

## Use of coatings to minimise acid emissions during ceramic tile firing

J. García-Ten\*, E. Monfort, M.P. Gómez-Tena, V. Sanz

*Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I, Campus Universitari Riu Sec, 12006 Castellón, Spain*

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### ABSTRACT

The manufacture of traditional ceramic products (ceramic tiles, roof tiles, and bricks) is often associated with the emission of F, Cl, and S compounds during the firing stage. According to the literature, fluorine emissions can be reduced by adding  $\text{CaCO}_3$  to the raw materials mixture used in fabricating these products. However, data available to the authors indicate that this procedure, which has been successfully applied in manufacturing structural ceramics (roof tiles and bricks), is ineffective in ceramic tile manufacture and modifies tile end properties.

This paper examines the possibility of reducing such emissions by applying coatings of alkaline-earth carbonates on to the ceramic tile bottom surface to retain the acid compounds emitted during tile firing. The effectiveness of  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$  coatings for retaining these acid emissions was studied, using the evolved gas analysis (EGA) technique with a TG-DSC-FTIR-QM instrument.

The  $\text{SrCO}_3$  coating was found to provide the greatest retention, showing that  $\text{SO}_2$  and  $\text{HCl}$  were retained more efficiently than  $\text{HF}$ . The presence of fluorides, chlorides, and sulphates of Ca, Sr, and Ba was verified in the respective fired coatings, confirming the existence of chemical reactions between the emitted acid compounds and the coating materials at high temperature.

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### 1. Introduction

The manufacture of traditional ceramic products (ceramic tiles, roof tiles and bricks) is often associated with the emission of fluorine compounds during the firing stage (Strohmeier, 1983; Kolkmeier, 1991; Denissen and Vries, 1998; Doreroğlu and Kara, 2002a, 2002b). As set out in the literature, the fluorine ion replaces  $\text{OH}^-$  groups in the crystalline structure of mica and many other clay minerals (montmorillonite, illite, etc.) (Fabbri, 1992; Reymer and de Jong, 1993), so that fluorine compound emissions usually start when these minerals dehydroxylate at temperatures between 500 and 700 °C (Brosnan, 1992; Galán et al., 2000; Chipera and Bish, 2002). The principal compounds that form are hydrofluoric acid, silicon tetrafluoride and, to a lesser degree, alkaline fluorides in particulate form (whose presence may be considered practically negligible) (Monfort et al., 2004). In the presence of water vapour – a typical situation in industrial combustion kilns – fluorine is mainly released as hydrofluoric acid (Reymer and de Jong, 1993; Monfort et al., 2010a).

One of the procedures described in the literature for reducing fluorine compound emissions involves adding  $\text{CaCO}_3$  to the raw materials mixture used in fabricating such ceramic products

(Denissen and Vries, 1998; Kolkmeier, 1979; Hauck et al., 1992; Schlandt, 1986). These studies show that, when  $\text{HF}$  (which evolves from the pieces in the high temperature zone) travels towards the preheating zone, it reacts with calcite to form  $\text{CaF}_2$ , which is thermally more stable, causing part of the fluorine to be retained in the products. However, data available to the authors indicate that this procedure (successfully applied in the manufacture of structural ceramics such as roof tiles and bricks) is ineffective in ceramic tile manufacture, where firing is much faster (35–90 min as opposed to 35–50 h) and occurs at higher temperatures (1130–1220 °C as opposed to 850–950 °C) (Monfort et al., 2008; Xie et al., 2003). In addition, the introduction of  $\text{CaCO}_3$  into ceramic tile body compositions modifies tile end properties, such as porosity, bending strength, and colour.

The ineffectiveness of  $\text{CaCO}_3$  in reducing fluorine compound emissions during ceramic tile firing is due to the fact that the arising fluorine-containing crystalline species – fluorite ( $\text{CaF}_2$ ) and cuspidine ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ ) – during firing are unstable in a ceramic matrix rich in silicon oxide ( $\text{SiO}_2$ ) and aluminium oxide ( $\text{Al}_2\text{O}_3$ ) at temperatures above 1100 °C (García-Ten et al., 2006). These conditions favour anorthite formation, and cause fluorine emissions to rise above 1100 °C.

In this study it was attempted to enhance the effectiveness of  $\text{CaCO}_3$  in retaining the emitted gaseous fluorine compounds, without the  $\text{CaCO}_3$  modifying tile properties, by applying a  $\text{CaCO}_3$  coating on to the tile bottom surface) (the tile top surface usually

\* Corresponding author. Tel.: +34 964342424; fax: +34 964342425.  
E-mail address: [jgarcia@itc.uji.es](mailto:jgarcia@itc.uji.es) (J. García-Ten).

being glazed, which also reduces gas emissions (Smith, 2004; Sanders and Brosnan, 1995; González et al., 2006; García-Ten et al. 2008a; Monfort et al., 2008). The formation of calcium aluminosilicates, which dissociate the fluorine-retaining crystalline phases, would thus be prevented.

