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ARTICULO

Characterisation of acid pollutant emissions in ceramic tile manufacture

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One of the environmental impacts associated with ceramics manufacture is the air emission of acid compounds stem from the presence of impurities in the raw materials and/or fuels.
The present study was undertaken to identify the significant gaseous pollutants of an acid nature, to determine their concentrations, and to obtain the characteristic emission factors in spray dryers and firing kilns.
The results show that, in spray dryers, the emission levels of the different acid pollutants are far below the current emission limit values applied in the European Union (EU). In firing kilns, the most significant acid pollutant emissions, compared with the recommended EU emission limit values (ELV-BAT), correspond to HF and HCl emissions, indicating that these emissions need to be corrected by appropriate cleaning systems before such emissions are released into the air. On the other hand, the results indicate that SO_2 and NO_x emissions in the Castellón industrial ceramic sector lie below the ELV–BAT proposed in the European ceramic industry BREF, owing to the widespread use of natural gas as fuel and of raw materials with reduced sulphur contents.

Keywords: Air emissions, acid pollutants, HF, HCl, SO_x, NO_x

Caracterización de las emisiones de contaminantes ácidos en la fabricación de baldosas cerámicas

Uno de los impactos medioambientales asociado a la fabricación de productos cerámicos es la emisión a la atmósfera de compuestos ácidos debido a la presencia de impurezas en las materias primas y/o combustibles.
Los objetivos del presente estudio son: identificar los contaminantes gaseosos de naturaleza ácida significativos, determinar su concentración y obtener factores de emisión de los secaderos por atomización y los hornos de cocción.
Los resultados obtenidos, en el caso de los secaderos por atomización, muestran que los niveles de emisión de los diferentes contaminantes ácidos se encuentran alejados de los valores límite de emisiones aplicados actualmente en la Unión Europea (UE). En cuanto a los hornos de cocción, la emisión más significativa de contaminantes ácidos, en comparación con los valores límite de emisión (VLE-MTD) recomendados en la UE, corresponde al HF y al HCl, e indican la necesidad de que dichas emisiones sean corregidas mediante la adopción de sistemas de depuración adecuados antes de su emisión a la atmósfera. Por su parte, los resultados indican que la emisión de SO_2 y de NO_x en las industrias ubicadas en el sector cerámico de Castellón, es inferior a los VLE-MTD propuestos en el BREF de la industria cerámica europea, debido al uso generalizado de gas natural como combustible y materias primas con reducidos contenidos en azufre.

Palabras clave: Emisiones atmosféricas, contaminantes ácidos, HF, HCl, SO_x, NO_x

1. INTRODUCTION

Gas emissions into the atmosphere are one of the main environmental impacts in ceramics manufacture. Such emissions may contain particulate matter and gas pollutants of an acid nature, in the form of fluorine, chlorine, sulphur, and nitrogen compounds (1)(2).

Acid compound emissions come from production stages in which combustion processes occur, resulting in high-temperature emissions. During ceramic tile production, hot emissions are generated in the slurry spray-drying stage, in the drying stage of freshly formed tiles, and in the ceramic tile firing stage. In tile drying, however, gas temperatures are usually below 250 ºC, and the ceramic material hardly becomes hotter than 100 ºC, so that pollutant emissions can be considered negligible (provided sulphur-free fuels are used) (3)(4).

1.1 Acid compound emissions in the ceramic industry

The origin of the acid compounds released in ceramic tile manufacture lies, essentially, in the use of raw materials and fuels that could contain them (except NO_x, as set out further below).

Fluorine compound emissions during ceramic tile firing are a key type of emission in these processes, fluorine compounds therefore being considered the most characteristic ceramic industry pollutants. Their emission stems from the presence of fluorine ions in clays used as raw materials in ceramic tile manufacture.

Fluorine ions replace OH^- groups in the crystalline structure of the mica, as well as in that of many other clay minerals (montmorillonite, illite, kaolinite, etc.) (5)(6), which is why fluorine compound emissions usually start with the dehydroxylation of these minerals at temperatures of the order of 500–700 °C (7)(8)(9). The major compounds that form are hydrofluoric acid, silicon tetrafluoride and, to a lesser extent, alkaline fluorides in particle form, the presence of these alkaline fluorides being practically negligible (10)(11)(12). In the presence of water vapour, a typical situation in industrial combustion kilns, fluorine is mainly emitted as hydrofluoric acid (13)(14)(15).

