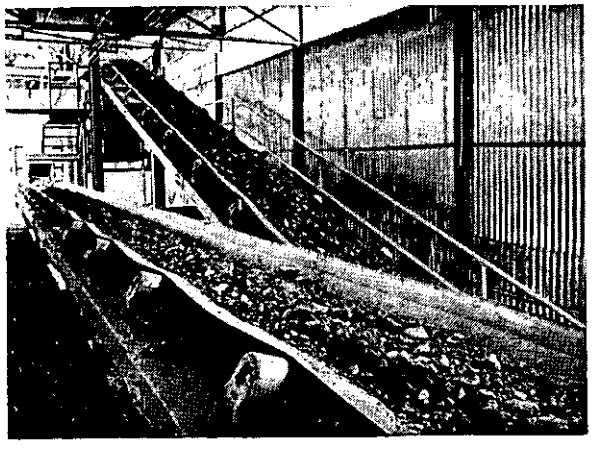


**FIG. 3.8. Bulk material conveyors:**
(a) Screw or auger conveyor (courtesy Screw Conveyor Corp.).

(b) Belt conveyors (courtesy Stephens-Adamson Division of Borg-Warner Corp.).

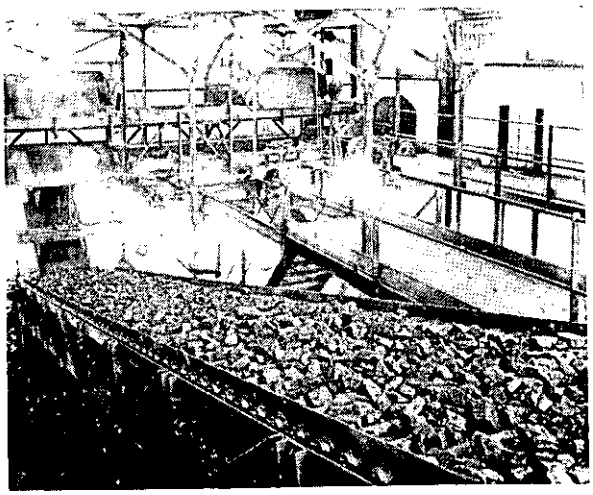
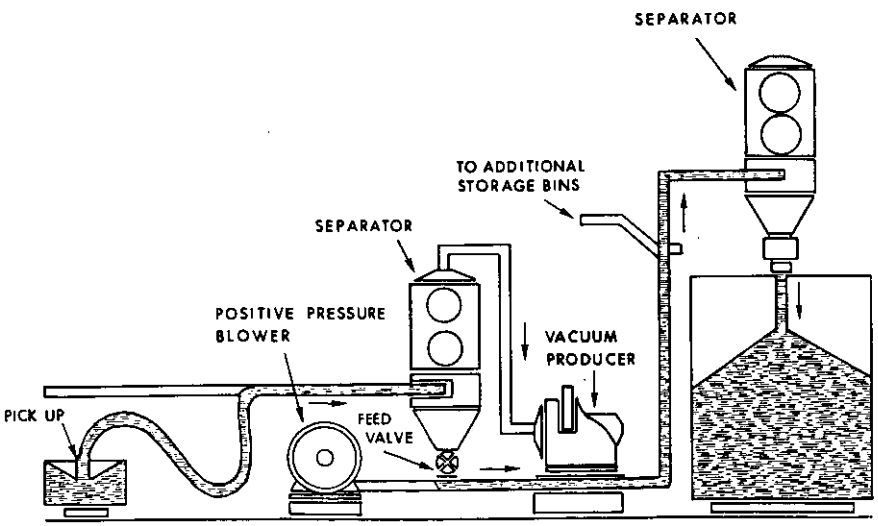
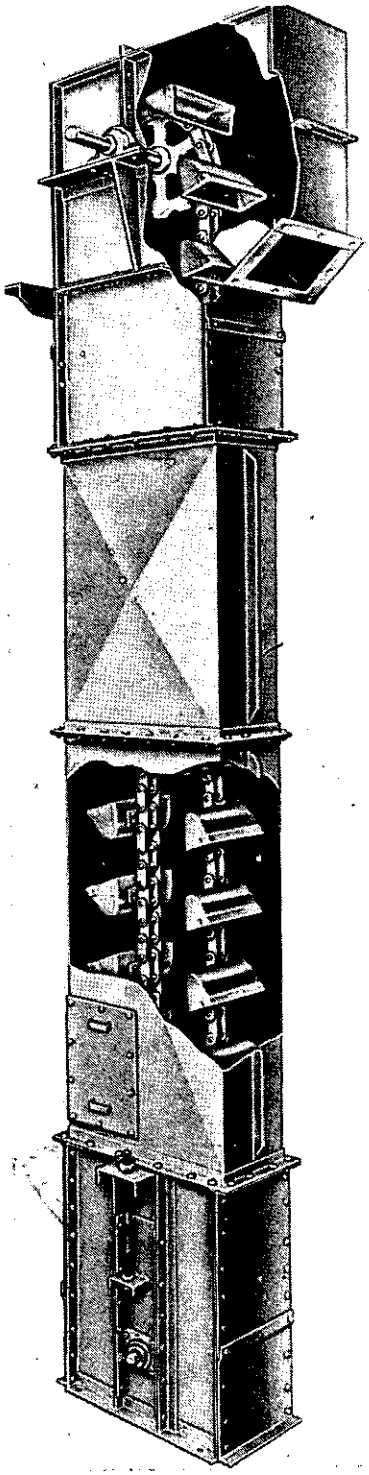


**FIG. 3.8. Continued:** (c) Flight conveyor (courtesy Jeffrey Manufacturing Co.).




(d) Pneumatic conveyor system with vacuum pickup and pressure distribution to bins (courtesy The Spencer Turbine Co., Hartford, Conn.).



(e) Bucket elevator (courtesy Stephens-Adamson Division of Borg-Warner Corp.).

side a trough and is useful for moving nonabrasive, nonfriable materials of fine particle size over short distances up to perhaps 100 feet. Vibratory conveyors are also useful for short distances and are particularly important for "dribbling" a small amount of additive into a blending operation. For medium- or long-distance conveying, endless belt conveyors are widely used either for horizontal or inclined movement of large tonnages of lumpy materials. Flight conveyors consisting of a series of vanes (flights) on an endless chain are sometimes used for medium-distance conveying of materials, especially if they are hot. Pneumatic conveyors that push or pull fine powders through a pipeline by means of air pressure or vacuum are replacing many other types in the ceramic industries. Many plants today receive dry bulk materials in specially constructed railroad tank cars or trucks which can be unloaded pneumatically in a few minutes. Pneumatic conveyors can move fine material vertically; many other types cannot do so. Bucket elevators are used for moving lumpy material vertically.

A popular new concept for clay users is the purchase of clay as a slurry delivered by tank truck. Other raw materials can be added directly to the slurry to form a slip for casting purposes. (See Ch. 4.)

## PROPORTIONING AND MIXING

The success of the modern ceramic industries is based on an ability to proportion correctly various raw materials of the proper purity and particle size distribution, mix them together, form them into useful shapes, and finally fire them at high temperatures. In the heavy clay products industries, the proportioning may consist of feeding a single pulverized shale into an extrusion auger at a controlled rate along with a controlled amount of water. In most of the ceramic industries however many different raw materials need to be carefully weighed out and mixed together.

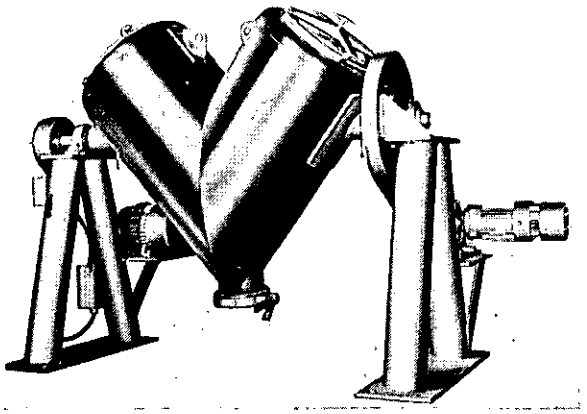
If the proportioning is to be done on a batch basis (i.e., if a definite amount of the mixture is to be prepared), the ingredients are weighed one by one into a weigh hopper. When the batch is complete, the weigh hopper is discharged into the mixing machinery. The weigh hopper may be stationary with a conveyor used to transfer the batch to the mixer, or the weigh hopper may be portable so it can be moved under each raw material bin to receive the proper amount of material and then moved to the mixer.

When proportioning is to be done continuously rather than in discrete batches, variable-speed belt or screw conveyors are used to carry each material from its storage bin into a continuous mixer. The relative speed of each raw material belt is fixed by the proportions of the raw material recipe and the demands of the process.

Bagged materials can be loaded directly into a batch mixer. In the technical ceramic industries, bags are usually weighed before and after emptying so that the actual weight added can be determined. This practice is necessary because small variations in composition of certain

technical ceramics can have profound effects on the material properties. Very small additions are carefully weighed on accurate table balances before being added to the batch.

Dry mixing is usually accomplished in either a shell mixer, a ribbon mixer, or an intensive mixer. The twin-shell mixer shown in Figure 3.9(a) consists of two hollow columns joined together into a V shell. As the shell rotates, the tumbling material is divided and poured together again and again to accomplish mixing. Another shell mixer configuration is the double cone shown in Figure 3.9(b). The ribbon



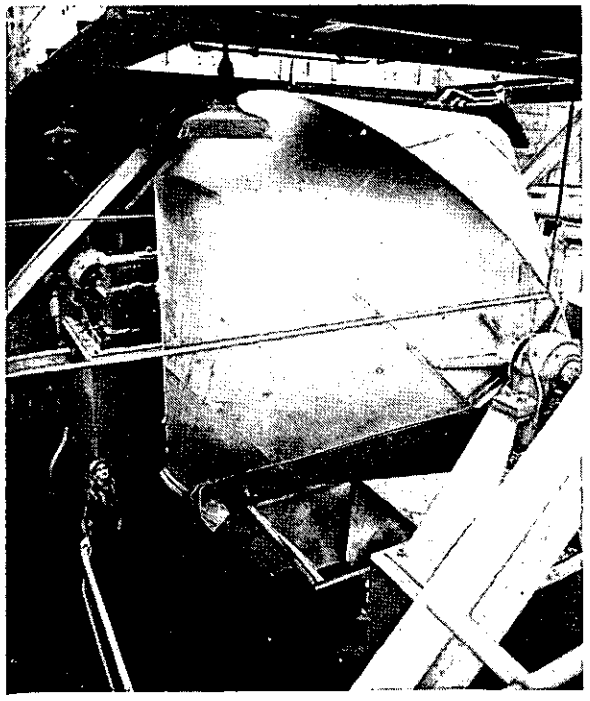


**FIG. 3.9. Shell mixers:** (a) Twin-shell or V mixer (courtesy Patterson-Kelley Co. Inc.). (b) Double-cone mixer (courtesy Patterson-Ludlow Division of Banner Industries, Inc.).

