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Influence of calcite content on fluorine compound emissions during ceramic tile firing

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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. According to the literature such emissions can be reduced by adding $CaCO_3$ 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. The present study has sought to establish why the $CaCO_3$ addition fails to reduce fluorine compound emissions during the ceramic tile firing stage. The study has thus determined the influence of $CaCO_3$ content on the evolution of the crystalline phases with firing temperature in a typical floor tile composition to which additions of CaF_2 were made; additions of BaF_2 and SrF_2 were also made to this floor tile body, and the thermal stability of these three fluoride compounds was studied. The study shows that the effectiveness of $CaCO_3$ in reducing fluorine compound emissions in roof tile and brick manufacture is due to the relatively low firing temperature (850-1000 °C) involved, which enables part of the CaF_2 to be retained in the pieces, and to the formation of cuspidine, which is stable up to 1050 °C. At higher temperatures (ceramic tiles are typically fired at temperatures of 1100-1200 °C), the fluorine-containing crystalline species (fluorite and cuspidine) are unstable, causing fluorine compound emissions to rise.

Key words: tile, fluorine, emission, calcite.

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 [1-3]. As set out in the literature, the fluorine ion replaces OH^- groups in the crystalline structure of mica and many other clay minerals (montmorillonite, illite, etc.) [4, 5], so that fluorine compound emissions usually start when these minerals dehydroxylate at temperatures between 500 and 700 °C [6-8]. 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) [9]. In the presence of water vapour – a typical situation in industrial combustion kilns – fluorine is mainly released as hydrofluoric acid [5].

One of the procedures described in the literature for reducing fluorine compound emissions involves adding $CaCO_3$ to the raw materials mixture used in fabricating these ceramic products [3, 10-12]. These studies show that when HF (which evolves from the pieces in the high temperature zone) travels towards the preheating zone, it reacts with calcite to form CaF_2, which is thermally more stable, causing part of the fluorine to be retained in the pieces. 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 (35-60 minutes as opposed to 35-50 h) and occurs at higher temperatures (1100-1200 °C as opposed to 850-950 °C). The ineffectiveness of $CaCO_3$ in reducing fluorine compound emissions during ceramic tile firing is evidenced by the typical emission values in kilns that process ceramic tiles with different $CaCO_3$ contents. Thus, the usual emission values in roller kilns that fire glazed stoneware (with $CaCO_3$ contents below 4.0%) range from 25 to 40 mg HF/Nm^3, which are similar to the values found in kilns that fire wall tiles (with $CaCO_3$ contents of 12-14%).

The present study seeks to establish why $CaCO_3$ is so ineffective in diminishing fluorine compound emissions, by examining the thermal stability of CaF_2 in a ceramic matrix whose $CaCO_3$ content is modified. The stability of BaF_2 and SrF_2 in this ceramic composition has also been studied, in order to determine the effectiveness of these three fluorides in fixing fluorine in the fired pieces.

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Table 1. Chemical composition of the GR body

Oxide	Content (wt%)
SiO_2	64.0
Al_2O_3	17.5
Fe_2O_3	6.0
CaO	1.1
MgO	0.8
Na_2O	0.4
K_2O	3.3
LOI	5.9
F	590 ppm

Experimental

Ceramic tile body compositions contain very little fluorine (500-700 ppm) [13, 14]. This prevents using X-ray diffraction (XRD) for monitoring the fluoridated crystalline phases that form during the firing stage. Mixtures have therefore been used in this study, obtained by adding CaF_2, BaF_2 and SrF_2 to a typical ceramic floor tile composition.

Materials

The study has been conducted using analytical grade (> 99% purity) CaF_2, BaF_2 and SrF_2. The floor tile composition used, referenced GR, is a typical industrial composition for manufacturing red-firing glazed stoneware bodies, and contains 1.1% CaO from the impurities (carbonates) in the red-firing clays. The chemical composition of the GR body is set out in Table 1.

Experimental procedure

– Test specimen preparation

To conduct the study, the different fluorides were mixed with the GR body in a tungsten carbide ring mill. The resulting mixtures were used to form cylindrical test specimens, 4 cm in diameter and 7 mm thick, by uniaxial pressing. The pressing variables applied were similar to those used in industrial practice to form ceramic tile bodies (powder moisture content of 0.055 kg water/kg dry solid and pressing pressure of 25 MPa). The test specimens obtained were dried in an electric oven at 110 °C and subsequently thermally treated at different peak temperatures, simulating industrial firing cycles, in an electric laboratory kiln with static air atmosphere. The heating rate was 25 °C/minute and the dwell time at peak temperature was 6.0 minute. Cooling was by forced air convection.

