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Pollutant Emission Factors for the Ceramic Floor and Wall Tile Industry

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After a short review on production technology of ceramic floor and wall tile, the main feature of pollutant emissions from each production phase are outlined. On the basis of thousands of measurements carried out by the Centro Ceramico of Bologna on most of the Italian ceramic factories, the variation ranges of pollutant concentrations in stack emissions are shown, and the respective emission factors are calculated. The results obtained show that the ceramic industry is relatively clean, in comparison with other industries, although some environmental problems were found in areas with particularly high concentrations of ceramic factories.

Ceramic floor and wall tile is a sector of the ceramics industry which is both qualitatively and quantitatively very important as a source of materials for the building industry. The manufacture of ceramic floor and wall tile is widespread; however Italy is the major world producer as illustrated in Figure 1.

The designation ceramic floor and wall tile includes a vast range of products. In Europe there are at least 150 different commercial names indicating the various types of products available. A classification of floor and wall tiles produced in Italy is given in Table I. This classification is based on characteristics of the tiles such as body color, porosity, surface nature, and use for which the tile is destined.[1]

Raw Materials

Raw materials for ceramic tile production are natural apart from some used in glazes and colors. They are of two kinds: clay and non-clay raw materials. The principal mineral constituents of clays are kaolinite, illite, chlorite, and montmorillonite. The mineral compounds of non-clay materials are mainly quartz, feldspar, calcite, and dolomite.

As far as clay raw materials are concerned, a great variety of types and compositions exist. According to the product required, clays may be used singularly if the working properties are adequate or mixed together. In Italy much use is made of clays containing carbonates and iron compounds (for porous, colored products: majolica, cottoforte, cotto) and clays containing no carbonates (for low-porosity materials: red stoneware, fully vitrified stoneware, clinker). In other cases, mixtures of pure kaolinic clays, mainly from abroad, are used (for white body products: soft and hard body earthenware).

The non-clay raw materials are mixed with clay materials when the clay materials themselves have no natural, non-clay content. The non-clay material fluxes to form a ceramic matrix within the body so altering the compactness. Many other natural or artificial compounds are used in the glazes and decoration such as lead, boron, zircon and titanium compounds, oxides of various metals such as manganese, iron, cadmium, chromium, etc.

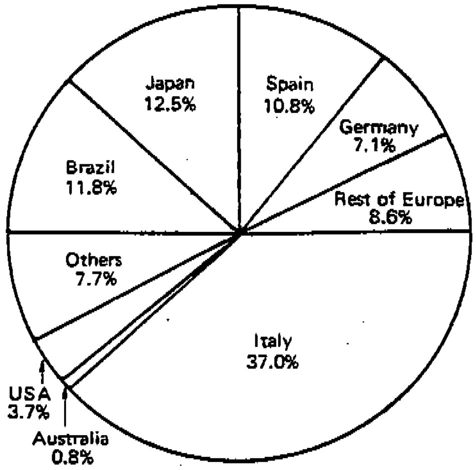

Figure 1. Shares of the world production of ceramic floor and wall tiles.

Production Technology

The production process is shown in Figure 2 and corresponds to glazed articles. The traditional technology is that of double firing; in recent years a glazed product, obtained from raw materials similar to those used in making stoneware and clinker, has been produced using a simplified process without the biscuit firing as this takes place simultaneously with the glost firing. This technology is that of single firing.

Raw Material Preparation

Raw materials are crushed using dry mills (hammer, toothed, swinging-arm, and runner types) or wet mills (ball and pebble types). Then, in the case of dry grinding, a quantity of finely milled fireclay grog (precalcined clay) and water is added to give the clay workability.

In this preparation stage the process is varied depending on the type of product being made. For majolica and cottoforte a single raw material is used and dry grinding may be sufficient, but for hard and soft body earthenware many materials are present and wet grinding is necessary. In this case each material will have different hardness and crushability, so the hard materials (quartz, feldspars, limestone) are usually ground separately while the softer materials (clays) are disintegrated in vessels provided with agitators. The two fractions are then put together in a single mixer from which they are pumped to a suitable drier. The latter operation is necessary to reduce the moisture content to suitably low levels for pressing the body in the form of a fine powder.

There are two methods for removing the water used in grinding and mixing: filter pressing and spray drying. If a filter press is used, the resulting cakes of material, still wet, are crumbled, dried, and milled to give a powder which is then re-moistened. If a spray drier is used, the clay suspension is introduced in droplet form into a drying tower, is dried within seconds, and is collected at a suitable grain size and moisture content ready for pressing.