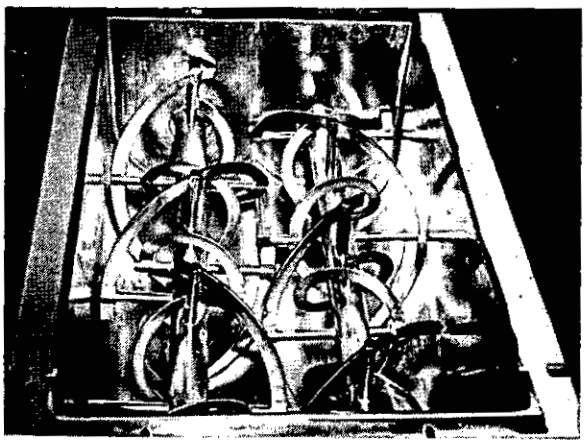


**FIG. 3.10. Conventional ribbon mixer** (courtesy The J. H. Day Co.).

mixer (Fig. 3.10) uses a helical vane (ribbon) rotating inside a closed chamber to accomplish mixing. Figure 3.11 shows a dry color agitator which utilizes a segmented ribbon. The intensive (turbine) mixer uses rapidly revolving plows to give coarse material a tumbling and folding action.

## TEMPERING

Tempering is the addition of water or other liquids to a dry ceramic powder to produce a mixture suitable for forming. The tempering operation usually combines mixing of dry materials with the incorporation of water by cutting and kneading the mass. The result can be ma-

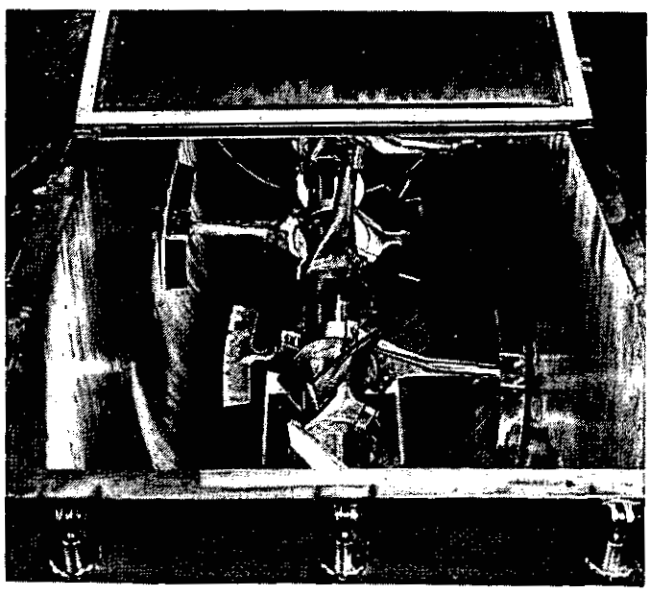


**FIG. 3.11. Dry color agitator** (courtesy The J. H. Day Co.).

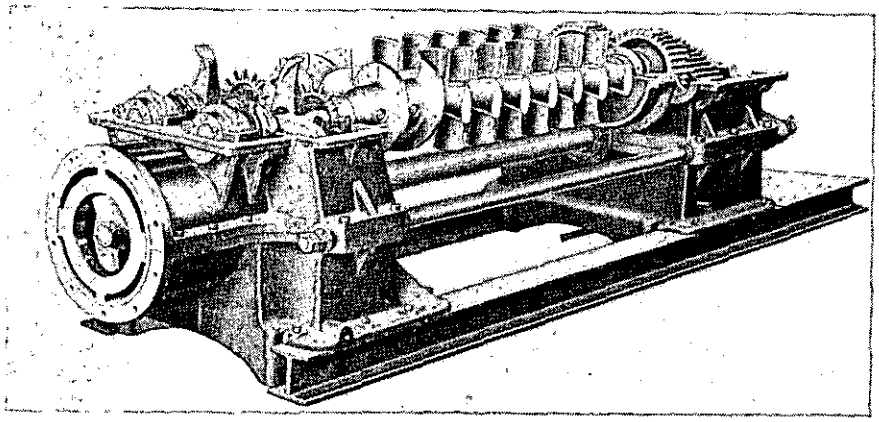


**FIG. 3.12. Pug mill with exterior shell removed to reveal pugging assembly** (courtesy Fate-Root-Heath Co.). **See also Figure 4.1(a).**

terial of a few percent moisture useful for dry press forming or can be a paste suitable for plastic forming. (See Ch. 4 for discussion of forming procedures.)

Shales and fireclays that are to be extruded are usually tempered in a pug mill (Fig. 3.12). The machine uses knives on a rotating shaft to cut through and fold together material in the shallow chamber. Pulverized clay and water are usually fed more or less continuously to one end of the pug mill, and the tempered mass exits at the other end, usually into an extrusion press.

Sigma blade mixers (Fig. 3.13) can give effective mixing of several dry materials in addition to water incorporation. Two oppositely rotating S blades force the powder and water together or against the steel body of the mixer.

The mix-muller (Fig. 3.14) consists of revolving rolls extending from a rotating pivot. The rolls ride in a shallow circular pan where plows guide material under them for tempering. Discharge of the tempered material is through an opening in the side of the pan.

Both the intensive mixer and the shell blender can also be used to add small amounts of moisture to a ceramic mixture. With the shell blender, water can be sprayed into the mix through the perforated hollow shaft on which the mixer turns.

## SLURRY PROCESSING

The whitewares and technical ceramics industries often find it necessary to add enough water to their raw material mixtures to form a slurry or slip. One reason for adding so much water is to aid in the mixing of a multiple-ingredient batch. A second reason for preparing such a slurry is to permit use of the slip casting method for forming ware. (See Ch. 4.)

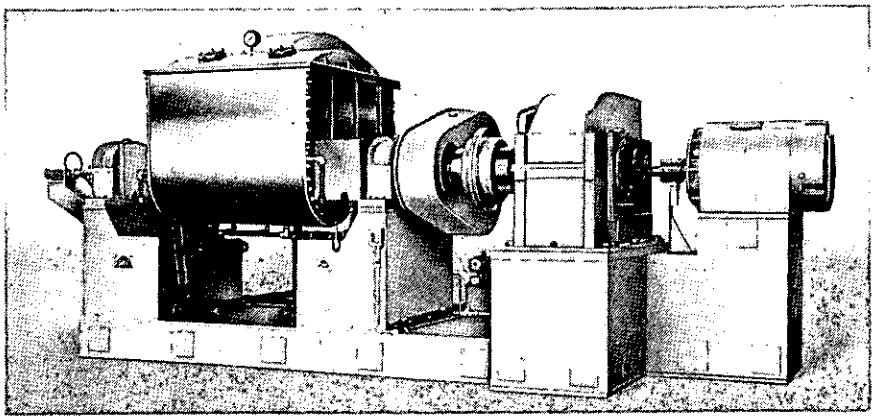
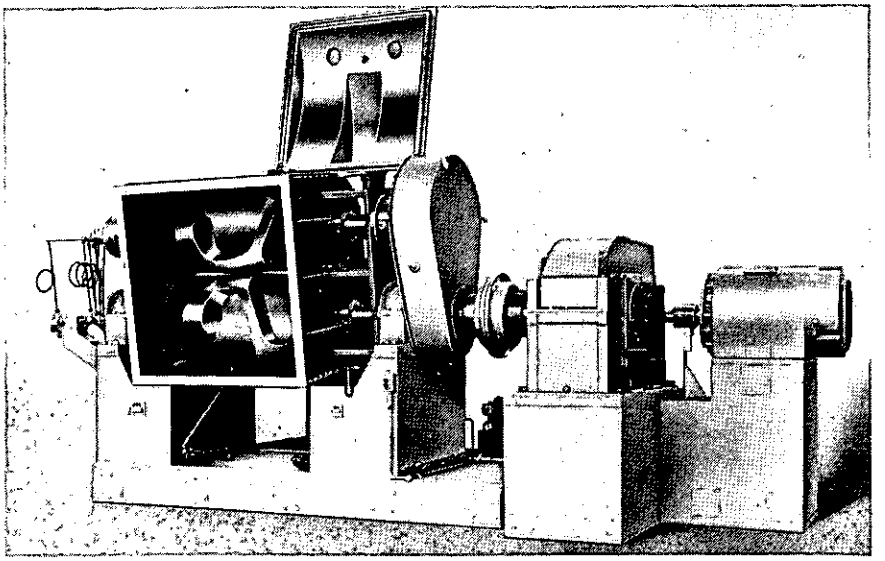


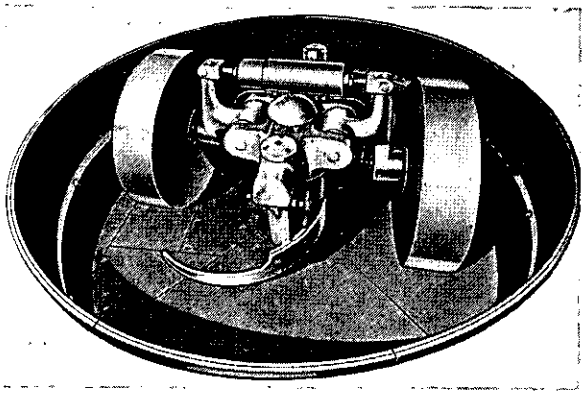
**FIG. 3.13. Sigma-blade mixer** (courtesy The J. H. Day Co.):
(a) Mixing position.

(b) Unloading position showing the mixer blades.



Frequently, slips are prepared by combining mixing, fine grinding, and water addition all in one operation. The ball mill is a useful device for accomplishing these objectives. A vibrating mill, shown in Figure 3.15, is also capable of combining mixing and fine grinding. This mill relies on the rubbing action of a bed of continuously vibrating ceramic cylinders to accomplish the grinding and mixing.

