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Fifth, Completely Revised Edition

Volume A 6:
Ceramics to Chlorohydrins

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Ceramics, General Survey

Ceramic Colorants; Ceramics, Advanced Structural Products; Ceramics, Ceramic-Metal Systems; Ceramics, Electronic; Construction Ceramics; Refractory Ceramics; and Whitewares are separate keywords.

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1. Traditional and Advanced Ceramics

This general survey covers the fields of traditional ceramics and advanced (or high-technology) ceramics, touching on the materials employed, processing and forming, firing and finishing, and the use of products. Advantages and disadvantages of various types of ceramic ware are discussed.

The word ceramic is a "general term applied to the art or technique of producing articles by a ceramic process, or to articles so produced" [24]. In general, it applies to any of a class of inorganic, nonmetallic products subjected to high temperature during manufacture or use. "High temperature" means any temperature above red heat, ca. 540 °C [13].

Typically, although not exclusively, a ceramic item is a metal oxide, boride, carbide, or nitride, or a compound of such materials. Thus, a *ceramic article* is "a glazed or unglazed object of crystalline or partly crystalline structure (or of glass), produced from essentially inorganic, nonmetallic substances; such objects are made from either a molten mass which solidifies upon cooling or which is formed and matured simultaneously or subsequently by action of heat" [1, p. 197].

The noun ceramic is derived from the Greek *keramos* meaning "burned earth." *Traditional ceramics* refers to ware prepared from an unrefined clay or to combinations of one or more refined clays in combination with one or more powdered or granulated nonplastic minerals or prereacted ceramic compositions. Traditional ceramics also refers to ware or products made from compositions or naturally occurring materials in which clay mineral substance exceeds 20%. Traditional ceramics and clay ceramics are synonymous expressions.

The past 50 years have seen an increasing interest in ceramic items made from highly refined natural or synthetic compositions designed to provide special properties [19, pp. 150–153]. These objects are termed *advanced*, new, or (in Japan) fine *ceramic products*, and find use as key components in such high-technology fields as electronics, computers, optical communication, cutting tools, metal forming dies, wear-resistant parts, high-temperature reactors, high-temperature engine parts, medical implants, and many other special purpose applications. Advanced ceramics must be considered as an enabling technology – one essential to competitive or functional performance of larger systems.

Advanced new roles for ceramics depend on properties inherent in basic structure and composition. Recognition of special capabilities of ceramics is largely due to progress over the past 30 years in relating physical to compositional and structural features [25]. Two recent developments are responsible for the exponential growth in applications for advanced ceramics: first, advances in systems that require special, highly developed ceramics; and second, advances in ceramic processing that permit production of usable ceramic parts.

Historical Aspects. The qualities of plasticity, dried strength, and fired hardness of clays were discovered and used possibly as long ago as 10 000 B.C. [26], and certainly by 5500 B.C. [27].

The earliest societies that give reasonable evidence of a ceramic industry seem to have been in the Near East, where a pottery tradition dates back ca. 7000–8000 years [28]. In the Far East, Neolithic villagers at Banpo in Shaanxi Province of China were making fine red, gray, black, and painted pottery at least as early as 4500 B.C. [8, pp. 135–162].

Urban planners at Mohenjo-Daro in the Indus Valley were using fired clay bricks and tile for public building, water-supply conduits, and an advanced sewer system 4000 years ago [29]. A cuneiform tablet of the 17th century B.C. describes the making of a copper–lead glaze [30].

By the Shang Dynasty (1500–1025 B.C.) the Chinese had changed Neolithic earthenware to a fine-grained white stoneware [8, pp. 135–162]. A primitive feldspathic glaze appeared during the Zhou Dynasty (1000–771 B.C.), followed by a soft green to brown lead silicate glaze in the Han Period (206 B.C.–220 A.D.). In the Six Dynasties time period (265–907 A.D.), marked developments occurred in art pottery. Ceramics of the Song Dynasties (960–1127 and 1127–1279 A.D.) and into the Ming Dynasty (1368–1644 A.D.) showed increasing use of hard-paste porcelain formulas. An egg-shaped kiln with a special stack designed for high draft was developed for firing Ming porcelains; the fuel was pine wood [31].

Beginning in the sixth century B.C., Attic vases of ancient Greece represented a ceramic art milestone. Use was made of a local illitic clay [32] to prepare a levigated glaze that was black under reducing conditions and red under oxidizing conditions. Rome seems to have had no ceramic tradition, but drew on ware and workmen from various parts of its empire. The famous Arretine ware was made near what is now Florence by Oriental Greeks, and terra sigillata, sometimes thought to have been invented by Romans, originated on the island of Samos [33].

Chinese ceramic technology is thought to have been transferred to the Near and Middle East by cultural contacts and by Chinese prisoners following defeat of a Chinese army by Persian Abbasids in 751 A.D. Islamic influence was felt late in Italy and France [34], and later still in Germany, the Netherlands, and England [35].

Salt-glazed stoneware was developed in High Germany near the end of the fourteenth century [36], and soft-paste

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porcelain was being manufactured in Meissen as early as 10 and in Sèvres, France, by 1751–1754. In England, COOKWORTHY developed and patented a hard-fire porcelain (1768), and sometime before 1750, calcined bone was being used in making chinaware [37].

Stoneware and hard porcelain served as prototypes for development in the United States, England, and Europe of mechanically strong, vitreous bodies for use in manufacture of sanitary ware, high-tension electrical porcelain, and impact-resistant dinnerware [11, p. 4]. The advent of steam power in the eighteenth century permitted WEDGWOOD and others in England to mechanize preparation and forming operations. Although acceptance of new ideas in the way of processing has been slow over the centuries, within the past two generations "felt wants" in industry have stimulated research in the areas of advanced ceramics.

1.1. Traditional Ceramics

Clay is the oldest ceramic material. The earliest ceramic ware was most likely made from natural clay, selected by the potter for its forming properties. However, at very early times, it was customary to add some other nonclay materials. A sticky, high-shrinkage clay might be modified by addition of crushed stone, sand, or crushed shell to reduce shrinkage and cracking. Currently, the major nonclay materials used in making clay-based ceramic items are silica powder and certain alkali-containing minerals added as fluxes. Traditional ceramics can be regarded as ware made from formulations in which clay provides the plastic and dry bonding properties required for shaping and handling. Analyses of natural clay bodies show that the actual clay mineral content is 25–40%.

Pottery is sometimes used as a generic term for all fired ceramic wares that contain clay in their compositions, except technical, structural, and refractory products [1, p. 201].

The term *whiteware* was originally applied to white tableware and artware [11, p. 4], but has been broadened to include ware that is ivory colored or has a light gray appearance in the fired state. Fine ceramic whitewares are conveniently divided into two classes: (1) formulas consisting primarily of clay minerals, feldspathics, and quartz; and (2) nontriaxial bodies made entirely or predominantly of other materials. For purposes of this discussion, ceramic whiteware is placed into five categories, namely, (1) earthenware, (2) stoneware, (3) chinaware, (4) porcelain, and (5) technical ceramics.

Earthenware is defined as glazed or unglazed nonvitreous (porous) clay-based ceramic ware. NORTON subdivides earthenware into four categories: (1) natural clay body, (2) refined clay body, (3) talc body, and (4) semivitreous triaxial body [11, p. 4]. Fired absorptions may range from 4–5% for semivitreous ware to 20% for the high-talc formulas. Fired color may range from red for high iron oxide bodies to white for the talc and triaxial formulas.

Stoneware is a vitreous or semivitreous ceramic ware of fine texture, made primarily from nonrefractory fireclay or some combination of clays, fluxes, and silica that matches the forming and fired properties of a natural stoneware. Thus, stoneware may be made either from a clay or may be a synthesized stoneware. Synthesized stoneware can range from highly refined, zero-absorption chemical stoneware to less demanding dinnerware and artware formulas.

Chinaware is vitreous ware of zero or low-fired absorption used for nontechnical applications. It can be either glazed or unglazed. The expression soft-paste porcelain has the same meaning [11, p. 4]. Formulas can be simple clay–flux–silica triaxial bodies or bodies containing significant percentages of alumina, bone ash, frit, or low-expansion cordierite or lithium mineral powders. Fired absorptions range from 0 to 5% for ovenware.

Porcelain is defined as glazed or unglazed vitreous ceramic ware used primarily for technical purposes. Formulations are generally of the triaxial type although some or all of the silica can be replaced by calcined alumina to increase mechanical strength. Firing of ware may be bisque (unglazed) at low temperature with glazing at high temperature or by single-firing at high temperature.

Technical ceramics include vitreous (i.e., nonporous) ceramic whiteware used for such products as electrical insulation, chemical ware, mechanical and structural items, and thermal ware.

The clays used for making *common brick* are usually of low grade and in most cases red-burning. The main requirements are that they are easy to form and fire hard at as low a temperature as possible, with a minimum loss from cracking and warping. An average of analyses of a number of brick clays from sources in New Jersey [38] showed approximately 67% SiO_2, 18% Al_2O_3, 3% Fe_2O_3, 2% alkaline-earth oxides, and 4% alkalies, with an ignition loss of about 4% (→ Construction Ceramics, Vol. A 7, p. 425).

Bodies [11, p. 2] can be classified as being either *fine* (having particles not larger than ca.

Table 1. Fine ceramic products

Type of product	Earthenware		Stoneware		Chinaware		Porcelain	
	% Absorption	Color	% Absorption	Color	% Absorption	Color	% Absorption	Color
Artware	10-20	red-white	0-5	red-white	0-1	white	0-0.5	white
Ballmill balls							0-0.2	white
Ballmill liners							0-0.2	white
Chemical ware			0-0.2	gray-white			0-0.2	white
Cookware			0-5	gray-white				
Drainpipe			0-5	gray				
Insulators							0-0.2	white
Kitchenware	10-15	white	0-5	gray				
Ovenware	10-20	white			1-5	tan		
Sanitary ware					0.1-0.3	tan-white		
Tableware	5-20	white	0-5	white	0-1	white	0-0.5	white
Tile	10-20	white	0-5	red-white				

Table 2. Coarse ceramic products

Porous (> 5% (+ 5%) absorption)		Dense (< 5% (− 5%) absorption)	
Building materials	Refractory	Chemical	Structural
bricks terra cotta roofing tile drain tile	flue linings fireclay bricks insulating bricks	acid-resistant bricks	quarry tile sewer pipe fireclay sanitary ware

0.2 mm) or *coarse* (having the largest particle ca. 8 mm). These can, in turn, be subdivided into bodies fired to a *porous* state and those with a fired absorption [1, p. 197] not exceeding 5%, i.e., a *dense* state. The classes of fine clay ceramics and product uses are arranged in Table 1 to show the percent absorptions and body colors. The classes of coarse clay ceramics and their fired porosities are given in Table 2.

1.2. Advanced Ceramics

Advanced ceramics are generally used as components in processing equipment by virtue of such ceramic properties as special electromagnetic qualities, relative chemical inertness, hardness and strength, and temperature capabilities, sometimes in combination.

A systematic classification of advanced ceramics based on function is presented in Table 3, and examples of materials and uses are shown. A broader system classifies all applications into structural, electronic, and other. *Structural* applications are mechanical, but do include chemical aspects where these are required to carry out the mechanical function. The *electronic* category covers electric, magnetic, and optical functions plus chemical functions that involve direct use of electronic properties. The *other* classification includes strictly chemical functions, for example, catalysis, as well as biological functions.

Of course, any classification is likely to be inexact because many applications involve simultaneous use of several functions. However, a functional classification system does point to the fact that, in contrast to metals, ceramics can be made to embody a wide variety of electronic functions while also having desirable chemical and mechanical properties.

Ceramics are already widely used in process industries, especially where corrosion, wear, and heat resistance are important. Excellent examples are found in metallurgical refractories [40], an area already feeling the effect of new developments in ceramics and the new demands of advanced metallurgical processing.

1.2.1. Advanced Structural Ceramics

(→ Ceramics, Advanced Structural Products)

The prominent families of advanced structural ceramics and structural materials involving ceramics include

alumina
silicon carbide

Porcelain	
% Ab- sorption	Color
0-0.5	white
0-0.2	white
0-0.2	white
0-0.2	white
0-0.2	white
0-0.5	white

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Structural
quarry tile
sewer pipe
fireclay sanitary ware

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Table 3. Classification of high-technology ceramics by function [39]

unction	Material	Uses
ectric functions Electri	insulation materials (Al_2O_3, BeO, MgO)	IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate
	ferroelectric material ($BaTiO_3$, $SrTiO_3$)	ceramic capacitor
	piezoelectric materials (PZT)	vibrator, oscillator, filter transducer, ultrasonic humidifier, piezoelectric spark generator
	semiconductor materials ($BaTiO_3$, SiC, ZnO Bi_2O_3, V_2O_5, and other transition-metal oxides)	NTC thermistor: temperature sensor, temperature compensation PTC thermistor: heater element, switch, temperature compensation CTR thermistor: heat sensor element thick-film thermistor: infrared sensor varistor: noise elimination, surge current absorber, lighting arrestor sintered CdS material: solar cell SiC heater: electric furnace heater, miniature heater
	ion-conducting materials (β-Al_2O_3, ZrO_2)	solid electrolyte for sodium battery ZrO_2 ceramics: oxygen sensor, pH meter, fuel cells
agnetic functions CMagnetic	soft ferrite	magnetic recording head, temperature sensor
	hard ferrite	ferrite magnet, fractional-horsepower motor
ical functions OPTICAL	translucent alumina	high-pressure sodium vapor lamp
	translucent magnesia, mullite	lighting tube, special purpose lamp, infrared transmission window
	translucent Y_2O_3–ThO_2 ceramics	laser material
	PLZT ceramics	light memory element, video display and storage system, light modulation element, light shutter, light valve
emical functions CHEMICAL	gas sensor (ZnO, Fe_2O_3, SnO_2)	gas leakage alarm, automatic ventilation fan, hydrocarbon detector, fluorocarbon detector
	humidity sensor ($MgCr_2O_4$–TiO_2)	cooking control element in microwave oven
	catalyst carrier (cordierite)	catalyst carrier for emission control
	organic catalyst	enzyme carrier, zeolite
	electrodes (titanates, sulfides, borides)	electrowinning aluminum, photochemical processes, chlorine production
functions CThermal	ZrO_2, TiO_2 ceramics	infrared radiator
nical ctions MECHANICAL	cutting tools (Al_2O_3, TiC, TiN)	ceramic tool, sintered SBN, cermet tool, artificial diamond, nitride tool
	wear-resistant materials (Al_2O_3, ZrO_2)	mechanical seal, ceramic liner, bearings, thread guide, pressure sensor
	heat-resistant materials (SiC, Al_2O_3, SiN_4)	ceramic engine, turbine blade, heat exchangers, welding-burner nozzle, high-frequency combustion crucible
ical functions SURGICAL	alumina ceramics implantation	artificial tooth root, bone, and joint
	hydroxyapatite bioglass	
ar functions NUCLEAR	nuclear fuels (UO_2, UO_2–PuO_2)	
	cladding material (C, SiC, B_4C)	
	shielding material (SiC, Al_2O_3, C, B_4C)	

rtesy of the American Ceramic Society)

silicon nitride
partially stabilized zirconia
transformation-toughened alumina
lithium aluminosilicates
ceramic–ceramic composites
ceramic-coated materials

These materials are widely used in diesel, turbocharger, and gas-turbine engines; in high-temperature furnaces; and in the machines and equipment needed for manufacturing.

Although *alumina* [*1344-28-1*] denotes pure Al_2O_3, the term is commonly applied to any ceramic whose major constituent is alumina, even if the ceramic contains other components. Commercial alumina microelectronic substrates with strengths above 350 MPa are obtained by conventional sintering. Hot-pressing techniques result in strengths of ca. 750 MPa, although parts are expensive with limited size and geometries. A recent development [41] involving a variation on conventional sintering produces a glass-bonded alumina with strengths of ca. 700 MPa. Although the glassy phase limits applications to moderate temperatures, this new alumina ceramic should compete with other more expensive, advanced ceramic items.

Fibrous alumina is employed as a reinforcing agent in metal matrix composites and offers promise for filtration of hot gases and as high-temperature insulation. Alumina is used with SiO_2 in making such fibers [42]. Pure Al_2O_3 fibers are made by a variety of solution processes to produce fibers with strength of 1400 MPa.

Silicon carbide [*409-21-2*], a synthetic product, has good wear and erosion resistance and can be produced in either cubic or hexagonal crystal structure. Unfortunately, SiC is inherently unstable in oxygen so that long life under oxidizing conditions requires a surface coating of protective oxide.

Silicon nitride [*12033-89-5*], Si_3N_4, is likewise a synthetic product, existing in two phases, alpha and beta, each having hexagonal crystal structures. Silicon nitride ceramics include hot-pressed, reaction-bonded, and sintered products. The SiAlON family is a solid solution of Al_2O_3 and/or other metal oxides in the β-Si_3N_4 structure [43]. Reaction-bonded Si_3N_4 is made by nitriding cast or cold-pressed shapes of silicon powder, whereas hot-pressed Si_3N_4 is made from silicon nitride powder as a sintered Si_3N_4 powder product. Reaction-bonded Si_3N_4 retains its strength at high temperature if it is protected from oxidation [44]. Hot-pressed Si_3N_4 has high short-term strength and better oxidation resistance, but needs additives to facilitate compaction [45].

The advanced cutting tool industry is dominated by cemented carbides [46]. Ceramic vapor-deposited coatings have extended tool life. Efforts are under way to increase tool use by basing tools on Si_3N_4 and SiAlON to reduce dependence on strategic W, Ta, and Co [47].

Silicon nitride possesses many interesting properties that suggest use in bearings [48]. Tests showed an estimated life for Si_3N_4 bearings of 8 times that of steel bearings. The economics of machining and finishing is the biggest obstacle to widespread use of Si_3N_4 bearings.

Zirconia [*1314-23-4*], ZrO_2, finds widespread use in a stabilized cubic form as an oxygen sensor in process industries and the automobile industries [49]. The destructive transformation of ZrO_2 at 1100 °C from monoclinic to cubic form has been overcome by keeping unstabilized particle size of ZrO_2 grains below 1 µm diameter. Then an alumina matrix toughens the Al_2O_3 ceramic [50]. Hot pressing was initially used, but slip-cast forming and sintering has been found to be feasible [51], [52].

Cordierite [*12182-53-5*], $2\,MgO \cdot 2\,Al_2O_3 \cdot 5\,SiO_2$, has a thermal expansion of $(8-12) \times 10^{-7}$ over the range 20–1000 °C and is widely used as a catalyst support for automobile emission control units. Similar materials are used as heat exchangers in automotive gas-turbine prototypes and can be considered candidates for other heat-exchanger applications where good thermal shock resistance and moderate crushing strength are required [53]. Silicon carbide and silicon nitride also find application in heat exchangers [54].