Table I. Classification of the main Italian products. Stoneware, red vitrified, fully vitrified, and clinker are also produced by the single fired process, which often gives them different and more pronounced characteristics than the corresponding twice fired articles.

Type	Description	Body colour	Water absorption %	Glazed surface	Main use
Coloured body	Majolica	Yellow-pink	15–25	Yes	Interior walls
	Cottoforte	Pink-red	4–15	Yes	Interior floors
	Cotto			No	
Earthenware	Soft body	White	15–25	Yes	Interior walls
	Hard body	White	5–15	Yes	Interior walls
Floor tiles	Red vitrified	Red	0–4	Optional	Interior or exterior floors
	Fully vitrified	Varied	<1	Optional	Interior or exterior floors
	Clinker	Varied	0–7	Optional	Interior floors exterior walls or floors

Fritting of glaze components is carried out in crucible or rotary kilns from which the fused material runs down and is wet ground in suitable porcelain ball mills.

Shaping and Drying

Shaping is by means of fly-wheel or hydraulic presses, the former type being more widely used. A sorting operation is necessary between pressing and drying of the tiles (also between biscuit and glost firing and after glost firing). The drying is generally carried out by tunnel driers, partially or completely supplied by recycled heat from the biscuit kilns.

Firing

Firing is by means of tunnel kilns without muffles. The ceramic article achieves its intended consistency through a series of physical and chemical reactions during this stage. In Italy the fuel prevalently used is natural gas.

Glazing and Decorating

Glazing machines with screen printing equipment and other accessories are used for this process. A second glost firing serves to fix the glaze and decoration. Tunnel kilns with muffles, roller-hearth kilns, etc. are the usual types employed.

Fast Firing

A recently introduced technique used for glost and single firing is that of fast firing. Fast firing is done in monolayer kilns where the material to be fired is spread out in a single layer rather than stacked as is done with traditional kilns. Fast firing monolayer kilns have considerable technical, economical, and operative advantages (better uniformity of firing, flexibility of operation and type of products which can be produced, lower energy consumption, etc.); in addition, the air pollution resulting from the use of these kilns is less than that from traditional kilns.

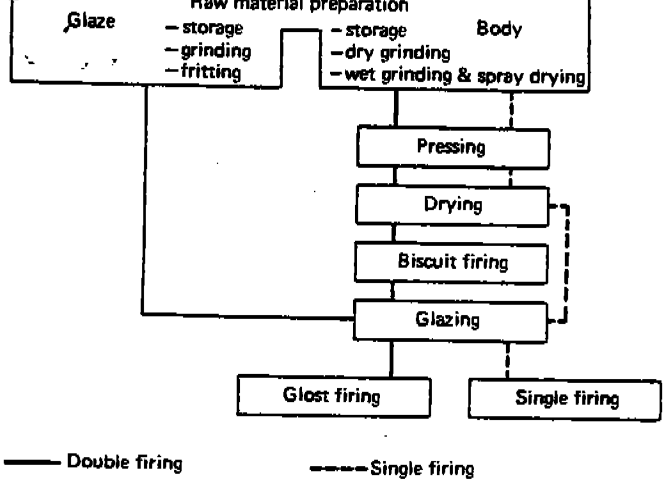

Figure 2. The production process.

Characteristics of the Emissions

Ceramic manufacturing processes result in the emission into the atmosphere of gaseous effluents containing various quantities of pollutants, mainly dust particles, lead and fluorine, in addition to other substances (oxides of sulphur, nitrogen, and carbon; boron, zinc, calcium compounds etc.) in minor or negligible quantities of little qualitative importance as regards contamination of the environment.

In fact, most of the Italian ceramic factories make use of natural gas as kiln fuel; therefore, both sulphur and nitrogen oxides emissions are rather low. In particular, sulphur oxides emission is related only to sulphur content in raw materials, which has been proven to be negligible.[2] However, an extensive investigation on air quality in the Ceramic Industry District of Sassuolo confirmed the low levels of SO_x air pollution.[2] Emissions of glaze constituents other than lead (such as boron, zinc, calcium compounds, etc.) are a minor environmental problem, as regards both the quantity (these compounds represent only a small percentage of the glaze) and the lower toxicity compared with lead.