The study also examined the efficiency of tile bottom coatings consisting of other alkaline-earth carbonates in retaining the acid compounds emitted by red-firing ceramic wall tile bodies during heat treatment. The efficiency of CaCO<sub>3</sub>, MgCO<sub>3</sub>, SrCO<sub>3</sub>, and BaCO<sub>3</sub> coatings in retaining tile fluorine, chloride, and sulphur compound emissions was thus determined.

## 2. Experimental

### 2.1. Materials

The study was conducted with an industrial spray-dried powder used in red-firing wall tile manufacture. Table 1 lists the chemical and mineralogical composition of the powder, which contained a mixture of clay minerals with an illitic-kaolinitic structure, calcite, dolomite, and an abundant quantity of quartz. The F, Cl, and S contents are typical of Spanish red-firing wall tile compositions.

The raw materials used to prepare the acid compound-retaining coatings were magnesium, calcium, barium, and strontium carbonates. Certain characteristics of these carbonates are given in Table 2. All samples had a high purity and a similar mean particle size (about 5 µm).

### 2.2. Experimental procedure

An aqueous suspension was prepared with each carbonate, 0.3% carboxymethylcellulose being added to enhance the coating bond strength to the tile and to provide the coating with sufficient mechanical strength. The suspension solids content was 65% by weight; apparent viscosity after a 1-min rest, measured in a Gallenkamp viscometer, was between 150 and 250 cP.

Cylindrical test pieces, 8 mm in diameter and 10 mm thick, were prepared from the industrial spray-dried powder by unidirectional pressing: pressing moisture content was 0.055 kg water/kg dry solids, and pressing pressure was 25 MPa. These test pieces, referenced STD, were then used to prepare the coated specimens. Before the STD pieces were dried, a number of these were respectively coated by spraying with the different carbonate suspensions, a continuous carbonate coating being deposited on the test piece sides and top surface. The references assigned to the coated test pieces were as follows:

**Table 1**  
Chemical and mineralogical composition of the spray-dried powder used.

Oxide	Content (wt%)	Mineral	Content (wt%)
SiO <sub>2</sub>	55.9 ± 0.3	Kaolinite	9
Al <sub>2</sub> O <sub>3</sub>	14.9 ± 0.2	Quartz	36
Fe <sub>2</sub> O <sub>3</sub>	5.02 ± 0.05	Microcline	8
CaO	7.39 ± 0.02	Illite/Muscovite	23
MgO	1.78 ± 0.02	Hematites	3
Na <sub>2</sub> O	0.45 ± 0.05	Calcite	7
K <sub>2</sub> O	3.58 ± 0.02	Dolomite	7
TiO <sub>2</sub>	0.64 ± 0.03	Chlorite	5
MnO	0.04 ± 0.01	Others	2
P <sub>2</sub> O <sub>5</sub>	0.13 ± 0.02		
L.O.I. (1000 °C)	10.1 ± 0.2		
F	735 ± 29 mg/kg		
Cl	280 ± 15 mg/kg		
S	320 ± 23 mg/kg		

**Table 2**  
Test carbonate characteristics.

Raw material	Purity (%)	d <sub>50</sub> (µm)	F/Cl/S (mg/kg)
MgCO <sub>3</sub>	94	6	85/194/55
CaCO <sub>3</sub>	98	4	138/278/45
BaCO <sub>3</sub>	99	7	70/206/681
SrCO <sub>3</sub>	98	5	80/202/807

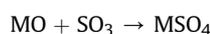
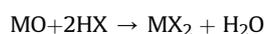
STD + Mg: STD piece coated with MgCO<sub>3</sub>

STD + Ca: STD piece coated with CaCO<sub>3</sub>

STD + Ba: STD piece coated with BaCO<sub>3</sub>

STD + Sr: STD piece coated with SrCO<sub>3</sub>

The deposited coating consisted of 0.045 ± 0.010 g, this quantity being chosen so that there would be excess alkaline-earth oxide with relation to the emitted HF, HCl and SO<sub>2</sub> in accordance with the stoichiometry given by the following simultaneous reactions:



Where: M: Mg, Ca, Sr, and Ba; and X: Cl and F

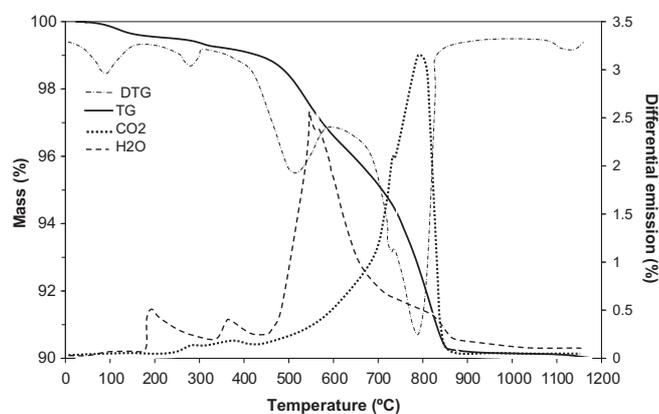
All test pieces were dried to constant weight in an oven at 110 °C before the emission tests. These were conducted in a NETZSCH STA 449 C Jupiter® TG-DSC instrument coupled to a QMS 403 Aëolos® quadrupole mass spectrometer and to a BRUKER TGA-IR Fourier transform infrared (FTIR) spectrometer. The test conditions were as follows: peak temperature: 1180 °C; heating rate: 10 °C/min; dynamic air atmosphere with a flow rate of 50 ml/min, and protection gas: helium with a flow rate of 25 ml/min.

## 3. Results

### 3.1. Determination of the emitted compounds during thermal treatment

The thermogravimetric analysis of the (uncoated) STD piece, which exhibited a series of weight losses related to the different transformations occurring during thermal treatment, is shown in Fig. 1. The temperature ranges in which each transformation took place, with the related weight loss, are detailed in Table 3.

Fig. 1 also shows the evolution of the major gaseous species emitted during thermal treatment, expressed as a differential percentage; the evolution of the minor species, expressed in mg/kg, is displayed in Fig. 2. The FTIR technique was used to analyse the



**Fig. 1.** Thermogravimetric analysis and H<sub>2</sub>O and CO<sub>2</sub> emissions of the (uncoated) STD test piece.

**Table 3**  
Interpretation of Figs. 1 and 2.

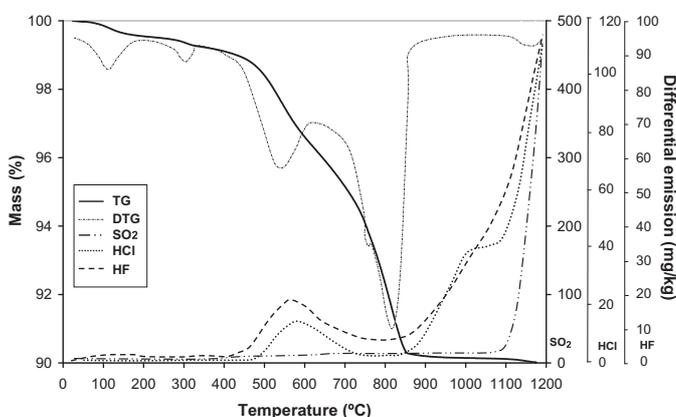
T (°C) <sup>a</sup>	Weight loss (%)	Peak emission (°C) of the compounds	Origin
25–200	0.45	140 °C	(H <sub>2</sub> O) Loss of moisture and adsorbed (interlaminar) water
200–400	0.44	210 °C, 385 °C 320 °C, 400 °C	(H <sub>2</sub> O) Decomposition of iron and aluminium hydroxides and combustion of organic matter (CO <sub>2</sub> )
400–650	3.19	565 °C 565 °C 570 °C	(H <sub>2</sub> O) Kaolinite dehydroxylation and chlorite dehydration (HF) (HCl)
650–900	5.72	825 °C 810 °C	(CO <sub>2</sub> ) Calcite and dolomite decomposition and removal of the water of constitution of micas and illites (H <sub>2</sub> O)
900–1180	0.19	945 °C, 1180 °C 930 °C, 1135 °C 1155 °C	(HF) Decomposition of micas, illites, chlorites, and sulphates (HCl) (SO <sub>2</sub> )

<sup>a</sup> The temperature ranges were established by assuming that the different transformations did not overlap.

emitted fluorine acid species; the sulphur and chlorine acid emissions were analysed by mass spectrometry. The other emissions, such as carbon dioxide and water, were also recorded by mass spectrometry. The results obtained indicate that fluorine was mainly emitted as HF, sulphur as SO<sub>2</sub>, and chlorine as HCl. No SiF<sub>4</sub> or SO<sub>3</sub> was detected.

The gaseous species emitted in the largest quantities were H<sub>2</sub>O and CO<sub>2</sub>. H<sub>2</sub>O displayed emission peaks at 210, 385, and 565 °C corresponding, respectively, to aluminium and iron hydroxide decomposition, combustion of the organic matter, and clay mineral dehydroxylation. The CO<sub>2</sub> emission began to become significant above 300 °C, owing to the combustion of organic matter, and peaked at 820 °C, at which calcite decomposition occurred. A secondary peak appeared at 750 °C, corresponding to dolomite decomposition.