Ceramic–ceramic composites and *ceramic–metal composites* (→ Ceramics, Ceramic–Metal Systems) are receiving increasing attention. Silicon carbide fibers in glass–ceramic matrices have shown toughness values up to 24 $MPa\,m^{0.5}$ at 1000 °C with cross-plied and unidirectional strengths of 500 and 900 MPa [55]. The reinforcing action of 60% alumina fibers in aluminum gave a tensile strength of 690 MPa up to 316 °C [56]. Use of as little as 3% of pure Al_2O_3 particles in aluminum increased strength and wear resistance [57].

A thickness of 10–15 mils (25–38 mm) of plasma-sprayed porous *ceramic coating* such as

ZrO_2 can reduce the temperature of the metal surface under the coating by 160 °C [58]. Such coatings are used on aircraft burners and aircraft afterburners, but not in critical parts of aircraft gas turbines. Pore-free coatings applied by chemical vapor deposition, sputtering, or reactive evaporation are 70–80 times as resistant to wear and erosion as porous coatings. High-temperature lubrication may make use of solid ceramic lubricants.

1.2.2. Electronic Ceramics

(→ Ceramics, Electronic)

Ceramics are involved in electronics as discrete units; however, as component sizes become progressively smaller, they are increasingly integrated into overall electronic assemblies. Fisher [59] has classified discrete ceramic parts into three categories: insulators, magnetic ceramics, and transducers.

Insulators represent a complex category including integrated circuit packages, insulating substrates, and a variety of special tube circuits. Electrical insulation materials are, in a sense, descended from traditional electrical porcelains, but property requirements plus the complex nature of integrated circuits make them a new family. Aluminum oxide is the dominant advanced ceramic insulator [11, pp. 426–429]. Tape-cast alumina ceramics dominate in uses requiring high heat dissipation and hermeticity. Alumina ceramics also compete with polymers and coated metals as supports for electronic chips. As excellent as alumina is for this purpose, alternative materials are being studied in an effort to lower the dielectric constant, permit higher frequency operation, and provide a closer match to silicon thermal expansion. Multiphase ceramics in the Al_2O_3–SiO_2–MgO family may be the second generation of ceramics, with Si_3N_4 as the third generation.

Several trends are apparent in the development of later-generation ceramic substrates. One line of development seeks to use low-firing, glass-bonded aluminas that can be cofired with copper, silver, or gold electrodes. A second line of development seeks to exploit the high thermal conductivity of AlN [*24304-00-5*]. Another candidate is BeO-doped SiC. A third line of development is concerned with finding lower-loss materials for microwave applications.

Ferroelectric ceramics, primarily high dielectric constant $BaTiO_3$ [*12047-27-7*] and related materials, find use in capacitors, which are indispensable in electronics. The use of cheaper metals as electrodes may lower unit costs [11, pp. 415–417].

Piezoelectrics are crystals whose charge centers are offset: a mechanical stress alters the polarization of the crystal just as an electrical field would. Piezoelectric crystals are widely used for voltage–pressure *transducers*. Piezoelectric ceramics, such as lead zirconate titanate [*12626-81-2*], are used in a wide variety of devices to convert motion into electrical signals and vice versa. Vibrators, oscillators, filters, loudspeakers, all using piezoelectric devices, are essential parts of many industrial and consumer products [19, pp. 55, 287].

Certain ceramics are termed semiconductors, electrical conduction occurring only if external energy is applied to fill energy gaps between filled and empty electron bands. An increase in temperature can also provide the required energy. Ceramic semiconductor materials include titanates, SiC, ZnO, NiO, and Fe_2O_3. In some instances, they are used as thermistors for temperature control. They may be used as voltage-sensitive resistors (varistors) to protect against voltage surges, as chemical sensors, or as miniheaters [19, pp. 47–50].

Ion-conducting ceramics, such as β-alumina and stabilized ZrO_2, are employed as oxygen sensors in automobiles and as electrolytes in fuel cells [60], [61].

Ceramic materials having magnetic properties are commonly termed ferrites. *Magnetic ceramics*, such as ferrites of Fe_2O_3 in combination with one or more of the oxides of Ba, Pb, Sr, Mn, Ni, and Zn, can be made into either hard or soft magnets. These are widely used in loudspeakers, motors, transformers, recording heads, and the like [11, pp. 417–421], (→ Magnetic Materials).

The optical properties of a material include absorption, transparency, refractive index, color, and phosphorescence. Optical transparency is often important. Glass and various ionic ceramics are transparent to visible light, and there are many applications for windows, lenses, prisms, and the like. Fiber optics offer enormous potential for communication; small fiber bundles transmitting coherent laser light can carry many times the information carried by wire cables. Magnesium oxide, Al_2O_3, and fused SiO_2 are transparent in the ultraviolet and a portion of the infrared and radar wavelengths. Magnesium fluoride, ZnS, ZnSe, and CdTe are transparent to infrared and radar wavelengths [19, p. 59].

Special pore-free Al_2O_3 is widely used as the inner envelope of high-pressure sodium vapor lights. Lead zirconate titanate ceramics are finding increasing use in light modulation and displays. Translucent $Y_2O_3-ThO_2$ ceramics are also useful optical materials.

Ceramic sensors can use bulk grain phenomena (such as piezoelectric effects, oxygen-ion conductivity, or negative temperature coefficient of resistivity), grain boundary phenomena (such as positive temperature coefficient of resistivity, voltage-dependent resistivity, or gas absorption), or controlled pore structure (moisture absorption). Occasionally all three microstructural features come into play, with different levels of importance. A broad class of sensors is based on optical fibers [62]. New types of optical sensors using optical fibers can measure temperature, pressure, sound, rotation, current, and voltage. A blood oxygen meter using optical fibers measures light transmission at eight different wavelengths, thus permitting blood oxygen determination.

1.2.3. Other Advanced Ceramics

One of the oldest uses of ceramics is as a thermal insulator at high temperature, and this role is continued in modern form, e.g., as super insulators such as the silica tile used on the U.S. space shuttle. Modern ceramics such as silicon carbide and silicon nitride are increasingly attractive as heat exchangers, as are low-expansion ceramics such as cordierite.

A potentially important market for new ceramics is as implants to replace teeth, bone, and joints.

Ceramics have long been used in the nuclear field as a fuel, cladding material, and shielding material. They are leading candidates as matrices to contain radioactive wastes for long-term storage.

1.3. Characterization of Ceramic Materials

The technology of ceramic manufacturing rests on measurement of the structural and chemical properties of the raw materials used in ceramic forming systems. The need for adequate test procedures is being met by continuing advances in materials science. Many sophisticated instruments and equally sophisticated techniques are available for evaluation of formula ingredients and of forming systems at various stages of manufacture [5, chap. 1].

Purity of ingredients has a profound influence on high-temperature properties of advanced ceramics, including strength, stress rupture life, and oxidation resistance. The presence of Ca^{2+} is known to sharply decrease the creep resistance of Si_3N_4 hot pressed with MgO sintering aid [63], but seems to have little effect on Si_3N_4 hot pressed with Y_2O_3 densifying aid [64]. Electrical, magnetic, and optical properties must be carefully tailored by additions of a dopant; slight variations in distribution or concentration can alter final properties significantly. Ceramic materials can occur in different geometries. As an example α-Si_3N_4 is preferred over β-Si_3N_4 for hot pressing or ordinary sintering.

In recognition of the importance of consistent properties of raw materials and synthetic powders used for advanced ceramic items, an ad hoc committee appointed by the Materials Advisory Board of the National Research Council (United States) gave the term *characterization* a special, restrictive meaning in the following definition [65]: "Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, and suffice for the reproduction of the material." True characterization involves a direct correlation between test results and properties. The mere taking of data is not characterization unless the test procedure serves a particular function in predicting properties of the material under test.

Although this definition was designed as an aid in establishing significant features for advanced ceramic products and their constituents, the concept has been successfully applied in the field of traditional ceramics. The many properties encountered in forming and firing are found to be consequences of the interaction of two or more of a limited list of fundamental characterizing features [66]. Table 4 provides a listing of significant, interacting features for traditional clay-based ceramics, with a partial list of the more important consequential properties encountered in forming and firing. An exhaustive survey of pertinent literature, in addition to a continuing review of plant and laboratory re-

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Table 4. Characterizing features and ceramic properties

	Characterizing features
	chemical composition
	mineral composition
	particle-size distribution
	specific surface
	colloid modifiers

Ceramic properties	
Unfired forming	Firing/fired
slip viscosity	vitrification
water of plasticity	shrinkage
workability	pyroplasticity
shrinkage	absorption
strength	strength
slip dispersion	color
casting rheology	thermal behavior
casting rate	microstructure

...its, has shown no exceptions to the list of characterizing features of Table 4.

Characterization, itself rapidly developing as a discipline, has suggested ways whereby selected properties of materials or a body can be used in development and control of clay bodies. Sanitary ware and vitreous chinaware are typical clay-based traditional ceramic products. The chemical, mineral, particulate, and surface data of Table 5 constitute complete characterizing descriptions of examples of formulas used in making these products.

Two terms require definition. The *mole of flux* is the sum of the percentages of CaO, MgO, K_2O, and Na_2O divided by their respective molecular masses. The *MBI* (methylene blue index) is the milliequivalents of methylene blue cation (chlorine salt) absorbed per 100 g of clay and is a measure of surface area [67].

Reproducibility of desired forming, firing, and fired properties is ensured by maintaining these characterizing features within prescribed limits [66].

Experience has shown that when any or all of the ingredients of a clay body must be replaced the 20-odd characterizing values of a full description may be reduced to 8–10 key indicators. A key indicator is a feature that is critical to controlling a particular property. The superscript *x*'s in Table 5 label the key indicators for the two examples.

Because fired body color is much more critical for vitreous chinaware than for sanitary ware, the coloring effect of Fe_2O_3 and TiO_2 must be taken into account when, for example, vitreous chinaware is reformulated [68]. The presence of mica in sanitary ware slip-casting significantly improves the casting rate and the quality of cast [69]. The presence of colloidal organic matter can increase response to deflocculants and result in significant increases in dry bonding power [70]. The rheology of clay-based forming systems can be altered adversely by apparently minor changes in subsieve particle-size distribution [71]: the percentage finer than 1 µm equivalent spherical diameter is an excellent indicator of any change [72]. The methylene blue indices (MBI) correlate with plastic forming properties and dry strength of unfired ware, both of which are functions of specific surface [67].

Table 5. Characterization of two clay-based bodies

Properties	Vitreous sanitary ware	Vitreous china
Chemical, wt%		
SiO_2	65.0^x	69.4^x
Al_2O_3	23.1^x	19.5^x
Fe_2O_3	0.44	0.30^x
TiO_2	0.28	0.14^x
CaO	0.33	1.33^x
MgO	0.13	0.11
K_2O	2.68^x	1.45^x
Na_2O	2.41^x	1.14^x
Ignition loss	5.67	6.46
Mole of flux	0.0766^x	0.0604^x
Minerals, wt%		
Smectite	3.7	3.0
Kaolin group	32.7	33.3
Mica	8.8^x	5.8^x
Free quartz	23.7^x	39.6^x
Organic	0.46^x	0.23^x
Auxiliary flux		2.0
Particle size		
% < 20 µm	76	76
% < 5 µm	47	45
% < 2 µm	33	36
% < 1 µm	25^x	28^x
% < 0.5 µm	19	21
Surface		
MBI, meq/100 g	3.3^x	2.7^x

^{x} Key indicators.

2. Raw Materials for Traditional Ceramics

Clay-based ceramics are predominant among ceramic products. Clay formulas (or bodies) may consist of a single clay or one or more clays mixed with mineral modifiers such as powdered quartz and feldspar. The special properties of the clay minerals that permit preparation of high-solids fluid systems and plastic forming masses are critical in the shaping of ware.

In developed countries, ceramic manufacturers and raw material suppliers usually work together in establishing standards [2]. The supplier assumes responsibility for continuity of material quality and works closely with the manufacturer in solving material-related plant problems.

However, in less developed countries, manufacturers may need to depend on suppliers who lack facilities and expertise for maintaining material uniformity. An alternative is that the manufacturer may be forced to mine and refine his own materials. In either case, the potter must be prepared to cope with variation in material properties, either by active supervision of supplier mining or through in-plant beneficiation prior to use. The characterization concept (Section 1.3) has permitted development of objective, simple test procedures for use in mining and beneficiation control [17].

2.1. The Structure of Clays and Nonplastics

The atomic structures of the common clay minerals are based on Pauling's generalizations for the structure of the micas and related minerals [73]. Two structural units are involved in most clay mineral lattices. One is the *silica sheet*, formed of tetrahedra consisting of a Si^{4+} surrounded by four oxygen ions. These tetrahedra are arranged to form a hexagonal network repeated to make a sheet of composition $Si_2O_5^{2-}$. The tetrahedral apex oxygens all point in the same direction with pyramid bases in the same plane.

The other structural unit is the *aluminum hydroxide, or gibbsite, sheet*, consisting of octahedra in which an Al^{3+} ion is surrounded by six hydroxyl groups. These octahedra make up a sheet, owing to sharing of edges: two layers of hydroxyls have cations embedded in octahedral coordination, equidistant from six hydroxyls. These octahedral sheets condense with silica sheets to form important clay minerals.

Kaolinite [*1318-74-7*] is the main mineral of kaolins, with usually tabular particles made up from units resulting from the interaction of gibbsite and silica sheets:

$$Al_2(OH)_6 + (Si_2O_5)^{2-} \longrightarrow Al_2(OH)_4(Si_2O_5) + 2OH$$

The kaolinite platelets have negative charges on their faces (or basal planes) due to an occasional Al^{3+} ion missing from the octahedral (gibbsite) layer or an Si^{4+} from the tetrahedral (silica) layer.

Disordered kaolinite is a variant of kaolinite in which Fe^{2+} and Mg^{2+} are thought to replace some Al^{3+} in the octahedral layer [23, p. 59]:

$$Al^{3+}_{1.8}Ca^{2+}_{0.1}Fe^{2+}_{0.1}(Si_2O_5)(OH)_4 \cdots M^{2+}_{0.1}$$

The M^{2+}, usually Ca^{2+}, is a balancing exchangeable cation. Hydrogen bonds between gibbsite and the silica layers can be weakened by changes in the octahedral dimensions caused by replacement of the small Al^{3+} (ionic radius of 0.051 nm) by the larger Fe^{2+} (0.074 nm) and Mg^{2+} (0.066 nm) ions. This produces the smaller grain size of disordered kaolinite found in some sedimentary kaolin and ball clay deposits.

Kaolinite crystals consist of a large number of two-layer units held together by hydrogen bonds acting between OH groups of the gibbsite structural layer of one unit and oxygens of adjacent silica structural layers. Unit layers are displaced regularly with respect to one another along the *a* axis. In the case of *halloysite*, the unit layers are stacked along both *a* and *b* axes in random fashion; because of less hydrogen bonding, water can penetrate between successive layers, thereby forming a hydrated variety of kaolinite.

$$Al_2(OH)_4(Si_2O_5) \cdots 2H_2O$$

According to KELLER [74], halloysite can exist as spheres, tubular elongates, or polygonal tubes; thus, kaolin occurs in a number of morphologies ranging from worms through stacks, irregular platelets, to euhedral kaolinite crystals. Particle morphology can have significant effects on ceramic forming systems [17].

The montmorillonites result from isomorphous replacements of portions of Al^{3+} or Si^{4+} in the three-layer mineral *pyrophyllite* [*12269-78-2*], which is formed by fusion of two silica sheets with one gibbsite sheet [75]:

$$Al_2(OH)_6 + 2(Si_2O_5)^{2-} \longrightarrow Al_2(OH)_2 \cdot 2(Si_2O_5) + 4OH^-$$

When Mg^{2+} replaces some of the Al^{3+} in the octahedral layer, the result is *montmorillonite* [*1318-93-0*] (smectite).

$$Al_{1.67}Mg_{0.33}(OH)_2 \cdot 2(Si_2O_5) \cdots M^+_{0.33}$$

M^+ lying between two adjacent three-layer units as an exchangeable cation, offsetting the excess atelets have negative charges basal planes) due to an occ- missing from the octahedral an Si4+ from the tetrahedral

amite is a variant of kaolinite Mg2+ are thought to replace tahedral layer [23, p. 59]:

[illegible]

ly Ca^{2+}, is a balancing ex- Hydrogen bonds between a layers can be weakened by hedral dimensions caused by small Al^{3+} (ionic radius of larger Fe^{2+} (0.074 nm) and ns. This produces the smaller ered kaolinite found in some and ball clay deposits.

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LER [74], halloysite can ex- r elongates, or polygonal ccurs in a number of mor- m worms through stacks, euhedral kaolinite crystals. can have significant effects ystems [17].

nites result from isomor- of portions of Al^{3+} or yer mineral *pyrophyllite* formed by fusion of two gibbsite sheet [75]:

[illegible] $(OH)_2 \cdot 2(Si_2O_5) + 4\,OH$

some of the Al^{3+} in the result is *montmorillonite*

[illegible]

adjacent three-layer units tion, offsetting the excess

Table 6. Layer lattice minerals

Mineral	Composition
Plastic	
Kaolinite	$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$
Fireclay	$(Al_{1.8} \cdot Fe_{0.1} \cdot Mg_{0.1})O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O \cdots Ca_{0.05}$
Montmorillonite	$(Al_{1.67} \cdot Mg_{0.33})O_3 \cdot 4\,SiO_2 \cdot 2\,H_2O \cdots Ca_{0.165}$
Illite group	muscovite → illites → montmorillonite
Halloysite [*12244-16-5*]	$Al_2O_3 \cdot 2\,SiO_2 \cdot 4\,H_2O$
Nonplastic	
Muscovite	$K_2O \cdot 3\,Al_2O_3 \cdot 6\,SiO_2 \cdot 4\,H_2O$
Pyrophyllite [*12269-78-2*]	$Al_2O_3 \cdot 4\,SiO_2 \cdot H_2O$
Talc [*14807-96-6*]	$3\,MgO \cdot 4\,SiO_2 \cdot H_2O$
Tremolite [*14567-73-8*]	$5\,MgO \cdot 2\,CaO \cdot 8\,SiO_2 \cdot H_2O$
Chlorite [*14998-27-7*]	$5\,MgO \cdot Al_2O_3 \cdot 3\,SiO_2 \cdot 4\,H_2O$

basal-plane negative charge. Because the SiO_2 of adjacent unit layers are held together only by weak van der Waals attraction, montmorillonite particles are thin and small.