Chlorine compound emissions stem, mainly, from the presence of chlorine ions in the water used as a raw material in ceramic tile manufacture. Many clays and admixtures contain trace levels of chlorine.

Chlorine compound emissions occur during the firing process at temperatures above 850 ºC, from the decomposition of chlorine-containing mineral salts. In addition, the decomposition of organic compounds that contain chlorine leads to HCl emissions in the 450–550 ºC range (16).

On the other hand, sulphur compound emissions stem from the sulphur content in the raw materials and the type of fuel used. The clays used in ceramic tile manufacture can contain sulphites in the form of pyrite or calcium and magnesium sulphates such as gypsum, and sulphur in organic compounds.

Fossil fuels can also generate sulphur emissions. Natural gas is the most widely used fuel, and contains practically no sulphur in its composition; however, if fuel oil, coal or coke is used, sulphur emissions can be higher (16)(17).

Nitrogen compounds are emitted in the form of nitrogen oxides, and are related to the formation of thermal NO_x in high-temperature processes when a reaction takes place between nitrogen and oxygen in the combustion air. This reaction is encouraged in processes that unfold at high temperature (particularly at temperatures above 1400 ºC). However, NO_x formation can even be significant at process temperatures below 1200 ºC, when the burners run at high flame temperatures (16).

The decomposition and combustion of nitrogen compounds present in the raw materials, admixtures, or fuels can also be a source of NO_x at lower temperatures.

1.2 EU legislation on air emissions in the ceramic industry

In the EU, the application of Directive on integrated pollution prevention and control, known as IPPC (18), obliges companies included in Annex I of the Directive to obtain an Integrated Environmental Authorisation (IEA), which includes emission limit values (ELV) for different atmospheric pollutants. When it comes to fixing the ELV applicable to each installation, authorities take into consideration the existing BREF Documents for those industries affected by the IPPC. BREF documents are EU reference documents that detail the Best Available Techniques for each sector and propose related emission values (ELV-BAT).

In July 2009, the EU criteria were reviewed for the award of the EU eco-label to rigid coverings (ceramic tiles)(19). These requirements are of a voluntary character: as a result, tiles that obtain the eco-label display demonstrable improvements in key ecological issues, such as air emissions.

Table I details the emission values defined for ceramic tile manufacture in the EU. The table presents both the ELV-BAT contained in the BREF Document on ceramics and those established in the criteria for the eco-label award.

2. SCOPE AND OBJECTIVES

The objectives of the present study on acid pollutant emission during ceramic tile manufacture were as follows:

- Identification of the significant gaseous air pollutants of an acid nature.
- Determination of the concentrations of these pollutants and, if possible, obtainment of specific emission factors for the ceramic industry in the Castellón district.

The purpose of this study has been to obtain updated and truthful sectoral information on the emission of these pollutants in order to be able to achieve the following objectives:

Table I. Emission values for ceramic tile manufacture in the EU.

Document	Stage	Units	HF	HCl	SO_2	NO_x (as NO_2)
BREF (ELV-BAT)	Spray drying	mg/m_0^3 at 18% O_2 and dry gas	--	--	--	500 (cogeneration)
	Firing		5	30	500	250
Eco-label (*)	Firing	mg/kg fired product	10	--	75	125

mg/m_0^3: concentration in standard conditions: temperature (273 K) and pressure (101,3 kPa).
** A mean value of 20 kg/m² tile has been considered*

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- Cost optimisation in air pollutant controls, establishing a realistic pollutant control system for the ceramic industry.
- Greater information transparency and better relationship with the administration.
- The fixing of emission factors that allow emission inventories to be made, in accordance with reality.

The emissions study was conducted in the ceramic tile manufacturing stages in which combustion processes occur and process temperatures above 500 ºC are reached. The facilities involved in these stages are as follows:

- Spray dryers (using bag filters or Venturi- type scrubbers for removing particulate matter)
- Firing kilns (without/before the acid cleaning systems)

The study addressed pollutants of an acid nature, emitted in the form of fluorine, chlorine, sulphur, and nitrogen compounds at the above emission sources, in relation to the tile types listed in Table II.