Dry materials of sufficiently fine grain size can be made into slips by mixing with water in blungers—large wood or metal tanks with paddles or turbines used for agitation. The tanks are usually baffled to



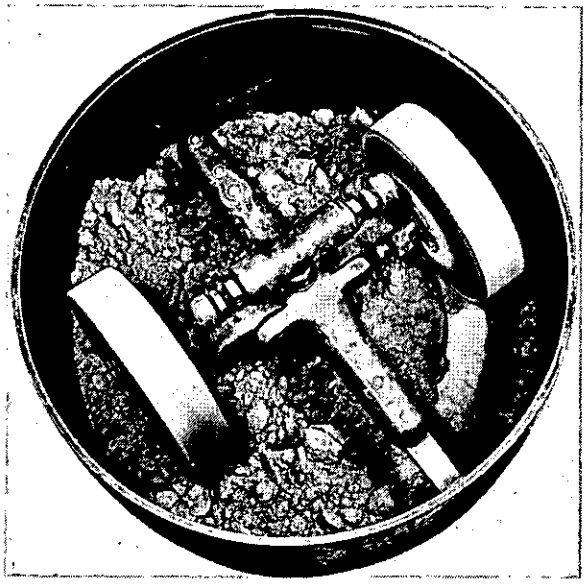


**FIG. 3.14. Mix-muller** (courtesy National Engineering Co.): (a) Details of construction showing mullers and plow.

(b) Mixing a tempered material showing the smearing action of the muller.

eliminate vortexing of the mixing fluids. After blunging, slips are usually stored in agitated holding tanks to prevent settling.

Because of the abrasive nature of ceramic slurries, they can be pumped only with centrifugal or diaphragm pumps that do not have close fitting parts. Transportation from holding tank to utilization point in the plant may be carried out using a pipeline or small portable tanks equipped with a pump for emptying.

If excess water has been added only to aid mixing, it is usually necessary to remove part or all of the water before forming. Partial dewatering can be accomplished by forcing the slip through a filter press such as that shown in Figure 3.16. These filters remove some of the water and leave behind a plastic filter mass (cake) that can be extruded for plastic forming or can be shredded for further drying.

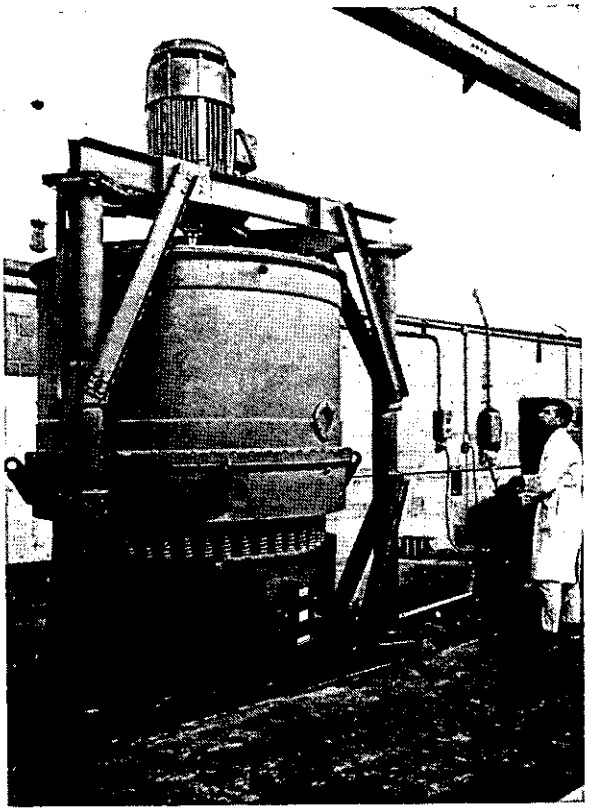
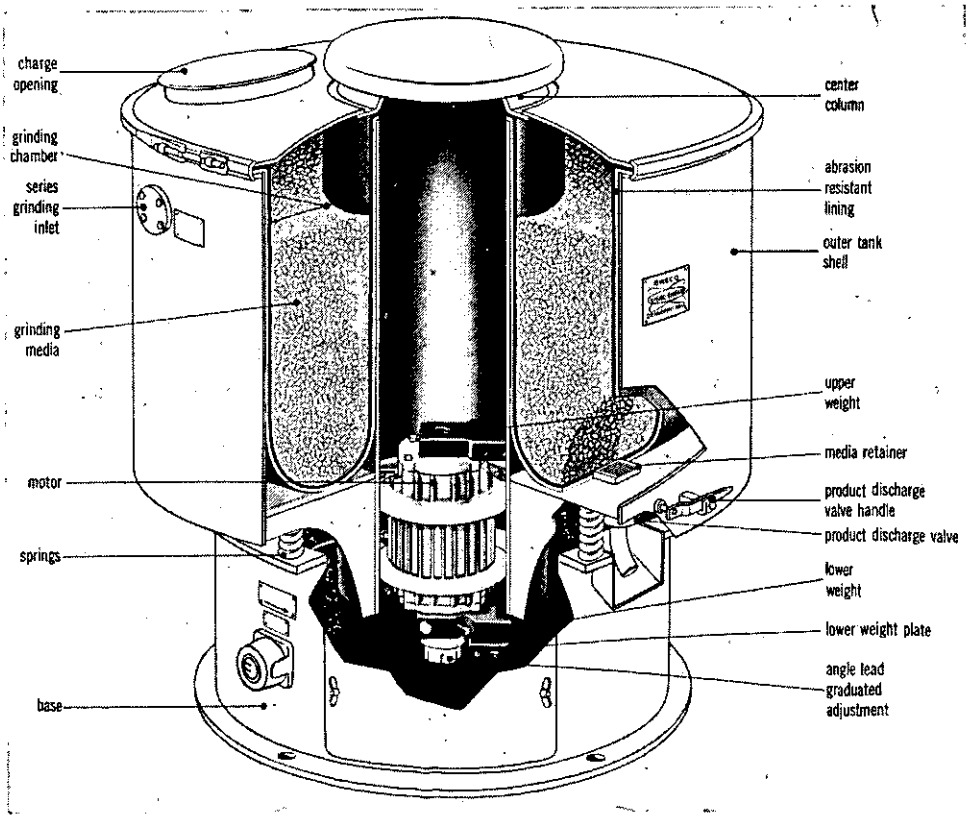


**FIG. 3.15. Vibro-energy mill** (courtesy SWECO, Inc.):
(a) Wet grinding mill.

(b) Schematic.



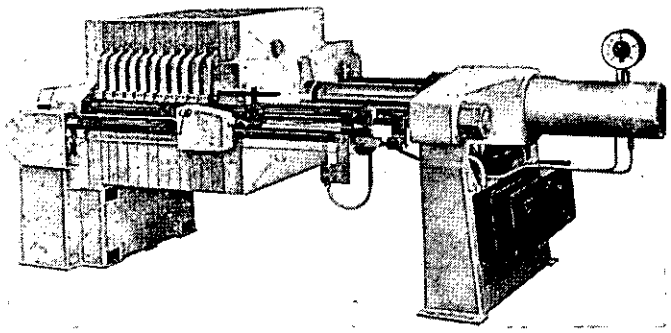


**FIG. 3.16. Filter press** (courtesy Gebrueder Netzsch, Selb, West Germany).

A particularly useful device for reducing a slurry to a granulated body suitable for dry forming is the spray drier (Fig. 3.17, a and b). The slip is pumped to an atomizer consisting of either a rapidly rotating disk or a nozzle usually located at the top of the spray drier. Droplets of slip are thrown out toward the edge of the drier where they fall through a rising hot air column, drying completely before they hit the walls or bottom of the drier chamber. The resulting product consists of

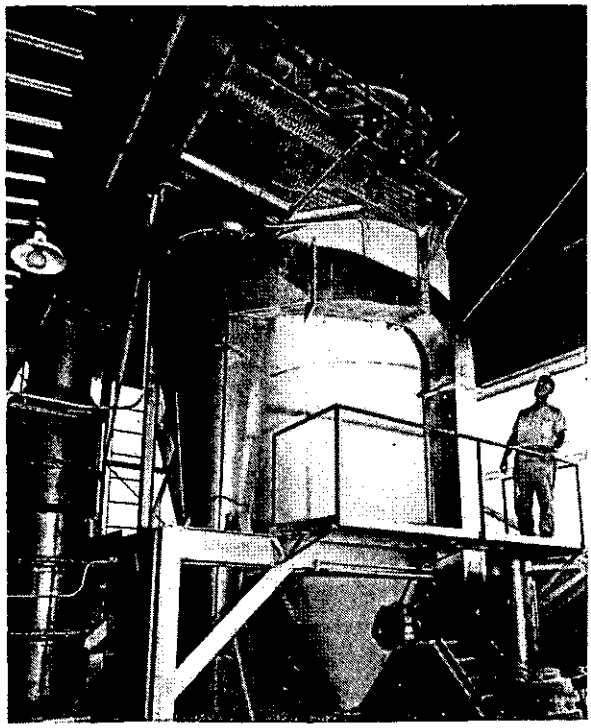


**FIG. 3.17. Spray drier for dewatering slurries** (courtesy Bowen Engineering, Inc., North Branch, N.J.):
(a) Drier chamber with air heater and cyclone separator.

CHAPTER FOUR

# FORMING CERAMIC WARE

THE GOAL of all the processing steps discussed in the previous chapter is the production of ceramic articles that will have properties tailored to a specific end use. To accomplish this goal the ceramic manufacturer is faced with the task of forming ceramic particles into solid, useful shapes that can later be densified by firing.

Ceramic pieces are more difficult to form than metal pieces because of the inherent brittleness and high melting temperatures of ceramics in general. Over the years a great variety of forming techniques have been developed for ceramics, and the more common of these will be discussed in this chapter. These techniques are grouped into the categories of plastic forming processes, slip casting, dry forming processes, and high-temperature forming processes. The forming of glass is discussed in a separate section.

## PLASTIC FORMING

The ease with which metals can be rolled, drawn, forged, and bent into intricate shapes results from the inherent ductility of the individual crystals making up the metal mass. Each individual crystal can deform under applied pressure and retain its new shape when the pressure is removed. Ceramic crystals are brittle and will fracture rather than flow under applied pressures. For this reason a dense mass of ceramic crystals cannot be formed by the same methods used for forming metals.

Prehistoric man discovered that clay-containing mineral mixtures when tempered with water were plastic enough to be formed by hand into useful shapes. The forming of such plastic mixtures can be accomplished by methods very similar to those used for low-yield-point ductile materials. The ability of clays to be formed when in the plastic condition and then to be made hard and durable by heat treatment is responsible for the great utility of these minerals in our everyday lives.