If one-quarter of the Si^{4+} ions of the tetrahedral layers of pyrophyllite are replaced by Al^{3+}, a charge of sufficient magnitude is produced to bind univalent cations in regular 12-fold coordination. If the cation is K^+, the result is *muscovite mica* [*1318-94-1*] [23, p. 23]:

$$KAl_2(OH)_2 \cdot 2\,(Si_{1.5}Al_{0.5}O_5)$$

If the cation is Na^+, the result is *paragonrite mica* [*12026-53-8*]:

$$NaAl_2(OH)_2 \cdot 2\,(Si_{1.5}Al_{0.5}O_5)$$

Many natural clays contain a micaceous mineral resembling muscovite but containing less Al^{3+} and more combined water than normal muscovite. This *illite* [*12173-60-3*] occurs in sedimentary clays sometimes associated with montmorillonite and kaolinite. Analyses of illites from various localities show K_2O contents of [illegible]%; SiO_2 of 38–53%; and Al_2O_3 of [illegible]–32%. Knowledge of illite is as yet incomplete [23, pp. 24–25].

Table 6 shows the names and chemical compositions of plastic clay minerals and nonplastic layered aluminum and alkaline-earth silicate minerals commonly encountered in ceramic clays.

2.2. Clay–Water System

When a clay is dispersed in water, its balancing *exchangeable cations* retreat to a distance from the clay determined by their size and charge, forming an electrical double layer. If the water contains cations of a different kind and charge, an exchange of solution cations for clay-held cations may occur. Some cations are attracted more strongly to the clay than others. Cations can be arranged in a lyotropic (Hofmeister) series [22, p. 24]; hydrogen is held most strongly and lithium least:

H Al Ba Sr Ca Mg NH_4 K Na Li

The capacity of a clay for absorbed cations is termed its cation exchange capacity (c.e.c.) and is a function of clay specific surface [76]. The usual measure of the cation exchange capacity is the MBI (see p. 9).

The stability of a suspension of clay particles in water depends on the *degree of deflocculation* of the particles. Deflocculation depends on the character of an electrical double layer made up of the following parts [22, pp. 92–110]:

1) Negative surface charge consisting of the inherent negative planar surface charge plus absorbed OH on normally positively charged edges
2) Absorbed layer of cations at the negative surface, the Stern layer
3) Diffuse cloud of cations that extends to a distance from the charged particle that is determined by the
    a) concentration of ions in the bulk solution away from diffuse cation cloud
    b) size and charge of the cations

The thickness of the electrical double layer is a maximum when the concentration of hydroxides or hydrolyzable salts of the monovalent cations of the Hofmeister series is the minimum needed to fully charge the clay surface. Excess deflocculant reduces the extent of the diffuse layer.

In the absence of a double layer, the bringing together of two clay particles by Brownian motion results in formation of a doublet. Attraction between platelets is either by edge–face attraction or by van der Waals force, or both. Where the normally positive edge has been neutralized or made negative, there is only van der Waals attraction. Particles provided with diffuse, extended counterion clouds cannot approach one another closely enough to allow the inherent van der Waals forces to function fully [21, pp. 183–212], so deflocculation or reduced flocculation is the result.

The very polar *water molecules* are attracted strongly to negative faces or positive edges of clay particles. The adsorbed water molecules, in turn, attract other water molecules, and these, in turn, attract yet other water molecules. Thus, a water structure is built on the surfaces of clay platelets or rods. The extension of the water envelope from the particle surface is thought [77] to depend on the size and valence of the cations present in the water. Exchangeable cations can adsorb water molecules and build up a structure whose extension from the clay surface depends on the amount and kind of cations present. Where large singly charged cations are present, a loose, wide extension occurs; for small multiply charged cations, the counterion cloud is compact and less extended [77]. Water of plasticity and plastic qualities are functions of surface area, particle geometry, and exchangeable cations.

However, if a clay is allowed to absorb *organic colloids*, such as tannic acid or humic acid colloids derived from soil organic matter or lignites, the attraction between clay particles is greatly reduced, water of plasticity drops significantly, response to deflocculants is enhanced, and dry strength rises [70]. Apparently the absorbed organic particles with their absorbed water layers neutralize positive edges and provide a measure of steric hindrance to the close approach of particles.

Deflocculation is, thus, a neutralization reaction between acidic groups of absorbed organic colloids and the monovalent cations and hydroxyl groups provided by the deflocculating compound, rather than a reaction between clay and the deflocculant. Some functional groups are more responsive than others; as a consequence, organic-bearing ball clays vary in their forming properties.

The hydroxyl ion is necessary in the deflocculation of clays [70]. The presence of any soluble sulfate or chloride salts in the clay–water system reduces the formation of OH^- and lessens the deflocculating effect of a given quantity of deflocculant.

2.3. Commercial Ceramic Clays

In the United States and the United Kingdom, the major classes of ceramic clays are termed kaolin (or china clay) and ball clay. *Kaolin* may occur at its point of origin in primary deposits or in sedimentary deposits composed of clay particles washed from the point of formation by stream action and laid down in quiet water. Kaolin deposits are widely distributed in the temperate zone. However, in the tropics alteration may be rapid, resulting in bauxite [78].

The term *ball clay* has no technological significance; it is derived from older mining practice in England, whereby cubes of moist, plastic clay were cut from the working face with a special tool, rolled down the clay face, assuming a vaguely spherical shape, and loaded onto wagons by women workers (ball maidens). A general definition of ball clay would be sedimentary clay of fine to very fine grain size, consisting mainly of ordered and disordered kaolinite with varying percentages of illite, mica, montmorillonite, free quartz, and organic matter.

Clays classified as ball clays are widely used in North and South America, England, and to an increasing extent, in Asia. Ball clay is far less used in Europe. The use of ball clays in clay-based forming systems is designed to improve plasticity, reduce water of plasticity, increase unfired strength, improve casting slip properties, and in some cases, improve firing and fired properties. The unfired functions of a ball clay can sometimes be matched by treating fine-grained kaolins with colloidal organic substances [70].

Table 7 characterizes representative china and ball clays from major producing areas in England and the United States. The china and ball clays from Thailand provide examples of ceramic clays available in less-developed nations. The mineral constituents of the clays of Table 7 were calculated from the chemical analyses with a procedure suggested by HOLDRIDGE [79].

The primary kaolins of the china clay deposits of England and Thailand contain more mica than the sedimentary kaolins of Georgia (United States), as demonstrated by their higher K_2O contents [66]. English ball clays are much higher in mica than their U.S. analogues [79]. Mica has favorable effects in slip casting and provides a measure of fluxing.

The flow diagrams of Figure 1 are representative of mining and refining practices in ball clay producing areas of Dorsetshire and Devon-

Table 7. Characterizations of typical clay

Properties	Clay*									
	A	B	C	D	E	F	G	H	J	K
Chemical, wt%										
SiO_2	45.7	46.7	50.5	60.4	46.6	47.2	48.5	59.8	49.0	58.5
Al_2O_3	38.3	38.2	28.7	27.0	38.1	37.6	32.3	26.4	34.6	24.4
Fe_2O_3	0.41	0.60	0.91	0.93	0.69	0.50	0.98	1.00	0.71	1.26
TiO_2	1.55	1.42	1.48	1.62	0.07	0.05	1.16	1.39	0.02	0.92
CaO	0.08	0.12	0.40	0.28	0.19	0.20	0.18	0.20	0.35	0.05
MgO	0.06	0.20	0.30	0.26	0.20	0.08	0.21	0.51	0.34	1.05
K_2O	0.06	0.15	0.89	1.70	1.47	1.35	1.89	2.42	2.52	2.36
Na_2O	0.14	0.03	0.18	0.50	0.08	0.07	0.19	0.38	0.48	0.12
Ignition loss	13.65	13.79	16.58	7.59	12.66	12.62	14.78	7.88	10.66	8.64
Minerals, wt%										
Montmorillonite	nil	3	8	7	6	2	6	14	9	29
Kaolin group	96	93	58	44	80	82	60	34	60	23
Mica	2	2	10	21	12	11	18	25	27	22
Free quartz	trace	1	14	26	1	1	9	23	3	19
Organic	trace	trace	8	0.5	trace	trace	5	2	nil	3
Particle size										
% < 20 µm	95	99	99	98	100	88	96	97	77	95
% < 5 µm	69	88	95	79	97	74	91	85	52	87
% < 2 µm	52	72	82	61	64	30	83	81	36	72
% < 1 µm	35	56	69	43	57	23	77	75	19	56
% < 0.5 µm	28	41	51	29	35	15	62	65	16	43
Surface										
MBI, meq 100 g	1.6	10.5	12.1	5.6	5.4	2.4	8.7	12.8	3.4	16.5

* Key to designations:
(A) Coarse kaolin, sedimentary, Washington County, Georgia, United States
(B) Fine kaolin, sedimentary, Wilkinson County, Georgia, United States
(C) Dark fine ball, Graves County, Kentucky, United States
(D) Coarse light ball, Weakley County, Tennessee, United States
(E) Fine china clay, Cornwall, England, United Kingdom
(F) Coarse china clay, Cornwall, England, United Kingdom
(G) Dark ball, Devonshire, England, United Kingdom
(H) Light ball, Dorset, England, United Kingdom
(J) China clay, primary, Thailand
(K) Ball clay, Thailand

shire and china clay deposits of Cornwall in England. The ball clay deposits are very thick with relatively thin overlaying soil. The china clay deposits are kaolinized granite and consist largely of mixtures of kaolinite, muscovite mica, quartz, and small amounts of accessory minerals. Over the past 40 years, the clay producers of England have raised mining and refining of their materials to a very high level of technology. As a consequence of already desirable clay properties, coupled with close control and technical competence, a large export trade has been developed.

The thin overburden and thick deposits of English ball clay permit both open-pit mining and underground mining. Open-pit operations are of two types: (1) excavating of uniform seams with backhoes and (2) selective mining of some clays with a spade-carrying version of the pneumatic jackhammer. Air-spaded clay is lifted from the pit with a boom, placed in a truck, and transported to a processing center. Backhoe-dug clay is placed directly into the truck for transport to a processing center. Underground ball clay mining is done either with air-spading for selective mining or by a rotating cutter that loads the clay directly into the mine car for transport to a processing, storage, and refining center.

English ball clays are stored in accordance with types determined by characterizing feature tests. Clays are sliced (shredded) into thumb-size pieces and often blended with one or more other selections to provide controlled, specified properties. Such blends may be extruded in the form of pellets for bulk shipment or dried and subjected to grinding to a refined powder in an air-elutriation grinding mill. Air-floated clay is usually bagged for shipment.

English china clay is recovered by subjecting the parent ore to "hydraulicking" (high-pressure jet of water). The clay and fine muscovite mica are separated from the ore and transported by the resulting stream to a classifier for removal of the coarser mica and quartz. Further nonclay impurities are removed with a hydrocyclone. The low-solids slip is thickened, characterized, and stored as a 20%

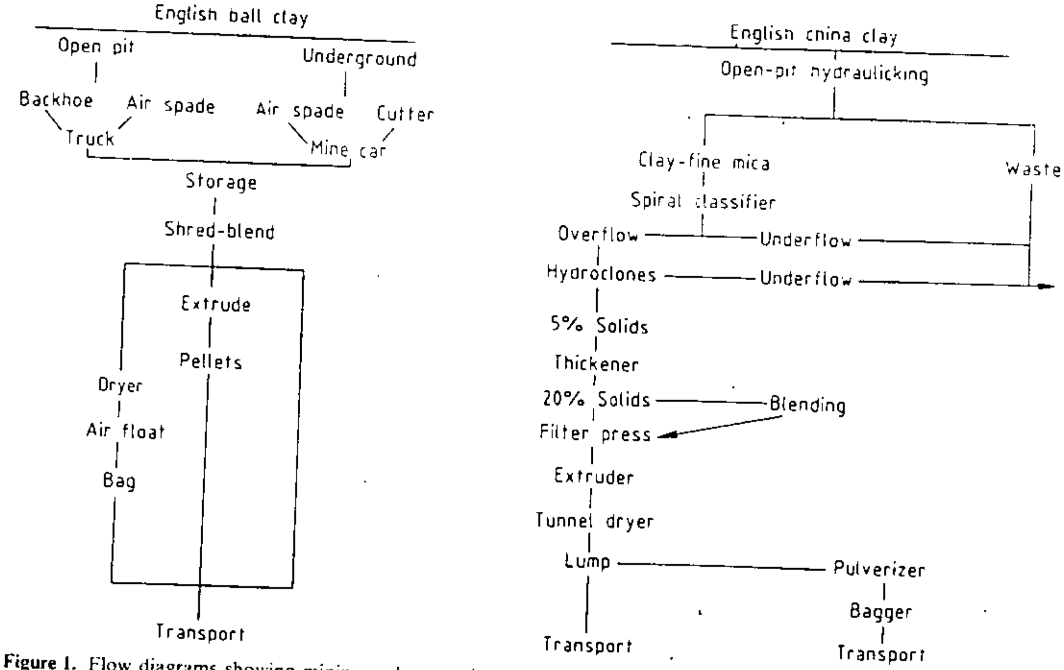

Figure 1. Flow diagrams showing mining and processing methods for the English ball clay deposits of Devonshire and Dorsetshire and the English china clay deposits of Cornwall

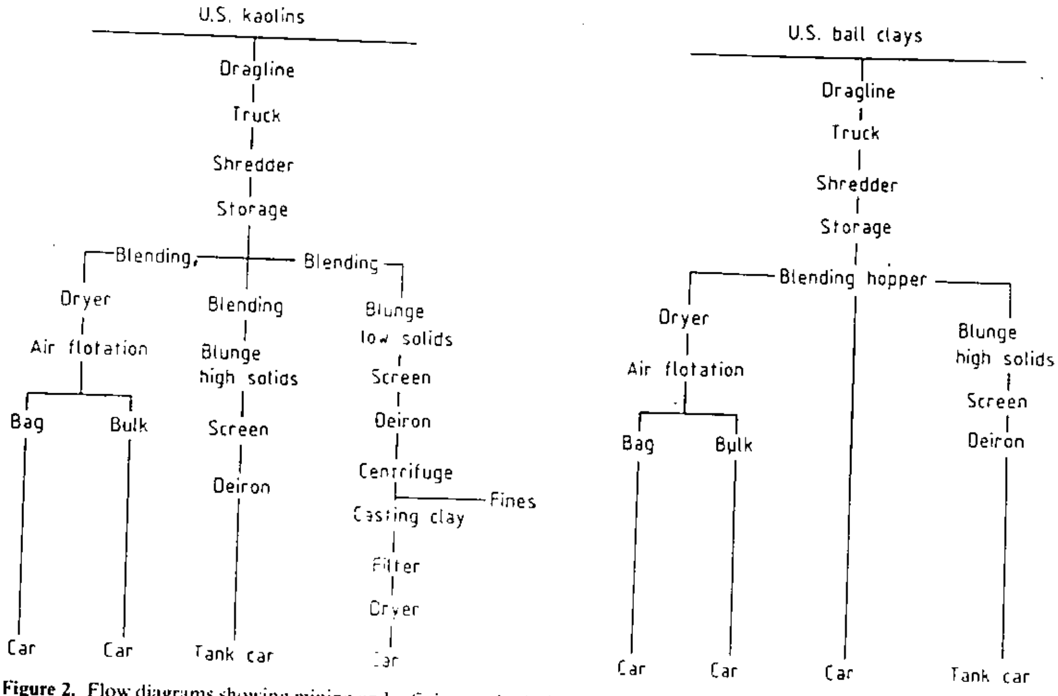

Figure 2. Flow diagrams showing mining and refining methods for the sedimentary kaolins of South Carolina and Georgia and the ball clay deposits of Kentucky and Tennessee

solids slurry. Two or more slurried china clay selections may be blended to give desired, controlled properties before filter pressing and drying. The dried clay may be shipped in bulk pellet form or passed through a pulverizer and shipped in bags.

Figure 2 provides flow diagrams representative of mining and refining methods employed in the sedimentary kaolin deposits of Georgia and South Carolina and in ball clay deposits of Tennessee and Kentucky. Overburden is usually no more than 8 - 10 m thick. Neither ball clay nor kaolin deposits exceed ≈ 15 m. All mining is open pit.

Selective mining based on drill hole and working face characterization tests is done with dragline or power shovel. Transport from pit to processing and storage sites is by trucks carrying 5 - 10 t up to 10 km. Storage is in the form of shredded clay.

Kaolins are blended to specification and either dry-ground for bulk or bagged shipment or subjected to wet processing. High-solids slurries (70%) are prepared for tank-car shipment to ceramic plants using slip-cast manufacturing. Low-solids slurries are subjected to centrifugal fractionation with subsequent thickening, filtration, and drying. The dried filter cake may be shipped in bulk, air-floated and sent in hopper cars as bulk, or pulverized for bagged shipment.

The ball clays are blended to specification and shipped as is, as high-solids slurries, or dried.

The processing of clays for use in ceramics is also described under → Clays.

2.4. Commercial Nonplastics for Ceramics

A large proportion of ceramic ware is made from clay-based formulas whose major constituents are clay minerals, powdered silica, and powdered feldspar or a related feldspathoid. Such bodies are termed triaxial [11, pp. 178–183]. The fluxing feldspathoids and silica minerals are termed nonplastics. The term *flint* is properly used only with reference to powdered flint pebbles.

The *feldspar group* of minerals is the most important source of fluxing oxides for clay bodies. All are framework aluminosilicates based on an SiO_2 structure. Replacement of Si^{4+} by Al^{3+} results in charge deficits that are balanced by K^+, Na^+, or Ca^{2+} lying in framework holes. The smaller Na^+ and Ca^{2+} ions confer a different crystal structure than the larger K^+ ion. Albite [*12244-10-9*] ($NaAlSi_3O_8$) and anorthite [*1302-54-1*] ($CaAl_2Si_2O_8$) are isomorphous and form the plagioclase solid-solution series. Albite and anorthite are triclinic, whereas microcline [*12251-43-3*] ($KAlSi_3O_8$) is monoclinic. Nepheline syenite is a type of rock consisting of nepheline [*12251-27-3*] ($K_2O \cdot 3\,Na_2O \cdot 4\,Al_2O_3 \cdot 9\,SiO_2$) mixed with microcline and albite.

An old saying, attributed to the Chinese [11, p. 92], says in effect that *silica* [*7631-86-9*] is the skeleton and clay the flesh of a ceramic body. There is a tendency to regard silica as an inert substance in the body. However, this is far from the case; the silica can have profound effects both in forming and firing.

Table 8 provides examples of fluxing feldspathoids and silicas used in clay-based ceramic formulations. The mineral constituents of the feldspars and silicas of Table 8 were calculated from the chemical analyses with a method by Koenig [80]. Feldspar A is a froth-floated feldspar recovered from North Carolina alaskite granite. Material C is dry-ground, selectively mined nepheline syenite from Ontario, Canada. Material E is wet-ground feldspar from Thailand. All are successfully used in clay-based ceramic formulations.

