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Review

Monitoring and possible reduction of HF in stack flue gases from ceramic tiles

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ABSTRACT

HF (hydrogen fluoride) emission control is one of the critical environmental parameters in the firing of ceramic materials at peak temperatures higher than 1000 °C. In this study, in-stack concentrations of HF were monitored on-line with laser-based equipment during the fast firing of ceramic tiles in continuous industrial roller hearth kilns under standard kiln operating conditions.

Three different ceramic tile compositions: porous red-body wall tiles, red-body stoneware tiles, and porcelain tiles were fired in industrial kilns customarily used to manufacture these types of tiles, modifying the heating rate and tile dry bulk density. The in-stack concentrations of HF can be explained on the basis of tile HF adsorption and emission processes in the kiln preheating and firing zones, analysed in previous studies.

The methodology used in this study has significant advantages for industrial studies compared with previous methodologies based primarily on laboratory-scale studies and analysis of solid material. The main advantages are: (a) rapid response, allowing abrupt changes in the HF emission to be studied; and (b) direct measurement of the in-stack concentration of HF, which is the most common parameter used as a legal limit for industrial emission control.

The study shows that tile HF adsorption in the preheating zone is very important. It also shows that HF stack emissions can vary significantly in continuous kilns depending on whether glazed or unglazed tiles are produced, or important changes occur in production (such as gaps in the kiln feed). The results indicate, furthermore, that HF stack emissions do not decrease significantly when realistic changes are made in industrial operating conditions if these industrial kilns are run at peak temperatures above 1100 °C. The most important reduction in in-stack concentrations of HF is observed when glazed ceramic tiles are fired, so further research in this field can be made in order to reduce HF emissions.

Contents

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1. Introduction

Industrial emission control has drawn growing attention in recent years, with increasingly stringent emission requirements aimed at achieving high productivity in an environmentally friendly manner. The development of the 1990 Clean Air Act and its amendments, and Directive 96/61/EC on Integrated Pollution Prevention and Control are key regulations in the heightened concern over environmental protection in the USA and EU, respectively.

A major environmental issue for the ceramic industry, particularly for ceramic tile manufacture, is the assurance of appropriate control of fluorine emissions in the firing stage [1–9], exhausted mainly as HF in continuous combustion kilns [10,11]. Legal limits are usually based on HF concentrations in stack flue gases (in the EU Member States, typically around 5–10 mg m^{-3}), measured during a set time under representative operating conditions [12].

The environmental legislation has imposed increasingly stringent emission limits of HF from ceramic factories in response to available evidence that such emissions have harmful effects on plants and animals [13,14]. On the other hand, in recent studies on air quality [15] significant concentrations of fluorine in particulate matter (0.2 $\mu g\ m^{-3}$ on an annual mean basis) have been found in the Castellón ceramic cluster, which has a high concentration of ceramic tile manufacturing companies.

In foregoing ITC studies, a laser-based, on-line HF measurement system was adapted to the specific conditions of stacks in ceramic tile-firing kilns [10,11]. This very useful tool enables in-stack concentrations of HF to be characterised and rapid variations in HF concentrations to be monitored. The mechanisms involved in HF emissions have also been analysed in previous studies [15–17]. These studies have shown that the final HF stack emission is not only highly influenced by the fluorine content and chemical composition of the raw materials, but also by peak firing temperature and the HF emission and adsorption processes inside the kiln between the kiln feed and the gases. Important variations in HF concentrations in flue gas emissions may therefore ensue when changes occur in the firing process [10,11]. These can affect the environmental impact and the response of the end-of-pipe cleaning systems typically used to minimise HF emissions; the most popular being based on dry neutralisation processes with the addition of reagents such as CaO, $Ca(OH)_2$, $CaCO_3$, or $NaHCO_3$ [2,8,12,18–20].

When basic primary measures have been applied, such as reducing the input of fluorine in the raw materials and optimising the calcium content in the body composition, the only way to minimise the fluorine emission by applying primary measures in products fired at peak temperatures higher than 1000 °C, is to optimise the process [12]. Previous laboratory-scale studies performed at ITC have shown that the main process variables affecting HF emissions are dry bulk tile density and firing rate. Dry bulk density determines the gas permeability of the tile during the emission process, while the firing rate controls tile residence time in every firing phase. These studies have shown that other variables, such as the degree of milling (that is, particle size distribution), only slightly affect the HF emission.