The emissions can be classified according to temperature and pollutants contained:

- *Cold emissions* are those which result from the processes of grinding the raw materials, pressing and glazing. They consist of the air aspirated from plants and working areas to limit the diffusion of dust in the work environment. These emissions are at room temperature and contain only particulate matter.
- *Hot emissions* are those which result from the drying and firing processes. They are at temperatures in general above 70 to 100°C and also contain gaseous pollutants, especially fluorine compounds (hydrofluoric acid, fluorosilicic acid, silicon tetrafluoride).

The dust pollutants, which from now on will be indicated with the symbol, Pv, include all the particulate matter, independent of its chemical composition. Particulate matter is present in the emissions from all the manufacturing phases, but is found in the greatest quantities in cold emissions. The chemical compositions are variable. The dusts resulting from the preparation of raw materials and from the pressing operation have essentially the same composition as that of the raw materials; which is a content of free crystalline silica of about 15–20%. Fine particles in the emissions from the firing operation have a more varied composition, since they include residues of unfired product, material coming from the product at various stages in the firing cycle, and material from the erosion of the kiln refractories; in these dusts, free crystalline silica concentration is lower (about 10–15%) compared with dusts resulting from previous operations. Finally dusts which result from the various operations involving the glaze, reflect the wide range of glaze compositions. Characteristic of the emissions from these operations (preparation and application of the glaze and firing of the glazed products) is the presence of lead, an element widely used in glaze formulations for ceramic floor and wall tile.

Emissions from the firing operation always contain fluorine compounds. In fact, traces of this element (0.02 to 0.3%) have been found in nearly all clays analyzed from all over the world.[3–11] Presumably, the fluorine in clays is present as F^{-1} ions in the crystal structure which substitute for some of the OH^{-1} ions. Such a substitution is possible since F^{-1} and OH^{-1} are approximately the same size. The emission of fluorine compounds (e.g., hydrofluoric acid, fluorosilicic acid, silicon tetrafluoride, or even alkali fluorides) results from the collapse of the clay mineral structure caused by the high temperatures of the firing operation. However, it should be noted that not all of the fluorine contained in the raw materials is released as a result of the firing operation; some of it remains bound in the fired product and can be released in varying amounts if a second firing is carried out. The parameters which have the greatest influence on fluorine emissions are the firing temperature and the length of the firing cycle.[12–14] In contrast, no significant correlation has been found between the fluorine content of a raw material and its ceramic utilization.

Variations in concentration of pollutants in the uncontrolled emissions of ceramic floor and wall tile manufacturing processes are reported in Table II. These data are the result of thousands of measurements carried out over the last seven years by the Centro Ceramico of Bologna, Italy.[2]

Table II. Pollutant concentrations in uncontrolled emissions for different production phases.

Production phase	Pollutant concentrations in uncontrolled emissions (mg/Nm³) F	Pv	Pb
Raw material grinding and pressing		100–800	
Spray drying		80–400	
Bisque firing			
—combustion gases stack	10–50	3–40	
—degassing stack	0–600	0–50	
—cooling air stack	0–15	1–5	
Glaze milling and glazing		30–200	0–40
Glost firing			
—combustion gases stack	8–30	1–20	0–5
—degassing stack	0–80	5–50	0–30
Single firing			
—combustion gases stack	10–50	4–50	0–2
—degassing stack	0–80	0–70	0–10
Fritting	0–200	80–800	0–220

Pollution Control

Pollutants in the emissions from ceramic manufacturing processes can be reduced using a variety of control systems (fabric filters, Venturi scrubbers, electrostatic dust collectors, etc.). The more commonly used control systems presently in use for the various types of emissions are the following:

- emissions from the preparation of raw materials for the body and from the pressing operation — fabric filters
- emissions from spray drying — Venturi scrubbers
- emissions from the glaze preparation and glazing operations — Venturi scrubbers

Table III. Pollutant emission factors, uncontrolled and controlled, for different production phases.