In addition to the feldspathics and silica, some clay-based bodies contain calcined Al_2O_3 to increase fired strength; ground limestone and/or dolomite as auxiliary flux; talc for special heatshock bodies and wall tile; chlorite to lower the maturing temperature of slip-cast porcelains; or wollastonite, a wall-tile body constituent.

The principal sources of pottery and glass grade feldspar in the United States are deposits in Connecticut, North Carolina, South Carolina, Oklahoma, and California [81]. Nepheline syenite, also widely used in ceramic formulations and in glass batches, is produced from deposits in Methuen Township, Ontario, Canada [82].

Prior to 1940 all feldspar mined in the United States was selectively quarried, crushed, and hand-cobbed on picking belts before being ground. Just after World War II a froth floating procedure began to be applied to mixed-mineral rocks containing feldspar. At the present time over 80 % of the feldspar produced in the United States is recovered by froth flotation from a variety of ores, including alaskite granite, pegmatite, graphic granite, beach sand, and weathered granite. The remaining feldspar, mainly high K_2O feldspar, is block mined, hand-cobbed, and processed dry. Nepheline syenite is also selectively mined and subjected to dry processing.

Figure 3 provides a generalized flow diagram for froth flotation recovery of feldspar from coarse granites.

Table 8. Characterizations of typical nonplastics

Properties	Feldspathic/Feldspathoid*					Flint/Quartz*				
	A	B	C	D	E	F	G	H	J	K
Chemical, wt%										
SiO_2	66.8	68.5	60.7	79.5	71.1	96.6	98.5	97.9	99.5	95.7
Al_2O_3	19.6	17.5	23.3	12.0	16.0	0.2	0.9	0.5	0.2	2.1
Fe_2O_3	0.04	0.08	0.07	0.08	0.26	0.10	0.09	0.40	0.06	0.03
TiO_2				0.01	0.34	0.01	0.06			0.09
CaO	1.70	0.30	0.70	0.20	1.54	0.20	0.02			0.20
MgO	trace	trace	0.10	0.09	0.37	0.09	0.03			0.20
K_2O	4.80	10.40	4.60	3.80	0.06	0.39	0.05			0.30
Na_2O	6.90	3.00	9.80	3.90	8.64	0.15	0.04			0.03
Ignition loss	0.20	0.30	0.70	0.45	0.42	1.58	0.17	0.20	0.12	1.60
Mole of flux	0.1728	0.1644	0.2220	0.1092	0.1768	0.0124	0.0028			0.0123
Minerals, wt%										
Feldspars	92	83	75	48	81					
Nepheline			24							
Mica	4	7			trace					2
Quartz	4	9		41	18	96	97	97	99	91
Clay				3		1	1		trace	6
Organic						trace				trace
Other			1	8	1	4	2	3	1	1
Particle size										
% < 20 µm	67	64	68	60	53	56	57	75	58	53
% < 5 µm	26	26	22	23	20	16	18	26	15	12
% < 2 µm	11	12	9	11	10	5	7	9	5	5
% < 1 µm	9	9	3	6	5	1	2	3	1	3
% < 0.5 µm	trace	6	trace	2	2			1		2

* Key to designations:
A) Flotation feldspar, Mitchell County, North Carolina, United States
B) Block feldspar, Custer County, South Dakota, United States
C) Nepheline syenite, Ontario, Canada
D) Cornish stone, Cornwall, England, United Kingdom
E) Feldspar, Thailand

F) Flint, France
G) Quartzite, Pennsylvania, United States
H) Quartzite, Venezuela
J) Silica sand, California, United States
K) Silica sand, Philippines

After (normally) thin overburden has been removed from the ore, the granite is blasted and transported to a processing plant. The large pieces are passed through, successively, a jaw crusher and cone crusher to prepare rodmill feed.

From the feed bins the thumb-sized pieces of ore pass through rodmills where they are reduced to millimeter-sized grains. The rodmilled pulp then goes onto rotating screens to remove oversize, which is returned to the rodmill for further grinding. Passage of screened pulp suspended in water through a hydroseparator removes most of the fines that might interfere with the chemistry of flotation processes. The sized, de-slimed pulp is then sent to a chemical conditioner where the mica particles are treated to promote bubble adherence. The underflow (feldspar, quartz, and garnet) is conditioned chemically to allow only the iron-containing garnet to be attracted to bubbles and so removed in the froth overflow. Next comes separation of feldspar from the quartz by adjusting the reagents to cause feldspar particles to adhere to the froth and the quartz to be rejected.

Final steps involve draining, rewashing to remove reagents and draining of the cleaned products, passage of drained material through a dryer and through a magnetic field, and finally storage. Pottery uses require fine grinding; glass grade requires no grinding of the granular feldspar or quartz.

Where a deposit is sufficiently pure, block feldspar may be processed as shown by the diagram of Figure 4.

The blasted block material is passed through a jaw crusher prior to passage through a rotary dryer into a surge bin. The crushed, dried product passes through a cone crusher onto a 2.4-mm vibrating screen, with any oversize being returned for further crushing.

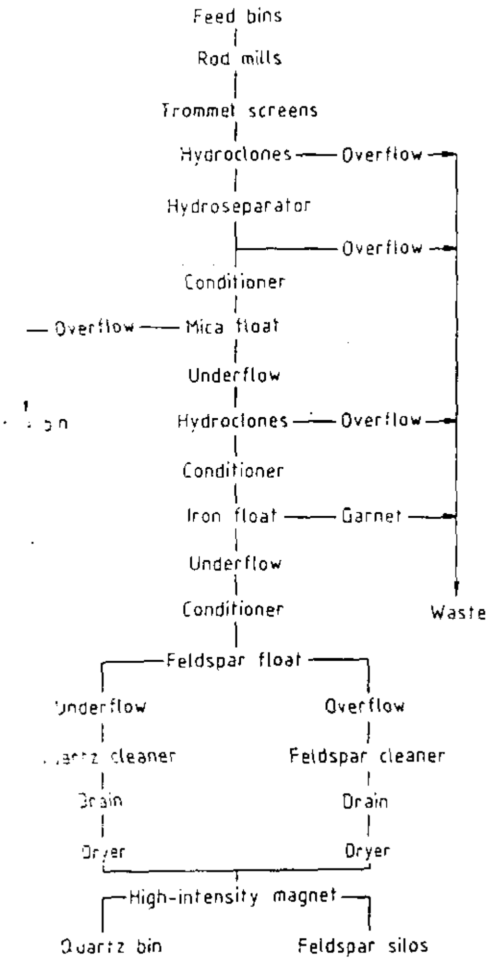

Figure 3. Flow diagram showing typical froth flotation re-…ery of muscovite mica, feldspar, and quartz from a …granite found in western North Carolina

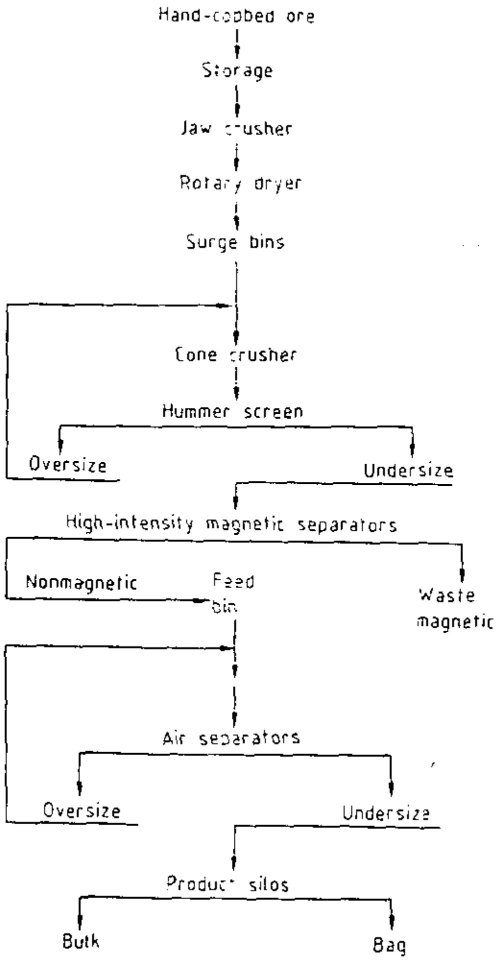

Figure 4. Flow diagram showing a typical cobbing (hand selection) method for mining and processing a pegmatite feldspar in southwestern South Dakota

The minus-2.4-mm product goes into a surge bin that feeds a high-intensity magnetic separator; magnetic particles pass to waste, while nonmagnetics go to mill feed bins. Milling is by pebble mills; ground product goes to air classifiers, with any oversize returned for further milling. Undersize passes to storage silos for bagged or bulk-loaded shipment. Nepheline syenite is processed in much the same manner, with an additional step designed to produce a minus-1.0-mm size for glass batching.

3. Raw Materials for Advanced Ceramics

Although traditional ceramics are composed of natural raw materials that are physically separated and reduced in size, advanced ceramics require chemical conversion of raw materials into intermediate compounds. These intermediates lend themselves to purification and eventual chemical conversion into a final desired form.

Oxides and carbonates available in powder form include those of Al, Sb, Ba, Be, Bi, Co, Mn, Mg, Ni, Si, Th, Ti, and Zr. Also available are carbides of Si, Ti, and W and the nitrides of Al, B, Hf, Si, and Zr. However, needs exist for specialized powders for some advanced ceramics, and a variety of chemical routes can be used to synthesize these powders. Chemical routes, such as sol-gel processing, can bypass the powder stage.

Requirements for high strength and smooth finishes, particularly of small parts, necessitate fine-grained powders. Thus, one line of advanced ceramic research aims at producing very fine, essentially spherical, monosize particle powders. These are typically made by colloidal chemistry for oxides. Nitrides and carbides involve controlled nucleation and growth in gas-phase reactions. However, most high-technology ceramics are still made from powders with broad size distributions in the submicrometer (under 1 µm) range.

3.1. Metal Oxides and Carbonates

Alumina [*1344-28-1*] is derived from bauxite by selective leaching with NaOH, precipitation of purified $Al(OH)_3$, and thermal conversion of the resulting fine-size precipitate to Al_2O_3 powder (→ Aluminum Oxide) for use in polycrystalline Al_2O_3-based ceramics. Antimony [*7440-36-0*] is derived from Sb_2S_3 (stibnite) by reduction with iron scrap, and antimony trioxide [*1314-60-9*] is formed by burning antimony in air.

Barium oxide [*1304-28-5*] is obtained by decomposition of $BaCO_3$ at high temperature; the carbonate itself is made by reaction of Na_2CO_3 with BaS. Beryllium oxide [*1304-56-9*] is prepared by heating $Be(NO_3)_2$ or $Be(OH)_2$. Bismuth oxide [*1332-64-5*] is obtained by heating $Bi(NO_3)_3$ in air.

Cobalt compounds are derived from ore concentrates by roasting and leaching with acid or ammonia; the oxide [*1307-96-6*] is formed by calcination of the carbonate or sulfate. Magnesium oxide [*1309-48-4*] is readily available as the 99.5% pure grade powder, but greater purity may require calcining of high-purity salt solutions. Manganese oxide [*1344-43-0*] can be prepared by calcination of manganous nitrate.

Nickel ores are either sulfidic or oxidic. Sulfides are flotation-separated and roasted to sintered oxide. Oxides are treated by hydrometallurgical leaching with ammonia. Nickel oxide [*1313-99-1*] is then prepared by gentle heating of $Ni(NO_3)_2 \cdot 6\,H_2O$. Strontium carbonate is formed by boiling celestite, $SrSO_4$, in a solution of $(NH_4)_2CO_3$; SrO [*1314-11-0*] is formed by decomposition of the resulting $SrCO_3$.

Vanadium pentoxide [*1314-62-1*] is prepared by ignition of alkali solutions from vanadium minerals. Zinc carbonate [*3486-35-9*] is prepared by action of sodium bicarbonate on a zinc salt, such as zinc chloride. Zirconia [*1314-23-4*], ZrO_2, is derived from $Zr(OH)_4$ or $Zr(CO_3)_2$ by heating.

3.2. Borides, Carbides, and Nitrides

Boron and carbon can be made into B_4C [*12069-32-8*] by heating B_2O_3 and carbon in an electric furnace. Boron nitride [*10043-11-5*] is made by heating B_2O_3 and tricalcium phosphate in an ammonia atmosphere in an electric furnace (→ Boron Carbides, Boron Nitride, and Metal Borides).

Boron, carbon, and nitrogen can be made into other synthetic compounds with refractory and wear properties. Examples are silicon carbide (SiC), silicon nitride (Si_3N_4), tungsten carbide (WC), titanium carbide (TiC), titanium nitride [*25583-20-4*] (TiN), tungsten boride (WB_2). A translucent AlN has been developed that is 5 times as thermally conductive as Al_2O_3 ceramics.

4. Processing Ceramic Ware

Traditional and advanced ceramic industries use many techniques for processing their products. The exact process is governed by the nature of the forming system, the size and geometry of the piece, product specification, and practices in various areas of the ceramic industry.

Most ceramic manufacturing processes start with formulas consisting of one or more particulate materials. These formulas are used for shaping products that are further processed by firing and by finishing of the fired items.

In many cases products have complex shapes made by use of one or another of such forming techniques as dry or isostatic pressing, plastic shaping, extrusion, slip casting, injection molding, tape casting, and green finishing. These shaping techniques are based on some old — the potter's wheel, for example — and some new procedures developed from recent research findings.

Forming systems employed in making traditional and advanced ceramic ware are (1) liquid suspensions, (2) plastic masses, or (3) more or less dry granulated or powdered formulations.

4.1. Preparation of Clay-based Forming Systems

The clay bodies of traditional ceramics are normally mixtures of clays and powdered nonclay minerals or else natural mixtures of clay

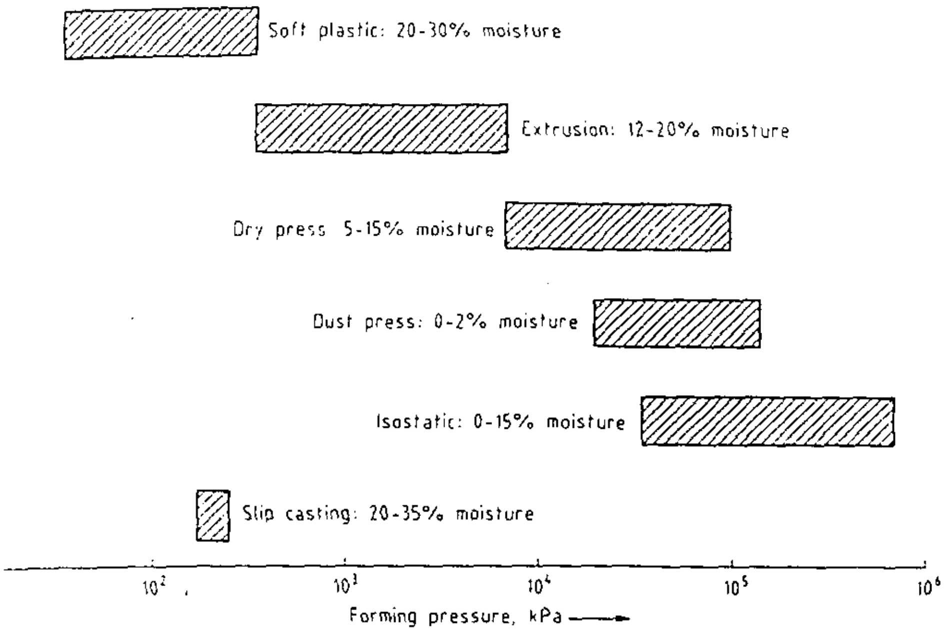

Figure 5. Moisture content and pressure ranges required for shaping clay-based forming systems

substances and nonclay particulate materials. Most clays occur as aggregates of clay particles. When contacted with water, such aggregates tend to break apart or slake. The development of a water structure on the surfaces of the particles results in plasticity (see Section 2.2. Clay–Water System). If sufficient water is added to the clay and the mixture is agitated, a dispersion forms. Because the powdered nonplastics, i.e., the nonclays, do not develop any great degree of plasticity when moistened with water, the various ceramic systems of traditional ceramics depend on the plastic component (usually but not always clay) to provide (1) the workability required in plastic forming or dry pressing, (2) the deflocculant response of fluid systems in slip casting, and (3) the green and dry strength of unfired ware.

Figure 5 shows the moisture-content variation and forming-pressure ranges for soft plastic shaping, extrusion, dry pressing, dust pressing, isostatic pressing, and slip casting of clay-based bodies.

Because the ingredients used by any given system may range from highly purified to as-mined lump materials, the body preparation process must vary with the particular circumstances. However, the main objectives of processing are always (1) to arrive at as intimate a mixture of clay and nonplastic particles as possible, (2) to provide uniformity of shaping properties from lot to lot, and (3) to maintain uniformity of firing and fired properties from lot to lot.

Preparation processes for these forming systems can be divided into two general classes: (1) wet processing and (2) dry processing.

Wet Processing. Wet processing is usually employed whenever one or more of the ingredients needs initial or supplementary beneficiation. General practice in the United States and the United Kingdom subjects dinnerware bodies (Table 5, Vitreous china, on p. 9) to wet processing to ensure adequate dispersion of clay constituents, permit sieving for removal of oversize, and allow magnetic treatment to remove iron particles. Such a process uses relatively unrefined shredded or lump ball clays and filter cake or coarsely pulverized china clay.

Third-world ceramic manufacturers may have access to producer-beneficiated materials but often must depend upon their own mines for at least a portion of their raw materials. In some instances beneficiation of local materials becomes an integral part of body preparation. In the People's Republic of China and Thailand, for example, the silica and fluxing feldspars may be received in block form and ground during the body preparation process.

Because grinding is readily accomplished by dry crushing, followed by wet ball milling, one approach is to wet-grind the nonplastics along with a small, fixed percentage of suspending fine clay. The nonplastic slop (suspension) is then sieved, deironed by magnets, and stored in agitators. Clays are wet-dispersed as suspensions, sieved and deironed, and then blended by formula with nonplastic slop in agitator tanks.

A modification of this method is to simply weigh all formula ingredients as a unit, transfer the batch to a ball mill with the required water, and mill to a specified sieve residue percentage.

For plastic or dry-press forming systems, wet processing is done in the flocculated state. Indeed, flocculation is often enhanced in preparation of high-tension electrical porcelain bodies by addition of $AlCl_3$ or $MgSO_4$. Sufficient water must be used to allow sieving and passage through a magnetic separator.