The present study has been undertaken to analyse on-line, on an industrial scale, the HF concentrations in stack flue gases before they enter the HF removal systems, under standard and modified firing conditions. The study was conducted at industrial kilns where the different types of ceramic tiles were fired under standard conditions, modifying the heating rate and dry bulk tile density. The performance of the study on an industrial level enables realistic, practical modifications to be implemented, though the changes that can be made are obviously much more limited than on a laboratory scale.

2. Materials and experimental procedure

2.1. Materials

The study was carried out on three standard tile body compositions used in the Castellón ceramic cluster (Spain), where about 40% of the ceramic tiles made in the EU are produced. The studied compositions were referenced as follows: A (porous red-body wall tiles), G (red-body stoneware tiles), and P (porcelain tiles). Tables 1 and 2 summarise the main characteristics of these compositions.

2.2. Heat treatment

The three types of ceramic tiles were fired in different continuous roller hearth kilns, fuelled by natural gas, used,

Table 1
Characteristics of the types of tiles studied.

Ref.	Type of product			Body characteristics	
	Industrial name	Finish	Group ISO 13006	Fired colour	Open porosity (%)
A	Wall tile	Glazed (GL)	BIII	Red	28.0
G	Floor tile	Glazed (GL)	BIIa	Red	8.0
P	Porcelain tile	Glazed (GL)	BIa	White	0.2

Table 2
Chemical and mineralogical composition of the bodies.

		A	G	P
Chemical composition (wt%)	SiO_2	57.5	64.0	65.8
	Al_2O_3	15.6	17.5	20.6
	Fe_2O_3	5.26	6.01	0.66
	CaO	6.25	1.21	0.72
	MgO	1.78	0.85	1.34
	Na_2O	0.41	0.47	4.48
	K_2O	3.23	3.34	1.60
	LOI	9.18	5.93	3.91
Fluorine content (mg kg^{-1})	F	650 ± 20	620 ± 20	290 ± 15
Mineralogical composition (wt%)	Illite	18	19	14
	Kaolinite	18	22	18
	Chlorite	2	–	5
	Quartz	36	39	24
	Albite	–	–	38
	Microcline	6	6	–
	Calcite	10	3	–
	Dolomite	2	2	
	Hematite	5	6	0.5

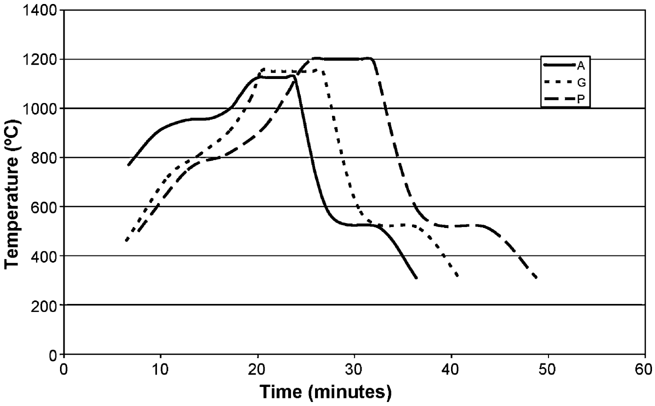

Fig. 1. Temperature–time curves in the industrial kilns used for the three studied compositions.