Production phase	Specific flow rate (Nm³/m²)	Emission factors (g/m²) uncontrolled F	Pv	Pb	controlled F	Pv	Pb
Raw material preparation and pressing	160		40			3.2	
Bisque firing	200		1.0			0.4	
—high porosity ware		1.4			0.2		
—medium porosity ware		2.6			0.3		
—coloured low porosity ware		3.2			0.4		
—light colour low porosity ware		8.5			0.7		
Glaze milling and glazing	160		20	4.0		1.4	0.5
Glost firing							
—slow	290	1.0	2.0	0.2	0.2	0.7	0.05
—fast	100	0.6	1.2	0.15	0.1	0.3	0.02
Single firing							
—slow	290		2.0	0.3		0.5	0.05
—coloured low porosity ware		3.2			0.4		
—light colour low porosity ware		8.5			0.7		
—fast	100		1.2	0.2		0.4	0.02
—coloured low porosity ware		1.0			0.2		
—light colour low porosity ware		2.5			0.3		
Fritting[a]	9	0.8	2.0	0.8	0.03	0.2	0.03

[a] For the production phase, fritting, both specific flow rate and emission factors refer to 1 kg of frit.

• emissions resulting from all types of firing operations	fabric filters precoated with a reactive solid (usually lime)

Various fabrics are available, which are suitable for the temperature range of kiln emissions; for example, fabrics based on aromatic polyamide can withstand temperatures up to 230–240°C, while fabrics of polytetrafluorethylene show a good resistance even at temperatures higher than 300°C.

The performance of these systems in general is quite satisfactory. Various studies carried out on some hundreds of control systems in operation have shown that the efficiency of systems applied to cold emissions is greater than 95 to 97% and that for systems applied to hot emissions is around 90%.[2,15]

At present, much research and experimentation are being carried out in this field. Other types of control systems (electrostatic purifiers, condensation systems, etc.) have been studied and developed but their still limited use by the ceramics industry is not sufficient for obtaining statistically significant data.

Emission Factors for the Various Manufacturing Operations

Emission factors for the pollutants (F, Pv, and Pb) relative to the various manufacturing operations, with and without control are reported in Table III. They are reported in terms of 1 m^2 of ceramic tile produced (the unit of production generally used in the ceramic floor and wall tile industry) with the exception of the data relative to the production of frit, where the data are referred to 1 kg of frit produced. The reason for this choice was two-fold: (1) conforming to the usual unit of production facilitated the calculations necessary to transform the pollution rate per unit product to pollution in terms of unit time and (2) for certain manufacturing operations such as that of glazing or second firing, it is more logical to refer the degree of pollution not to the weight but rather to the surface area of the product. In addition, the passage from one unit of reference to the other is quite easy since it can be assumed to a sufficiently good approximation that 1 m^2 of ceramic tiles weighs 20 kg and that the glaze applied to 1 m^2 of tiles will weigh about 1 to 1.2 kg.

Significant differences in fluorine emissions were found as a function of the type of tile produced. In confirmation of what was said previously, the differences in fluorine emissions were influenced more by the differences in the firing temperatures (higher in the products with low porosity and in those with light-colored bodies) rather than by the fluorine content of the respective raw materials. Especially significant for fluorine emissions was the influence of firing time. Emissions of fluorine were considerably reduced in going from traditional kilns (with 20 to 30 h firing cycles for single firing and bisque firing and 10 to 15 h for the second firing) to monolayer kilns (with 1 to 2 h firing cycles for single firing and ½ to 1 h cycles for the second firing).[12]

The results reported in Table III illustrate the preceding general remarks regarding the efficiency and performance of the control systems presently being used.

Overall Emission Factors for the Various Types of Production

Overall emission factors for the various types of production are given in Table IV. These values are the sum of the emission factors for the individual manufacturing operations. The emission factors for the operations of frit production however, were not included in calculating the overall emission factors because the major part of the factories do not produce their own frits, which in general are produced by factories specializing in frit production.

The following conclusions can be drawn from the resulting data: single layer fast firing considerably reduces the impact which the production of ceramic floor and wall tiles has on the environment; in comparison with other industries such as the phosphoric acid, aluminum, phosphate fertilizers, foundry and metal industries, etc., the ceramic floor and wall tile industry is relatively clean.[15,16] However, it must not be forgotten that before control systems were generally adopted, quite serious environmental problems were found. This was especially true in areas with a high concentration of ceramic factories such as the ceramic district around Sassuolo (Provinces of Modena and Reggio Emilia, Italy), where in an area of a few tens of km^2 there are located about 250 ceramic factories which produce about ¼ of the world's production of ceramic floor and wall tile.[2]

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Table IV. Total emission factors, uncontrolled and controlled, for different production technologies.