Fig. 2 shows the acid compound and sulphur oxides emissions. The HF emission displayed two emission peaks: the first began at about 450 °C, coinciding with clay mineral dehydroxylation, and continued up to about 700 °C. A second HF emission occurred above about 850 °C and increased progressively up to the peak test temperature. The fluorine present in these compositions replaced the OH<sup>-</sup> groups in the octahedral sheets of some clay minerals. Chipera and Bish (2002) point out that fluorine in kaolinite behaves in a similar manner to hydroxyl, while fluorine in smectites and



**Fig. 2.** Thermogravimetric analysis and HF, SO<sub>2</sub>, and HCl emissions of the (uncoated) STD test piece.

illites is significantly stabilised in these structures. It may therefore be inferred that the first fluorine emission came from kaolinite and the second from illite.

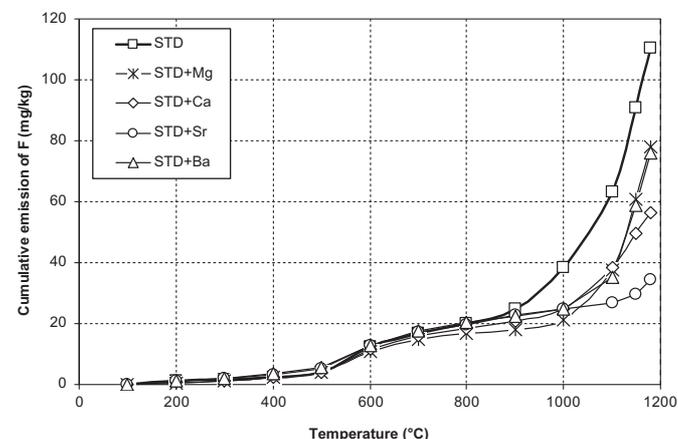
The SO<sub>2</sub> emission occurred at higher temperatures, starting at 1110 °C, and increased progressively up to the peak test temperature (1180 °C). The absence of any SO<sub>2</sub> emission between 400 and 550 °C indicates that the STD test piece contained no pyrite: the sulphur-contributing minerals are therefore mainly sulphates (Sanders and Brosnan, 1995).

The STD test piece exhibited a small HCl emission between 500 and 700 °C, coinciding with clay mineral dehydroxylation. This could be due to the presence of chloride in the clay mineral crystal structure, released jointly with the hydroxyls. A second HCl emission occurred above 850 °C, coinciding with the second HF emission, which increased progressively with temperature. Studies on emissions in fired-clay products report that the HCl emissions are small, owing to the low chloride content usually found in clays (contributed for example by halite) (Sanders and Brosnan, 1995; González et al., 2006). In the compositions used for ceramic tile manufacture by semi-dry pressing, however, the HCl emissions are of greater importance, owing to the chloride contributed by the water used in wet milling such compositions (García-Ten et al., 2008b), in particular in water that has previously undergone cleaning and/or disinfection treatments.

### 3.2. Influence of the coating on the acid compound emission

The evolution of the cumulative emission of HF, expressed as F, with firing temperature of test pieces coated with the different carbonates is presented in Fig. 3. The figure shows that the coatings were unable to retain the HF emitted between 500 and 650 °C, possibly because the carbonates making up the coatings had not yet decomposed at these temperatures, thus reducing their ability to react with the emitted HF.

The second HF emission began at 800 °C in the (uncoated) STD piece. In the coated test pieces, however, the beginning of the second HF emission was delayed by 200 °C, indicating that the coatings were very effective in reducing the HF emission up to 1000 °C. This result is consistent with the findings reported in studies on fixing HF in fired-clay products, in which CaCO<sub>3</sub> was added to the body composition and the firing temperature usually did not exceed 1000 °C (Denissen and Vries, 1998; Kolkmeier, 1979; Hauck et al., 1992; Schlandt, 1986). This increase in HF-fixing efficiency could stem from the fact that, at these temperatures, the carbonates had already begun to decompose, facilitating the reaction between HF and the alkaline-earth oxides.



**Fig. 3.** Cumulative emissions of fluorine of the coated and uncoated test pieces.

The SrCO<sub>3</sub> coating, in which the second HF emission was delayed up to 1100 °C, is particularly to be noted. At higher temperatures, the emission increased slightly, indicating that the arising crystalline species (SrF<sub>2</sub>, as will be observed below) began to destabilise.

The evolution of the HF emissions in the test pieces coated with MgCO<sub>3</sub> and BaCO<sub>3</sub> was very similar, and was characterised by a rapid increase in HF emissions above 1000 °C. The test piece with the CaCO<sub>3</sub> coating behaved analogously up to 1100 °C, though the HF emission was not as high at higher temperatures.