Consistency of plastic masses is controlled by four major factors: (1) specific surface of the body, (2) modifying inorganic ions such as Ca^{2+}, Mg^{2+}, Al^{3+}, SO_4^{2-}, and Cl^-, (3) the amount and kinds of organic colloid present, and (4) the proportion and temperature of water present.

The water content of plastic forming systems is reduced to a working level by filter-pressing and, when necessary, by further drying of the filter cake. Air is removed from the filter cake by passage through a vacuum pug mill.

Pressing dust can be made from filter cake by drying the cake and passing the dried cake through a granulating hammer mill. Otherwise, sieved and deironed slip can be diverted to a spray drier and formed into pressing-size granules.

Dry Processing. The flow diagrams of Figures 1–4 (Chap. 2) indicate that finely ground, deironed clays and nonplastics can be obtained in both North America and the United Kingdom. Such materials make it possible to prepare both plastic forming systems and pressing dust without a slip stage. Dry pressing dusts are prepared by dry blending the ingredients with ribbon blenders or rotating cone mixers and then incorporating the required moisture with a muller mixer. If sufficient water is mulled into the mix and the resulting plastic mass is passed through a vacuum pug mill, the resulting forming system can be used for plastic forming.

Refractories and heavy clay products are usually made from combinations of clay and coarse nonplastics by crushing them in a wet pan (heavy rollers revolving in a pan) and adding water plus other modifiers. By variation of the moisture, the mulled mixes can be made into pressing dusts by granulation or into plastic systems by a deairing operation.

Casting Slip. Although filter-cake clay body is sometimes made into casting slip by addition of deflocculating agents, by far most casting slips are made by direct wet methods.

Clay-based casting slips must be made to cast to a firmly plastic state within a prescribed time range. Casting properties, such as rate, amount of retained water, and plastic quality of casts, are each in some way related to freshly stirred consistency of the slip and its tendency to thicken on standing. Common practice in industry is to control casting properties by maintaining a constant *solids concentration* by measuring slip specific gravity and adjusting *slip rheology* to targeted freshly stirred viscosity and thixotropic gelling. Unfortunately, the mere meeting of a targeted rheology is no guarantee of constant casting performance.

Variation in *slip temperature* can alter slip viscosity and casting rate significantly [83]. Thus, it is possible for two slip batches at different temperatures to have identical viscosities and thixotropies, yet to cast in decidedly different ways. RYAN and WORRALL [84] found that the nature of exchangeable cations in casting slip governs the rate of cast under constant temperature and rheological conditions. The custom in sanitary ware slip control is to buffer the effect of deflocculant-enhancing organic colloid by addition of divalent alkaline-earth-metal carbonates or sulfates to control the rate and structure of the cast [85].

The rheology and casting properties of casting slips are strongly influenced by apparently minor changes in the distribution of *particle sizes* in the subsieve region. BROCINER and BAILEY [86] have shown that the coarse kaolin component of a casting slip can be made variably finer as the input of energy imparted in blunging or ball milling is varied: the mixing or milling operation must be very carefully controlled, and both equipment and time of mixing should be kept constant.

In direct preparation of casting slips, on occasion a standard sequence and timing of additive and raw material introduction into the mixer is not followed. If, for example, a light ball clay is added first with the Na_2CO_3, followed

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organic-bearing ball clay, the amount of adjusting sodium silicate required is significantly greater than if the reverse order were used, and the resulting slip requires a longer aging period. If deflocculation is initiated with sodium silicate and the Na_2CO_3 is added later, the aging time is greatly extended. When slips prepared by using differing sequences of addition are adjusted to the same viscosity and thixotropy, their casting rates and cast structure are also likely to differ significantly.

Equipment. Those plants that grind their own nonplastics use *ball milling*, either continuous dry grinding in an air-swept conical ball mill or batch wet grinding in a cylindrical ball mill. Dry grinding demands that the feed material be dry to avoid packing and to allow air sweeping of fines to a collector. Wet grinding is claimed to require less power than dry grinding, but dry grinding produces less wear on the mill lining and grinding media [88, sect. 6, pp. 20–25].

Ball mills belong to a class of grinding devices termed tumbling mills. The rotating container is a cylinder mounted with its axis horizontal. The grinding action is due to the tumbling of the grinding media, which are cast iron or steel balls, hard rock (e.g., flint pebbles), or some nonmetallic material such as high-alumina porcelain [88, sect. 6, pp. 20–25].

Blunging refers to the agitation or blending of ceramic materials in a mixing tank equipped with an impeller to stir the suspension and baffles to direct the suspension to the impeller. Impellers can be simple paddles or specially designed shapes for increased efficiency of dispersion [89].

Screening (or sieving) of fluid dispersions is termed wet screening. Two general types are employed in the sieving of blunged or ball-milled slips: (1) an inclined rectangular panel of wire mesh having the proper openings and (2) circular screens. The *inclined rectangular panels* are subjected to vibration that agitates and separates the coarser particles during transit of the slip. Vibration can be by shaking or electromagnetic pulse [88, sect. 7, pp. 34–37].

Circular vibratory screens can [90] effectively separate particles as fine as 44 μm in diameter. The basic arrangement consists of a motor plus interchangeable frames that hold screening wire cloth and discharge ports. The frame is held rigidly to a main screen assembly. The motor has a vertical upward and downward extended shaft fitted with eccentric weights. The main screen assembly is mounted on a circular base by springs that permit the assembly to vibrate freely while preventing vibration of the floor. A number of three-dimensional patterns of the suspension on the screen can be developed by varying the angle between top and bottom weights. This type of screen is widely used in the United States and the United Kingdom.

Screens used for pressing-dust sizing are relatively coarsely meshed (2.0–3.0 mm), whereas those used for plastic body systems and casting slips are much finer (0.20–0.05 mm).

To remove magnetic particles, granular nonclay ball-mill feed can be subjected to a *magnetic separator*, passage either through a magnetic field or over a magnetic pulley prior to the grinding operation. Suspensions of clays or nonclay powders can be passed through the grid of an electromagnetic purifier prior to the dry or pugging operations. High-gradient magnetism is capable of removing such colorants as TiO_2 from kaolin slurries; this can transform the high-TiO_2 Georgia and South Carolina kaolins into very white-firing fine-china constituents [91].

Dewatering of slips for preparation of plastic forming systems or pressing dusts is usually by *filter pressing*. The basic concept of filter presses involves feeding the slurry under pressure into the space between square, round, or rectangular plates. This space is created by frames that alternate with the plates. Plates are hollow and normally covered with filter cloth. As the space fills with suspension under pressure, the liquid is forced through the cloth and drains away as the solids form a cake [92].

Pugging is the process of blending clays and water by manual or mechanical means. A pug mill is an open trough with a lengthwise shaft on which are mounted blades that blend the clay and water to a plastic forming system of the desired consistency. Filter-cake bodies are subjected to a combination of pugging in an auger trough, coupled with passage through a vacuum chamber, followed by extrusion. Vacuum pug milling (or deairing) makes the plastic mass more workable and cohesive by elimination of the air from the system [13, p. 267].

A fluid suspension of particulate material can be dried and formed into pressing dusts or granules by *spray drying*. A spray dryer consists essentially of a drying chamber. A downward flow of heated air is introduced at the top of this chamber. A flow of suspension is transformed into an upward flowing cloud of droplets by a nozzle atomizer. The droplets are dewatered and fall to a product outlet at the bottom of the drying chamber. An attached exhaust removes excessively fine particles to a cyclone collector.

Relatively uniform spheres are formed, and moisture content is also uniform [93].

When fully purified clays and nonclay powders are available, *dry blending and tempering* are employed. A shell or ribbon mixer may be used as an initial step, followed by addition of water in a mixing muller. Otherwise, dry blending and tempering may be done in stages in a mixing muller. Mixing mullers normally have heavy wheels, under which the moistened body rotates. First, a smearing action occurs, and second, a rotating plow scrapes the compressed body up and turns it under the mullers for additional mulling [94]. The tempered body then goes to dust mill/sieving operation for lower-moisture-dust processing or dry pressing or to a deairing pug mill for plastic systems.

4.2. Preparation of Advanced Ceramic Systems

Traditional ceramic forming systems are nearly always polydisperse, with particle size ranging more or less continuously from an upper to a lower limit. As a distribution ranging between definite limits approaches linearity on an arithmetic plot, optimum packing results in minimum voids [95]. The more extended the range between upper and lower limiting sizes, the lower the void volume for a given distribution [96]. However, the more extended the distribution is, the more sensitive it is, with respect to void volume, to deficits or excesses of intermediate particle sizes. This finding has been related to differences in calcined alumina slip occasioned by altering particle-size distribution size limits and intermediate size distribution [97].

Although a controlled optimum particle size distribution is needed for maximum, reproducible strength, sometimes a mono-size distribution must be approached to avoid growth of larger particles at the expense of the smaller: very fine particles are much more reactive than larger particles, and quite porous initial compacts can be sintered at high temperature to nearly theoretical density. Transparent polycrystalline Al_2O_3 is an example. The finer the powder, the more rapid the sintering and the lower the densification temperature, thereby reducing grain growth and increasing fired strength.

Sizing of Advanced Ceramic Materials. Because particle size and distribution are so important for controlling properties of advanced ceramic products, the manufacturer must often further refine an already refined as-received material to meet his specifications. A variety of techniques are used for modifying particle size and distribution:

screening
air elutriation
ball milling
attrition milling
vibratory milling
fluid energy milling
liquid elutriation
precipitation
freeze drying
laser
plasma
calcining
sol–gel

Dry *screening* is used for sizing particles down to 44 µm, whereas wet, slurry screening is often employed for subsieve sizes. *Air elutriation* (or classification) is used to separate coarse and fine fractions. Special air classifiers are available for separating minus-20-µm particles, but care must be exercised to avoid contamination. *Liquid elutriation* can be used to separate a single specific material into fractions or to separate materials having different specific gravities.

Ball milling [16, pp. 410–438] consists in placing either a dry or a suspension charge in a closed container with appropriate grinding media and rotating the container to create a cascading action of the media. Media selection is important. Higher density pebbles or cylinders will grind more quickly than lower density media. Wear of media creates contamination that can be controlled by careful selection of wear-resistant mill lining and hard grinding media. Wet ball milling requires removal of water from the powder. Dry ball milling requires additional grinding aids such as a lubricating stearate. A very small amount of moisture has been found to prevent packing of high-alumina prereacted body during dry grinding.

Attrition milling is similar to ball milling, but the container is held in a fixed vertical position and the grinding media agitated by arms attached to a rotating shaft. The attrition mill can be used for dry grinding or wet grinding with vacuum or various controlled atmospheres [16, pp. 439–443].

Vibratory milling uses fixed containers typically lined with polyurethane or rubber. Suitable grinding media are placed in the container with the material to be ground, and a vibration is transmitted through the bottom center. The resulting cascading–mixing action leads to shear and impact breaking of particles between grinding media [16, pp. 410–438].

Fluid energy milling functions by causing particles of the material to be ground to impact one another. They are carried at high velocity in a fluid: air, water, superheated steam. Jet mills are lined with wear-resistant materials [98].

Precipitation of soluble salts and pyrolysis to the oxide has been used to provide controlled particle size and high purity. Calcined alumina has been made by precipitating alumina trihydrate from solution by changing pH and using seed crystals. The very fine, reactive alumina greatly extends the uses for alumina [19, p. 165].

Freeze drying involves forming drops from solutions of metal salts, freezing them rapidly, removing water by sublimation under vacuum, and calcining the crystallized salts [99]. Another method for preparing pressing granules is by dispersing the powder and additives as a slurry and drying by spraying the slurry or solution into a chamber where the drops fall through hot gases. Surface tension holds the drops in spherical form. These drops, when dry, flow readily into a die [100].

Slip-cast advanced ceramic forming systems require a particle distribution [97] that provides maximum packing. Often sizing is accomplished by blending several narrow distributions [95], or the material may be ball-milled with binder, wetting agents, deflocculants, and densification aids. Disk mills [16, pp. 468–488] are especially effective in dispersing agglomerated powder. The liquid phase normally used in mold casting is water, whereas in tape casting the liquid is usually nonaqueous [101]. In each instance, all bubbles must be removed from slips by vacuum treatment prior to use [102].

A number of glasses have been prepared in the laboratory by hot pressing or sintering gels of single oxides or combinations of two or more oxides, such as SiO_2, Al_2O_3, and TiO_2. Carefully controlled processing makes monolithic objects possible [103]. Commercial uses of *sol–gel* are fibers, powders, bulk shapes, and oxide coatings or films [104]. Of these uses, film or oxide coatings are regarded as very important.

Processing of a sol–gel starts with a metal alkoxide: $Si(OC_2H_5)_4$, $Ti(OC_2H_5)_4$, as well as $Al(OC_2H_5)_3$ are examples. Alcohol and distilled water are hydrating reagents. A wide variety of silicate and aluminosilicate systems have been made with other cations, such as those of Li, Na, K, Rb, Mg, Ca, Sr, Ba, Pb, Ga, Fe, Ln, Ti, Zr, and Th, as well as ternary or quaternary compositions with two or more of these elements [105].

The basic procedure for making SiO_2 and metal oxide gels is to dissolve $Si(OC_2H_5)_4$ in ethyl alcohol and add alcohol or water solutions of the desired metal nitrate. Hydrolysis is effected with an excess of distilled water. At 60 C the SiO_2 precipitates as a stiff gel.

Preconsolidation of Advanced Ceramics. Preparation of a pressing dust sometimes involves addition of a binder, a lubricant, possibly a sintering aid, and finally, development of a free-flowing powder by granulation. This may be done by blending the fine, low-bulk-density powder with binder solution and lubricant, and then compacting the mass into blocks that are chopped, crushed, or coarsely pulverized. The resulting granules are screened to obtain proper size for die filling.

4.3. Forming Ceramic Articles

Forming systems used to make traditional and advanced ceramic ware include slip casting, soft plastic, stiff plastic, dust pressing, dry casting, and a number of modified or special systems for advanced ceramics (see Fig. 5, p. 19).

Soft Plastic Forming. The simplest method of forming plastic masses is by hand molding. This requires a soft plastic system. Currently, soft plastic forming systems are used in the production of soft mud bricks; pottery by throwing; jiggered or roller-formed tableware; hot-plunge insulators; and ram process products. In *soft mud brick making*, the selected clays are prepared by wet panning and passed through a pug mill that forces the plastic clay through a die into wooden molds. *Throwing* on the wheel is a soft plastic method for making vases and the like, used in simple cultures and by art potters. The wheel is a disk on top of a shaft turned by a weighed kickwheel or by a motor.

Jiggering was developed from throwing. A measured slug of soft plastic body is placed on a plaster form that revolves on a wheel head. A template tool is brought down onto the moist bat, pressing it down onto the plaster mold and so forming the upper part of the piece. At the same time, the template tool scrapes away excess body from the moist piece with the aid of a spray of water. Automation requires carefully controlled, deaired forming masses [106].

The *roller-head method* for soft plastic forming is an alternative to the jigger, especially for less plastic formulations such as bone china and hard porcelain. Instead of a scraping témplate blade, a polished (and sometimes heated) contoured metal roller is brought down and rolls out the plastic body onto the plaster form. In this case, the form remains stationary [107].

Hot-plunging or jollying of plastic body articles involves the placing of a measured slug of body in a plaster mold and having a heated, revolving polished metal tool press down and form hollow objects, such as pin insulators or cups. The term *hot pressing* is sometimes applied to the hot-plunging operation, but hot pressing is more generally used for special, advanced ceramics processed by application of high pressure to fine-grained oxides in refractory molds held at high temperature [108].

The *ram process* involves pressing a lump of soft plastic body between two hard plaster molds and squeezing them together to form a plate, ash tray, or similar object. In the pressing stage, water is squeezed out of the piece and a vacuum pulls moisture into the molds. In the removal step, the vacuum is maintained on the upper mold and pressure is applied to the lower mold to release the piece. The upper mold then lifts the piece free, and pressure is applied to free the object from the upper mold. Pressure is also applied to blow moisture from the mold halves before another cycle starts [109].

Stiff Plastic Forming. Stiff plastic systems are extruded through a die, either by auger extrusion or piston extrusion. Auger extrusion is a continuous operation, whereas piston extrusion is necessarily intermittent. *Piston extrusion* is used for extruding fine-grained refractories, cermets, and electronic bodies. A preformed, deaired slug is placed in the cylinder and forced through a die at pressures up to 35 MPa. Pieces as small as 1 mm in diameter with a half-dozen 0.1-mm-diameter holes can be made. Large sewer pipes are piston-extruded with a vertical piston extruder [11, p. 147].

Auger extrusion finds use in extruding bricks and hollow tile on a continuous basis. Short sections are cut off at desired lengths. The auger device consists of a pugging trough that feeds a screw, which in turn pushes the clay through a shredder into a vacuum chamber. The deaired shreds are recompacted with a screw and pushed through the die. High-tension insulator blanks of up to 1 m in diameter [12, pp. 111–112] are extruded with auger deairing pug mills and are used in lathe-turning segments of very large electrical insulators.

Dust Pressing. The term applied to forming of damp, granulated body batches containing 5–15% moisture that are formed at high pressure in a steel die is dust pressing. All wall tile, floor tile, some quarry tile, and most low-tension electrical porcelain is formed by dust pressing. More than 85% of all fireclay brick and nearly all silica brick and basic brick are formed by dust pressing. Hydraulic presses and hydraulic toggle presses are used [11, pp. 149–151].

Dry Pressing. Dry pressing is similar to dust pressing, but the moisture content is < 2.0%, so that a binder and internal lubricant must be employed. Dry pressing is employed for advanced ceramic products in two ways [11, pp. 149–151]. Small shapes are pressed by *uniaxial compaction* [11, pp. 151–152], wherein the pressure is applied (usually) in a downward, vertical direction, thereby producing pressure variations due to wall friction and particle–particle friction. This results in nonuniform density. *Isostatic compaction* involves application of pressure equally to all sides of the charge. An isostatic press consists of a thick-walled pressure vessel. Powder is enclosed in a liquid-proof rubber mold that is immersed in a noncompressible fluid. The fluid is pressurized and transmits pressure equally to all sides of the mold; pressures can range from 35 MPa to as much as 1400 MPa, but usually ca. 210 MPa [110].

Slip Casting. Deflocculated liquid systems are made into ware by slip casting [17, chap. 10]. Formation is accomplished by consolidation of the particles into a semirigid state through removal of a portion of the liquid phase by an absorbent, porous mold. The most common mold material is the hemihydrate of gypsum, $CaSO_4 \cdot 0.5\,H_2O$ [*10034-76-1*], which when mixed with water rehydrates and forms needles of gypsum crystals as an interlocked mass [111], thus forming continuous capillary pores (→ Calcium Sulfate, vol. A4, p. 555). The size and liquid-carrying capacity of plaster molds is controlled by varying the plaster:water ratio.