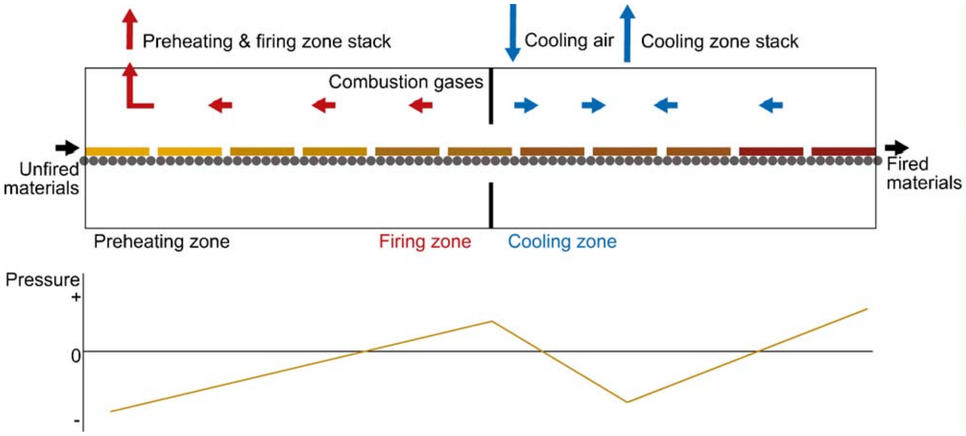

Fig. 2. Schematic illustration of the roller kiln with gas flow and static pressure curve.

respectively in industrial practice to manufacture these types of tiles.

The tiles were subjected to the standard thermal cycles used at the companies where the tests were carried out, with total firing times (cold to cold) of 40–55 min, and peak firing temperatures of about 1125, 1150, and 1200 °C for compositions A, G, and P, respectively. The complete temperature–time curves are shown in Fig. 1.

Fig. 2 schematically illustrates one of these kilns. The most significant operating feature in relation to HF concentrations in the kilns is the movement of the combustion gases, which circulate counter current to the tiles in the preheating and firing zones according to the static pressure curve (see Fig. 2 below).

2.3. Monitoring of HF concentrations in stack flue gases

The in-stack concentrations of HF in the studied kilns were monitored on-line, thus allowing variations in the concentrations to be observed in real time, and enabling their relation to the manufacturing process and/or emission treatment variables to be studied.

The HF emissions were always monitored in the common stack exhausting the preheating and firing zone flue gases, since recent studies [17] have shown that no significant fluorine emissions occur during the cooling stage. The use of the in-stack concentrations of HF as a parameter is of particular interest, because it usually enables almost direct comparison with legal limits to be made, conversion only being needed to comply with legally required conditions. Thus, in this study, in accordance with the European recommendations for firing ceramics [10], all in-stack concentrations of HF are always referred to the following conditions: 273.15 K, 101.3 kPa, 18% oxygen content by volume, and dry basis.

The HF measuring system used was a commercial apparatus (supplied by Boreal Laser Inc.) adapted for measuring HF concentrations in flue gases during ceramic tile firing, validated elsewhere [10,11]. Fig. 3 schematically shows the equipment and the probe designed for in-stack sampling. In this instrument, a TDL (tuned diode laser) selects the HF absorption band that displays no interferences with any other gases, which makes these instruments with infrared spectrometry and tuned lasers highly selective.

One of the instrument's basic features is its continuous calibration system, in which a fraction of the generated laser radiation passes through a reference cell with known HF content. The fact that the analyser has a self-calibrating system is of