3. MEASUREMENT METHODOLOGY

The methodology used to determine the gaseous pollutants considered in the present study (fluorine, chlorine, and sulphur) is based on the extraction, by means of an appropriate probe, of a known volume of gases that are put through an absorption system that captures these compounds. The pollutant at issue in the capturing solution is then determined and its concentration in the gas stream is calculated. This methodology is described in various specific test standards, outlined in Table III.

ITC is accredited by the Spanish National Accreditation Body (ENAC) for the determination of fluorine, chlorine, and sulphur concentrations.

Parallel to the determination of acid pollutants, a further series of key gas stream parameters were measured, such as volumetric flow rate, gas humidity, and other gases in these streams (O_2, CO_2, and CO): these last gases were determined using automatic batch methods based on electrochemical sensors.

4. EXPERIMENTAL DEVELOPMENT

Measurements were performed of the pollutants at issue in the studied process stages: spray drying and firing. The selection of the sources in each studied stage was made as a function of the following parameters:

- Type of product made: earthenware tile (A), stoneware and/or porcelain tile (G)
- Colour of the body composition: red (R) or white (B)

4.1 Spray drying

Table IV presents the distribution of the sources measured in this study stage. The table also indicates the type of spray-dried granule made (type and colour), and indicates whether the spray dryer is connected to a cogeneration turbine, since the BREF also identifies these two possibilities. The parameter characterised in this stage was the concentration of the different studied pollutants.

Table III. Standards on air pollutant measurement

Pollutant	Reference standard
Fluorides (expressed as HF)	ISO 15713:2007
Chlorides (expressed as HCl)	EN 1911:1998
SO_2	EN 14791:2006
NOx	ASTM 6522

Table IV. Distribution of the sources measured in the spray drying stage.

Installation	Type of product	Cogeneration
1	Spray-dried granule for red earthenware tile (AR)	Yes
2	Spray-dried granule for red earthenware tile (AR)	Yes
3	Spray-dried granule for red stoneware tile (GR)	Yes
4	Spray-dried granule for porcelain tile (GB)	Yes
5	Spray-dried granule for porcelain tile (GB)	No

Table II. Most common types of ceramic tiles in Spain

Reference in the study	Body colour	Type of tile	Forming	Body	Glazed	Group according to EN 14411
AR	Red	Earthenware tile	Pressing	Porous	Yes	BIII
AB	White					
GR	Red	Glazed stoneware tile	Pressing	Non porous	Yes	BIb/BIIa
GB	White					
	White	Porcelain tile	Pressing		Yes	BIa

4.2 Firing kilns

The distribution of the sources measured in the firing stage in this study is detailed in Table V. The following parameters were determined in this case:

- Pollutant concentration (mg/m_0^3), this being the parameter customarily used to establish the ELV-BAT
- Emission factors, because they are considered of great usefulness for setting up environmental registers or inventories. Two types of emission factors are distinguished:
  – Emission factor (g/h), customarily used to characterise the emissions of continuous processes and to draw up regular environmental reports (Pollutant Release and Transfer Register (PRTR)). The emission factor depends directly on the mass production of the studied kilns, which is why it is necessary to take this into account when it comes to interpreting the findings.
  – Specific emission factor (mg/kg fired product), used to compare different processes, independently of the actual production of each process.

The data set out in Table V enable the following to be noted:

- The number of data available for each studied parameter does not coincide for the different pollutants considered, since in certain cases not all the necessary information was available such as, for example, the flow rate values of the gases or tile production data.
- The data on white stoneware and porcelain tile have been treated together, since their emissions display very similar behaviour.

5. RESULTS

5.1 Spray drying

Table VI presents the results corresponding to acid compound emissions in the spray drying stage. Since the results obtained display no significant variations as a function of the use of cogeneration, or of the type of product made, they are shown together with the ELV-BAT, thus enabling the current situation in relation to these values to be readily evaluated.

The results presented in Table VI indicate that the acid pollutant emissions in the spray-drying stage are relatively insignificant, even for NO_x. It may be noted in this sense that, in the studied facilities, no great differences were found in nitrogen compound emissions owing to the use of cogeneration systems.

The results obtained display high uniformity, probably because of the low temperature (between 50 and 60 ºC) reached inside the spray-dried granule during drying, which does not lead to thermal decomposition of the raw materials, as is the case in the firing stage. For this reason, the lack of measurement data on granulate sources for white earthenware tile manufacture (AB) is not considered significant. These findings are consistent with the information in the BREF Document for the ceramic industry (15).