– Determination of crystalline phases

The crystalline phases were determined by X-ray diffraction (XRD) of the powder samples, with a PHILIPS PW 1840 diffractometer. The test conditions were as follows:

- Cu tube
- Use of monochromator
- 40 kV, 40 mA
- Step size: 0.01 (2θ)
- Acquisition time: 1s
- Slit: 0.2 mm

Results

CaF_2, BaF_2 and SrF_2 stability in a ceramic matrix during thermal treatment

A number of tests were conducted first to determine the XRD detection limit (minimum detectable quantity) and quantitation limit (minimum quantity that provides a signal which can be quantified by calculating the peak area) of the test fluorine compounds (CaF_2, BaF_2 and SrF_2) in a ceramic matrix.

For this, compositions were prepared by adding 0.5%, 1.0% and 5.0% by weight, respectively, of the test fluorides to the GR body. The maximum intensity peak of each fluoride was then recorded, which was not overlapped with reflections of other possible crystalline compounds (quartz, anorthite, hematite, etc.) present in the fired pieces.

The selected measurement angle and crystalline spacing for each compound are detailed in Table 2.

The diffractograms obtained for these compositions exhibit similar trends. As an example, Fig. 1 shows the region of the diffractogram corresponding to the CaF_2 maximum intensity peak for the GR composition with the CaF_2 additions. The diffractograms of the three test fluorides indicate that very good signals are obtained with 5% additions. The fluorides of the alkaline-earth cations can also be detected and quantified at considerably lower percentages, since they display quite well-defined peaks without notable interferences.

These results allowed establishing the detection limits (DLs) and quantitation limits (QLs) for the test fluorides in the GR composition (Table 3). Thus, in these compositions, SrF_2 can be detected and quantified at lower concentrations, whereas a larger quantity of BaF_2 is required for detection and quantitation. In view of these values, since the fluorine present in this type of composition (500-700 ppm) does not allow formation of fluoride concentrations above the QLs, the study was conducted with mixtures obtained by adding CaF_2, BaF_2 and SrF_2 respectively to the GR body.

After the DLs and QLs had been established, CaF_2, BaF_2 and SrF_2 stability in the ceramic matrix during firing was determined. This was done by adding 1% and 5% by weight, respectively, of these fluorides to the GR composition, monitoring the maximum intensity peak of each fluoride (Table 2) with maximum thermal treatment temperature. These results were compared with those obtained when pure fluorides were tested.

Table 2. Measurement angle and crystalline spacing for each test fluoride

Compound	Measurement angle 2θ (º)	Crystalline spacing d (Å)
CaF_2	47.00	1.932
BaF_2	41.13	2.193
SrF_2	44.12	2.051

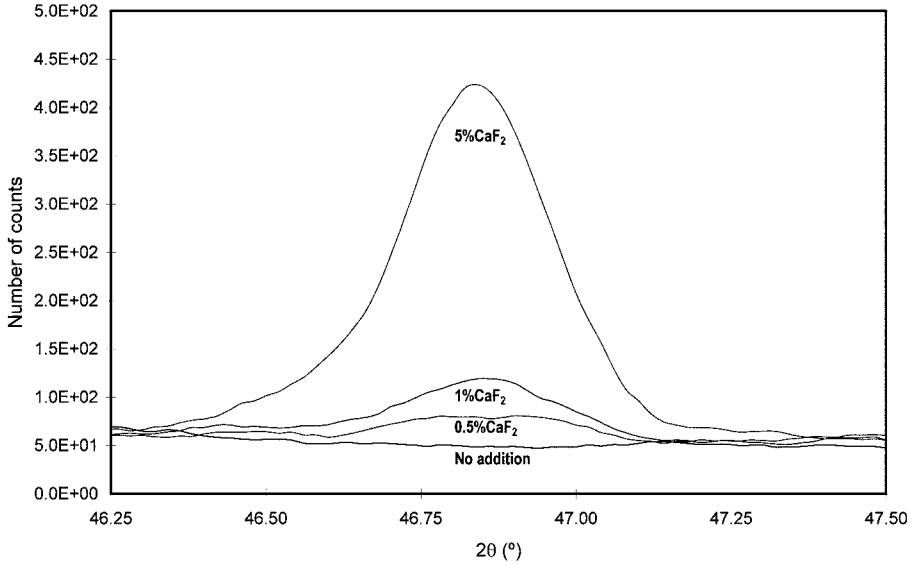

Fig. 1. Signal of the maximum intensity peak of calcium fluoride with increasing additions of CaF_2 to the GR body.