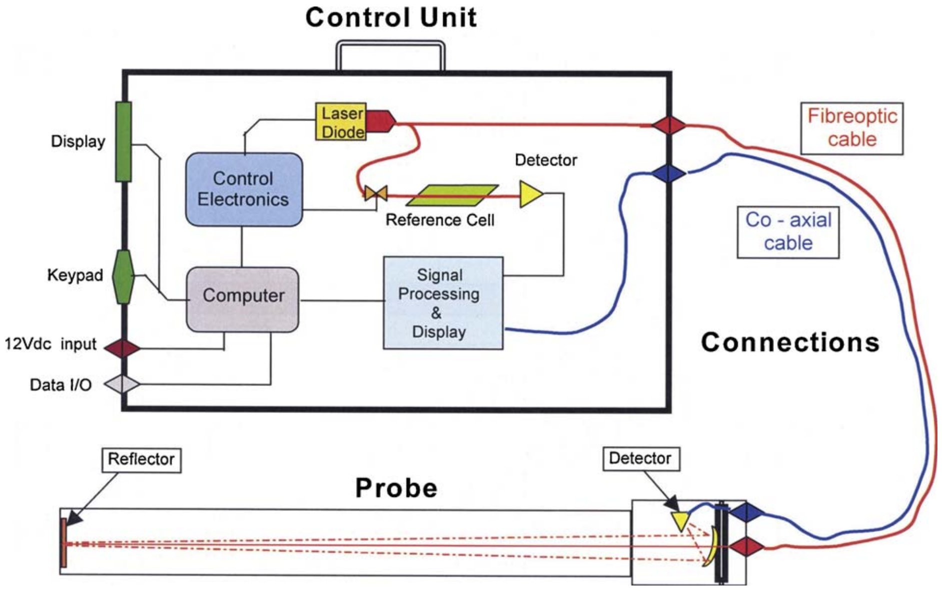

Fig. 3. Schematic illustration of the equipment used and probe designed for in-stack sampling.*Source*: Boreal Laser Inc.

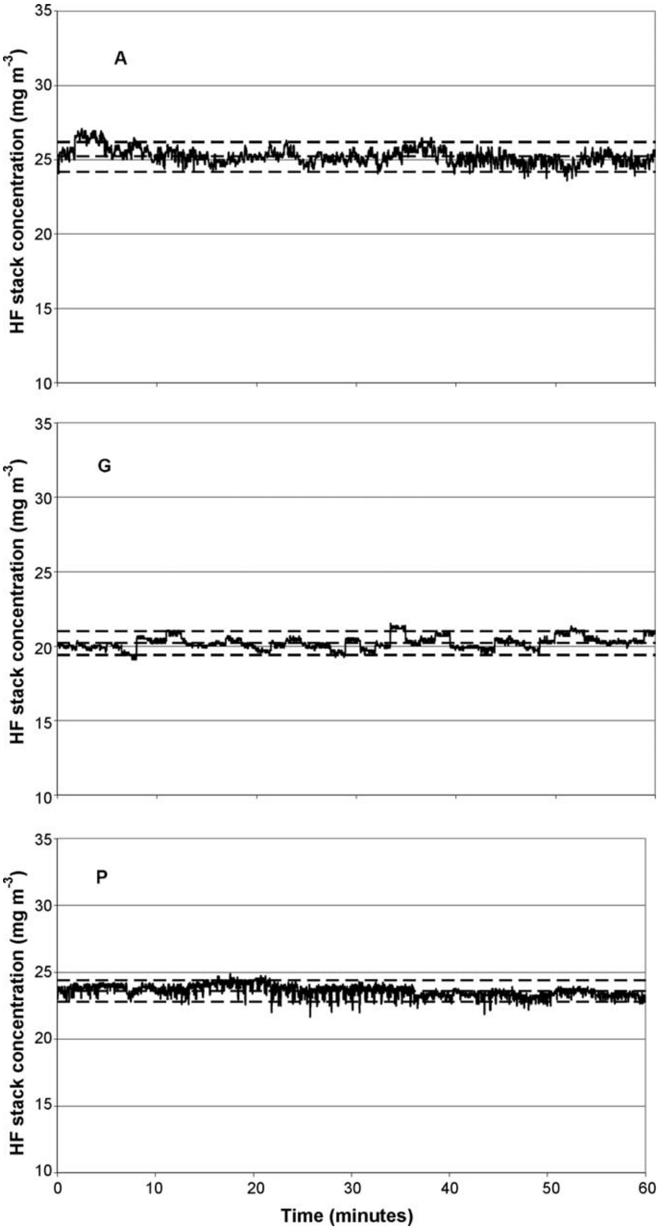

Fig. 4. Evolution of in-stack concentrations of HF under standard kiln operating conditions with bodies A, G, and P.

enormous practical importance since no standard gases need be used, thus simplifying the fieldwork.

3. Results

3.1. HF concentrations in stack flue gases under standard operating conditions

A series of assays were performed, related to the evolution of HF in-stack concentrations under standard kiln operating conditions in the three studied body compositions (A, G, and P), shown in Fig. 4. In all cases, the variation in HF concentrations is observed to fluctuate in a relatively narrow margin with only slight swings around a mean value that, to all practical purposes, may be considered constant. The absolute values of the in-stack concentrations of HF obviously varied, depending on body composition, production throughput, and firing schedule.