TABLE V. DISTRIBUTION OF THE NUMBER OF DATA CONSIDERED IN THE FIRING STAGE.

Pollutant	Studied parameter	Total no. of data	Earthenware tile		Stoneware tile	
			Red (AR)	White (AB)	Red (GR)	White (GB)
HF	Concentration (mg/m_0^3 at 18% O_2)	72	11	7	35	19
	Emission factor (g/h)	65	11	5	30	19
	Specific emission factor (mg/kg fired product)	56	11	6	22	17
HCl	Concentration (mg/m_0^3 at 18% O_2)	43	7	6	15	15
	Emission factor (g/h)	43	7	6	15	15
	Specific emission factor (mg/kg fired product)	30	5	4	13	8
SO_2	Concentration (mg/m_0^3 at 18% O_2)	18	4	5	3	6
	Emission factor (g/h)	18	4	5	3	6
	Specific emission factor (mg/kg fired product)	18	4	5	3	6
NO_x	Concentration (mg/m_0^3 at 18% O_2)	42	8	6	14	14
	Emission factor (g/h)	30	6	5	6	13
	Specific emission factor (mg/kg fired product)	19	5	4	4	6

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TABLE VI. ACID POLLUTANT CONCENTRATIONS (mg/m_0^3 AT 18% O_2 AND DRY GAS) DURING SPRAY DRYING.

Pollutant	No. of data	Maximum concentration	BREF (ELV-BAT)
HF	5	<2	--
HCl	5	<25	--
SO_2	5	<50	--
NO_x (as NO_2)	5	<100	500 (cogeneration)

5.2 Firing kilns

5.2.1 CONCENTRATION

The results corresponding to firing kilns for the different studied parameters are shown in Figure 1 in the form a median (50th percentile). The median is considered a more robust estimator than the arithmetic mean, since the extreme values affect it less. The figure also shows the ELV-BAT applicable to this process stage.

The most significant emissions of the studied acid pollutants in the firing stage correspond to HF and HCl compared with the different applicable ELV-BAT, which indicates that these emissions need to be corrected by means of appropriate cleaning systems before such emissions are released into the air. In the case of the white earthenware tile, however, it is necessary to study the cleaning need in each particular case, because white earthenware tile emissions (AB) are significantly lower than those recorded for the other products (20)(21)(22).

The SO_2 and NO_x emissions in the studied ranges are clearly lower than the ELV-BAT proposed for this process stage (16).

5.2.2 EMISSION FACTORS

This section summarises the emission factors obtained in the present study for the firing stage. The emission factors (g/h) are presented in Figure 2. These values depend directly on the mass production of the studied kilns, this being a factor that must be taken into account when it comes to interpreting the results obtained. The specific emission factors (mg/kg fired product) are presented in Figure 3.