Production technology	Total emission factors (g/m^2) uncontrolled F	Pv	Pb	controlled F	Pv	Pb
Double firing	2.4–9.5	63	4.2	0.4–0.9	5.7	0.55
Slow single firing	3.2–8.5	62	4.3	0.4–0.7	5.1	0.55
Fast single firing	1.0–2.5	61	4.2	0.2–0.3	5.0	0.52

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Predicasts Reports Filter Equipment, Media Shipments Will Top $14 Billion by 1995

Continued air and water pollution control standards, recovery of increasingly expensive raw process materials, increased water recirculation rates and an increase in industrial production are expected to create a $14 billion market for filter equipment and media by 1995, according to Predicasts, Inc., the Cleveland-based business information and market research firm.

In a recently completed study, Predicasts reports that U.S. shipments of filter products will grow at an annual rate of more than 11 percent through 1995, slightly slower than the 13 percent per year growth exhibited from 1967 to 1980. The drop off in real growth rate will result from the larger installed base of equipment and the Federal Environmental Protection Agency's so-called "bubble" policy, which lessens the financial burden on companies by giving them more flexibility in complying with emission standards.

The mix of filter media and equipment, split almost equally in 1967, has changed in favor of equipment. By 1977, about 60 percent of total sales was for equipment, but this dropped to about 58 percent in 1980. This mix is expected to remain relatively stable through 1995, when equipment will total nearly $7.8 billion and media over $5.4 billion.

Equipment and media sales in the U.S., totaling $2.7 billion in 1980, were dominated by particle emissions collectors, which accounted for 23 percent of the total market. Electrostatic precipitators and fabric filters comprise the bulk of this category.

This dominance is expected to remain through 1995, when particle emissions collectors will total nearly $3 billion, with fabric filters gaining some market share as the result of advances in fabric technology (especially for high temperature applications) and innovations such as electrostatically charging filter fabrics to increase particulate removal efficiency.

Gaseous emissions controls, such as scrubbers and flue gas desulfurization systems, are expected to exhibit the highest rate of growth, approaching 13 percent annually, and reaching $760 million in 1995. This will be the result of more coal burning by electric utilities and political or environmental pressures brought about by the acid rain problem.

In the filter media category, HVAC filters will exhibit the highest growth through 1995, followed by fabric filter media. HVAC filters are expected to benefit from the awareness that dirty filters cause a pressure drop which forces heating or cooling system motors to work harder and use more energy. Most of the growth, to more than $1.6 billion in 1995, will continue to come from large capacity HVAC systems used in commercial, industrial or institutional buildings.

Electric utilities are the largest market for filter equipment. Most of the $785 million sold to this sector in 1980 was for capital equipment such as fabric filters, electrostatic precipitators, flue gas desulfurization systems, and scrubbers.

The chemicals industry is the second largest end-use market for filter products. This industry uses virtually every type of filtration available, from pollution control devices to cartridge filters used in manufacturing processes.

Sales to most end-use sectors will grow about 11 percent annually, with electric utilities reaching more than $3.8 billion in 1995, chemicals approaching $1.5 billion and water and sewerage about $1.3 billion.

FILTER EQUIPMENT AND FILTER MEDIA (No. 263), a 111-page report, is available from Predicasts, Inc., 11001 Cedar Avenue, Cleveland, Ohio, 44106 at a cost of nine-hundred and ninety-five dollars ($995.00) per copy.

Control Technology News . . .

A concept being developed by researchers at Battelle's Columbus Laboratories may enable industries to inexpensively burn certain wastes to produce energy. Under a one-year grant from the U.S. Environmental Protection Agency, experts are using spouted-bed technology in a novel way—to help industries dispose of hard-to-burn wastes while saving on fuel and capital. According to Dr. Herbert A. Arbib, who heads Battelle's study team, conventional incineration of low heating-value industrial wastes requires additional energy and equipment, such as expensive heat exchangers.

Using a 2-inch diameter bench-scale model, Battelle's researchers have demonstrated the spouted-bed combustor's efficiency as an incinerator for gaseous and liquid wastes. Researchers are now evaluating the spouted-bed concept in a 6-inch diameter model. Their study includes an examination of scaling tactics and combustion efficiency for commercially significant fuels and wastes in solid, liquid or gaseous states.

The spouted bed, which has been used since the late 1950s for a number of applications—such as grain drying, blending, and pharmaceutical tablet coating—consists of a cylindrical vessel with a conical base, partly filled with relatively coarse