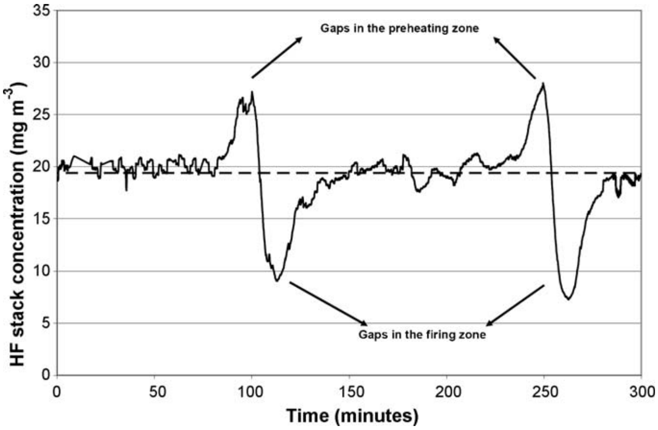

Fig. 5. Evolution of the in-stack concentration of HF with 15-min gaps in the tile feed (body P).

The results indicate that the batch sampling procedure, sampling gas for a relatively short period of time (20–40 min), allows adequate determination of the HF concentrations in a kiln running under standard conditions [21], since the in-stack concentrations of HF do not vary significantly with time and can be appropriately characterised as a mean concentration, provided no changes occur during sampling (i.e. constant production throughput, body composition, etc.).

Table 3 shows the mean in-stack concentrations of HF during the period of time analysed, together with a 95% confidence range ($C_{HF} \pm 2\sigma$). The parameter ($2\sigma/C_{HF}$) has a value of 3–4% for the three studied body compositions, confirming that the HF concentrations are quite constant in this process under standard operating conditions.

3.2. HF concentrations in stack flue gases under modified operating conditions

3.2.1. Gaps in the kiln feed

The kiln feed is quite often interrupted for several reasons (maintenance, model changeovers, etc.), leading to tile feed gaps. In order to study the effect of tile feed gaps on HF concentration in the end stream, the evolution of the fluorine concentration was monitored in the three kilns after the kiln feed was stopped for periods of 5 and 15 min. In these experiments, the operating conditions (type of processed material, temperature profile, etc.) were kept constant.

The results obtained in the different studied tile compositions (A, G, and P) were qualitatively similar. For the sake of simplicity, only the results for porcelain tiles (P) are therefore presented graphically.

The evolution of the in-stack concentrations of HF during a period of time in which two 15-min breaks occurred is shown in Fig. 5. This shows that an abrupt change takes place in the in-stack

Table 3
In-stack concentrations of HF under standard kiln operating conditions.

Ref.	Mean HF concentration C_{HF} (mg m^{-3})	Standard deviation σ (mg m^{-3})	2σ (mg m^{-3})	$C_{HF} \pm 2\sigma$ (mg m^{-3})	$(2\sigma)/C_{HF}$ (%)
A	25.2	0.5	1.0	25.2 ± 1.0	4.0
G	20.2	0.4	0.8	20.2 ± 0.8	4.0
P	23.6	0.4	0.8	23.6 ± 0.8	3.4

Table 4
Changes in in-stack concentrations of HF with gaps in the tile feed.

Body	Increase in HF concentration (%) (gaps in preheating)	Decrease in HF concentration (%) (gaps in firing)
A	80	50
G	60	70
P	40	55

concentration of HF, with an initial increase followed by a decrease stage. This can be explained by tile HF adsorption and emission processes during preheating and firing, respectively, in continuous kilns [17]. The initial increase is caused by the absence of tiles in the preheating zone. The HF in the gases flowing through this area is therefore not adsorbed and the stack HF concentration peaks at a value that is 40% higher than the HF concentration under standard conditions. Under these modified conditions, almost all the emitted HF goes to the stack, without any adsorption in the preheating zone, as occurs in batch kilns.

When the gap reaches the peak temperature zone, the HF concentration in the stack decreases significantly, minimising at a value that is approximately 55% lower than the initial value (under standard operating conditions), as a result of two simultaneous effects. On the one hand, the gap reaches the firing zone minimising the HF emissions, that is, the emission at peak temperature is very low, and as a result, the gases entering the stack from this area have a very low HF content. On the other hand, the presence of unfired material in the adsorption zone (preheating) adsorbs HF from the flue gases. As a result, the in-stack concentration of HF plunges, which may explain why the second peak (gap in the firing zone) is larger than the first (gap in the preheating zone).

