

11.7 Ceramic Products Manufacturing

11.7.1 General¹⁻³

Ceramics are defined as a class of inorganic, nonmetallic solids that are subjected to high temperature in manufacture and/or use. The most common ceramics are composed of oxides, carbides, and nitrides. Silicides, borides, phosphides, tellurides, and selenides also are used to produce ceramics. Ceramic processing generally involves high temperatures, and the resulting materials are heat resistant or refractory.

Traditional ceramics refers to ceramic products that are produced from unrefined clay and combinations of refined clay and powdered or granulated nonplastic minerals. Often, traditional ceramics is used to refer to ceramics in which the clay content exceeds 20 percent. The general classifications of traditional ceramics are described below.

Pottery is sometimes used as a generic term for ceramics that contain clay and are not used for structural, technical, or refractory purposes.

Whiteware refers to ceramic ware that is white, ivory, or light gray in color after firing. Whiteware is further classified as earthenware, stoneware, chinaware, porcelain, and technical ceramics.

Earthenware is defined as glazed or unglazed nonvitreous (porous) clay-based ceramic ware. Applications for earthenware include artware, kitchenware, ovenware, tableware, and tile.

Stoneware is vitreous or semivitreous ceramic ware of fine texture, made primarily from nonrefractory fire clay or some combination of clays, fluxes, and silica that, when fired, has properties similar to stoneware made from fire clay. Applications for stoneware include artware, chemicalware, cookware, drainpipe, kitchenware, tableware, and tile.

Chinaware is vitreous ceramic ware of zero or low absorption after firing that are used for nontechnical applications. Applications for chinaware include artware, ovenware, sanitaryware, and tableware.

Porcelain is defined as glazed or unglazed vitreous ceramic ware used primarily for technical purposes. Applications for porcelain include artware, ball mill balls, ball mill liners, chemicalware, insulators, and tableware.

Technical ceramics include vitreous ceramic whiteware used for such products as electrical insulation, or for chemical, mechanical, structural, or thermal applications.

Ceramic products that are made from highly refined natural or synthetic compositions and designed to have special properties are referred to as advanced ceramics. Advanced ceramics can be classified according to application as electrical, magnetic, optical, chemical, thermal, mechanical, biological, and nuclear.

Most ceramic products are clay-based and are made from a single clay or one or more clays mixed with mineral modifiers such as quartz and feldspar. The types of commercial clays used for ceramics are primarily kaolin and ball clay.

11.7.2 Process Description^{1,3-5}

Figure 11.7-1 presents a general process flow diagram for ceramic products manufacturing. The basic steps include raw material procurement, beneficiation, mixing, forming, green machining, drying, presinter thermal processing, glazing, firing, final processing, and packaging. The following paragraphs describe these operations in detail.

11.7.2.1 Raw Material Procurement -

To begin the process, raw materials are transported and stored at the manufacturing facility. The raw materials used in the manufacture of ceramics range from relatively impure clay materials mined from natural deposits to ultrahigh purity powders prepared by chemical synthesis. Naturally occurring raw materials used to manufacture ceramics include silica, sand, quartz, flint, silicates, and aluminosilicates (e. g., clays and feldspar).

11.7.2.2 Beneficiation -

The next step in the process is beneficiation. Although chemically synthesized ceramic powders also require some beneficiation, the focus of this discussion is on the processes for beneficiating naturally occurring raw materials. The basic beneficiation processes include comminution, purification, sizing, classification, calcining, liquid dispersion, and granulation. Naturally occurring raw materials often undergo some beneficiation at the mining site or at an intermediate processing facility prior to being transported to the ceramic manufacturing facility.