Modern man has learned that nonclay ceramic materials, although not rendered plastic by the simple addition of water, can be brought into a plastic condition by the addition of certain organic materials. These materials may be classified as binders or lubricants according to the functions they serve in the plasticizing process. Binders serve to give

CHAPTER FIVE

# DRYING, FIRING, AND FINISHING CERAMIC WARE

MANY CERAMIC-FORMING PROCESSES involve the intentional addition of water to the material mixture. Since the ware thus formed will be fired at high temperatures which would turn this water to steam and literally explode the ware, the water must be removed prior to firing. Drying is the removal of mechanically combined water and sometimes also involves vaporization of additives such as plasticizers and binders. Ceramic products formed without the addition of water, including many electronic components, certain refractory shapes, and spark plug insulators, do not require a drying step prior to firing.

Firing (burning) ceramic ware is probably the most important single step in the overall production process. It is during firing that the final properties and the final usefulness of the ceramic product are developed. Detailed descriptions of the physical and chemical changes that take place while the material is maturing in the kiln are complex, and only a general description of these processes is given here. A variety of kilns and furnaces are utilized to carry out the firing of ceramic ware and glass melting. A representative selection of these will be described along with a brief discussion of combustion and furnace atmospheres. The methods used to finish ceramic ware after firing, including grinding, glazing, and bonding to other materials, will also be described.

## DRYING

The removal of water from ceramic ware can take place only at the surface by evaporation. The water on the interior of the article must travel to the surface by seeping through interconnected pores. Both processes—evaporation and seepage toward the surface—are accelerated by heating. Since the individual particles that make up the wet-formed ware are held apart by thin layers of water, the removal of this water will cause the particles to pull together, resulting in an overall decrease in the volume of the piece. This drying shrinkage is discussed in some detail in Chapter 7. The greater the amount of water originally added to aid in forming the ware, the greater will be the amount of drying shrinkage occurring when that water is removed.

If the rate of evaporation of water from the surface of a drying piece is greater than the rate at which water can seep through the pores from the interior toward the surface, the surface of the piece will dry much faster than the rest of the piece. This very dangerous condition (case hardening) allows the surface layers of the piece to shrink a large amount while the interior remains unchanged, and cracks will almost certainly occur across the surface. A similar situation can develop in a piece having both thin cross-sections and thicker cross-sections. Here the thin cross-sections would dry completely before the thicker sections, and the difference in shrinkage would probably cause cracking to occur.

The solution to the first of these problems lies in preventing the rapid evaporation of water from the surface of the piece while large amounts of water still remain in the interior. This can be accomplished by heating the piece initially in an enclosure where the relative humidity is kept high. The higher the humidity of the air surrounding the drying piece, the slower the evaporation rate from the surface of the piece will be. Combining heating to encourage seepage toward the surface with high humidity to suppress evaporation results in a situation where the rates of these two processes are nearly equal and the piece dries uniformly. As drying progresses, the temperature can gradually be raised and the humidity gradually lowered so that evaporation and seepage rates remain reasonably high. Finally the last bit of drying will be done at very low humidity and at temperatures exceeding 212° F, the boiling point of water. This should result in a bone dry piece that is free of shrinkage cracks.

The problem of preventing shrinkage cracks due to nonuniform cross-sections cannot be overcome by this procedure. Instead the thinner cross-sections are usually prevented from drying faster than the thicker sections by selective wrapping with moist cloths that suppress the rate of evaporation. This kind of drying can be done at room temperature or at warmer temperatures if the humidity is kept high. Whenever ceramic pieces of thick cross-sections are to be dried and a controlled humidity enclosure is not available, the use of moist rags will also prevent formation of drying cracks due to surface shrinkage.

Since air at normal drying temperatures holds only a limited quantity of water before reaching saturation (100 percent relative humidity), and since evaporation takes place only if the air surrounding a drying piece is at less than 100 percent humidity, fans are used to circulate air over a drying piece constantly. If the rate of air circulation is increased without changing its humidity or temperature, the rate of evaporation will also increase. Thus the important quantities to control in any drying operation are air temperature, relative humidity, and air flow rate.

A final important consideration in driers is the dew point of the air being introduced. The dew point for a moisture-containing gas such as air is the temperature at which it will start to condense out water. The higher the moisture content of air, the higher its dew point will be. If moist air encounters a solid which is at a temperature below its dew

point, water will condense onto the solid. Thus very high-humidity air passing through a relatively cool portion of the drier system (such as a metal flue) may condense out water, resulting in serious corrosion problems. The dew point problem is also a serious one in the initial heating stage of ceramic firing.

Ceramic pieces of thin cross-section and low water content can be dried by simply placing them in a warm area with good air circulation. Most ceramics which require drying however must be processed in special drier enclosures where the temperature, humidity, and air flow can be controlled. The source of heat for these driers is generally a set of gas or oil burners, although often a considerable amount of waste heat from kilns is transferred to the drier. Some driers are heated by infrared lamps, but electrical resistance heating is too expensive for anything but the very smallest production and laboratory driers. For ease of handling, the ware is usually stacked on cars that can be wheeled in and out of the driers on rails.

Periodic (batch) driers (Fig. 5.1) are necessary when a great variety of articles are being produced and fired in periodic kilns. These driers consist of a single chamber which is filled with ware and then cycled through a specific time-temperature-humidity schedule to achieve complete drying. The drier is then at least partially cooled and the dried ware is removed. When the drier is empty, a new charge of wet ware is rolled in, and the cycle is repeated.

Tunnel driers (Fig. 5.2) are continuous driers that are best suited to a continuous firing operation. They consist of a long chamber through which the ware is slowly pushed. Various zones of constant temperature and humidity are maintained along the length of the tunnel. The formed ware is usually placed directly on refractory-topped kiln cars which can then be passed through a drier and directly into a tunnel kiln without further handling of the ware.

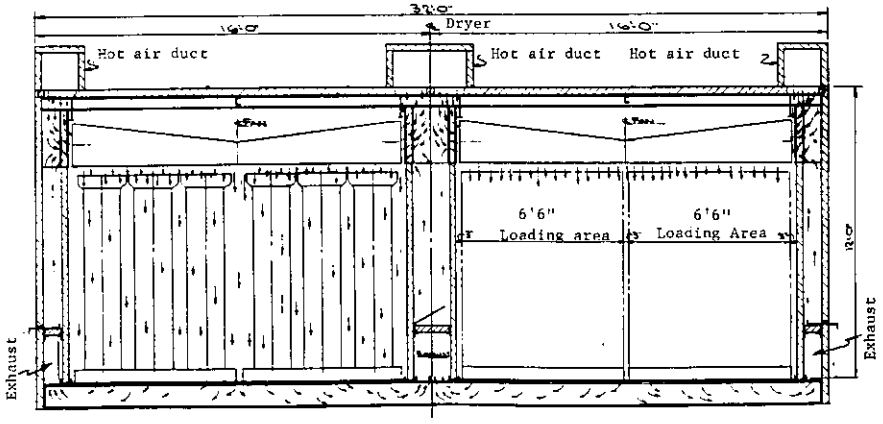



**FIG. 5.1. Schematic of periodic drier for sewer pipe** (courtesy Swindell-Dressler Co.).

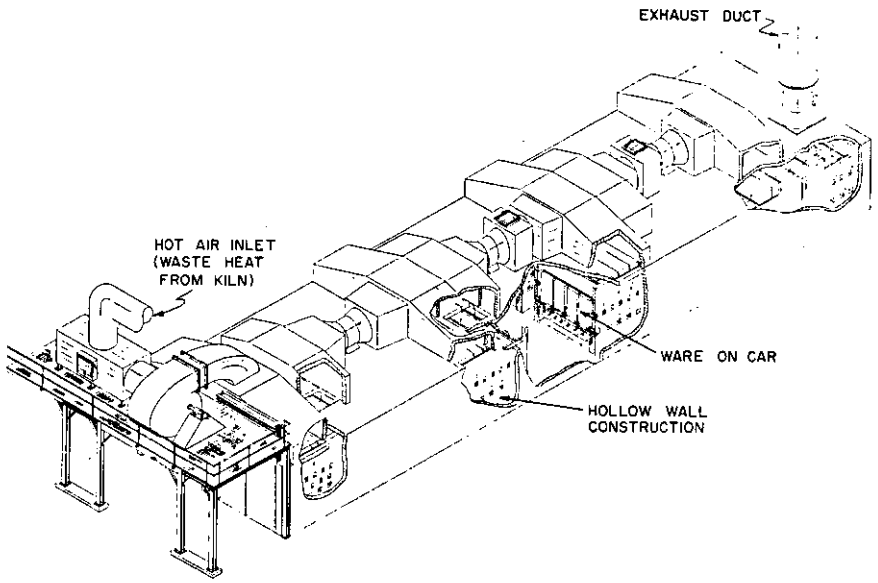



**FIG. 5.2. Schematic of tunnel drier, having several zones of controlled humidity and temperature** (courtesy Swindell-Dressler Co.).

It is sometimes necessary to dry ceramic materials in the unconsolidated condition. For drying moist agglomerated materials such as filter cakes or the products of various wet separation processes, tray driers may be used in which the material is spread on trays that move progressively through a drying chamber. Such material can also be dried in a rotary drier (Fig. 5.3) which consists of a long cylinder tilted slightly from the horizontal and slowly rotated about its axis. Hot dry air is blown into the lower end and exhausts from the higher end. The moist material is fed into the higher end, and because of the action of the rotating tilted cylinder walls, slowly tumbles its way to the lower end where it is discharged dry.

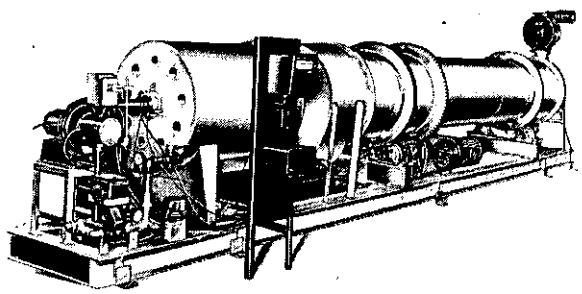


**FIG. 5.3. Rotary drier** (courtesy Davenport Machine & Foundry Co.).

If a ceramic slurry or slip is to be dried, filtering and conventional drying can be eliminated by spray-drying as discussed in Chapter 3.