These experiments were replicated in the different kilns used for bodies A and G, respectively, which yielded similar results. Table 4 shows the increase and decrease in in-stack concentrations of HF, expressed as a percentage of the mean value under standard conditions for the three body compositions. For the G and P bodies, the decrease in in-stack concentrations of HF is larger when the tile gap reaches the firing zone than the increase in HF concentrations when the gap reaches the preheating zone, as set out above. However, body A displays the opposite behaviour: the increase in in-stack concentration of HF is larger than its decrease. Previous studies [16] suggest that this difference could be due to the higher calcite content in body A (6.25% CaO compared with 1.21 and 0.72% CaO for compositions G and P, respectively), which improves HF adsorption in the preheating zone. As a result, when the gap in the calcite-rich composition reaches the preheating zone, the absence of adsorption causes the in-stack concentration of HF to rise much more (80%) than when the tile gap is related to compositions with a lower calcite content (40 and 60%).

These outcomes are consistent with those obtained in previous studies, in which the fluorine content was monitored in solid material and in gas samples throughout the kiln [16,17], and can be explained by tile HF emission and adsorption processes during preheating and firing.

3.2.2. *Effect of heating rate*

Firing time was lengthened by 10% in the kiln that produced glazed porcelain tiles (P) in order to reduce production throughput by a similar percentage. This was done by reducing tile speed through the kiln, extending cycle time (cold to cold) from 40 to 44 min, decreasing production throughput from 1.25 to 1.15 kg/s (thus meaning a reduction of 8%).

The results obtained in monitoring the evolution of HF during this change are shown in Fig. 6 and Table 5. Though no great changes could be made in this test owing to industrial constraints, the graph shows that when the heating rate decreased (equivalent to an increase in residence time in the kiln and a drop in production throughput), the in-stack concentration of HF rose slightly. These findings match those of previous laboratory-scale studies in which it was possible to make greater changes [17]. In fast-cycle processes, not all the initial HF content is released at peak firing temperature: HF is released progressively, so that longer residence times at temperatures at which HF is released raise HF emissions. This is because at temperatures above 1000 °C, the crystalline phases in which the fluorine might be retained – fluorite (CaF_2) and cuspidine ($Ca_4Si_2O_7F_2$) – are unstable [16].

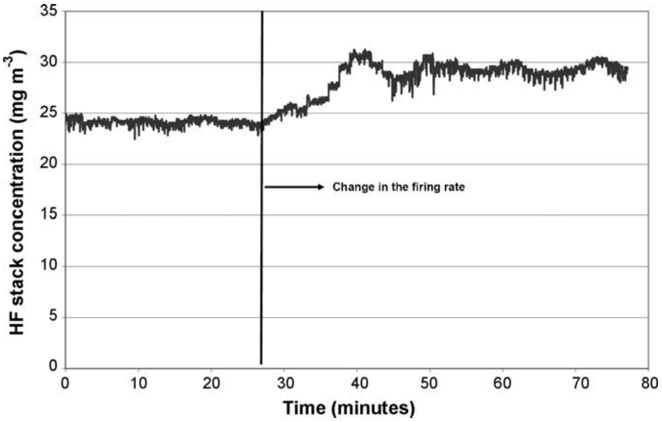

Fig. 6. Evolution of the in-stack concentration of HF during the change in firing rate (body P).

Table 5
Effect of heating rate on in-stack concentrations of HF (body composition P).

Cold to cold cycle (min)	Production throughput (kg s^{-1})	HF concentration (mg m^{-3})	
		Mean	σ
40	1.25	22.2	3.4
44	1.15	24.1	2.1

These findings match industrial experience and are consistent with the results reported by other authors [22–24] in relation to firing cycles, which show that, for a given body composition, the resulting emission factors decrease when faster firing cycles are used. Moreover, the foregoing explains why ceramic tile manufacture by fast single-firing cycles leads to lower fluorine compound emissions than double-firing processes.