Comminution entails reducing the particle size of the raw material by crushing, grinding, and milling or fine grinding. The purpose of comminution is to liberate impurities, break up aggregates, modify particle morphology and size distribution, facilitate mixing and forming, and produce a more reactive material for firing. Primary crushing generally reduces material up to 0.3 meter (m) (1 foot [ft]) in diameter down to 1 centimeter (cm) (0.40 inch [in.]) in diameter. Secondary crushing reduces particle size down to approximately 1 millimeter (mm) (0.04 in.) in diameter. Fine grinding or milling reduces the particle size down to as low as 1.0 micrometer (μm) (4×10^{-5} in.) in diameter. Ball mills are the most commonly used piece of equipment for milling. However, vibratory mills, attrition mills, and fluid energy mills also are used. Crushing and grinding typically are dry processes; milling may be a wet or dry process. In wet milling, water or alcohol commonly is used as the milling liquid.

Several procedures are used to purify the ceramic material. Water soluble impurities can be removed by washing with deionized or distilled water and filtering, and organic solvents may be used for removing water-insoluble impurities. Acid leaching sometimes is employed to remove metal contaminants. Magnetic separation is used to extract magnetic impurities from either dry powders or wet slurries. Froth flotation also is used to separate undesirable materials.

Sizing and classification separate the material into size ranges. Sizing is most often accomplished using fixed or vibrating screens. Dry screening can be used to sizes down to $44 \mu\text{m}$ (0.0017 in., 325 mesh). Dry forced-air sieving and sonic sizing can be used to size dry powders down to $37 \mu\text{m}$ (0.0015 in., 400 mesh), and wet sieving can be used for particles down to $25 \mu\text{m}$ (0.00098 in., 500 mesh). Air classifiers generally are effective in the range of $420 \mu\text{m}$ to $37 \mu\text{m}$