## FIRING

The maturing of a ceramic body may take place in one of two ways: if formation of glass by partial melting occurs during firing, the maturing process is called vitrification; if no liquid is present during firing, the maturing process is called sintering. (Sintering can also occur when a liquid phase is present, especially when that liquid phase tends to aid in the rate of atomic movement from one particle to another. An example is the use of liquid cobalt to aid in the sintering of tungsten carbide.) In either case, the end results of firing are the same, i.e., the reduction or near elimination of pores accompanied by shrinkage and increased density, and a bonding together of crystalline grains to form a strong, hard mass. The great majority of ceramics, including all whitewares, structural clay products, and fireclay refractories, undergo vitrification during firing. The terms unvitrified, simivitrified, and vitrified are descriptive of the amounts of porosity remaining in the final product. (See ASTM C 242–60.) Most of the vitrifiable ceramic wares contain clays along with other silicates. As the temperature of the body is raised, carbonaceous impurities burn out, chemical water is evolved, and carbonates and sulfates begin to decompose. All of these processes produce gases that must escape from the ware by passing to the surface through interconnected pores. On further heating, some of the minerals begin to break down into new forms, and the fluxes present react with the decomposing minerals to form liquid silicates or glasses. (If this glass formation proceeds far enough to begin blocking pores before all gases are vented, the body will swell up in an undesirable process called bloating.) More glass forms as the temperature is raised, and it begins to pull the unmelted grains together by surface tension forces, causing shrinkage and an increase in bulk density. If the glass-forming process is allowed to go too far (either to too high a temperature or for too long a "soak" time at the temperature), so much of the mass will become liquid that it will no longer support its own weight. If this occurs, the mass will deform or slump, and the article will become worthless. Slumping can often be eliminated by supporting the piece with special refractory shapes called kiln furniture. When the proper degree of maturity, i.e., the proper amount of remaining porosity, has been achieved, the article is cooled. The cooling causes the liquid glass to become rigid and thus form a strong bond between the remaining crystalline grains. Figure 5.4 shows the microstructure of ceramics that have undergone vitrification. The features are identified in the caption.

The role of the silica grains in a vitrifying ceramic is a critical one. Silica undergoes several changes in crystal structure during heating and cooling. These changes, called polymorphic transformations, result in a change in volume with a consequent tendency to cause cracking of the

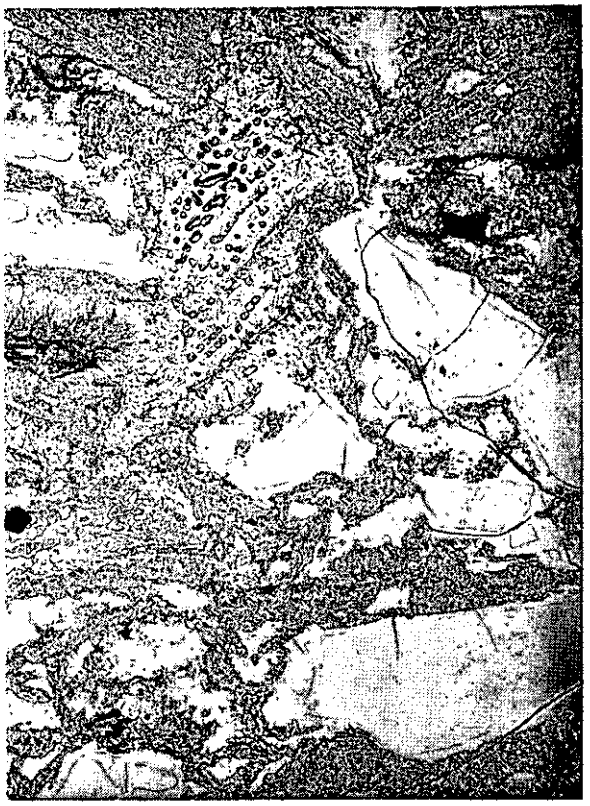
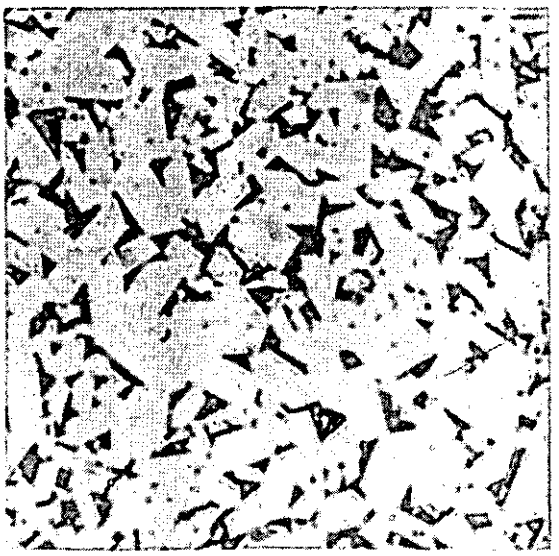


**FIG. 5.4. Microstructure of vitrified ceramics:** (a) Porcelain, showing large quartz grains surrounded by glass. Very fine needle-like crystals are mullite. Major fine grain areas are clay matrix. Cracks in quartz grains are due to polymorphic transformation on cooling (courtesy American Standard) (approx. 2,200×).



(b) High alumina body. The light gray areas are alumina grains; the darker gray areas are glassy bonding phase (courtesy V. E. Wolkadoff and R. E. Weaver, Coors Porcelain Co.) (400×).

ware. Ordinary quartz transforms abruptly into high quartz when heated above 573° C. The sudden large volume change does not cause serious strains to develop in the unmatured ceramic mass. When liquid is present, the high quartz can very slowly transform into other forms on further heating: to tridymite above 867° C and to cristobalite above 1470° C. Some cristobalite is often found in ceramics that have been fired to high temperatures.

Since large silica grains remain relatively unreacted even at maturity, the probability of their going back through the polymorphic transformations during cooling must be considered. Generally, any cristobalite and tridymite formed will remain on cooling, but the majority of the silica grains in many ceramics never transform beyond the high quartz form. When cooled below approximately 600° C, these high quartz grains will transform abruptly back into low quartz with a sudden volume change. In the relatively dense matured body, this abrupt volume change on cooling can cause serious strains to develop and may even cause cracking (dunting) of the ware. For this reason cooling through the 600–500° C temperature range must be done very slowly. Fine grinding of the flint is sometimes helpful in overcoming this limitation. In fast-fire ceramics, alumina is often substituted for some or all of the silica to avoid such cooling problems.

Pure oxides such as $Al_2O_3$, MgO, $BaTiO_3$, and the ferrites, which do not contain any glass-forming constituent, cannot undergo vitrification. Instead, when an article consisting of a mass of these oxide grains is heated, atoms move one at a time from pore walls to points of contact between the grains, resulting in the bridging together of the individual grains into a coherent mass. This process, sintering, may actually be

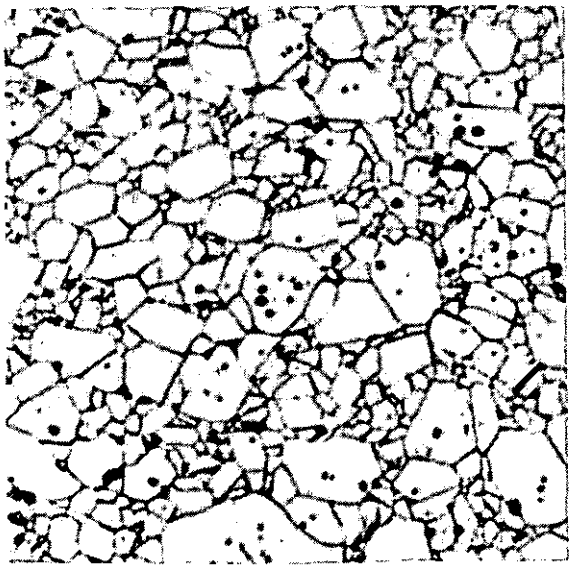


**FIG. 5.5. Microstructure of a sintered alumina ceramic. Small dark areas are porosity** (courtesy V. E. Wolkadoff and R. E. Weaver, Coors Porcelain Co.) (400×).

accomplished by several different atomic mechanisms. Very high temperatures are usually necessary to carry out the densification at a reasonable rate. The rate of densification is usually found to be increased if the initial grain size is decreased. Often, small additions of other nonglass-forming oxides can greatly increase the sintering rate of a pure material. When most of the porosity has been removed, a coarsening of the grain size (grain growth) is usually observed. Figure 5.5 shows the microstructure of a sintered ceramic.

### Furnace Atmosphere

The composition of the atmosphere in which a ceramic is being fired has a strong influence on the results of the operation, regardless of whether the ceramic matures by vitrification or by sintering. The oxygen content of the atmosphere inside the furnace is particularly important. If the atmosphere has sufficient oxygen to allow the ceramic to absorb some, it is said to be an oxidizing atmosphere; if the atmosphere tends to remove oxygen from the ceramic, it is said to be a reducing atmosphere. When the ceramic can absorb oxygen from the atmosphere, it can burn out carbon and can convert all salts present to oxides. If reducing conditions occur, variable-valence ions in the ceramic will tend to change to their least positive valence, resulting in changes in optical (especially color), electrical, and other characteristics.

In furnaces heated by combustion, the furnace atmosphere will contain a mixture of $CO_2$, $N_2$, CO, $O_2$, $H_2O$, and usually some $SO_2$. The latter is often harmful to ceramics, especially if present in large quantities. When this is the case, common practice is to place a muffle in the furnace. This is a protective inner enclosure in which the ware can be placed so that the combustion gases flow around the outside of the muffle and never actually contact the ceramic. If a muffle is not available, or if extra protection is required, saggers—individual closed refractory containers—are utilized to protect the firing ware. The muffle also protects the ceramic from flame impingement which can cause differential shrinkage during firing.

### Ceramic Kilns

The furnace in which firing takes place, commonly called a kiln, can be classified as either a periodic (intermittent or batch) kiln or a tunnel (continuous) kiln, depending upon its construction and mode of operation. A periodic kiln is one in which the entire furnace is heated and cooled in accordance with the particular firing schedule used for the ware; a tunnel kiln, on the other hand, maintains certain temperature zones continuously, and the ware is pushed from one zone to another to accomplish the required time-temperature cycle. The periodic kiln is the more flexible type since its time-temperature cycle can be tailored to a wide variety of different ceramic products. The tunnel kiln is the more economical of fuel and labor, but is relatively inflexible, being

limited to firing long runs of one kind of product. Many plants employ both kinds of kilns, the periodics being used for special products, and the tunnels for standard product lines. Initial investment for a tunnel kiln is high, and more sophisticated control systems are usually required than for a periodic kiln.