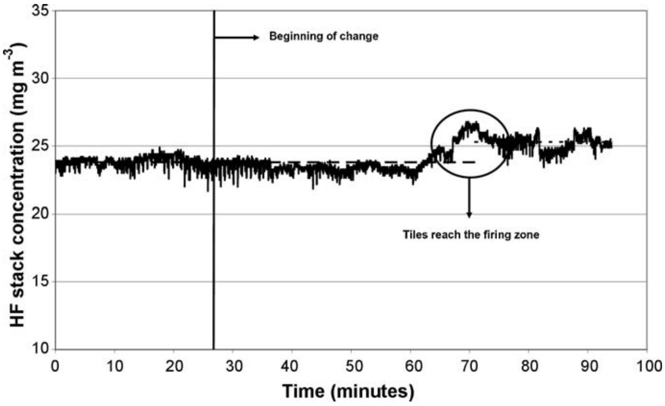

Fig. 7. Evolution of the in-stack concentration of HF during the change in dry bulk density (body P).

Table 6
Effect of dry bulk density on in-stack concentrations of HF (body composition P).

Dry bulk density (kg m^{-3})	HF concentration (mg m^{-3})	
	Mean	σ
2030	23.8	0.7
1945	25.3	0.6

Table 7
Evolution of in-stack concentrations of HF with the introduction of unglazed tiles (body composition A).

Parameter	Value
Mean HF concentration (mg m^{-3})	26.3
Standard deviation (σ) (mg m^{-3})	0.3
Decrease in HF concentration (%)	25
Increase in HF concentration (%)	45

3.2.3. Effect of dry bulk density

An important process variable that can affect HF emissions according to previous laboratory-scale studies is dry bulk tile density, which is directly related to tile porosity. Several experiments were performed on an industrial level to verify these results.

The results obtained in the stack of the kiln producing glazed porcelain tile (P), whose dry bulk density was changed from 2030 to 1945 kg/m^3 (thus involving a reduction of about 4%) by reducing the pressing pressure are presented in Fig. 7 and Table 6. As in previous trials, in order to keep end-product quality steady, no large changes were made. The outcomes indicate that the HF concentrations in the stack rose when tiles with low bulk density reached the kiln firing zone. No changes were detected in HF emissions when the low-density tiles reached the preheating zone. This behaviour is related to the effect of the pressing stage on body microstructure: lower pressing pressure raises body porosity and pore size, while it also reduces pore tortuousness [25]. These effects lead to increased gas permeability of the body, facilitating the movement of HF from within the body to the gaseous phase (kiln environment). Therefore, despite the small change made in tile bulk density, it may be inferred that the overall effect of reducing bulk density raises HF emissions in the firing stage.

3.2.4. Effect of the glaze

Industrial trials were conducted in the three kilns to establish the effect of the presence of a glaze coating on the tile body. In these trials, kilns firing standard glazed tiles were partly fed with unglazed tiles (i.e. tile bodies), the number of unfired tiles being about 10–15% of kiln throughput. The evolution of the HF concentration was monitored in the flue gas emissions (stack) in the three studied kilns, before and after unglazed tiles were fed into the kilns.

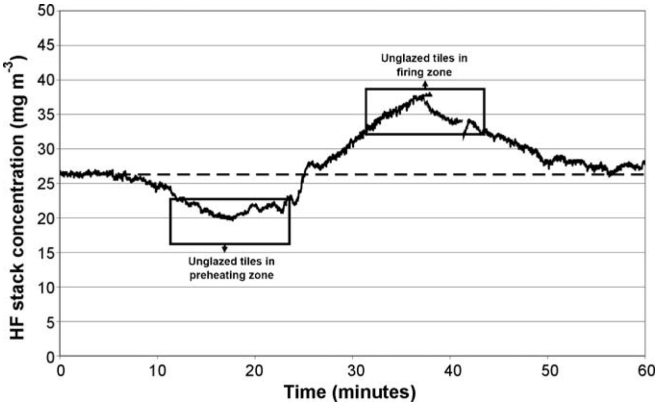

Fig. 8. Evolution of the in-stack concentration of HF with the introduction of unglazed tiles (body A).

Table 8
Effect of the glaze coating.