Table 3. Detection limits (DLs) and quantitation limits (QLs) of the different fluorides in the GR body

Compound	DL (% by weight)	QL (% by weight)
CaF_2	0.20	0.25
BaF_2	0.25	0.50
SrF_2	0.15	0.20

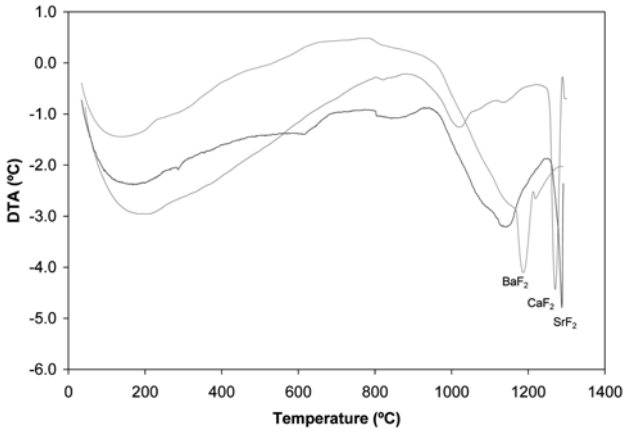

Fig. 2. Differential thermal analysis (DTA) of CaF_2, BaF_2 and SrF_2.

Figure 2 and 3 show the differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the pure calcium, barium and strontium fluorides. The graphs show that these fluorides are thermally stable up to 910 ºC, 960 °C and 960 °C, respectively, after which an endothermal tendency develops until they reach their respective melting temperatures at 1260 ºC, 1190 °C and 1290 °C (Fig. 2). In view of these findings and the fact that the industrial peak firing temperature of the GR body is around 1140 °C, the GR compositions with 1% and 5% additions of the fluorides were heat treated at

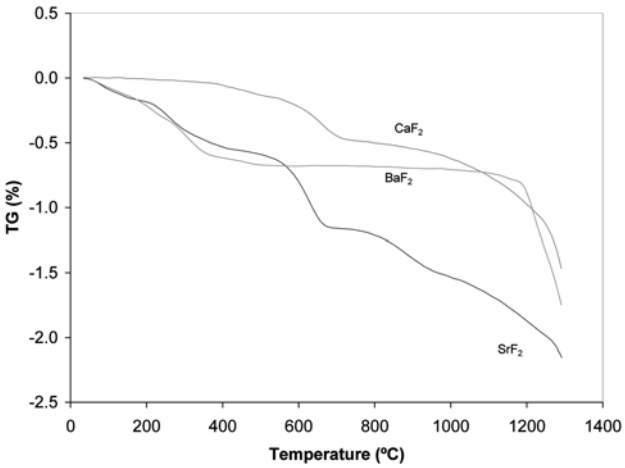

Fig. 3. Thermogravimetric analysis (TG) of CaF_2, BaF_2 and SrF_2.

peak temperatures of 950 °C, 1000 °C, 1100 °C and 1150 °C, simulating the industrial firing cycles.

Figure 4, 5 and 6 depict the diffractograms corresponding to the series of tests in which 5% by weight of each fluoride was added. In order to determine the respective fluoride concentrations in the fired pieces, the area of the maximum intensity peak (Table 2) obtained in each heat-treated sample was compared with the peak area obtained in the green samples. These data are set out in Table 4.