WALKER [112] observed that as water rises from the stoichiometric 18.5 kg of water to the range of 60–100 kg (depending on the processing and ore source of the plaster) per 100 kg of $CaSO_4 \cdot 0.5 H_2O$, the rate of casting increases to a maximum and then decreases with greater water. Both the specific gravity and the compressive strength decrease with further increases in water.

Although the suction pressure of porous plaster decreases as the amount of water increases, a larger pore size allows freer passage of water from the developing cast and provides a larger reservoir for liquid as it is removed from the cast [112]. The loss of moisture from the exterior of the mold by evaporation is a significant controlling factor in governing the rate and condition of casts: high external humidity reduces, and low external humidity raises, the rate of cast and time of setup.

Slip casting takes two general forms. In the first, slip is poured into the mold where water is absorbed, leaving a semirigid layer of particles next to the mold wall. After a sufficiently thick layer has developed, the excess slip is poured out. The cast wall continues to pass moisture into the mold, thus reducing the moisture gradient from the wall, and allowing the cast to assume the plastic state needed for cast removal. This is *drain casting*, which is used for hollow items. In the second, a slip at a somewhat higher solids concentration (55 vol% against 50 vol% for the drain-cast slip) and a greater thixotropy (reversible thickening) is poured into the mold and allowed to cast solid. This is termed *solid casting*. On occasion, solid casting and drain casting are used in the same piece. The character of the cast and rate of buildup are controlled by manipulation of the particle size [72] and colloid modification [7, chap. 1].

Special Systems for Advanced Ceramics. Advanced ceramics can be consolidated and formed by the following methods:

1) Pressing
    uniaxial pressing
    isostatic pressing
    hot pressing
    hot isostatic pressing
2) Casting
    slip casting
    soluble-mold casting
    thixotropic casting
3) Plastic forming
    extrusion
    injection molding
    transfer molding
    compression molding
4) Others
    tape forming
    flame spraying
    green machining

To this point discussion has focused on the shaping methods originally used for the less-demanding clay-based formulas, but which have been refined for use in making small, more-demanding advanced ceramics. Certain advanced ceramic products require very thin sheets. A method for making such products makes use of casting or spreading a specially prepared slip or slurry onto a moving carrier surface and controlling its thickness with a doctor blade [113]. In such cases, the system resembles an oil-base paint. The powder is dispersed in a volatile solvent (nonaqueous organic liquid) with unsaturated organic acids of 18–20 carbons, and a polymer binder and plasticizer are added. Drying consists primarily in removal of the volatile solvent, which leaves a thin flexible tape.

An interesting and useful modification of slip casting also involves an adaptation of investment casting. First, a water-soluble wax is injection molded to make a pattern. The pattern is then coated with a water-insoluble wax, and the water-soluble part is dissolved away. The wax mold is fastened to an absorbent plaster block and is filled with slip. Once casting is completed, the water-insoluble wax is dissolved from the cast with an organic solvent, and the cast is dried, machined as needed, and fired to the proper temperature for densification [19, pp. 197–199].

Injection molding makes use of the techniques for molding plastic combs and the like, the difference being that the polymer, either thermosetting or thermoplastic, serves only to disperse the ceramic powder and to provide lubrication [114]. A sized powder is milled dry with organic binders and made plastic by preheating. The plastic mass may require as little as 24% or as much as 50% binder by volume, depending on particle size and particle-size distribution. Complex shapes can be made [19, pp. 200–203].

4.4. Drying and Finishing

Drying of ceramic products is one of the more critical processing operations. The moisture must be removed as rapidly as possible without generating stresses great enough to cause cracking or distortion.

A plastic ceramic piece contains liquid in three forms: (1) adsorbed liquid on the colloidal particles; (2) liquid films on particles of noncolloidal dimensions; and (3) free liquid held in pores between the particles. Liquid must leave the system in three distinct stages [20, pp. 82–84]:

1) By evaporation from the surface of the piece, bringing the particles closer together, decreasing the volume of the piece proportionately, and eventually allowing the particles to come into contact, at which time shrinkage ceases
2) By removal of the remaining free moisture
3) By removal of the adsorbed moisture

As moisture leaves the piece, a gradient is established between the surface and interior of the ware. Because of the shrinkage factor, this gradient must not be too great; otherwise, excess shrinkage at the surface will cause cracking.

Moisture Stress. Many mechanisms affect the behavior of clay-based ceramic forming systems during dewatering processes such as slip casting, filtration, and drying. Some of the mechanisms involved are capillarity, adsorption, osmotic pressure, the electrical double-layer, and pore water structure [115]. The moisture changes in unfired ceramic bodies can be studied by measuring the specific energy of the water as the fundamental parameter. This energy concept is termed moisture stress [116], [117].

Moisture stress is defined as the work done per unit mass of water when a small amount of the water is moved from the clay–water system to a free water surface at the same temperature. The SI unit is J/kg. Expressed in simpler terms, moisture stress is a measure of the affinity of a porous system, such as a moist clay body or liquid slip, for its moisture.

A number of methods have been proposed for measuring moisture stress. PACKARD [117] employed a direct suction device in which moist clay was placed on a water-saturated, fritted glass plate that was in contact with water. A tube connected to the water vessel could be raised and lowered to increase or decrease suction, thus altering the moisture content of the clay. COLEMAN and MARSH [118] used a pressure-membrane apparatus for very high moisture stress. PACKARD [117] proposed use of a series of evacuated closed containers where moist clay was suspended over solutions of known relative humidity. SAMUDIO [119] was able to assign moisture stress (pF) values to casts made from slips containing small percentages of various inorganic salts by using a pressure-membrane method.

Moisture stress ranges from nearly 0 for dilute suspensions to ca. 10^6 J/kg for oven-dried clay bodies. Soft plastic bodies have moisture stresses in the region of 40–50 J/kg. Leather-hardness occurs at moisture stress of in the region of 5×10^3 J/kg, whereas air-dried clay bodies have moisture stresses of ca. 10^5 J/kg.

Rate of Drying. The moisture stress concept implies that for a body of a given particle-size distribution, the rate of drying depends on a structure imparted by the interaction of many factors. A simple example is the control of permeability and water holding in slip-cast pieces by interaction of organic matter, deflocculants, and flocculating salts [120]. Organic colloids are known to reduce the water of plasticity of fine-grained clays [17, p. 45], yet that same organic matter has a strong affinity for water and can retard moisture loss [121]. Similarly, the presence of fine-grained muscovite mica in plastic clay bodies or moist cast appears to slow drying [69].

If a granular solid is involved, moisture loss proceeds at about the same rate as from a pan of water under the same conditions [11, p. 161]. However, from a plastic mass of fine clay, the rate of moisture loss may be less than that of the coarser system [122]. Ceramic clay bodies would be expected to show loss rates between those for granular masses and clay masses. In any one of these circumstances, the drying rate is constant until particles touch and shrinkage stops. At this point the continuum of the pore water ceases and flow of water from the interior of the piece cannot maintain the surface film needed for rapid evaporation. The rate of drying then falls.

The shrinkage properties of clay bodies are useful in setting up an efficient drying schedule. Natural clays give shrinkage traces that vary with clay fineness and packing characteristics of the noncolloidal particles [122]. Contrary to other opinion [4, p. 554], NORTON stated that the rate of water removal from the surface of a plastic clay piece is approximately one half that from a free water surface under the same conditions. Accordingly, evaporation rate from a moist granular solid is much greater than that from a plastic fine-grained clay [123]. The rate of flow of liquid from the interior can be increased by decreasing the viscosity of the liquid and this is accomplished by raising its temperature.

Speed of drying is also governed by the moisture capacity of the air surrounding the piece, i.e., the relative humidity, and the volume of air passing over the ware. Because the moist piece is a porous system, a balance must be struck between loss of moisture at the surface and movement of moisture through the particles from the interior to the surface. If liquid loss at or near the surface exceeds liquid movement from interior pores, differential shrinkage can result in cracking or warping.

Defects. Drying defects can originate wherever there are discontinuities in the formed piece. *Cracks* can develop at these points during shrinkage associated with drying. Clay particles tend to orient with their long dimension normal to the direction of pressure. Because shrinkage is least in the direction parallel to particle orientation and greatest in the normal direction, solid-cast test bars made in an open mold tend to *warp* on the exposed face away from the oriented mold-face layer. Similarly, frictional forces in extrusion force moisture into the interior and cause orientation of clay particles parallel to the direction of extrusion. Differential shrinkage and excessive moisture gradient are leading causes for cracking and warping.

Even though a moist object has a uniform distribution of moisture, it warps unless it is evenly dried. A wall tile, for example, placed on a plate so that one face is protected from air flow and evaporation warps. During initial drying, an originally uniformly moist piece can develop a moisture gradient through (1) loss of moisture at the surface or (2) uneven heating of the pore water, which lowers its viscosity at the warmer surface but not in the cool interior.

Some operations subsequent to slip casting can cause livering (dilatant consolidation) in one part of the cast and not in adjacent areas, resulting in a lower moisture-release rate and lower shrinkage in the livered area than in the adjoining portion.

Even after defect sources originating in the forming operation have been eliminated, the problem of removing the moisture without rupturing or warping the ware remains. This objective is achieved through the techniques of *humidity drying* that (1) lower the viscosity of the water, (2) uniformly warm the pore water without causing differential shrinkage, and (3) remove the water economically with respect to both time and fuel consumption.

The principle of humidity drying involves (1) heating greenware all the way through in a saturated atmosphere, (2) reducing the humidity as fast as possible without stressing the ware, and (3) once shrinkage ceases, raising the temperature and reducing the humidity to zero relative humidity [20, pp. 82–84].

Drying Methods. Drying methods fall into two classes: (1) convection and (2) radiation [124], [125]. *Convection methods* circulate warm air around the ware being dried, the warm air serving the dual purpose of heating the pieces and removing moisture by convection circulation.

A *simple tunnel dryer* requires passage of cars loaded with ware through the dryer, while heat is supplied by steam coils underneath, hot air from a heater, or waste heat from kilns. Drying is likely to be uneven from top to bottom of the load in tunnel dryers, but cross-circulation of heated air by fans or jets improves uniformity in such dryers.

Controlled humidity can also be attained in a tunnel dryer by introducing the moist ware at one end into hot moist air sent in originally as warm dry air at the exit end, the *counterflow method*. The dry air picks up moisture in its passage over the loaded cars, thus becoming saturated with moisture. Sometimes an auxiliary heating unit is located at the ware entrance end. In this way the moist ware is heated uniformly with no initial loss of moisture or shrinkage. As the ware moves toward the exit end, the surrounding air becomes progressively cooler and drier. The exterior parts of the pieces are reduced in temperature, owing to evaporative cooling, while the interior remains warmer; in a clay mass with a temperature gradient moisture moves toward the cooler part [126].

A refinement of the counterflow method has the *tunnel divided into sections*, each with its own independent heat and humidity controls. The ware enters a hot, saturated zone and is warmed without moisture loss. The car then passes through progressively drier zones, each held at constant but higher temperature.

A *chamber humidity dryer* operates by stages on a stationary load. Hot, saturated air warms the ware. When the chamber is at a uniformly high temperature, drier and slightly cooler air is passed through the load and evaporation occurs.

Ware can be dried more quickly if air is directed at right angles than if it is blown parallel to a surface [127]. For small, simple shapes, a method termed *jet drying* is sometimes used: air is blown in a definite pattern at right angles to the surface of the piece, thereby saving fuel, space, and time [11, p. 167].

Radiation methods involve transfer of heat to the moist ware as infrared or high-frequency radio waves. The principle of heat transfer by radiation methods is being employed increasingly in the drying of ceramic ware. Over 40 years ago, infrared lamps were used to dry large slip-cast units in open settings while ordinary air movement was used to remove the moisture. Drying times were reduced from 14 days to 12 h [128]. Hotel china from automatic jiggers can be dried sufficiently for removal from the bat in 10–15 min [125]. The infrared drying is followed by hot-air jet drying [127].

Finishing. Nearly all ceramic ware, however formed, must be subjected to finishing operations. These may be as simple as removal of casting spares, mold seams, and fins. However, the operation may involve the turning of a foot on a leather-hard cup or an elaborate turning of a high-tension insulator from a 1-m-diameter extruded blank. The term *trimming* means the shaving away of seams from a cast piece or cutting off the casting spare. *Fettling* refers to removal of fins, mold seams, and rough edges from dry, or nearly dry, ware.

4.5. Firing Ceramic Products

The terms used to describe the densifying processes that occur during heat treatment of ceramic items can be confusing. The expression *sintering* is used [13, p. 232] to describe a process by which a substance is bonded together, stabilized, or agglomerated by being heated to a point close to, but below, the melting point. *Vitrification* is defined as a progressive reduction of the pores of a ceramic piece as a result of heat treatment [1, p. 202], but says nothing about formation of a liquid, glassy phase. However, the dictionary definitions [129] dealing with the terms vitreous, vitrify, vitrification, and vitrifiable all center on some aspect of glass. BURKE [130] notes that the word sintering is generally used in referring to processes that assume no liquid is formed during heat treatment.

Here the term *densification* [19, chap. 7] is applied to processes where removal of pores from a ceramic product by heat treatment can take place either by formation of a glassy phase or by solid-state material transport, or both. However, traditional ceramics and advanced ceramics are described separately because clay-based products invariably involve development of some glass, whereas advanced ceramic products nearly always involve solid-state reactions.

4.5.1. Firing Traditional Ceramics

The main reactions occurring in the course of heating a clay-based product to maturity are summarized in Table 9 [11, p. 267]. As shown by the expansion curves in Figure 6 [131], in the initial stages of firing clay-based bodies, there is an expansion to a peak at ca. 600 °C with a small inflection (the quartz inversion) at 573 °C, followed by a gradual drop up to ca. 775 °C. After remaining level to ca. 850 °C, a rise in expansion follows to a peak at ca. 900 °C. Shortly thereafter, the bodies begin a decided contraction. Above 1300 °C (not shown in Figure 6) irreversible thermal expansion occurs in all types of clay-based bodies [132], and this expansion must be taken into account in devising firing schedules [131]. The expansion on heatup of body A, which contains pyrophyllitic South American clays, is much greater than that of body B, a U.S. clay body containing no pyrophyllite.

Shrinkage and porosity changes with increasing temperature vary, depending on the body composition and the porosity at maturity.

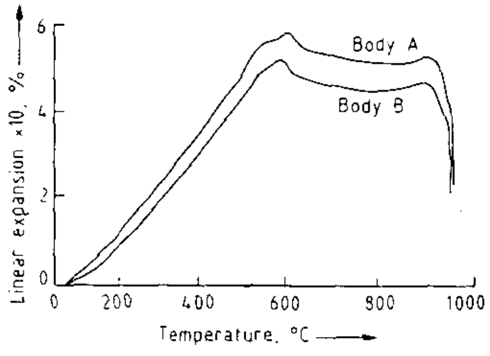

Figure 6. Irreversible heatup thermal-expansion traces for vitreous sanitary ware bodies containing pyrophyllite and sericite (A) and no pyrophyllite and little mica (B)

Table 9. Reactions occurring in firing clay bodies

Temperature, °C	Reactions in the course of firing
100	free moisture removed from the piece
100–200	loss of adsorbed moisture
200–400	gradual loss of H_2O from halloysite and montmorillonite, pyrophyllite and fine sericitic mica begin decided expansion
400–700	organic matter oxidized, breakup of clay mineral structures, pyrophyllite starts sharp expansion
573	quartz inversion
700–950	pyrophyllite attains maximum expansion, spinel forms in clays
950–1000	muscovite structure destroyed, γ-Al_2O_3 or mullite forms
1000–1100	mullite, $3\,Al_2O_3 \cdot 2\,SiO_2$, forms from clay
1100–1200	feldspars melt, clay and cristobalite dissolve, porosity decreases, shrinkage increases rapidly
1300	glass increases, ware expands, absorption increases, strength decreases

Vitrification/shrinkage curves can be shifted downward in the maturing range while their configuration and the forming properties of the bodies can be maintained by the judicious selection of auxiliary fluxing constituents [133]. An understanding of those factors affecting the nature of the glassy phase permits ready control of the pyroplastic deformation characteristic of large clay body units [134] without altering the unfired forming properties of the body.

4.5.2. Densification of Advanced Ceramic Products

The densification of formed advanced ceramic items is generally referred to as sintering. Sintering is, in simple terms, removal of voids (pores) of the formed piece, accompanied by shrinkage. Criteria to be met before sintering can take place are (1) an available means for material transport and (2) an energy source to initiate and promote material transport. Diffusion and viscous flow are transport mechanisms. Heat is the primary source of energy, functioning with particle–particle contact and surface tension to produce energy gradients [19, pp. 217–223].

Vapor-Pressure Sintering. Difference in vapor pressure as a function of surface curvature provides the driving energy. Material goes from particle surfaces with a positive curvature radius and high vapor pressure to contact regions with negative curvature radius and much lower vapor pressure. The smaller the particles, the greater the driving force. While vapor-phase sintering bonds particles, it does not eliminate pores.

Diffusion Sintering. Diffusion can be the movement of atoms or vacancies along a surface or grain boundary through the body. Only grain boundary or body diffusion results in sintering. The driving force is differential free energy or chemical potential between free surfaces and contact points of adjacent particles. Finer particles sinter more rapidly and at lower temperatures than coarser particles. Uniformity of particle shape, size, and distribution governs the uniformity of the final product.

Liquid-Phase Sintering. The main densification mechanism for most silicate systems is liquid-phase sintering. The sintering occurs best where the liquid phase thoroughly wets the solid grains at sintering heat. Capillary pressure in narrow pores between particles may be ≥ 7 MPa. Because small particles have higher surface energy and form smaller pores, there is more densification driving energy than for compacts of larger particles. Temperature strongly affects sintering; generally, small increases in temperature cause significant increases in the amount of liquid. In some cases, this is desirable, but in others excessive grain growth and fire distortion occur. The amount of liquid at a given temperature can be predicted from phase equilibrium diagrams.

Hot Pressing. Hot pressing resembles sintering except that temperature and pressure are applied at the same time [135]. Pressure speeds densification by increasing particle packing and by stressing points of contact. The densification energy can be increased 20-fold by applying pressure. *Hot isostatic pressing* can be done with special heat-treating equipment [136] and provides results superior to those attained with conventional hot pressing. Hot pressing injection-molded items gives results superior to those obtained with simple isopressing sintering, slip-casting/sintering, or injection molding/sintering. The Weibull probability plot of Figure 7 (on p. 38) shows the superior uniformity and higher strength of hot-pressed, injection-molded products.