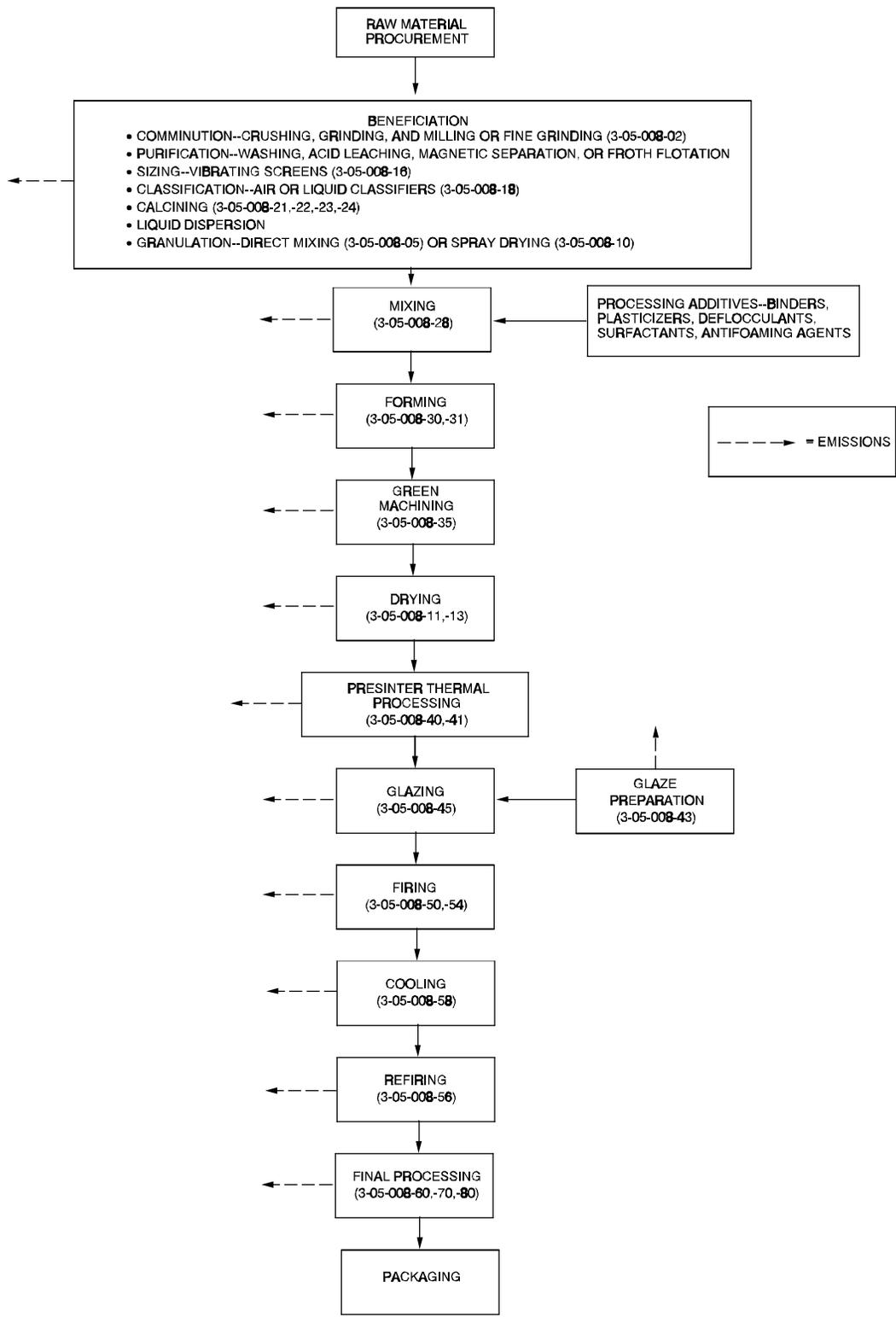


Figure 11.7-1. Process flow diagram for ceramic products manufacturing.
(Source Classification Codes in parentheses.)

(0.017 to 0.0015 in., 40 to 400 mesh). However, special air classifiers are available for isolating particles down to 10 μm (0.00039 in.).

Calcining consists of heating a ceramic material to a temperature well below its melting point to liberate undesirable gases or other material and to bring about structural transformation to produce the desired composition and phase product. Calcining typically is carried out in rotary calciners, heated fluidized beds, or by heating a static bed of ceramic powder in a refractory crucible.

Liquid dispersion of ceramic powders sometimes is used to make slurries. Slurry processing facilitates mixing and minimizes particle agglomeration. The primary disadvantage of slurry processing is that the liquid must be removed prior to firing the ceramic.

Dry powders often are granulated to improve flow, handling, packing, and compaction. Granulation is accomplished by direct mixing, which consists of introducing a binder solution during powder mixing, or by spray drying. Spray dryers generally are gas-fired and operate at temperatures of 110° to 130°C (230° to 270°F).

11.7.2.3 Mixing -

The purpose of mixing or blunging is to combine the constituents of a ceramic powder to produce a more chemically and physically homogenous material for forming. Pug mills often are used for mixing ceramic materials. Several processing aids may be added to the ceramic mix during the mixing stage. Binders and plasticizers are used in dry powder and plastic forming; in slurry processing, deflocculants, surfactants, and antifoaming agents are added to improve processing. Liquids also are added in plastic and slurry processing.

Binders are polymers or colloids that are used to impart strength to green or unfired ceramic bodies. For dry forming and extrusion, binders amount to 3 percent by weight of the ceramic mixture. Plasticizers and lubricants are used with some types of binders. Plasticizers increase the flexibility of the ceramic mix. Lubricants lower frictional forces between particles and reduce wear on equipment. Water is the most commonly used liquid in plastic and slurry processing. Organic liquids such as alcohols may also be used in some cases. Deflocculants also are used in slurry processing to improve dispersion and dispersion stability. Surfactants are used in slurry processing to aid dispersion, and antifoams are used to remove trapped gas bubbles from the slurry.

11.7.2.4 Forming -

In the forming step, dry powders, plastic bodies, pastes, or slurries are consolidated and molded to produce a cohesive body of the desired shape and size. Dry forming consists of the simultaneous compacting and shaping of dry ceramic powders in a rigid die or flexible mold. Dry forming can be accomplished by dry pressing, isostatic compaction, and vibratory compaction.