The SO<sub>2</sub> emission began at 1100 °C in all test pieces, owing to the absence of sulphur compounds in the spray-dried powder used. Fig. 4 therefore only shows the cumulative emissions (expressed as S) at temperatures above 1000 °C. It may be observed that, except for the MgCO<sub>3</sub> coating (which exhibits a moderate SO<sub>2</sub>-retention efficiency), the other coatings are able to retain practically all the emitted SO<sub>2</sub>.

Fig. 5 depicts the cumulative emissions of HCl (expressed as Cl) above 500 °C. The main effect of the coatings was to delay the second HCl emission, which began at 900 °C. The MgCO<sub>3</sub>, BaCO<sub>3</sub>, and SrCO<sub>3</sub> coatings delayed the HCl emissions up to 1100 °C. Beyond this temperature, the HCl emissions increased slightly in the pieces coated with SrCO<sub>3</sub> and BaCO<sub>3</sub>, whereas the increase was very pronounced in the MgCO<sub>3</sub>-coated piece. The CaCO<sub>3</sub> coating, which exhibited high HCl retention at low temperatures, did not appear to be as effective at temperatures above 900 °C since the HCl emissions increased.

### 3.3. Coating efficiency in acid compound retention

The HF, SO<sub>2</sub>, and HCl emissions at 1180 °C of the (uncoated) STD test piece, expressed as F, S, and Cl, respectively, are detailed in Table 4. The STD piece emitted 15% F under the test conditions. This F emission was slightly lower than the average F emission reported for wall tiles fired in industrial roller kilns, which is about 20% (Monfort et al., 2008). The lower value obtained in the laboratory could be due to the presence of water vapour in industrial kilns, which favours HF emissions (Reymer and de Jong, 1993). Tile HF adsorption in industrial roller kilns may be assumed not to have a significant influence on the observed difference, since it has been verified that all the adsorbed HF is subsequently emitted at high temperature (Monfort et al., 2008).

The Cl emissions were much higher (83%) and, according to our experience, close to those observed in industrial kilns, which are usually higher than 90% (Galán et al., 2002; IPTS, 2006; Monfort et al., 2010b).

The S emission was close to 80%, in contrast to the S emissions observed in industrial kilns, which are usually much lower (10–20%)

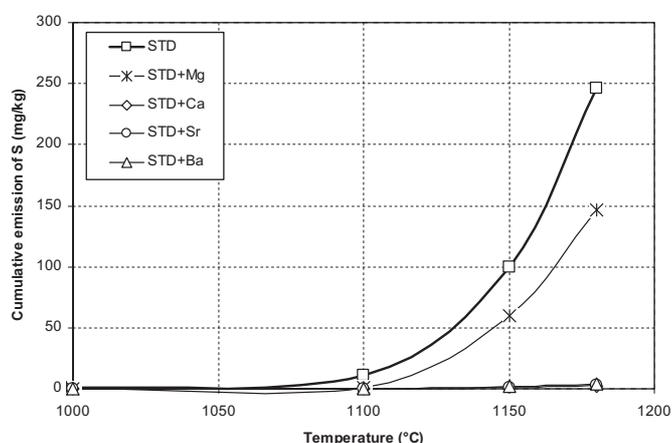


Fig. 4. Cumulative emissions of sulphur of the coated and uncoated test pieces.

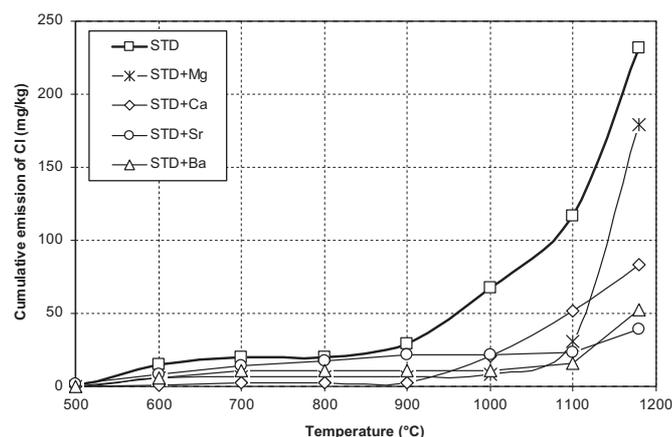


Fig. 5. Cumulative emissions of chlorine of the coated and uncoated test pieces.

(IPTS, 2006; Monfort et al., 2010). This difference stems from the fact that, in those kilns, the tiles advance counter-current to the combustion gases, which encourages adsorption during tile pre-heating in the kiln of a large part of the sulphur compounds that are emitted at high temperatures (Genel et al., 2001). The absence of adsorption phenomena in the laboratory tests explains the greater emission observed on a laboratory scale (García-Ten et al., 2008a, 2008b).