Body	F content (mg kg^{-1})					
	Glazed tiles			Unglazed tiles		
	Unfired	Fired	Emission	Unfired	Fired	Emission
A	660	560	100	660	470	160
G	630	530	120	630	440	190

The experiments were conducted for A, G, and P bodies. Since the results were qualitatively similar, only the wall tile (A) data, whose variation was the most significant, are presented.

The findings are shown in Fig. 8 and Table 7. The dotted line in Fig. 8 indicates the HF emission when glazed wall tiles are being produced under standard operating conditions. An examination of the figure allows the following to be inferred:

- When unglazed tiles reach the *preheating zone*, the HF concentration recorded in the stack decreases progressively. This reduction may be assigned to the absence of a glaze coating on the tile face, which increases the contact area between the gases and the ceramic body. The HF-rich, counter-current gas stream circulates from the peak temperature zone to the stack. The adsorption process is therefore favoured and the HF content in the gases drops. These results also indicate that HF adsorption by the glaze layer may be considered almost negligible.
- When unglazed tiles reach the *peak temperature zone*, the HF emission is higher than when glazed tiles are fired. This could be due to two effects. First, glazed tiles release less HF at high temperatures because of two possible mechanisms: the glaze can fuse and seal the body, preventing HF emission through the tile's top surface, and/or some HF may dissolve in the glassy phase at high temperature. Secondly, unglazed tiles contain more fluorine (caused by fluorine enrichment in the preheating zone), leading to higher HF emission as a result of the low thermal stability of the fluorine crystalline compounds (CaF_2 and $Ca_4Si_2O_7F_2$) that form in preheating [16].

A number of further experiments were conducted, varying the type of glaze, but no significant differences were found amongst the different glazes. The glazes tested were always of the industrial type, and no changes were made to heighten HF absorption.

In order to confirm the effect of the glaze, fluorine was analysed in unglazed and glazed ceramic tile bodies (A and G bodies) before and after heat treatment, according to the procedure described elsewhere [16,17]. The results are presented in Table 8. They show that the glazed tiles have a higher fluorine content compared with that of the unglazed tiles. This corroborates the results obtained by monitoring the in-stack concentrations of HF: that is, glazed tiles release significantly less HF (approximately 35% less in recorded experiments). Further research needs to be carried out in order to study the mechanisms involved in this emission reduction process.

4. Conclusions

In this study, HF concentrations were measured in the stack flue gases of industrial roller kilns firing different types of ceramic tiles. The following conclusions may be drawn:

- The methodology used in this study with a laser-based, on-line HF analyser allows HF emission behaviour in continuous kilns to be efficiently monitored, because it allows rapid HF measurement when changes are made in the kiln.

- Under standard kiln operating conditions, the HF emissions in industrial ceramic tile kilns fabricating different types of tiles remained very steady with time, only slight fluctuations occurring around a practically constant mean value.
- When the standard firing conditions were modified, the variation in HF emissions was qualitatively similar for the three types of studied tiles (porous red-body wall tiles, red-body stoneware tiles and porcelain tiles).
- Interrupting the tile feed into the kilns produced two effects, depending on the location of the feed gap in the kiln: a feed gap in the preheating zone led to a significant rise in HF emissions as a result of decreased tile HF adsorption; in contrast, a feed gap in the firing zone caused the HF emissions to drop notably, owing to the absence of tiles in the kiln high-temperature zone.
- The study shows that realistic adjustments of certain industrial process variables (dry bulk tile density and heating rate) only lead to a very limited reduction in HF emissions.
- The results indicate, further, that glazing is an effective way of reducing HF emission, probably because of the formation of an impermeable coat by the fusion of glaze components at temperatures above the sealing temperature and/or dissolution at high temperature of some fluorine in the glassy phase. The glazes tested in this study were always of the industrial type, and no modified or special glazes were used. The outcomes encourage further research into the enhancement of the glaze fluorine retention capacity, as a way of reducing the environmental impact of the ceramic process in order to avoid or minimise the use of the end-of-pipe cleaning systems. Therefore, it opens up very interesting new possibilities, since the glazes may be used not only to improve the aesthetic and technical properties of ceramic tiles (or ceramic materials in general), but also to reduce the environmental impact in the firing stage.

Acknowledgements

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