4.6. Kilns and Firing Conditions

The furnaces in which ceramic products are heat-treated are usually termed *kilns*. Kilns, depending on the manner of operation, can be termed periodic (intermittent) or tunnel (continuous):

1) Intermittant firing kilns
   - stationary periodic
   - lifting charge
   - lifting kiln
   - moving charge
   - moving kiln
2) Continuous firing kilns
   - chamber
   - conveyor belt
   - roller slab
   - muffled tunnel
   - direct-fire tunnel

Periodic kilns are heated and cooled in accordance with prescribed schedules that differ with the kind of product. A *tunnel kiln* has temperature zones held at specific temperatures through which kiln cars (or other supports) are passed to provide the specified time–temperature cycle. Tunnel kilns are adapted to firing one type of body in long runs, whereas periodic kilns can be adapted to a variety of products.

Periodic kilns can be heated by electrical elements or fired with gas or oil. Traditionally, where hot gases are involved, heating is accomplished by having the combustion products pass through the load of ware, either upward (updraft kiln) or downward (downdraft kiln), before going out in a flue. The disadvantages of such kilns is that (1) they must be loaded and unloaded by hand, (2) there is a long cooling period, and (3) the entire kiln must be reheated in the next firing.

4.6.1. Modern Periodic Kilns

Elevator kilns are of three types: (1) ware to be fired is placed on a refractory protected car that is pushed in position under a suspended kiln that is then lowered over the car (a top-hat kiln); (2) the car with its ware is elevated into the kiln that is permanently fixed; and (3) an elevated kiln is moved horizontally over a series of cars and placed over any one of them, as desired.

Shuttle kilns are positioned permanently. One end has a movable door. Ware is loaded onto a car that is then run on rails into the kiln, the door is closed, and the ware is fired. A variant is the envelope kiln, which is rolled over and encloses ware placed on a permanent hearth.

4.6.2. Tunnel Kilns

Tunnel kilns are refractory chambers, sometimes 90–100 m long, through which ware is moved to achieve gradual heating and cooling. The entry section is the preheat zone, the middle section is the firing zone, and the exit portion is the cooling zone.

Cooling air is blown into the cooling zone, is heated, and moves into the firing zone, where it improves combustion and preserves an oxidizing atmosphere. Combustion gases from the firing zone are conveyed into the preheat zone to heat and dry the ware.

Refractory-topped cars riding on insulated rails carry the ware into and through tunnel kilns. Pushing is done on a prescribed schedule, expressed in terms of "cars per 24 hours." Some smaller tunnel kilns have positively rotated refractory (alumina) rollers, on which refractory slabs carry the ware. Other tunnel kilns use sled hearths, which are intermediate between cars and roller slabs, for smaller fast-fired products.

Advances in ceramic-fiber technology [136], [137] have provided alumina, silica, and kaolin fiber products for use in place of high-density castables for kiln cars and for insulating replacements for higher-density brick. This has made possible kiln designs that greatly reduce fuel consumption and permit faster firing of ware [138].

4.6.3. Advanced Ceramics Furnaces

Because advanced ceramic products often have special sintering requirements, the furnaces differ from those of ordinary ceramic kilns and require new furnace technology [139]. A common requirement is the need for total control of kiln atmosphere, as well as control of temperature and time scheduling. Atmospheric control can be achieved by sintering in a vacuum furnace or an autoclave. Initial air can be pumped out so that contaminants are vaporized and evacuated. The atmosphere around the ware can then be controlled with respect to composition and pressure.

Separate furnaces may be needed to eliminate lubricants and volatile binders. However, delubing can be done at low temperature, along with degassing, and the ware can be fired in an inert atmosphere on a controlled schedule to a required temperature.

4.6.4. Kiln Atmosphere

The atmosphere has a profound influence on the fired properties of clay-based ceramics. If there is enough O_2 to permit the piece to absorb some, the atmosphere is regarded as oxidizing. An oxidizing atmosphere helps eliminate carbon and converts salts to oxides. A low-oxygen atmosphere reduces multivalent ions to their lowest positive state, thus causing color and other changes.

Sulfur-bearing fuels provide SO_2, which is harmful to body and especially to glazes of clay-based ceramics. The ware must be protected by saggers (refractory boxes) or by keeping the combustion gases away from the work with a refractory wall (muffles), through which heat is radiated.

Electric kilns of all types [11, pp. 305–306], which avoid contamination from burned fuels, are used widely in Europe. In the United States, such kilns are mainly used for decorating, special ceramic products, and wall tile. The heating elements are nichrome, kanthal, or silicon carbide. Nichrome (a nickel–iron–chromium alloy) elements are used for decorative materials firing, kanthal (iron) for intermediate-temperature kilns, and silicon carbide for high-fire kilns.

4.6.5. Fired Ware Finishing

Postfiring processes fall in the category of finishing. Finishing may include grinding to size and removing kiln marks (grains of kiln dirt). Technical ceramics must be examined for flaws.

5. Glazes and Glazing

Glazes are applied to clay-based ceramic products to provide a shiny, generally smooth surface that seals the body. The surface may be either matt or bright. Glazes resemble glass in structure and texture, but have greater viscosity in the molten state. Glaze adheres strongly and uniformly to the ware. Application of glaze suspension to ware is by spraying or dipping.

Glazes can be made for maturing from ca. 600 °C up to ca. 1500 °C, depending on the items to which they are applied. If necessary, surfaces can be made resistant to various corrosive liquids and gases. Semiconducting glazes can be prepared for electrical porcelains.

5.1. The Nature of Glazes

Glasses and glazes used by ceramists are normally combinations of oxides (Table 10). Oxides that form glasses by themselves are termed *network formers;* by Zachariasen's rules [11, p. 130], SiO_2, B_2O_3, and P_2O_5 should, and do, form glasses. The holes in the network are filled by network *modifiers*, which weaken the bonds. Such modifiers are usually Na_2O, K_2O, CaO, and MgO. Generally speaking, the more modifier present, the lower the glass viscosity and chemical resistance. Oxides such as Al_2O_3, PbO, ZnO, ZrO_2, and CdO can enter the network by replacing some Si^{4+} or B^{3+}. These are the *inter-*

Table 10. Oxide glasses [140]

Oxide	Oxidation state	Coordination number	Bond strength, relative
Network formers			
SiO_2	4	4	106
B_2O_3	3	3	119
Intermediates			
Al_2O_3	3	4	90
Al_2O_3	3	6	60
ZnO	2	2	72
ZnO	2	4	36
PbO	2	2	73
PbO_2	4	6	39
Modifiers			
Na_2O	1	6	20
CaO	2	8	32
Substitutions for Na_2O			
K_2O	1	9	13
Rb_2O	1	10	12
Cs_2O	1	12	10
Li_2O	1	4	36
Substitutions for CaO			
MgO	2	6	37
BaO	2	8	33
SrO	2	8	32

mediate glass formers. The relative single-bond strengths of the oxides correlate with glass formation: network formers have high bond strengths, modifiers have low bond strengths, and intermediates fall in between.

The conventional representation of glaze formulas is the Seger convention, by which the formula is expressed with the fluxing oxides R_2O and RO, including PbO and ZnO, adding up to unity on a molar basis. The Al_2O_3 and SiO_2 plus B_2O_3 are listed as separate items, also on a molar basis, in the following manner:

$$1.0\,(R_2O + RO)\cdot x\,Al_2O_3\cdot y\,(SiO_2 + B_2O_3)$$

Glazes can be classified as raw glazes and fritted glazes. In the case of *raw glazes*, the oxides are introduced in the form of compounds or minerals, such as feldspar, which melt readily and act as solvents for the other ingredients. A *frit* is a prereacted glass containing ingredients, such as Na_2CO_3, which are soluble in water. Fritting fixes the desired oxide in a relatively insoluble form. Fritted glazes are used for whitewares. Frits may form only a part of the whiteware glaze formula, or the glaze may be composed entirely of frit [11, p. 190].

Raw Glazes. Raw glazes include (1) porcelain glazes, (2) Bristol glazes, (3) raw lead glazes, (4) raw leadless glazes, and (5) slip glazes. According to the Seger convention the basic *porcelain glaze* is expressed as follows [141]:

0.3 K_2O	0.4 Al_2O_3	4.0 SiO_2
0.7 CaO		

It matures as a bright glaze in the region of Orton pyrometric cones 8–10 (1236–1285 °C). When Al_2O_3 is raised to 0.5 and SiO_2 to 5.0, a bright glaze is obtained at cone 12 (1306 °C). At SiO_2 7.0 and Al_2O_3 0.5, the maturity of a bright glaze rises to cone 14 (1388 °C), whereas at SiO_2 8.0 and Al_2O_3 1.0, maturity occurs at cone 16 (1455 °C). Increasing the Al_2O_3 and SiO_2 content produces semimatt and matt low-gloss surfaces.

Bristol glazes are raw glazes containing ZnO, which are used on terra-cotta clayware and sometimes on stoneware items [142]. A typical Bristol glaze falls near the following molar composition:

0.40 K_2O	0.5 Al_2O_3	3.4 SiO_2
0.35 CaO		
0.25 ZnO		

Maturity occurs at cones 4–8 (1168–1236 °C).

Raw lead glazes [143] are used only on artware, never on commercial ware, owing to health hazards from soluble lead. A typical bright glaze maturing at ca. cone 05 (1031 °C) has roughly the following composition:

0.55 PbO	0.23 Al_2O_3	1.55 SiO_2
0.36 CaO		
0.09 Na_2O		

Lead-free glazes, or leadless glazes, are designed to provide lower maturity than true porcelain glazes without the use of lead oxide. A typical glaze has the following composition [144]:

0.2 K_2O	0.3 Al_2O_3	3.0 SiO_2
0.3 SrO		
0.1 CaO		
0.4 BaO		

Glazes built around this composition have an excellent maturing range as low as cone 03 and up to cone 9 (1086–1260 °C), but lack the covering power and brightness of lead glazes.

Slip glazes [145] are natural clays having the following approximate composition:

0.20 K_2O	0.60 Al_2O_3	4.00 SiO_2
0.45 CaO	0.08 Fe_2O_3	
0.35 MgO		

Such clays are used for artware glazing and often for high-tension electrical porcelain insulators. Slip clay glazes have a maturing range from ca. 1200 °C to 1300 °C.

Frits. Because B_2O_3 and most borates are soluble in water, the B_2O_3 must be added in a frit. A typical lead-free borate frit has the following composition:

0.69 CaO	0.37 Al_2O_3	2.17 SiO_2
0.19 Na_2O		1.16 B_2O_3
0.12 K_2O		

Although lead bisilicate [*11120-22-2*] (PbO · 2 SiO_2 or $PbSi_2O_5$) is relatively insoluble in water, lead is normally introduced into commercial glazes in fritted form. A more complex frit might have a composition such as the following:

0.50 PbO	0.10 Al_2O_3	2.70 SiO_2
0.30 Na_2O		
0.20 K_2O		

Boric oxide and lead oxide often appear together in low-temperature glaze. A typical composition is the following:

0.50 PbO	0.10 Al_2O_3	2.70 SiO_2
0.10 Na_2O		0.60 B_2O_3
0.10 K_2O		
0.30 CaO		

Special Glazes. Low-expansion glazes are required by zircon, cordierite, and low-expansion lithium silicates [146]. Recommended glazes for zircon porcelain in the range of cones 10–14 (1285–1400 °C) approximate the following composition:

1.00 RO	0.6–0.7 Al_2O_3	9–11 SiO_2

Semiconducting glazes are used to remove charges from surfaces of electrical insulators. This property can be produced with a high concentration of Fe_2O_3 in the glaze, crystals of SnC_2O_4, or activated SnO_2 [11, p. 197].

Glaze opacity is obtained by mill additions of zirconium-type opacifiers [147].

Lithium oxide additions increase the hardness of commercial glazes [148]. High-compression glazes resist scratching. Crystalline glazes grow large crystals in the firing and cooling of the glaze. NORTON [149] demonstrated that crystals grow when temperatures of nucleation and crystal growth do not overlap. For example, proper control of the heating schedule allowed the growth of large willemite crystals.

Salt glazing is an old method for glazing stoneware. The glaze is formed by throwing damp common salt into the kiln during the sintering stage of firing. The NaCl decomposes to form Na_2O and HCl, the Na_2O combining with the Al_2O_3 and SiO_2 of the body to form complex silicates. BARRINGER [150] found the limits of the $Al_2O_3:SiO_2$ ratio within which it is commercially possible to produce good salt glaze to be 1:4.6–1:12.5.

5.2. Preparation of Glazes

Prepared frit, clay, and materials not incorporated in the frit are ground generally in ball mills with water. Grinding is followed by sieving and magnetic treatment.

The ball mills are large steel drums lined with quartzite or ceramic blocks. Flint pebbles of various size grades are frequently used. Recently, high-density (usually high-alumina) balls or cylindrical rods have found favor for this operation. The higher-density media reduce grinding times and lessen contamination from pebble wear. The media, batch, and water occupy ca. 60% of mill volume. Media weight is around 3 times that of batch. Water content runs 30–50%, depending on the material being processed. Mill speed varies with mill size: the smaller the mill, the faster the rotation.

The practice of grinding to a stated percentage of residue remaining on a test sieve does not take into account differences in particle-size distribution brought about by changes in media size and size distribution and linear wear. PHELPS [151] has shown that apparently minor differences in glaze and enamel slip particle-size distribution can cause marked differences in slip rheology.

While fine grinding improves glaze brightness, hardness, and chemical stability, grinding too fine can result in crawling (parting of the glaze, which leaves bare spots) or peeling (flaking away) of the glaze. Changes in the soluble materials content of the water can lead to difficulties in consistency and fineness of glazes.

5.3. Glaze Application

The prepared glaze slip is adjusted with additives designed to control consistency and adhesion. Hand dipping of prefired (bisque) ware in glaze slip was the general practice prior to 1920. However, spraying then became common. Automatic spraying on a conveyor line is now used. Tiles are glazed by spraying or by passing them unter a falling sheet of glaze slip.

Aside from grinding-induced differences, the nature of the materials can result in glaze settling. Suspending agents, such as bentonite or organic agents, are then used. Flocculants, such as $MgSO_4$ or $CaCl_2$, can be used.

6. Glass (→ Glass)

Glass has been defined in simple terms as a fusion product of an inorganic material that has been cooled to a reasonably rigid, noncrystalline state [2, p. 42]. Objects made of glass are simply called glass, although specific kinds of glass are qualified by types, such as flint, barium, lead, container, or window glass.

As shown by Table 10 (see p. 31) glasses consist of the following types of oxides: (1) network formers (form glasses by themselves); (2) network modifiers (alkali-metal ions and alkaline-earth-metal ions); (3) intermediate glass formers (partial substitutes for network formers).

A fairly high PbO content (10–45%) is characteristic of *flint glasses*. Low-expansion, chemically stable glasses contain significant levels of B_2O_3 (6–12%). Optical glasses contain variable percentages of lead and barium oxides.

Soda–lime–silica glass represents the major proportion of commercial glass [12, chap. 13]. It is made by melting more or less pure silica sand by fluxing with soda (Na_2O) and stabilizing with CaO or CaO · MgO.

Container glass is a typical soda–lime–silica glass containing smaller percentages of materials having special functions. Alumina (from feldspar or nepheline syenite) helps chemical stability, sodium nitrate functions as an oxidizing agent, and arsenic is a fining agent (for elimination of bubbles and undissolved gases). Clear glass requires low Fe_2O_3 content, whereas high Fe_2O_3 materials are used in colored glasses [152]. Manganese blanks out the green color of iron.

Container glass production is usually large scale. Batches are weighed automatically, blended, and conveyed to glass melting tanks (refractory containers for melting). Tanks hold 180–275 t of glass. Batches are fed into tanks as layers 15–20 cm thick and melted by heat from side burners fired with oil or gas. Exhaust heat passes into checker chambers below the burner ports; flow is reversed 3–4 times per hour. Combustion air passes through the heated checkerwork.

Large refractory blocks made of fusion-cast Al_2O_3 or Al_2O_3–ZrO_2–SiO_2 mixtures function as side walls and end walls, while the bottom is $ZrSiO_4$ and the roof is SiO_2. A container glass tank may have melting areas of 90–150 m² with glass depths of 1–1.5 m. A campaign (working life before major repair) of a tank may be 4–5 years.

Sheet glass tanks, holding 1200–1500 t, are much larger than container glass tanks. Such a tank can supply 180–275 t every 24 h.

Optical glass tanks are much smaller, with outputs of perhaps 40–200 kg every 24 h.

Forming is by pressing, vacuum, or blowing (using air pressure to transform the gob, i.e., mass of molten glass, into a hollow piece). Otherwise, a sheet is formed by pulling (drawing) a continuous sheet of molten glass from the tank and passing it through a flattener or roller. Float glass involves a process in which the sheet floats on a bath of molten tin with heaters above and in the bath; the glass settles to an even ribbon and is allowed to cool slowly. Sheet glass requires polishing and grinding for use as plate glass, whereas float glass does not.

Fiberglass takes two forms: (a) continuous thread for textiles or (b) discontinuous fiber for insulation, filtering, or reinforced fiberglass. Glass marbles are fed continuously into a melting chamber, and filaments are pulled through platinum spinnerets. Discontinuous fibers are blown by striking a molten stream of glass with a high-velocity steam jet. Such glass generally has a lower viscosity than textile fiberglass. Fiberglass, with its high surface area, also must be chemically stable.

Certain glasses [153] and glass-bonded ceramics [154] have application as refractory substances. Included are vitreous silica, high-silica glasses, aluminosilicate glasses, aluminate glasses, mullite glass, and barium feldspar glass ceramics.

7. Refractories (→ Refractory Ceramics)

Refractory materials are essential to the manufacture of all forms of ceramic products, including refractories themselves. Table 11 [1, pp. 13–15] gives classes and types of refractory brick. Insulating firebrick are rated in eight progressively more refractory groups where reheat shrinkages are not more than 2% at testing temperatures of 845 °C (group 16), 1065 °C (group 20), 1230 °C (group 23), 1400 °C (group 26), 1510 °C (group 28), 1620 °C (group 30), 1730 °C (group 32), and 1790 °C (group 33) [1, p. 104].

Special refractories include zircon ($ZrSiO_4$), zirconia (ZrO_2), silicon carbide (SiC), chromic oxide (Cr_2O_3), and graphite (C). Refractory specialties include nonformed products such as mortars, castables, plastics, and ramming mixes. Basic refractories include the chrome brick, chrome–magnesite brick, and magnesite brick used in basic oxygen steelmaking [155].