The results obtained for CaF_2 indicate that even at temperatures below 950 ºC an important part of the initial CaF_2 addition is lost, making monitoring by XRD unfeasible in the compositions with 1% CaF_2 additions. When 5% was added, half the CaF_2 content had disappeared at 950 ºC. These results are in contrast to those obtained for pure CaF_2, which is stable up to 910 °C. At higher temperatures the CaF_2 content diminishes progressively up to 1100 ºC, at which the presence of CaF_2 is

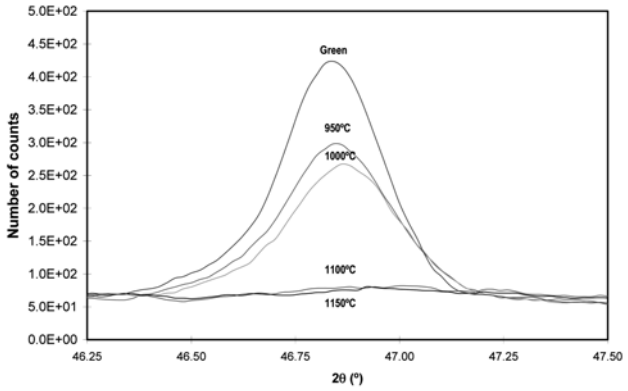

Fig. 4. Variation of the maximum intensity peak signal of CaF_2 with temperature.

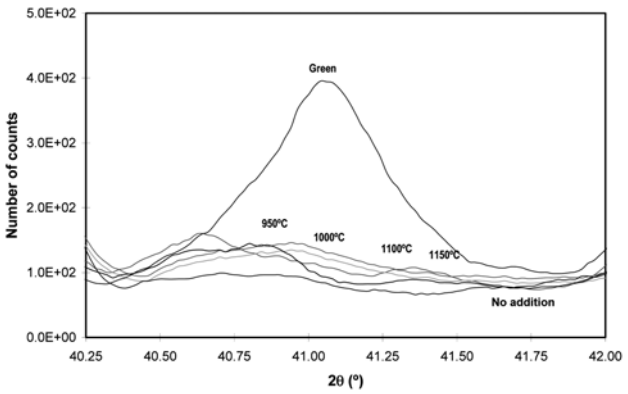

Fig. 5. Variation of the maximum intensity peak signal of BaF_2 with temperature.

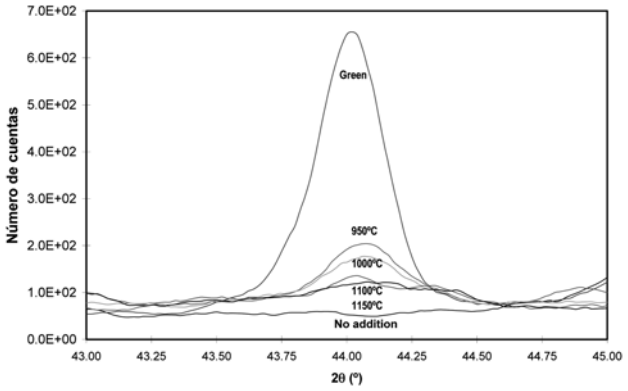

Fig. 6. Variation of the maximum intensity peak signal of SrF_2 with temperature.

hardly 5% of the original addition.

Although BaF_2 is one of the thermally most stable fluorides when found in isolation (even more so than CaF_2), the BaF_2 content decreased even further than that of CaF_2. The BaF_2 content with temperature could, therefore, not be monitored for the 1% BaF_2 addition. In the 5% BaF_2 additions, only 25% of the initial BaF_2 was left at 950 ºC, and BaF_2 could no longer be quantified at 1100 ºC.

The SrF_2 results are similar to those of BaF_2. Thus, the 1% SrF_2 additions could not be monitored; in the 5% additions the SrF_2 content diminished appreciably at 950 °C. When the temperature was raised further, SrF_2 decreased progressively up to 1150 °C, at which it could no longer be quantified.

Table 4. CaF_2, BaF_2 and SrF_2 content in the GR body after thermal treatment at different temperatures

Compound	Addition (wt%)	Fluoride content (wt%)			
		950ºC	1000ºC	1100ºC	1150ºC
CaF_2	1.0	0.5	<0.25	<0.25	<0.25
	5.0	2.5	1.9	0.25	<0.25
BaF_2	1.0	<0.5	<0.5	<0.5	<0.5
	5.0	1.3	1.1	<0.5	<0.5
SrF_2	1.0	<0.2	<0.2	<0.2	<0.2
	5.0	1.5	1.1	0.5	<0.5

These results indicate a pronounced reduction in CaF_2, BaF_2 and SrF_2 thermal stability in a ceramic matrix. The differing behaviour of these fluorides in the GR body could be due to their dissolution in the liquid phase that GR develops at high temperature [15], or to the formation of other, more stable compounds. With a view to establishing whether other crystalline phases evolved during thermal treatment, the complete diffractograms were studied.