Plastic molding is accomplished by extrusion, jiggering, or powder injection molding. Extrusion is used in manufacturing structural clay products and some refractory products. Jiggering is widely used in the manufacture of small, simple, axially symmetrical whiteware ceramic such as cookware, fine china, and electrical porcelain. Powder injection molding is used for making small complex shapes.

Paste forming consists of applying a thick film of ceramic paste on a substrate. Ceramic pastes are used for decorating ceramic tableware, and forming capacitors and dielectric layers on rigid substrates for microelectronics.

Slurry forming of ceramics generally is accomplished using slip casting, gelcasting, or tape casting. In slip casting, a ceramic slurry, which has a moisture content of 20 to 35 percent, is poured into a porous mold. Capillary suction of the mold draws the liquid from the mold, thereby consolidating the cast ceramic material. After a fixed time the excess slurry is drained, and the cast is dried. Slip casting is widely used in the manufacture of sinks and other sanitaryware, figurines, porous thermal insulation, fine china, and structural ceramics with complex shapes. Gelcasting uses in situ polymerization of organic monomers to produce a gel that binds ceramic particles together into complex shapes such as turbine rotors. Tape casting consists of forming a thin film of ceramic slurry of controlled thickness onto a support surface using a knife edge. Tape casting is used to produce thin ceramic sheets or tape, which can be cut and stacked to form multilayer ceramics for capacitors and dielectric insulator substrates.

11.7.2.5 Green Machining -

After forming, the ceramic shape often is machined to eliminate rough surfaces and seams or to modify the shape. The methods used to machine green ceramics include surface grinding to smooth surfaces, blanking and punching to cut the shape and create holes or cavities, and laminating for multilayer ceramics.

11.7.2.6 Drying -

After forming, ceramics must be dried. Drying must be carefully controlled to strike a balance between minimizing drying time and avoiding differential shrinkage, warping, and distortion. The most commonly used method of drying ceramics is by convection, in which heated air is circulated around the ceramics. Air drying often is performed in tunnel kilns, which typically use heat recovered from the cooling zone of the kiln. Periodic kilns or dryers operating in batch mode also are used. Convection drying also is carried out in divided tunnel dryers, which include separate sections with independent temperature and humidity controls. An alternative to air drying is radiation drying in which microwave or infrared radiation is used to enhance drying.

11.7.2.7 Presinter Thermal Processing -

Prior to firing, ceramics often are heat-treated at temperatures well below firing temperatures. The purpose of this thermal processing is to provide additional drying, to vaporize or decompose organic additives and other impurities, and to remove residual, crystalline, and chemically bound water. Presinter thermal processing can be applied as a separate step, which is referred to as bisque firing, or by gradually raising and holding the temperature in several stages.

11.7.2.8 Glazing -

For traditional ceramics, glaze coatings often are applied to dried or bisque-fired ceramic ware prior to sintering. Glazes consist primarily of oxides and can be classified as raw glazes or frit glazes. In raw glazes, the oxides are in the form of minerals or compounds that melt readily and act as solvents for the other ingredients. Some of the more commonly used raw materials for glazes are quartz, feldspars, carbonates, borates, and zircon. A frit is a prereacted glass. Frit manufacturing is addressed in AP-42 Section 11.14.

To prepare glazes, the raw materials are ground in a ball mill or attrition mill. Glazes generally are applied by spraying or dipping. Depending on their constituents, glazes mature at temperatures of 600° to 1500°C (1110° to 2730°F).

11.7.2.9 Firing -

Firing is the process by which ceramics are thermally consolidated into a dense, cohesive body comprised of fine, uniform grains. This process also is referred to as sintering or densification. In

general: (1) ceramics with fine particle size fire quickly and require lower firing temperatures; (2) dense unfired ceramics fire quickly and remain dense after firing with lower shrinkage; and (3) irregular shaped ceramics fire quickly. Other material properties that affect firing include material surface energy, diffusion coefficients, fluid viscosity, and bond strength.