The reduction in F, S, and Cl compound emissions at 1180 °C of the coated test pieces, compared with those of the uncoated (STD) test piece, are presented in Fig. 6. The figure shows that practically all the tested coatings had a certain effectiveness in reducing these acid compound emissions.

The reduction in the F compound emissions by the coatings, with respect to those of the STD piece, ranged from 25% to 70%, depending on the carbonate involved. The most efficient F-retaining coating was the SrCO<sub>3</sub> coating, which reduced the F emissions by almost 70%. The efficiency of the CaCO<sub>3</sub>, BaCO<sub>3</sub> and MgCO<sub>3</sub> coatings in reducing the F emission was less significant, accounting for 45, 30, and 25% reduction, respectively.

The different test coatings also retained Cl acid compounds, the emission reduction ranging from 55 to 85%, except for the MgCO<sub>3</sub> coating which displayed a scarce Cl emission-retention capability, with relation to the Cl emission of the STD piece. The SrCO<sub>3</sub> coating was highly efficient and reduced these emissions by 85%. The CaCO<sub>3</sub> coating reduced the Cl emissions by 65%, while the BaCO<sub>3</sub> coating exhibited a lower retention capability, reducing the Cl emissions by 55%.

The CaCO<sub>3</sub>, SrCO<sub>3</sub>, and BaCO<sub>3</sub> coatings provided high S acid compound retention efficiencies. The test piece emissions ranged from 77% for the (uncoated) STD piece to below 10% for the coated pieces, the latter entailing a 95% reduction in S emission. The MgCO<sub>3</sub> coating was much less efficient than the other carbonate coatings, reducing the S emission by 35%.

These results indicate that, except for the MgCO<sub>3</sub> coating (which provided acid compound emission reductions below 35%), the other studied carbonates displayed high acid compound retention

Table 4

F, Cl, and S initial contents and emissions at 1180 °C of the (uncoated) STD test piece.

	Initial content (mg/kg)	Emission at 1180 °C	
		(mg/kg)	(%)
F	735	110	15
Cl	280	232	83
S	320	246	77

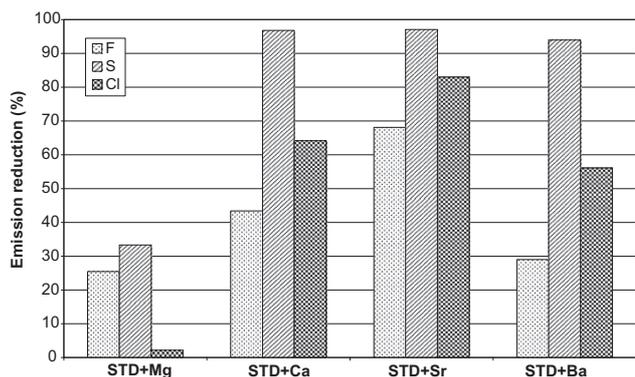


Fig. 6. Reduction of the F, S, and Cl compound emissions by the test coatings with relation to the (uncoated) STD piece emissions.

capabilities during heat treatment of a standard red-firing wall tile body. The  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$  coatings were particularly efficient in retaining S compounds, with emission reductions exceeding 90%. They also displayed high Cl compound retention capabilities, especially when  $\text{CaCO}_3$  and  $\text{SrCO}_3$  were used, with reductions ranging from 65% to 85%. The fluorine compounds were the most difficult to retain, with F emission reductions between 30 and 70%.

The retention mechanism of the emitted acid compounds is based on adsorption, with or without a chemical reaction, of these compounds on to the coating materials (alkaline-earth carbonates) when the compounds travel through the coating. The main compound emissions began at temperatures above 900 °C (Fig. 2), at which the carbonates had already decomposed. As a result, the main coating constituents at high temperature were MgO, CaO, BaO, and SrO. The presence of HF and HCl emissions at low temperatures (450–700 °C) could explain the lower efficiency of the tested coatings to retain these acid compounds.

With a view to determining the existence of a chemical reaction in the coatings, the fired coatings with the highest acid compound retention efficiencies were analysed by X-ray diffraction (XRD). To perform the XRD analysis, the entire coating was separated from the substrate with a stainless steel blade, trying not to draw along part of the substrate. Since only a small quantity of coating had been applied on to each test piece, the coating powder was randomly deposited on a silicon monocrystal in the most uniform possible way for the XRD analysis.

The results obtained are presented in Fig. 7. The material used to prepare the coatings and the crystalline phases detected in the fired

Table 5

Crystalline species detected by XRD in the fired test coatings.