The study of these diffractograms revealed the presence of anorthite ($CaAl_2Si_2O_8$) in the experiments with 1.0% and 5% CaF_2 additions, and celsian ($BaAl_2Si_2O_8$) in the 5% BaF_2 additions. No new crystalline species was detected in the series of SrF_2 additions. The anorthite and celsian contents detected in the above compositions at the different test temperatures are respectively detailed in Tables 5 and 6.

As CaO is the most widely found oxide in the compositions used for ceramic tile manufacture, it was decided to study the effect of CaO content in the composition on the crystalline phases formed during firing. Thus, the results could therefore foreseeably be extrapolated to analogous industrial processes and products.

Table 5. Anorthite ($CaAl_2Si_2O_8$) content in the GR body with CaF_2 additions at different peak heat-treatment temperatures

CaF_2 addition (wt%)	Anorthite content (wt%)			
	950°C	1000ºC	1100ºC	1150ºC
1%	5	6	5	3
5%	9	10	10	7

Table 6. Celsian ($BaAl_2Si_2O_8$) content in the GR body with BaF_2 additions at different peak heat-treatment temperatures

BaF_2 addition (wt%)	Celsian content (wt%)			
	950°C	1000ºC	1100ºC	1150ºC
5%	4	4	4	4

Table 7. Compositions prepared to study the influence of CaO content on CaF_2 thermal stability

Component	M0	M5	M10	M15
GR	95	90	85	80
CaF_2	5	5	5	5
$CaCO_3$	–	5	10	15

Influence of CaO content on the crystalline phases formed during firing

To carry out the study, test compositions were prepared of the GR body with CaF_2 and $CaCO_3$ additions, as set out in Table 7. The $CaCO_3$ contents in the compositions encompass the range of $CaCO_3$ contents found in ceramic tiles, from very low porosity to highly porous tiles.

The resulting mixtures were used to form cylindrical test specimens, which were fired at 800, 900, 950, 1000, 1050, 1100 and 1150 °C. A composition M0, to which no $CaCO_3$ was added, was also thermally treated at lower temperatures to establish CaF_2 stability at low temperatures.

Figure 7 shows the crystalline phases present in the heat-treated M0 specimens. At 800 °C clay minerals and calcite are no longer detected. This indicates that the former are dehydroxylated and the latter have fully decomposed, together contributing to the presence of SiO_2, Al_2O_3 and CaO in the ceramic matrix. The figure evidences a progressive reduction in CaF_2 content, which starts at low temperatures (200 °C) and becomes more pronounced between 600 and 850 °C. The tendency then reverses and exhibits a small peak at 900 °C. The presence of this small peak indicates that fluorite is forming, probably from the fluorine evolving from the GR body and from the CaO stemming from the decomposition of $CaCO_3$, present as an impurity in composition M0. At higher temperatures the CaF_2 content again diminishes, and practically disappears at 1100 °C.

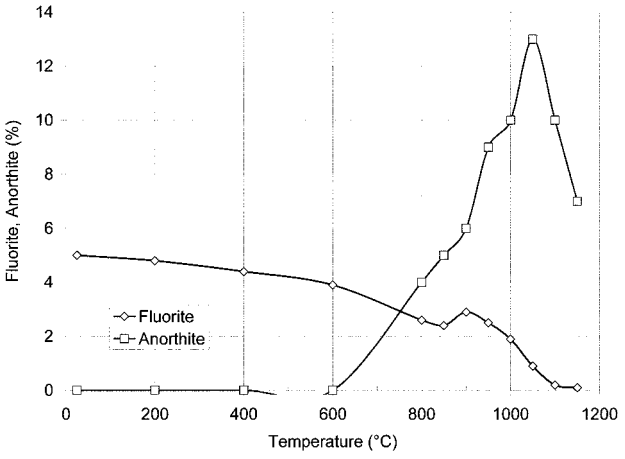

Fig. 7. Evolution of the crystalline phases with thermal treatment temperature. Mixture M0.