Parameters that affect firing include firing temperature, time, pressure, and atmosphere. A short firing time results in a product that is porous and has a low density; a short to intermediate firing time results in fine-grained (i. e., having particles not larger than 0.2 millimeters), high-strength products; and long firing times result in a coarse-grained products that are more creep resistant. Applying pressure decreases firing time and makes it possible to fire materials that are difficult to fire using conventional methods. Oxidizing or inert atmospheres are used to fire oxide ceramics to avoid reducing transition metals and degrading the finish of the product.

In addition to conventional firing, other methods used include pressure firing, hot forging, plasma firing, microwave firing, and infrared firing. The following paragraphs describe conventional and pressure firing, which are the methods used often.

Conventional firing is accomplished by heating the green ceramic to approximately two-thirds of the melting point of the material at ambient pressure and holding it for a specified time in a periodic or tunnel kiln. Periodic kilns are heated and cooled according to prescribed schedules. The heat for periodic kilns generally is provided by electrical element or by firing with gas or oil.

Tunnel kilns generally have separate zones for cooling, firing, and preheating or drying. The kilns may be designed so that (1) the air heated in the cooling zone moves into the firing zone and the combustion gases in the firing zone are conveyed to the preheat/drying zone then exhausted, or (2) the air heated in the cooling zone is conveyed to the preheat/drying zone and the firing zone gases are exhausted separately. The most commonly used tunnel kiln design is the roller hearth (roller) kiln. In conventional firing, tunnel kilns generally are fired with gas, oil, coal, or wood. Following firing and cooling, ceramics are sometimes refired after the application of decals, paint, or ink.

Advanced ceramics often are fired in electric resistance-heated furnaces with controlled atmospheres. For some products, separate furnaces may be needed to eliminate organic lubricants and binders prior to firing.

Ceramic products also are manufactured by pressure firing, which is similar to the forming process of dry pressing except that the pressing is conducted at the firing temperature. Because of its higher costs, pressure firing is usually reserved for manufacturing ceramics that are difficult to fire to high density by conventional firing.

11.7.2.10 Final Processing -

Following firing, some ceramic products are processed further to enhance their characteristics or to meet dimensional tolerances. Ceramics can be machined by abrasive grinding, chemical polishing, electrical discharge machining, or laser machining. Annealing at high temperature, followed by gradual cooling can relieve internal stresses within the ceramic and surface stresses due to machining. In addition, surface coatings are applied to many fired ceramics. Surface coatings are applied to traditional clay ceramics to create a stronger, impermeable surface and for decoration. Coatings also may be applied to improve strength, and resistance to abrasion and corrosion. Coatings can be applied dry, as slurries, by spraying, or by vapor deposition.

11.7.3 Emissions And Controls^{1,3,5,12-31}

The primary pollutants associated with raw material beneficiation are particulate matter (PM) and PM less than 10 μ m in aerodynamic diameter (PM-10). Filterable PM and PM-10 are emitted from comminution, sizing, classifying, handling, transfer, and storage. In addition, raw material calciners emit filterable and condensible PM, which may include metals and other inorganic pollutants. Calciners also emit products of combustion such as nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), carbon dioxide (CO₂), and volatile organic compounds (VOC). Emissions of SO_x are a function of the sulfur content of the fuel used to fire the calciners and the sulfur content of the raw materials used to manufacture ceramics. Emissions of VOC result from incomplete combustion and volatilization of the organic material associated with the raw material. Other beneficiation processes that are associated with emissions include acid leaching and granulation. Emissions of hydrochloric acid (HCl) or other acids may arise from leaching. In addition, PM and products of combustion are emitted from spray dryers used for granulation.