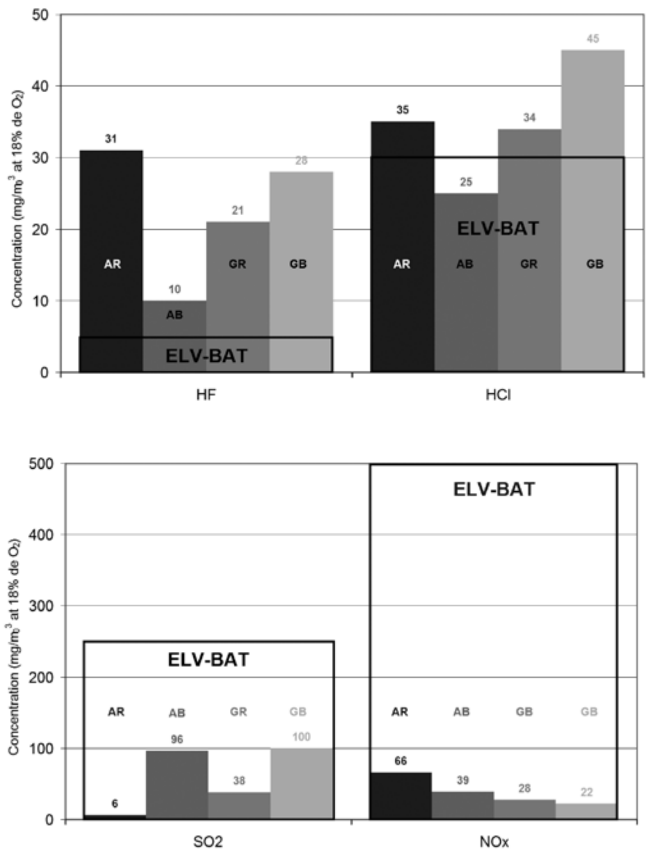

Figure 1 Median acid pollutant concentrations (mg/m_0^3 at 18% O_2 and dry gas) for earthenware and stoneware tile in the firing stage.

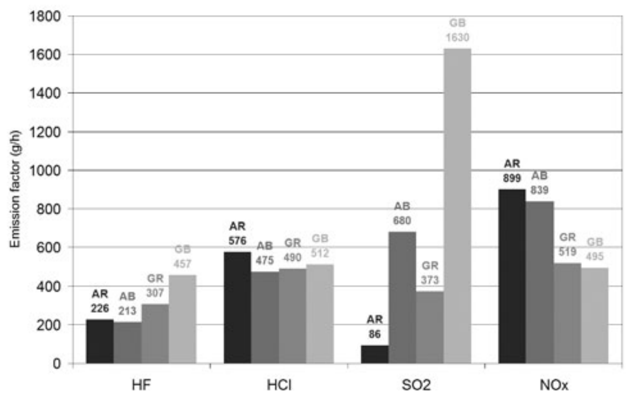

Figure 2 Median emission factors (g/h) for earthenware and stoneware tile in the firing stage.

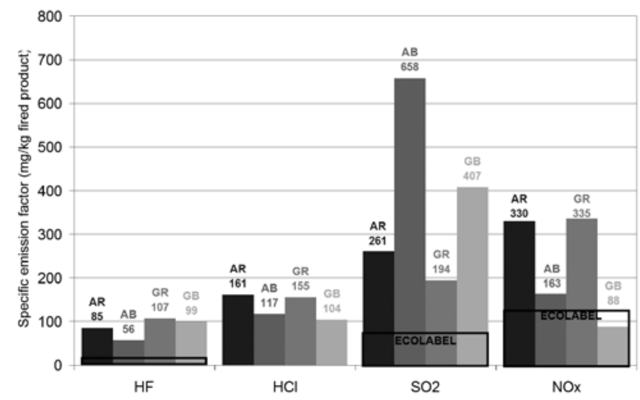

Figure 3 Median specific emission factors (mg/kg fired product) for earthenware and stoneware tile in the firing stage.

Figure 3 also shows the ecological criteria established for the EU eco-label award for rigid coverings (ceramic tiles). The figure clearly shows that these criteria, in relation to air emissions, are quite restrictive compared with the usual emission values for these types of products.

CONCLUSIONS

The results of the study allow the following conclusions to be drawn in relation to the studied process stages:

Spray dryers:

- No significant differences were found between the acid compound emissions of the different types of studied products, nor were significant differences found owing to the use of cogeneration turbines.
- The emission of fluorine and of the other acid pollutants in the spray-drying stage is of little significance, compared with the ELV-BAT currently established in the EU.
- From an air emission control standpoint, provided no changes occur in the process that justify the need for such control, it is possible to reconsider the need for regular SO_2 and NO_x emission controls in view of the low emissions detected in these facilities.

Firing kilns:

- HF and HCl emissions are the most significant acid pollutant emissions in the firing stage compared with the different ELV-BAT proposed in the EU BREF. The study outcomes indicate the need to correct the great majority of these emissions by adopting appropriate primary measures and cleaning systems before such emissions are released into the air.
- The SO_2 and NO_x emissions in all the studied companies are clearly below the ELV-BAT applicable to this process stage, so that if there are no changes in fuels or raw materials, no type of correction is required.
- The emission factors corresponding to the firing stage have been determined with narrow variation ranges for each type of studied pollutant, solely as a function of the type of product made, without any other manufacturing process characteristics being considered. The information obtained is considered to be representative of the current situation in the Spanish ceramic tile manufacturing sector and can be used to draw up regular environmental reports, such as the Pollutant Release and Transfer Register (PRTR), and to prepare limit proposals in future BREF document reviews.

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