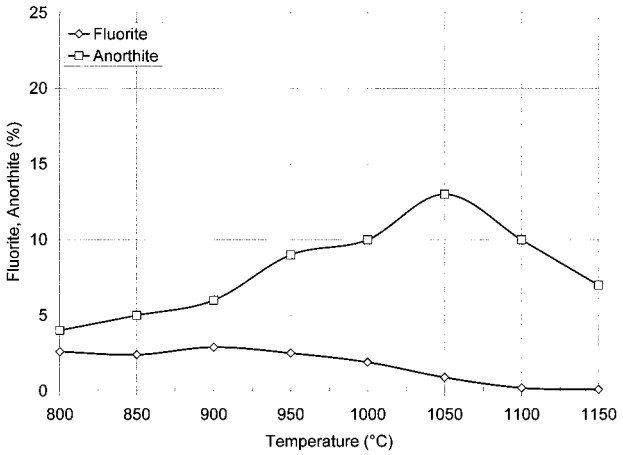

Fig. 8. Evolution of the crystalline phases present with thermal treatment temperature. Mixture M0.

Anorthite starts forming above 600 °C and increases up to 1050 °C, at which it peaks. The anorthite content then diminishes up to 1150 °C, as a result of anorthite crystal dissolution in the liquid phase generated by GR at high temperature [15].

Comparison of these results with those obtained in the thermal treatment of pure CaF_2 indicates that CaF_2 stability diminishes notably in a ceramic matrix, particularly when the matrix develops an abundant quantity of liquid phase at temperatures exceeding 800-900 °C. On the other hand, when the CaO needed to form the anorthite was calculated, it was observed that the CaO present in the GR body (1.1%) only sufficed to form 5.5% anorthite. Therefore, the formation of larger anorthite contents requires part of the calcium from the CaF_2 to contribute to anorthite formation by reacting with SiO_2 and Al_2O_3 from clay mineral dehydroxylation. Moreover, the formation of anorthite at the expense of fluorite appears to be favoured thermodynamically at high temperature, to judge by the free energies of formation from their elements ($\Delta G^{\circ}_{f,1300K} = -3259$ kJ/mol for anorthite and $\Delta G^{\circ}_{f,1300K} = -1012$ kJ/mol for fluorite). Fluorite is, therefore, likely to destabilise in the presence of SiO_2 and Al_2O_3 and form anorthite at temperatures exceeding 800 °C. These findings could explain the ineffectiveness of the CaF_2, which forms from the CaO present in stoneware compositions, to retain fluorine when these products are fired.

Figure 9 to 11 show the results, respectively, for mixtures M5, M10 and M15 in the range of temperatures from 800 to 1150 °C; the results for mixture M0 in this temperature range are shown in Fig. 8. Note that at 800 °C, clay minerals and calcite are no longer detected in any of the test compositions.

The evolution of CaF_2 content in mixtures M5, M10 and M15 closely resembles that observed previously in M0, and consists of a progressive reduction in CaF_2 content with rising temperature, until detection of CaF_2 ceases between 1050 and 1150 °C. The small differences

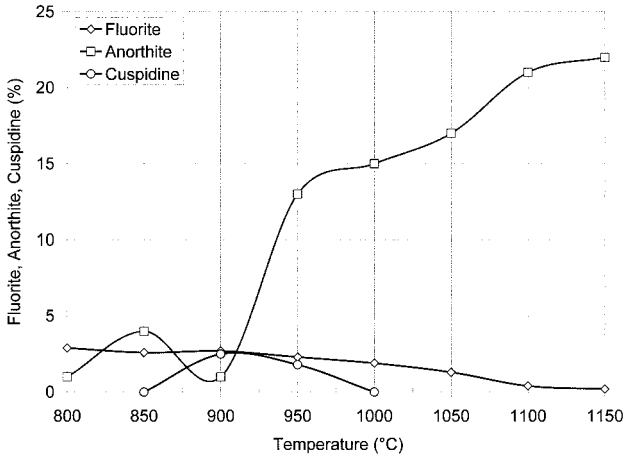

Fig. 9. Evolution of the crystalline phases present with thermal treatment temperature. Mixture M5.