Periodic kilns usually consist of a single large refractory-lined, sealed chamber having burner ports and flues for carrying away combustion products. Unless it is constructed with a muffle, the kiln will heat the ware by passing the hot combustion gases through the loosely stacked ware. In the downdraft kiln (also called the beehive kiln if round in shape) (Fig. 5.6), the flat refractory floor is perforated with many openings leading to an underground flue. The ware is loosely stacked on this floor so that vertical "chimneys" exist between pieces. The hot gases

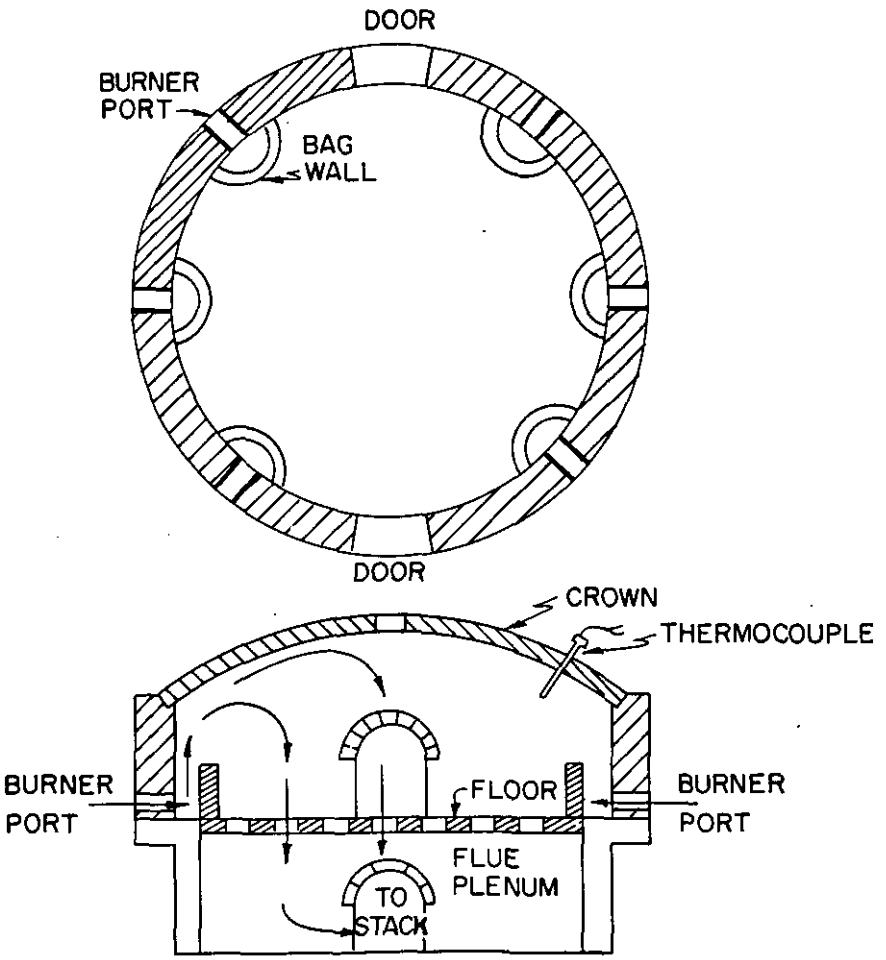



FIG. 5.6. Top and side views of downdraft kiln.

from the burners enter through the sidewalls, sweep up around the inside of the curved crown, then pass down through the ware and into the flue system. Care must be taken during initial heating that these high dew point combustion gases do not begin to condense water on the ware in the cooler, bottom part of the furnace. A less common periodic kiln is the updraft kiln where the hot gases from a plenum below the floor are distributed through a refractory grating and pass up through the ware to exhaust at the crown. Both kilns are set (loaded) and drawn (unloaded) by hand, resulting in considerable labor cost. They cannot be drawn until the kiln is cool enough to permit men to work inside, which means that very long cooling periods are necessary during which the kiln is unproductive. A total cycle time of several weeks is common for downdraft kilns.

The shuttle kiln is a popular periodic type in which the ware is loaded onto a car and rolled into the chamber for firing (Fig. 5.7). After

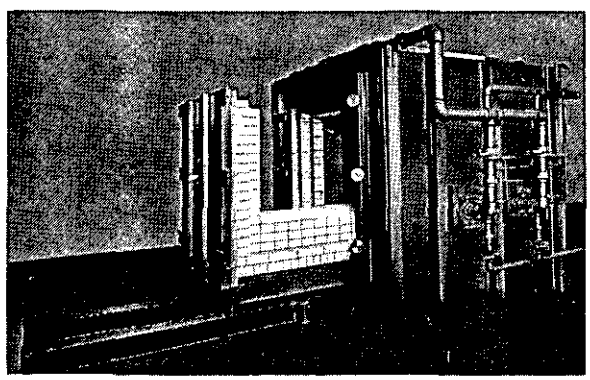
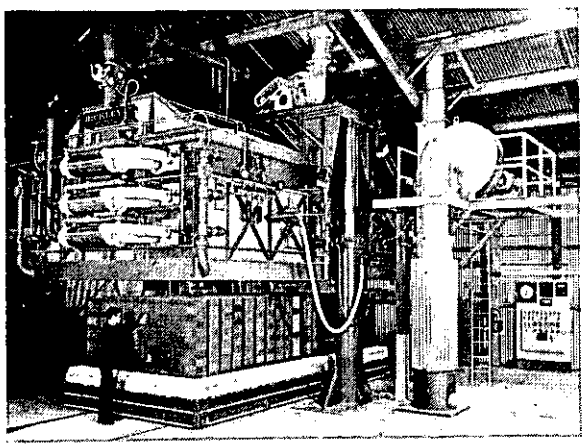


**FIG. 5.7.**
(a) Shuttle kiln (courtesy Harrop Ceramic Service Co.).

(b) Large porcelain insulators fired in a shuttle kiln (courtesy Bickley Furnaces, Inc.).

firing, the kiln door can be opened and the kiln car rolled out as soon as the kiln refractories and the ware have cooled enough to withstand the thermal shock involved in the process. In this way, the kiln need not be completely cooled, and less time is lost between cycles.

Elevator kilns (Fig. 5.8) are also popular fast turn-around periodic kilns. The furnace shell (walls and crown) can be elevated, while the



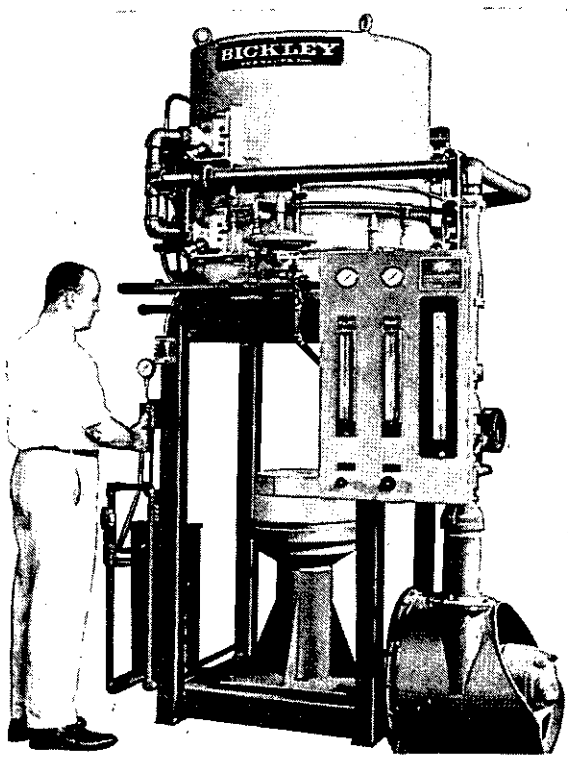



**FIG. 5.8. Elevator kilns** (courtesy Bickley Furnaces, Inc.): (a) Bell-top production kiln. (b) Small elevator hearth kiln.

hearth (bottom) remains on ground level. After the ware is placed on the hearth (often on a car rolled into place), the rest of the furnace is lowered around it. After firing, the furnace shell can be raised before the ware is completely cooled, shortening the long unproductive cooling cycle. In some elevator kiln designs the furnace shell is fixed above the plant floor, and the hearth is raised into place for firing.

The tunnel or continuous kiln (Fig. 5.9) consists of a refractory chamber, often several hundred feet in length, through which ware is slowly moved to accomplish gradual heating and slow cooling. The highest temperature zone, or firing zone, is generally near the middle of the tunnel length; this is where most of the burners are located. The first section of the tunnel where the greenware enters the furnace is called the preheat zone. A few burners are located in this zone with most of them concentrated near the entrance to the firing zone. The final section of the tunnel is called the cooling zone.

Cooling air is forced into the cooling zone of the kiln by large fans. This cool air travels over and through the cooling ware, picking up heat from it and accelerating the cooling process. The hot air resulting from this cooling process is blown back into the firing zone, where it improves combustion efficiency and also assures an oxidizing atmosphere. Hot combustion products are blown back from the firing zone into the preheat zone to help bring the unfired ware up to temperature. Finally these combustion products are exhausted through the crown of the preheat zone before they encounter ware that is cool enough to cause condensation of moisture. (See dew point discussion, this chapter.) The resulting pattern of flow in the tunnel is as follows: the ware moves through the tunnel in one direction, picking up heat in the preheat and firing zones and giving it up in the cooling zone; gases move through the tunnel in the opposite direction, picking up heat from the ware in the cooling and firing zones, and giving up heat in the preheat zone. Very high thermal efficiency is the result of this complicated operation. Very often, outside air is blown through a double wall and the crown in the cooling zone to pick up waste heat for use in driers.

The movement of ware through large tunnel kilns is accomplished by using refractory topped cars riding on insulated rails. The cars are generally pushed into the preheat end on a fixed schedule. Since the tunnel is completely filled with cars, pushing one into the preheat end forces one out the cooling end—at the same time every car in the kiln moves one car length forward. Certain small tunnels, especially those using a very fast firing cycle, employ positively driven refractory rollers as the tunnel hearth. The ware is usually flat or is placed on a flat refractory plate which moves forward through the kiln on these rollers.