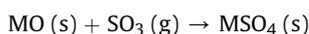
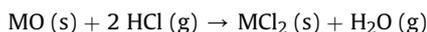
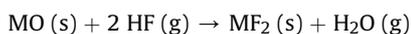
Coating	Crystalline phases with F, Cl, or S	Other detected crystalline phases
$\text{CaCO}_3$	$\text{CaF}_2$ , $\text{CaCl}_2$ , $\text{CaSO}_4$	$\text{Ca(OH)}_2$ ,
$\text{BaCO}_3$	$\text{BaF}_2$ , $\text{BaCl}_2$ , $\text{BaSO}_4$	$\text{BaAl}_2\text{Si}_2\text{O}_8$ , $\text{Ba}_2\text{SiO}_4$
$\text{SrCO}_3$	$\text{SrF}_2$ , $\text{SrSO}_4$	$\text{Sr(Al}_2\text{Si}_2\text{O}_8)$

coatings are detailed in Table 5. The presence of crystalline phases containing F, Cl, and S, involving mainly fluorides, chlorides, and sulphates, was observed in all fired test coatings. Usovite, a more complex crystalline phase with the formula  $\text{Ba}_2\text{Mg(AlF}_6)_2$ , was also detected in the fired  $\text{BaCO}_3$  coating. These results confirm the existence of chemical reactions between the emitted acid compounds and the coating materials. Since there were insufficient quantities of the coatings to obtain continuous homogeneous layers of powder in the diffractometer sample holder, the crystalline species that had formed during thermal treatment could not be quantified.

The presence of portlandite ( $\text{Ca(OH)}_2$ ) and vaterite ( $\text{CaCO}_3$ ) was also detected in the fired  $\text{CaCO}_3$  coating, which indicates that not all the CaO present had reacted. The unreacted CaO hydrated in the ambient air, initially forming  $\text{Ca(OH)}_2$ , which then carbonated giving rise to  $\text{CaCO}_3$ . These types of crystalline species were not observed in the fired  $\text{SrCO}_3$  and  $\text{BaCO}_3$  coatings.

The presence of barium and strontium silicates and aluminosilicates, which must come from the coating–tile interface, was also detected.

The ability of the different coatings to retain F, Cl, and S acid compounds depends on thermodynamic factors (formation of new crystalline phases and thermal stability of these phases at high temperature) and on chemical reaction kinetics. To determine the thermodynamic stability of the arising phases, the Gibbs energy of fluoride, chloride, and sulphate formation from alkaline-earth metal oxides (where M = Mg, Ca, Ba, and Sr) was calculated, based on the following reaction schemes:



The data used in the calculations were drawn from the literature (NIST, 2008). By way of example, Fig. 8 shows the evolution of the variation of the Gibbs function of the fluoride formation reactions with temperature. The negative values of  $\Delta G^0$  indicate that all the fluoride formation reactions considered tended, thermodynamically, to unfold over the entire range of working temperatures. In addition, the higher the atomic number of the alkaline-earth element, the greater this trend became, which explains the results obtained in Fig. 6 in which the fluorine retention capability increased in the order  $\text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3$ . The  $\text{BaCO}_3$  coating did not follow this trend, indicating that there must be other factors, beside its thermodynamic properties, which influenced the unfolding of the chemical reaction.

The same trend was also observed when the values of  $\Delta G^0$  for the chloride and sulphate formation reactions were plotted. The values of the reduction in the  $\text{SO}_2$  emissions displayed in Fig. 6 matched the values of  $\Delta G^0$ , though there was a great difference between the retention provided by  $\text{MgCO}_3$  (35%) and that provided by the other carbonates (>90%). With regard to the HCl retention, the HCl emission reduction also matched the values of  $\Delta G^0$ , except for the  $\text{BaCO}_3$  coating, which presented a lower value than expected.

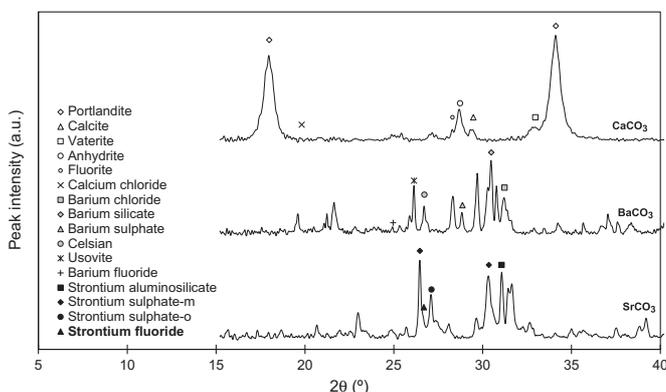


Fig. 7. Diffractograms of the fired test coatings (being a.u.: arbitrary units).