Mixing generally is a wet process. However, VOC emissions from this step may arise from the volatilization of binders, plasticizers, and lubricants. Forming generally is performed in sealed containers and often is a wet process; emissions from this step in the process are likely to be negligible. However, tape casters are a source of VOC emissions. For ceramic bodies that are dry-formed, PM is likely to be emitted from grinding, punching, and other green machining activities.

Particulate matter emissions consisting of metal and mineral oxides also arise from glaze preparation, which includes mixing and grinding. Emissions of PM from glaze application also are likely, if the glaze is applied by spraying.

Emissions associated from green ceramic heat treating processes, which include drying, presinter thermal processing, and firing, include combustion products and filterable and condensible PM. Particulate matter emissions consist in part of metals and the inorganic minerals associated with the raw materials. Emissions of the products of combustion are a function of fuel type, raw material constituents, process temperature, and other operating parameters.

Emissions of fluorine compounds also are associated with firing. Fluorine is present in ceramic raw materials in the range of 0.01 to 0.2 percent. As the temperature of green ceramic bodies reaches 500° to 600°C (930° to 1110°F), the fluorine in the raw material forms hydrogen fluoride (HF) and other fluorine compounds such as silicon tetrafluoride. Much of the fluorine is released as HF. However, if lime is present in the ceramic body, HF reacts with the lime to form calcium fluoride (CaF₂), thereby reducing potential HF emissions.

Other emission sources associated with ceramics manufacturing include final processing operations and fugitive dust sources. The final processing steps include grinding and polishing, which can emit PM and PM-10, and surface coating, annealing, and chemical treatment, which can emit VOC. Fugitive dust sources, which consist of vehicular traffic, wind erosion of storage piles, and materials handling and transfer, emit PM and PM-10.

Several techniques have been used to control PM emissions from the mechanical processing of ceramic raw materials and finished products. Fabric filters are the most commonly used control device, but wet scrubbers and electrostatic precipitators (ESPs) also are used. Fabric filters, wet scrubbers, and ESPs also are used to control emissions from clay calciners and dryers. Venturi scrubbers and fabric filters are used to control emissions from granulation (spray dryers) and from

glaze preparation and application. Afterburners have been used to control VOC emissions from tape casting operations. Emissions from kilns generally are uncontrolled.

Emissions of HF from kilns can be reduced through process modifications such as increasing the raw material lime content and reducing kiln draft, kiln exhaust temperature, and kiln residence time. Dry sorption scrubbing also has been used to control HF emissions in the brick and ceramic industries in Germany and in the brick industry in the United States. These devices use limestone as a sorption medium to produce CaF_2 , which is removed by means of a rotating screen, drum, or fabric filter. Control efficiencies of 95 to 99 percent have been reported for this type of scrubber.

Table 11.7-1 presents emission factors for PM and lead emissions from various ceramic products manufacturing processes. Table 11.7.2 present emission factors for SO_2 , NO_x , CO, CO_2 , VOC, HF, and fluoride emissions from ceramic kilns and tape casters.

Table 11.7-1. EMISSION FACTORS FOR CERAMIC PRODUCTS
MANUFACTURING OPERATIONS^a

Source	Filterable PM (lb/ton) ^b	EMISSION FACTOR RATING	Lead (lb/ton)	EMISSION FACTOR RATING
Comminution--raw material crushing and screening line with fabric filter ^c (SCC 3-05-008-02)	0.12	D	ND	NA
Dryer ^d (SCC 3-05-008-13)	2.3	E	ND	NA
Cooler ^d (SCC 3-05-008-58)	0.11	E	ND	NA
Granulation--natural gas-fired spray dryer (SCC 3-05-008-10)				
with fabric filter ^e	0.060	E	ND	NA
with venturi scrubber ^f	0.19	D	ND	NA
Firing--natural gas-fired kiln ^g (SCC 3-05-008-50)	0.49	D	ND	NA
Refiring--natural gas-fired kiln ^h (SCC 3-05-008-56)	0.067	E	ND	NA
Ceramic glaze spray booth (SCC 3-05-008-45)				
uncontrolled ^j	19	E	3.0	E
with wet scrubber ^k	1.8	D	ND	NA

^a Emission factor units are lb of pollutant per ton of fired ceramic produced, unless noted. To convert from lb/ton to kg/Mg, multiply by 0.5. Factors represent uncontrolled emissions unless noted. SCC = Source Classification Code. ND = no data. NA = not applicable.