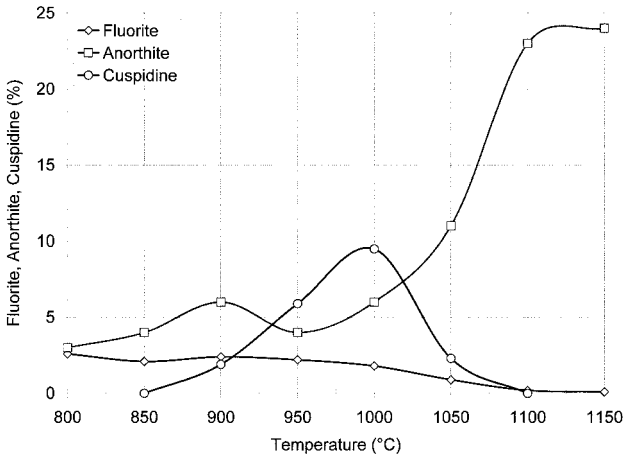

Fig. 10. Evolution of the crystalline phases present with thermal treatment temperature. Mixture M10.

noted in CaF_2 content when the $CaCO_3$ addition is modified are not considered significant, and are associated with the accuracy of the technique used.

The figures also evidence the appearance of a new crystalline species, cuspidine ($Ca_4Si_2O_7F_2$), which was not detected in M0. Cuspidine begins to crystallise above 850 °C, and the cuspidine content in the pieces depends on the $CaCO_3$ addition. Thus, in mixture M5 the cuspidine content maximises at 900 °C and is only 2.5%. In the mixtures with larger $CaCO_3$ additions, the cuspidine content maximises around 1100°C, and increases to 9.5% (M10) and 15.5% (M15).

The appearance of this crystalline species in the temperature range in which the CaF_2 content decreases (900-1100 °C) fixes the fluorine in the piece, which reduces fluorine compound emissions into the atmosphere in this range of temperatures. However, the cuspidine content diminishes rapidly above 1000 °C, and disappears completely at 1100 °C, with the ensuing increase in fluorine compound emissions. This could help explain the effectiveness of the $CaCO_3$ addition in reducing such

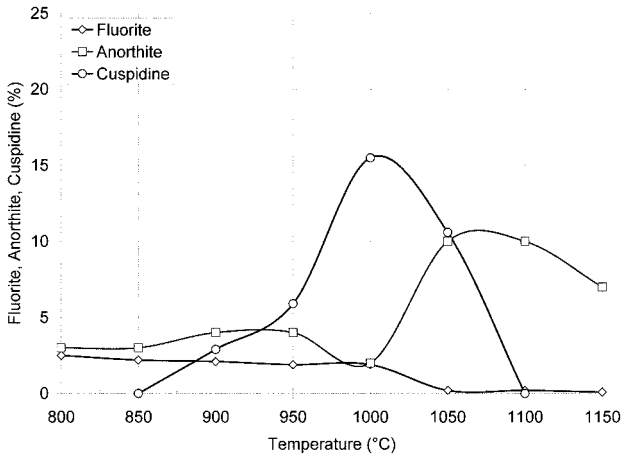

Fig. 11. Evolution of the crystalline phases present with thermal treatment temperature. Mixture M15.

emissions in products fired at temperatures below 1000 °C (roof tiles and bricks), and its ineffectiveness in products fired at higher temperatures (ceramic tiles).

Mixture M0 exhibits a progressive rise in anorthite content with heat-treatment temperature up to 1050 °C. The anorthite content then decreases at higher temperatures, owing to dissolution in the liquid phase in the piece. This tendency changes noticeably in the mixtures with $CaCO_3$ additions. Thus, in M5 (Fig. 9) the anorthite content decreases between 850 and 900 °C, coinciding with cuspidine formation, suggesting that cuspidine formation is thermodynamically favoured ($\Delta G^{\circ}_{f,1300K}$ = −6271 kJ/mol [16]) at these temperatures. Cuspidine disappears at higher temperatures, while the anorthite content increases notably up to 1150 °C. Mixture M5 displays no peak in anorthite content.

The evolution of anorthite content in mixtures M10 and M15 (Fig. 10 and 11) resembles that in M5. Thus, anorthite content decreases in the temperature ranges 900-950 °C and 950-1000 °C for calcite contents of 10% and 15%, respectively, coinciding with cuspidine formation. After this there is a significant rise in anorthite content, concurrently with the disappearance of cuspidine. These results indicate that cuspidine formation is encouraged between 850 and 1000 °C, whereas anorthite formation is favoured at temperatures above 1000 °C.