Unconsolidated ceramic materials can be calcined in rotary kilns, i.e., refractory-lined rotating, cylindrical steel tubes (Fig. 5.10). Rotary kilns may be as much as 500 feet long and 12 feet in diameter. The tube is slightly inclined and rotates slowly on its axis. The burners

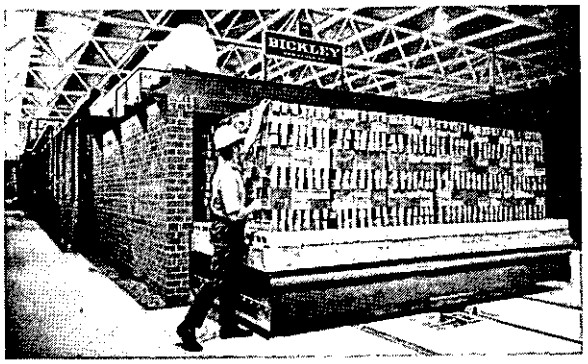
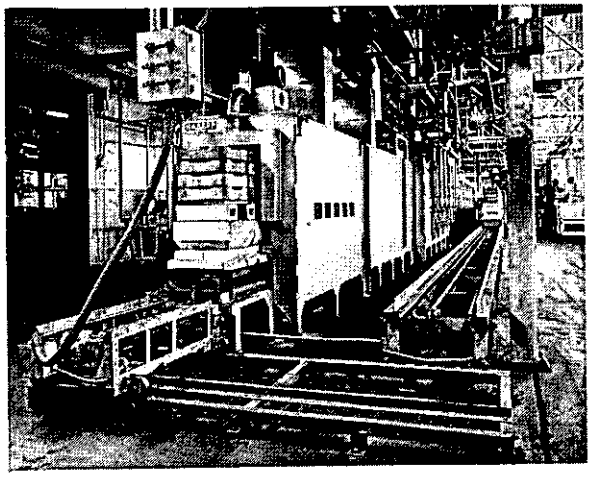
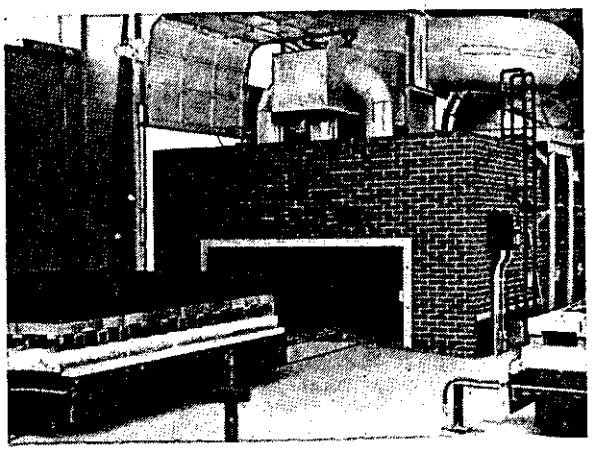



**FIG. 5.9. Tunnel kilns:** (a) Kiln for firing brick showing loaded kiln car (courtesy Bickley Furnaces, Inc.).



(b) Kiln for firing technical ceramics in saggers. Transfer car in foreground (courtesy Harrop Ceramic Service Co.).



(c) Kiln for "one-high" firing of brick (courtesy Harrop Ceramic Service Co.).

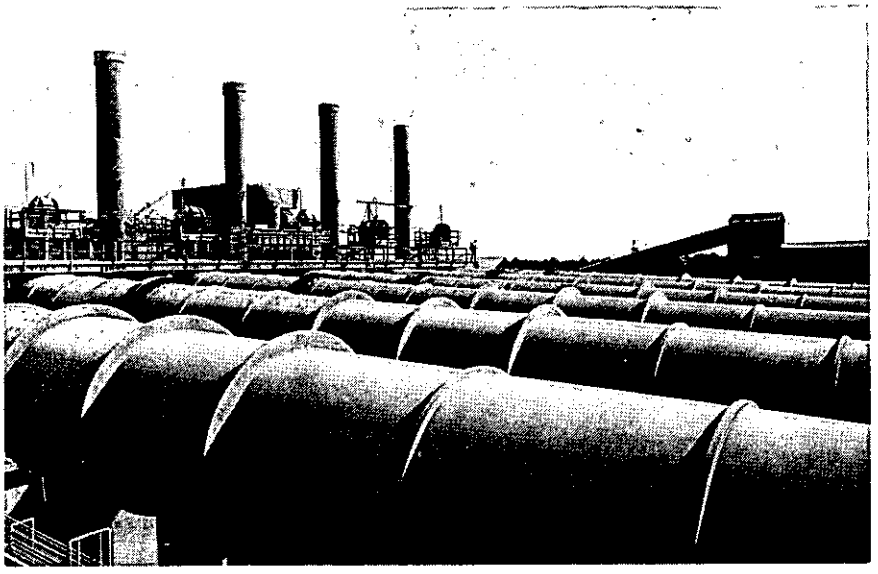


**FIG. 5.10. Rotary kilns** (courtesy Alcoa).

are located at the lower end of the tube, and the material to be fired is fed into the elevated end. The rotating action tumbles the material down through hotter and hotter zones until the final desired temperature is reached just before discharge at the low end. The heat drives off any water or gases combined in the raw material and greatly densifies the individual ceramic particles. Many ceramic materials are calcined on a definite heating schedule, which preserves the reactivity of the material. This is particularly important in the production of reactive aluminum oxides and cements. Other materials, such as MgO, are "dead-burned" to minimum reactivity for use as grog to reduce the shrinkage in refractories and other ceramic products.

### Glass Melting

The melting together of raw materials to form glasses is usually accomplished in large furnaces called glass tanks. The tank is constructed of special refractory blocks to hold a pool of molten glass several feet deep. Above the level of the glass surface are short walls topped by an arched crown. Heat is supplied by rows of burners along the length of the furnace. Firing occurs alternately from one side and then from the other, with the flames streaming across the tank between the glass surface and the crown. Heating takes place primarily by radiation from the hot crown down to the glass. Large refractory-filled compartments, called checker chambers or regenerators, are placed along and below either side of the tank. The purpose of these regenerators is to recover some of the heat in the exhaust gases and use it to preheat the air to be used in combustion (Fig. 5.11).

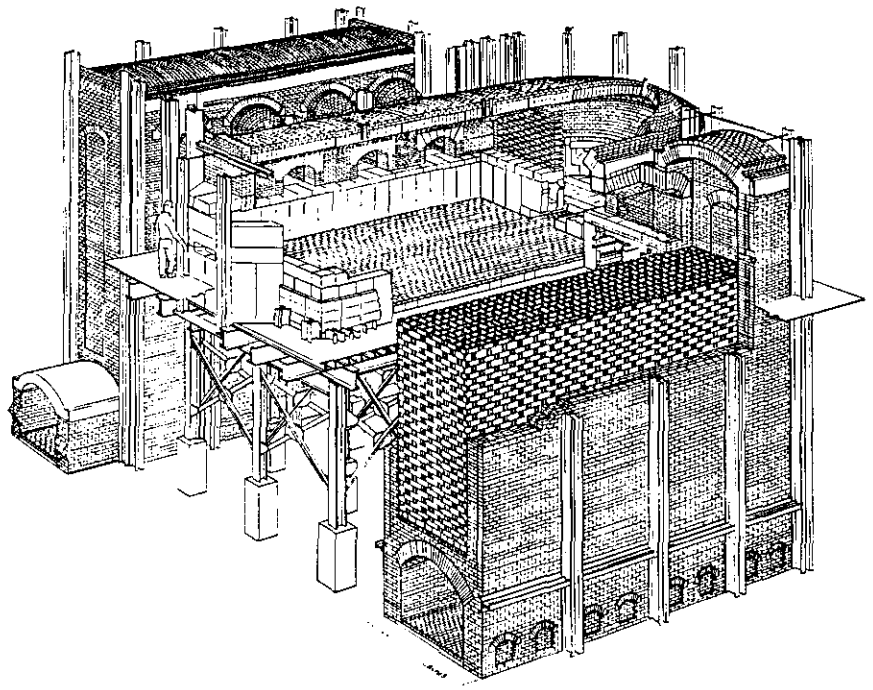


**FIG. 5.11. Schematic of glass tank showing checker-filled regenerator chambers in either side. Raw materials *enter at left, are melted, and pass to the refining* zone at the right for conditioning prior to forming.** (Drawing courtesy Harbison-Walker Refractories Division of Dresser Industries, Inc. Caption by authors.)

A refractory wall, called the bridge wall, stretches across the inside of some tanks and divides them into two distinct sections. In the melter section, raw materials are continuously fed in and melted to give a bubble filled glass. In the refining section, the glass is allowed to free itself of bubbles (i.e., to fine) and is conditioned to the proper viscosity for forming. In some tanks, the glass flows from the melter section into the refining section through a hole in the bridge wall. This hole, the throat, is submerged below the glass surface so that no unmelted batch floating on the surface in the melter can find its way into the refining section. Other tanks use an anchored "floater block" of refractory to retain the unmelted batch. The flow of glass from the melter into the refining section occurs because glass is continuously being removed from the refining end for forming.

It is common practice to augment combustion heating of the tank with some electrical heating. This procedure, called *boosting*, uses the glass itself as a resistor and passes large electric currents through the glass pool from refractory metal electrodes immersed in the melt.

Specialty glasses and optical glasses are not normally melted in

tanks. Instead, large refractory containers called pots are used for both the melting and fining of such glasses. The pots are placed inside a large furnace for heating.

### Combustion

The source of heat for most industrial processes, including the drying and firing of ceramics, is the direct combustion of a fuel with air. The fuels most used in the ceramic industries are natural gas, fuel oil, liquid petroleum (LP) gases, producer gas, occasionally powdered coal, and rarely lump coal. All of these fuels are made up of various combinations of the combustible chemical elements carbon and hydrogen with usually a very small amount of sulfur also present. When these elements are burned using oxygen from the air they produce various gaseous combustion products plus heat. If carbon is burned completely, it forms $CO_2$; if combustion of carbon is not complete, a mixture of $CO_2$ and CO results. When hydrogen is burned, it forms water vapor ($H_2O$). Sulfur burns to produce $SO_2$.

In order to assure complete combustion and to generate large quantities of hot gases, air in excess of the quantity theoretically necessary for reaction is generally used. The combustion products from a sulfur-free fuel burned with excess air usually consist of a mixture of the gases $CO_2$, CO, $H_2O$, $O_2$, and $N_2$. The $N_2$ comes from the air used to supply the oxygen for combustion. The relative amounts of these gases depend upon the amount of excess air and the overall combustion efficiency of the operation. It is common practice to monitor the chemical composition of the combustion products to optimize the operation. The Orsat analyzer gives an analysis complete except for the amount of water vapor. Other instruments automatically monitor the furnace atmosphere for only one or two of the more important gases. One common portable instrument monitors excess oxygen and unburned combustibles.

Natural gas is the most convenient fuel to use, but in order to make it more economical, it is usually purchased at a reduced rate on an interruptible basis. During times of limited gas supplies, especially in winter, the user's gas supply will be interrupted by the commercial gas supplier, and a standby fuel system will be needed. Such standby systems often employ fuel oil, although LP gas is gaining popularity for such uses. Burners are available which burn both natural gas and the standby fuel, making changeover more convenient.

## FINISHING

Many ceramic products can be taken directly from the kiln, inspected, and shipped to the customer. Certain other products however require additional processing to meet customer specifications. These postfiring processes are grouped under the general category of finishing operations and may include grinding to meet critical size requirements

and application of coatings for protection, decoration, or other special needs.