^b Filterable PM is that PM collected on the front-half of an EPA Method 5 (or equivalent) sampling train. Although condensable organic and inorganic PM emissions are expected from dryers and kilns, no data are available to estimate these emissions.

^c References 12-13. Raw material processing for production of quarry tile, which is an unglazed tile product similar to structural clay products. Emission factor units are lb of pollutant per ton of material processed.

^d Reference 15.

^e Reference 16. Emission factor units are lb of pollutant per ton of dry material produced.

^f References 26-29. Emission factor units are lb of pollutant per ton of dry material produced.

^g References 7,9-11,15,23-25.

^h Reference 6. Kiln is used for refiring tile after application of decals, paint, or ink screening.

^j Reference 30. Emission factor units are lb of pollutant per ton of glazed used. Glaze contains about 24 percent lead oxide.

^k References 20-22. Emission factor units are lb of pollutant per ton of glaze used.

Table 11.7-2. EMISSION FACTORS FOR GASEOUS POLLUTANT EMISSIONS FROM CERAMIC PRODUCTS MANUFACTURING^a

EMISSION FACTOR RATING: E

Source	SO ₂	NO _x	CO	CO ₂	VOC ^b	HF ^c	Fluorides ^d
Firing--natural gas-fired kiln (SCC 3-05-008-50)	44·S ^e	0.54 ^f	3.3 ^g	780 ^f	0.43 ^g	0.46 ^h	0.56 ^j
Refiring--natural gas-fired kiln ^k (SCC 3-05-008-56)	ND	ND	ND	97	ND	ND	0.019
Forming--tape casters ^m (SCC 3-05-008-31)	ND	ND	ND	ND	58	ND	ND

- ^a Emission factor units are lb of pollutant per ton of ceramic product produced, unless noted. To convert from lb/ton to kg/Mg, multiply by 0.5. Factors represent uncontrolled emissions unless noted. SCC = Source Classification Code. ND = no data.
- ^b VOC reported on an "as propane" basis; measured using EPA Method 25A. Emission factor may include nonphotochemically reactive compounds that are not considered VOC. No data are available to estimate emissions of these non-VOC compounds.
- ^c Hydrogen fluoride measured using EPA Method 26A. This compound is listed as a hazardous air pollutant under Section 112(b) of the Clean Air Act, as amended in November 1990. A mass balance on fluoride will provide a better estimate of HF emissions for individual facilities.
- ^d Total fluorides measured during EPA Method 13A or 13B. Measurements include HF and other fluorine compounds. A mass balance on fluoride will provide a better estimate of fluoride emissions for individual facilities.
- ^e Reference 10. For facilities using raw material with a sulfur content greater than 0.07 percent. The variable S represents the raw material sulfur content (percent). For facilities using raw material with a sulfur content less than or equal to 0.07 percent, use 9.5·S lb/ton to estimate emissions (References 9,11). Emissions of SO₂ are dependent on the sulfur content of the raw material and the fuel used to fire the kiln.
- ^f References 9,11,15. EMISSION FACTOR RATING: D.
- ^g Reference 15. EMISSION FACTOR RATING: D.
- ^h Reference 15.
- ^j References 7,9-11, 23-25.
- ^k Reference 6.
- ^m Reference 14. Emission factor units are lb of pollutant per ton of formed product. Emissions controlled by an afterburner.

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