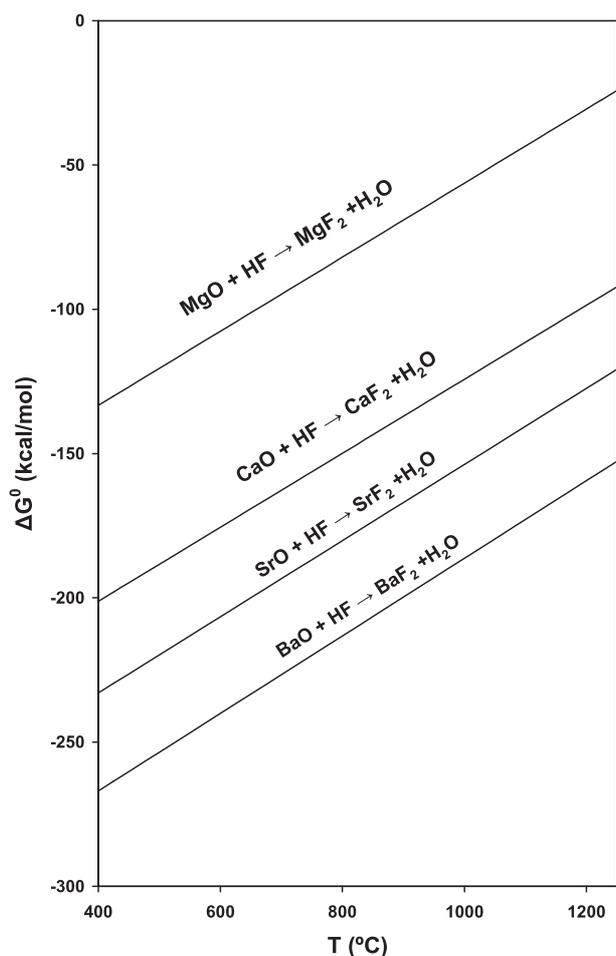


Fig. 8.  $\Delta G^0$  of the fluoride formation reactions as a function of temperature.

#### 4. Conclusions

The evolution with temperature of the acid compounds that are emitted during heat treatment of red-firing ceramic wall tile bodies and the effectiveness of using coatings of alkaline-earth carbonates ( $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$ ) to minimise such emissions were examined in this study. The study allows the following conclusions to be drawn:

- The emitted acid compounds were HF, HCl, and  $\text{SO}_2$ . No  $\text{SiF}_4$  or  $\text{SO}_3$  was detected in the tests, in contrast to what has been reported in the literature.
- HF and HCl were emitted in two temperature ranges: the first emission taking place at about 600 °C and the second starting at 850 °C. In the case of HF, the first emission was related to kaolinite dehydroxylation and second to the fluorine present in the illite structure.
- The  $\text{SO}_2$  emission began at higher temperatures, namely 1080 °C, and increased progressively with heat treatment temperature.
- The emissions measured in the laboratory were similar to those found in industrial practice, except for  $\text{SO}_2$ , for which much lower values are detected in industry due to  $\text{SO}_2$  absorption by the unfired tiles located in the preheating zone in industrial roller kilns.
- The application, respectively, of  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$  coatings significantly reduced these emissions. The emission reduction was particularly high for  $\text{SO}_2$ , though it was less effective for HF.

- After the tile bodies had been fired, the coatings exhibited various phases, including fluoride, chloride, and sulphate phases of Sr, Ba, and Ca, indicating that one of the acid compound retention mechanisms was chemical reaction of the emitted gaseous species with the coating. However, this retention might also have taken place by adsorption of these compounds on to the particles in the coating, an issue that it was not possible to confirm in this study.
- The calculation of the variation of the Gibbs function of the fluoride and sulphate formation reactions indicated that the thermodynamic trend for these reactions to unfold increased with the atomic number of the alkaline-earth elements. The  $\Delta G^0$  values enable the retention capability of the different coatings, except that of the  $\text{BaCO}_3$  coating, to be explained. This discrepancy could stem from the fact that coating emission-retention efficiencies also depend on other characteristics, such as coating specific surface area and porosity, which influence the reaction kinetics, or the formation of barium aluminosilicates of high thermodynamic stability, possibly favoured by the fluxing effect of  $\text{BaCO}_3$ , which could interfere the acid compound retention.
- At present, coatings (called roller engobes) are being applied on to the bottom surface of ceramic tiles to minimise tile contact with the kiln rollers conveying the tiles. It would appear feasible, therefore, to modify the composition of these coatings with the additional purpose of retaining the emitted acid compounds. This approach would have the advantage, compared with the methods that incorporate admixtures into the tile body composition, of not altering tile technical and aesthetic properties.

Further laboratory tests are planned to study the possible degradation of ceramic rollers in kilns by coating components. Pilot plant tests will subsequently be conducted in an industrial roller kiln to determine the quantity of coating that needs to be applied to reduce emissions below current limits and, thus, enable the economic implications of this procedure to be assessed.

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