## Grinding

Most ceramic products can be fired to meet customer specifications on dimensions without further processing. By calculating the proper dimensions of the formed part from dimensions specified by the customer, and by knowing the shrinkage of the ceramic materials under particular forming conditions, the manufacturer can usually fire to a given specification. Frequently, special firing techniques are required to insure meeting a specification. The ceramic parts may have to be supported by refractory kiln furniture to prevent slumping during firing. Solid refractory setters or setters of the same composition as the parts being fired may be placed under certain parts to help control shrinkage and warpage. A layer of refractory grain such as calcined clay or fused alumina may be required to keep parts from reacting with setters or refractories during firing. Tubes and rods are frequently hung by collars into refractory saggers so that the force of gravity tends to keep them straight during firing.

If the manufacturer cannot meet the dimensional and surface finish specifications of the customer by special firing techniques, then the ceramics must be ground and (or) polished after firing. Diamond tooling is usually required to grind hard materials such as alumina, but silicon carbide, alumina, or other abrasives may be used for softer materials. Disks may be lapped to the proper thickness and surface finish. Centerless grinders are often used to grind the outer diameters of cylinders and rods. Small parts as well as the diameters of disks or the ends of cylinders may be ground on tool post grinders.

Very close tolerances are frequently required on technical ceramic parts. The dimensions of these parts are frequently measured under carefully controlled humidity and temperature conditions with very specialized measuring devices.

Special surface finishes are sometimes required on ceramic parts. This is particularly true of valves and valve seats used in medical equipment where human life may be involved. These valves must have not only an essentially flawless surface but also must meet extremely rigid dimensional requirements. Special grinding and polishing techniques are always required under these circumstances.

Technical ceramics are carefully examined for flaws before shipment to the consumer. Cracks and pits can sometimes be detected visually as shown in Figure 5.12 or by dye penetration tests.

## Glazing

Many ceramics are glazed after firing. A glaze is a special glass designed to melt onto the surface of a ceramic body and to adhere to that surface during cooling. Glazes are used primarily to seal the surface of

**FIG. 5.12. Inspection of a radome for flaws following precision grinding** (courtesy Corning Glass Works).

a porous ceramic to prevent absorption of water or other substances. The resulting smooth impermeable surface is attractive and easy to clean. In high-tension insulators a glaze insures maintenance of good electrical properties. Special colors and textures can be developed within the glaze to provide decoration and sales appeal.

The major constituent of a glaze is generally silica, with the addition of alkalies such as sodium and potassium oxides to lower the melting point of the glaze and alkaline earths such as calcium oxide to retain chemical durability. Lead oxide and boric oxide are also frequent glaze constituents. The overall composition is always adjusted in order to control the thermal expansion of the glaze which must be equal to or slightly less than that of the underlying body. Additives are used to color the glaze or make it opaque. Techniques for formulating a glaze of known composition are discussed in Chapter 8.

Most glazes are prepared by grinding together various raw materials along with a specially prepared frit. The frit is a glass containing all soluble materials, all coloring oxides, and those materials which are toxic in uncombined form. Frits are produced commercially by melting and quenching a glass made up of the required chemical constituents. Quenching may be accomplished by pouring the molten frit directly into water or by roll quenching in which the frit is quenched between water-cooled steel rolls. After quenching, the frit is ground, dried, bagged, and shipped to ceramic or enameling firms for use in glazes or enamels.

The frit is placed in a ball mill with clays and other insoluble ma-

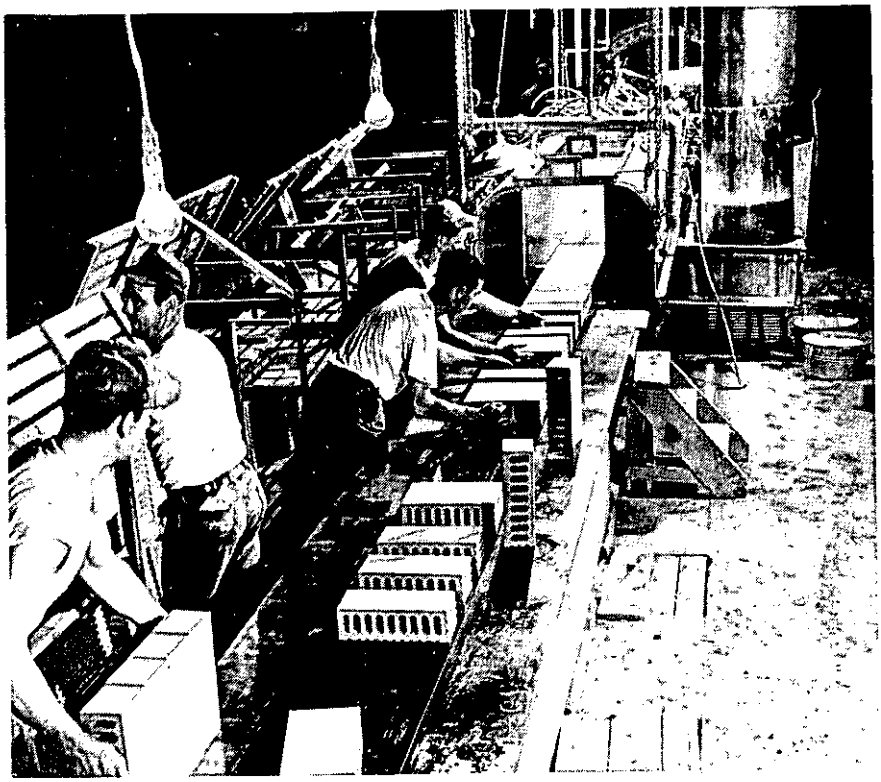


**FIG. 5.13. Glaze application methods:** (a) Continuous glaze spraying of structural tile (courtesy Schweitzer Equipment Co., 3764 Ridge Road, Cleveland, Ohio).

(b) Dipping (courtesy The Haeger Potteries, Inc.).

terials and milled to a definite particle size with the proper amount of water. Binders such as dextrine or gum arabic may be added to aid in application. The milled glaze may be applied to the ceramic by spraying, dipping, or painting (Fig. 5.13). Spraying is used in many automated processes. The glaze dries rapidly on the ceramic surface, and special drying is usually not required before firing.

Glazes can be applied to green ceramics, to bisque-fired ceramics, or to completely vitrified ceramics, depending on the nature of the body. However, parts are generally bisque-fired before glazing. Bisque-firing is a low-temperature firing which removes the volatiles from the body and part or all of the firing shrinkage thus assuring better success in the glazing operation. The body and glaze are then fired together (glost-fired) at the same temperature. Electrical ceramic ware is frequently matured and then glazed at a lower temperature than the maturing temperature of the body. Low-cost items such as ashtrays can frequently be sprayed in the green state and the body and glaze can be matured together. (In the china process the ceramic body is first fired to maturity; then the glaze is applied and matured by firing at a lower temperature. In the porcelain process the body and glaze are matured together in the same firing operation. [See ASTM specification C 242–60T.]) It is usually necessary to preheat previously vitrified ware before the glaze is applied or it will not adhere properly.

Various glaze defects can occur in the different stages of production. Crawling occurs when the glaze does not satisfactorily wet the body. This can often be corrected by changing or increasing the amount of organic binder in the glaze slip. Crazing occurs because a glaze has a higher coefficient of thermal expansion than the body. Shivering occurs when the glaze has too low a coefficient of thermal expansion. Pitting can be traced to volatiles in the glaze or body. Descriptions of these and other defects and methods for correcting them are given in Singer and Singer (1964) and Parmelee (1951).

### Metallizing

Ceramics are sometimes bonded directly to metal parts, a process that is especially common in the electronics industry (Fig. 5.14). The process consists of first metallizing the ceramic and then soldering or brazing the metal to the metallized ceramic surface. In one process a mixture of molybdenum and manganese metal powders is ground in organic solvents and binders and painted or sprayed onto the ceramic surface. The coating is then fired onto the ceramic in a furnace containing a cracked ammonia (hydrogen plus nitrogen) atmosphere at a temperature depending on the exact composition of the ceramic. Metal parts with expansion coefficients near that of the ceramic may then be soldered to the metallized coating using alloys of metals such as copper or silver. The metallized areas are often plated with nickel, silver, or gold before soldering.

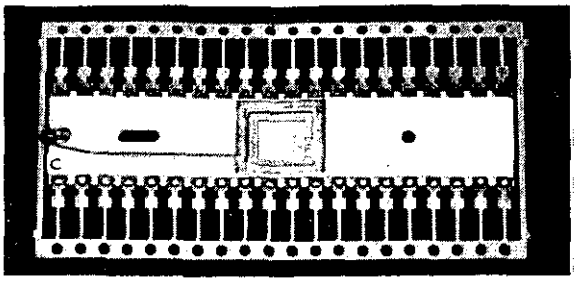


*FIG. 5.14. Example of metals soldered to a metallized ceramic part* (courtesy Coors Porcelain Co.).

Active metals such as titanium may be used to metallize ceramics in a hydrogen atmosphere (titanium hydride process), usually allowing lower metallizing temperatures. After metallizing, the procedure for soldering is similar to that for the molybdenum-manganese process.

### Glass-to-Ceramic Seals

Many glasses have been developed which can be used to solder ceramics to other glasses. Techniques of application of the glass solder to the joint vary with the products being produced. Sometimes solder glass rings can be used to form the joint, and solder glass powders are used in other applications. The thermal expansion coefficient of the solder glass must be compatible with both the ceramic and the glass being bonded. The seal is made by heating the glass and ceramic together until they become hot enough to soften the solder glass. Glass-to-ceramic seals are extremely common in a wide range of products from automobile spark plugs to electronic tubes.

PART TWO

# MEASUREMENTS AN

PHYSICAL MEASUREMENTS and calculations are procedures used in the ceramic industry to maintain quality control during production and to characterize the final product.

It is important at the outset to realize that no attempt has been made to include the step-by-step "recipe" for making these measurements. A great variety of standardized testing methods exists for nearly every common property, and it is important that one of these be selected by mutual agreement of the interested parties and then rigidly adhered to. The importance of this rule is obvious when it is realized that using two different testing methods for the determination of the same property on the same sample may very well give different results. Many firms use their own detailed testing methods, and others prefer to use those methods adopted by the American Society for Testing and Materials (ASTM) or the American Ceramic Society (e.g., 1921–22 Yearbook of the Society). Certain specialized industrial organizations have adopted their own standards, some of which have become ASTM standards, e.g., Standards of the Alumina Ceramic Manufacturers Association.

The complete set of ASTM standards is reviewed, revised, and reissued each year as a set (33 volumes in 1971 plus an index). The standards of most interest to the ceramic industries are found in Part 13—Refractories, Glass, and other Ceramic Materials; Manufactured Carbon and Graphite Products. Impor-