Table 11. Classes and types of refractories

Class	Type	PCE*	MOR**, MPa
Fireclay	Super duty	33	4.14
	High duty	31.5	3.45
	Medium duty	29	3.45
	Low duty	15	4.14
High Al_2O_3	50% Al_2O_3	34	
	60% Al_2O_3	36	
	70% Al_2O_3	36	
	80% Al_2O_3	37	
	90% Al_2O_3		
	99% Al_2O_3		

* PCE pyrometric cone equivalent.

** MOR modulus of rupture.

8. Abrasives

(→ Abrasives, Vol. A 1, pp. 1 16)

Several natural minerals are employed as abrasives for cutting, grinding, and polishing. These include quartz, garnet, corundum, emery, and diamond. Manufactured abrasives include silicon carbide, boron nitride, diamond, fused alumina, silicon carbide, titanium carbide, tungsten carbide, and zirconium silicate. Abrasive products include loose grains, wheels, coated abrasives, and grinding pebbles.

9. Cement (→ Cement and Concrete, Vol. A 5, pp. 489 – 537)

Cement is a synthetic mineral mixture (clinker) that when ground to a powder and mixed with water forms a stonelike mass, and is thus a ceramic product [156]. A primary requirement for cement manufacture is a source of CaO: this can be limestone, oyster shell, slag, etc. Also necessary is a source of Al_2O_3 and SiO_2, most commonly clay and, where needed, a quartz rock or sand.

Processing involves (1) grinding of rock material, (2) blending of ground materials to a desired chemical composition or slurry blending of the powders, (3) burning the blended material to form a clinker, (4) blending the clinker and gypsum, and (5) grinding the gypsum – clinker. Grinding can be accomplished by dry grinding ball milling, rod milling, roller, race, tube mill with air classification. Oversize is recycled.

The American Society for Testing and Materials has listed specifications for eight types of cement in accordance with chemical composition and physical requirements [157].

10. Properties of Ceramic Materials and Products

Ceramic products have relatively high strength associated with brittle fracture, high thermal stability, and low electrical conductivity. These properties are related to structure and depend on the size and arrangement of multiphase polycrystalline constituents and the glassy phase. Size, type, and distribution of pores must be considered because pores affect strength, thermal expansion, heat insulation, corrosion and weathering resistance, and electrical properties.

Table 12 shows mechanical properties of a number of representative ceramic products. In all cases, there is a characteristic direct transition from a small elastic deformation, with no or small plastic deformation, to fracture. Irreversible deformations from above the elastic region up to fracture may be due to viscous processes within the particle structure.

Important ceramic oxides have high melting points (°C):

Al_2O_3	2050	Fe_3O_4	1600
MgO	2800	FeO	1360
CaO	2600	$MgO \cdot Al_2O_3$	2135
SiO_2	1780	$2\,MgO \cdot SiO_2$	1890
ZrO_2	2700	$3\,Al_2O_3 \cdot 2\,SiO_2$	1810
Cr_2O_3	2265	$ZrO_2 \cdot SiO_2$	1775

Table 12. Mechanical properties of ceramic materials

Type of material	Compressive strength, MPa	Flexural strength, MPa	Modulus of elasticity, GPa
Solid brick	10 – 25	5 – 10	5 – 20
Roof tile	10 – 25	8 – 15	5 – 20
Steatite	850 – 1000	140 – 160	1 – 3
Silica refractories, 96 - 97% SiO_2	15 40	30 80	8 14
Fireclay refractories, 10 – 44% Al_2O_3	10 – 80	5 – 15	20 – 45
Corundum refractories, 75 – 90% Al_2O_3	40 – 200	10 – 150	30 – 120
Forsterite refractories	20 – 40	5 – 10	25 – 30
Magnesia refractories	40 – 100	8 – 200	30 – 35
Zircon refractories	30 60	80 – 200	35 – 40
Whiteware	30 – 40	20 – 25	10 – 20
Stoneware	40 – 100	20 – 40	30 – 70
Electrical porcelain	350 – 850	90 – 145	55 – 100
Capacitor ceramics	300 – 1000	90 – 160	

Table 13. Thermal expansion coefficients, $10^{-6}\,K^{-1}$, of components of ceramic materials

Component	Temperature ranges, C		
	20 – 300	20 – 900	20 – 1400
Silica	36.5	15.5	10.0
Magnesite	10	12.7	14.2
Chrome magnesite	8.3	9.4	10.5
Chromite	8.3	9.1	9.5
Corundum 99	7.3	7.2	*
Corundum 90	4.3	5.2	6.5
Zircon	2.7	3.8	**
Sillimanite	3.3	4.4	4.8
Silicon carbide	1.6	3.5	4.4

* 7.9 over the range 20 – 1200 C.

** 4.5 over the range 20 1200 C.

Table 14. Thermal conductivity of refractory brick

Material	% Porosity	Thermal conductivity, $W\,m^{-1}\,K^{-1}$	
		371 °C	1000 °C
28% Al_2O_3	22	0.84	1.72
42% Al_2O_3	19	1.21	1.42
72% Al_2O_3	22	1.55	1.42
99% Al_2O_3	24	3.77	2.47
Silica	23	1.34	1.76
Mullite	23	0.92	1.76
94% MgO	20	6.86	2.76
Chrome magnesite	22	1.72	1.80
Zircon	17	2.76	2.38

Table 15. Thermal conductivity of electrical ceramics at room temperature

Body type	Thermal conductivity, $W\,m^{-1}\,K^{-1}$
Electrical porcelain	0.8-1.7
Steatite porcelain	2.1-2.5
Cordierite	1.3-2.1
Zircon porcelain	4.6-5.0
Titania porcelain	2.9-4.2
Titanate	3.3-4.2

Table 16. Resistivities of some metals, ceramic insulators, and semiconductors at room temperature

Ceramic material	Resistivity, Ω cm
Insulators	
Low-voltage porcelain	$10^{12}-10^{14}$
Steatite porcelain	10^{14}
Mullite porcelain	10^{13}
Cordierite porcelain	10^{13}
Zircon porcelain	10^{14}
Alumina porcelain	10^{16}
Silica	10^{19}
Semiconductors	
Silicon carbide	10
Boron carbide	0.5
Ferric oxide	10^{-2}

Table 13 gives thermal expansion coefficients for a number of ceramic product constituents. Because high melting points generally correlate with low thermal expansion, these materials generally have low coefficients of thermal expansion. The anisotropic structure results from polycrystalline mixed phases and varying amounts of glassy phases, which explains the relatively poor thermal-shock resistance.

Most ceramic products have thermal conductivities lower than platinum, for example, but higher than, for example, insulating firebrick or organic polymers. Table 14 shows thermal con-

Table 17. Properties of advanced ceramics [158]

Material	Crystal structure	Theoretical density, Mg/m^3	Knoop or Vickers hardness, GPa	Transverse rupture strength, MPa	Fracture toughness K_{IC}, $MPa \cdot m^{0.5}$	Young's modulus, GPa	Thermal expansion, $10^{-6}\,K^{-1}$	Thermal conductivity, $W\,m^{-1}\,K^{-1}$		Specific heat, $J\,kg^{-1}\,K^{-1}$
								400 K	1400 K	
Alumina, Al_2O_3	hexagonal	3.97	18-23	276-1034	2.7-4.2	380	7.2-8.6	27.2	5.8	1088
Mullite, $3\,Al_2O_3 \cdot SiO_2$	orthorhombic	2.8		185	2.2	145	5.7	5.2	3.3	1046
Partially stabilized zirconia, ZrO_2	cubic, monoclinic, tetragonal	5.70-5.75	10-11	600-700	8-9	205	8.9-10.6	1.8-2.2		400
Titanium dioxide, TiO_2	tetragonal (rutile)	4.25	7-11	69-103	2.5	283	9.4	8.8	3.3	799
Silicon carbide, SiC	hexagonal (α) cubic (β)	3.21	20-30	230-825 (hot pressed)	4.8-6.1	207-483	4.3-5.6	63-155	21-33	628-1046
Silicon nitride, Si_3N_4	hexagonal (α) hexagonal (β)	3.18-3.19	8-19	700-1000 (hot pressed)	3.6-6.0	304	3.0	9-30		400-1600
Titanium nitride, TiN	cubic	5.43-5.44	16-20			251	8.0	24	67.8*	628

* At 1773 K.

ductivity coefficients for a number of refractory brick products [4, p. 942], and Table 15 provides thermal conductivity ranges for a number of electrical porcelain types [19, p. 47].

Table 16 gives resistivities for a number of ceramic products that serve as electrical insulators: their resistivities are of the order of 10^{12} - 10^{13} Ω cm several orders of magnitude higher than for metals [19, p. 47].

Table 17 provides a tabulation of mechanical and thermal properties of materials employed in making advanced ceramics articles. The temperature for which these values are valid is room temperature or somewhat above, unless specified otherwise.

Chemical stability of nonporous ceramic products in the presence of acids or alkalies is adequate although it decreases as the temperature is increased. Nonporous ceramics can withstand atmospheric effects up to their melting points.

11. Testing Ceramic Raw Materials and Products

A distinction is made between tests made to determine the suitability of raw materials or ceramic products for particular applications and quality control test procedures. Tests for suitability can be very involved, whereas acceptance tests agreed upon between the raw materials supplier and the user or employed by the supplier in mining and refining and the manufacturer in processing can be simple. The characterization concept is considered the basis for determining the suitability of raw materials and products [2], pp. 195–249], [65].

11.1. Raw Material and Product Tests

Various ceramic manufacturers and suppliers of raw materials for ceramic products have joined together in "the development of standards on characteristics and performance of materials, products, systems, and services; and the promotion of related knowledge" [2, p. iii].

Table 18 lists the volume identifications and subject areas of interest to the several areas of ceramic endeavor [2, pp. vi - vii].

Table 18. Listing of ASTM book of standards (1985) for ceramic-related test compilations

Volume identification	Subject area
03.05	chemical analysis of metals and metal-bearing ores
03.06	emission spectroscopy; surface analysis
04.06	thermal insulation
10.01	electrical insulation: solids, composites and coatings
10.02	electrical insulation (II), wire and cable, heating and electrical tests
10.04	electronics (I)
10.05	electronics (II)
11.01	water (I)
11.02	water (II)
11.03	atmospheric analysis; occupational health and safety
12.01	nuclear energy (I)
12.02	nuclear energy (II), solar and geothermal
14.01	analytical methods -- spectroscopy; chromatography; temperature; computerized
14.02	general test methods -- nonmetal; lab apparatus; statistical methods; durability
15.01	refractories, carbon and graphite
15.02	glass; ceramic whitewares, porcelain enamels

11.2. Simplified Testing of Clay Body Materials

The tests listed in Table 19 were derived from the characterization concept to serve as control tests by miners and refiners of clay body materials and by manufacturers in acceptance testing and for plant control. Table 19 lists suggested control tests for clays and nonplastics. These tests are designed as surrogate procedures for the methods that require complex, expensive equipment and highly trained personnel. Chemical analysis, particle-size distribution, and mineral constituents govern fired properties and glaze fit of clay-based bodies. A simple test, using two clear glazes (one fitted to a standard kaolin and the other to a standard ball clay) make possible detection of variation in free silica. The presence of specking impurities is shown more strongly by clear glazes than by bisque clay. Deflocculation tests indicate changes in particle size and soluble salts. The solubles test also relates to deflocculation and the rate of cast. Nonplastics should be evaluated in a standard body for deflocculation, rheology, and fired properties. A fusion test, compared against standard specimens [159], is indicative of changes in mineral composition and particle size.

Table 19. Suggested control tests

China clay	Ball clay	Feldspar	Silica
residue: 100, 200, 325 mesh	residue: 100, 200, 325 mesh	residue: 100, 200, 325 mesh	residue: 100, 200, 325 mesh
solubles: hardness, Cl^-, SO_4^{2-}	solubles: hardness, Cl^-, SO_4^{2-}	particle-size analysis	particle-size analysis
methylene blue index	methylene blue index	body deflocculation	body deflocculation
particle size analysis	particle size analysis	casting cups and bars	casting cups and bars
fired shrinkage and absorption	fired shrinkage and absorption	firing shrinkage and sag bars	firing shrinkage and sag bars
glaze fit	glaze fit	glaze fit and absorption	glaze fit and absorption
fired color, specking	fired color, specking	fusion	
chemical: TiO_2 and Fe_2O_3	ignition loss		
neat clay deflocculation	clay–flint deflocculation		
casting	casting		

11.3. Quality Control of Advanced Ceramics

The degree of quality control needed in a ceramic manufacturing depends on the critical requirements of the application. In advanced ceramic manufacture, most end uses need a specified manufacturing procedure in writing in addition to certification that this procedure has been followed. The more demanding applications must have proof tests, destructive sample tests, and nondestructive inspections of various kinds [19, chap. 9].

A popular method for characterizing flaw distribution is the use of the Weibull approach [160], based on the weakest link theory. This theory assumes that a given volume of a ceramic material under uniform stress will fail at the worst flaw. Data is shown as a probability of failure F (a function of stress σ and volume V or area A under stress) plotted against σ. The probability F can be estimated from $Fn/(N+1)$, where n = rank of sample and N = total number of samples. When plotted on a log normal grid, as in Figure 7, the result is a straight line.

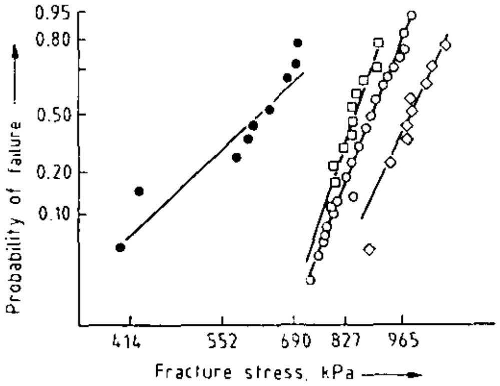

Figure 7. Weibull probability plot showing the effect of forming methods for silicon nitride on the range and level of stress fracture

● Isopressed/sintered; □ Slipcast sintered; ○ Injection molded/sintered; ◇ Injection molded hot isopressed

The data of Figure 7 show the effect of forming technique on the uniformity of an advanced ceramic material, with respect to stress fracture. A vertical plot at a particular fracture stress indicates absolute uniformity. Slip cast and injection-molded parts are much more uniform than simple isopressed items after sintering. Slip-cast pieces are more uniform than injection-molded parts. Hot isopressing of injection-molded pieces gives a significant increase in fracture stress over sintered injection molding, but at about the same level of uniformity.

12. Economic Aspects

The cost of a ceramic product at its point of manufacture depends on such factors as (1) cost of raw materials; (2) cost of energy for processing, forming, firing, and finishing; (3) capital cost and maintenance; and (4) cost of labor. The impact of the various factors necessarily vary with the product being made.

Raw material cost involves the cost of mining, refining, and transporting a given commodity to a point of ceramic manufacture. Equipment cost depends on the country where it is manufactured. However, countries with highly developed, technologically advanced manufacturing capability, coupled with moderate wage scales, can compete in domestic markets of countries having comparable manufacturing ability but higher wage levels. Countries with skilled workers and low wage scales can export products that require detailed handwork and can undersell domestic manufacturers with high wage rates. For example, countries of the Far East, having highly skilled but low-wage labor, make and deliver high-quality tableware to European and American markets at prices lower than domestic potteries can [161].

Other high-quality, less labor-intensive products, such as vitreous plumbing ware, are less vulnerable to imports. However, as developing countries gain expertise and improve quality, it is possible that sanitary ware imports may take over some of the sanitary ware markets in developed countries.

In terms of unit weight, the cost of making and delivering a ceramic product depends on the nature of the product and can vary widely. The fine ceramic products of Table 1, in general, cost more to make per unit weight than the coarse ceramic products of Table 2. Furthermore, a vitreous china plumbing fixture costs far less per unit weight than a highly decorated fine china platter. By the same token, a building brick costs far less per unit weight than a high-alumina refractory brick of comparable volume.

Physical and economic geographical factors are likely to limit exports of relatively heavy products from countries where mountains make road or rail transport difficult. The distance from market is a factor in the cost of transport. In the United States, where rail, water, and road transport are reasonably good, the cost of transporting desirable raw materials from sources in the southeast to points on the West Coast can exceed the FOB cost of the raw material. This has encouraged use of local, less desirable raw materials. In glass manufacturing, plants will seek out closest possible sources of silica sand and glass feldspar or nepheline syenite. In smaller countries, transport costs are of less consequence.

Specialty products, such as high-tension electrical porcelain insulators, have stringent mechanical and dielectric strength requirements. Careful processing of controlled compositions is the key to superior quality. Those countries with lower wage scales and good technical capabilities can often meet or exceed these requirements at a lower or equivalent cost than in higher wage North American markets.

Manufacture of structural clay products, such as brick, clay pipe, and tile, has been historically located as close as possible to a given market area, consistent with access to cheap raw material, fuel, and labor. However, structural clay product companies are increasing in size and becoming correspondingly more conscious of the necessity for controlling raw materials and servicing an expanding market [162]. Research is being done on forming methods to reduce losses and improve quality [163]; automated plants are increasingly more common.

The economic health of *traditional, clay-based ceramic* manufacture is closely tied to the state of the economy, especially the level of building [164]–[166]. Traditional ceramics continue to evolve from an art to a science as more use is made of the findings of materials science in better control over raw materials, body preparation, and automated forming. As noted earlier, improvements in kilns and body composition will permit faster firing, lower fuel and refractory costs, and lowered losses.

By way of contrast, *advanced ceramics* is a rapidly developing field of large, although somewhat undefined, potential for growth. Market forecasts for high-technology ceramics vary from one to another with respect to absolute size; although starting bases differ, growth rates are more consistent.

Bowen [167] estimated sales rising from 1.5×10^9 to 7.0×10^9 dollars in the period 1980–1995 at an annual rate of 11% in the United States. For Japan, the figures are 1.9×10^9 to 9.0×10^9 dollars, also at an annual growth rate of 11%. For the world market, the values are 4.1×10^9 to 17.0×10^9 dollars at an annual growth of 10%. Toshiba [168] forecasts a rise in the Japanese market from 1.26×10^9 to 11.4×10^9 dollars from 1982 to 2000, with an overall growth of 32%. The U.S. Department of Commerce [169] predicts estimated sales for advanced ceramics rising from 0.60×10^9 to 5.9×10^9 dollars over the period 1980–2000 at an annual growth rate of 12–15%.

The Western world in general and the United States in particular depend for economic strength on abundant, readily available natural resources. The countries of Western Europe, the United Kingdom, and North America are either self-sufficient in traditional ceramic materials or have ready access to such materials. This does not appear to be the case for many materials required for advanced ceramics. Of 27 basic industrial minerals or metals listed by the U.S. Department of the Interior, 18 are imported at levels above 50 %, including cobalt, manganese, and chromium [170].

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