Finally, the theoretical fluorine retention in the fluoridated crystalline phases present in the pieces at the different test temperatures has been calculated. The results are plotted in Fig. 12. The figure shows:

- The fluorine retained in the crystalline phases diminishes progressively up to 850 °C, owing to the reduction in CaF_2 content. Above 850 °C the retained fluorine content rises, due to CaF_2 formation from the fluorine evolving from the GR body, and to cuspidine crystallisation.
- In the compositions with lower $CaCO_3$ contents (M0 and M5) the retained fluorine content peaks at 900 °C. At higher temperatures the quantity of retained

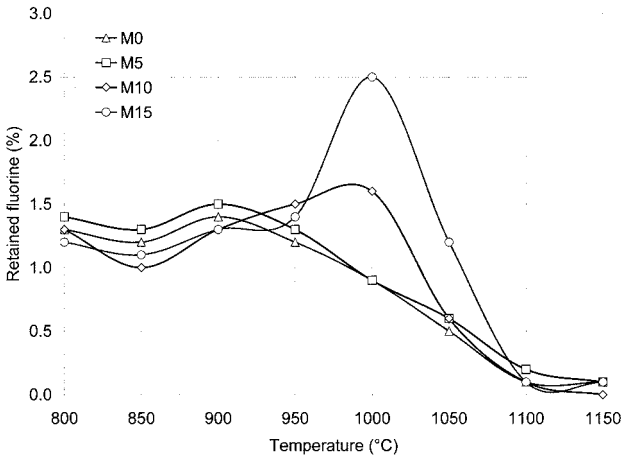

Fig. 12. Evolution of the fluorine retained in the crystalline phases with thermal treatment temperature.

fluorine decreases again, owing to the disappearance of CaF_2 and cuspidine. This trend is observed up to 1150 °C, at which practically no fluorine is retained.

- The compositions with larger $CaCO_3$ contents (M10 and M15) also display a maximum retained fluorine content, albeit at higher temperatures (1000 °C). In these compositions the decrease in retained fluorine content caused by the reduction in CaF_2 content above 900 °C is offset by the formation of important quantities of cuspidine, causing the retained fluorine content to rise between 850 and 1000 °C.

Above 1000 °C the retained fluorine content decreases sharply in compositions M10 and M15, owing to the drop in CaF_2 and cuspidine content. This trend continues up to 1150 °C, at which practically no fluorine is retained in the crystalline phases.

Conclusions

The present study has determined the influence of $CaCO_3$ content on the evolution of the crystalline phases with firing temperature in a typical floor tile composition to which additions of CaF_2 were made; additions of BaF_2 and SrF_2 were also made to this floor tile body, and the thermal stability of these three fluoride compounds was studied. The following conclusions can be drawn from the study:

1. The thermal stability of CaF_2, BaF_2 and SrF_2 decreases notably in a ceramic matrix. Their content in the matrix diminishes progressively, starting at low temperatures (200 °C for CaF_2), and is no longer detected at temperatures around 1100 °C.
2. During thermal treatment of the composition with CaF_2 (without any $CaCO_3$ addition), CaO displays a high tendency to form anorthite at temperatures exceeding 800 °C. This increases as temperatures rise further, even causing CaF_2 destabilisation. The same behaviour is observed in the composition with BaF_2, in which celsian formation is detected.
3. In the compositions with larger $CaCO_3$ contents, cuspidine formation is favoured between 850 and 1050 °C. This prevents the anorthite content from increasing, even causing it to diminish notably in this temperature range. The cuspidine content decreases sharply above 1000 °C, while the anorthite content rises up to 1150 °C.
4. The effectiveness of the $CaCO_3$ addition in reducing the emission of fluorine compounds in the compositions used in manufacturing structural ceramics (roof tiles and bricks) is due to two factors: the relatively low firing temperature of these products (850-1000 °C) enables fixing part of the CaF_2 that forms during firing in the pieces; and secondly, the presence of CaO in these compositions encourages the formation of cuspidine, which is stable up to temperatures between 1000 and 1050 °C. Both factors favour fluorine retention in the pieces, provided the firing temperature does not exceed 1050 °C.
5. The reason why the $CaCO_3$ addition is ineffective in reducing fluorine emissions during ceramic tile firing is due to the higher processing temperature required for these products. Thus, the study shows that the crystalline species which contain fluorine (fluorite and cuspidine) are unstable between 1100 and 1150 °C, causing fluorine emissions to rise at temperatures above 1100 °C.
6. These results, obtained in an electric kiln with an static air atmosphere using a standard floor tile body to which the different fluorides were added, could change when ceramic products are processed on an industrial scale. Thus, the presence of water vapour in industrial combustion kilns favours CaF_2 destabilisation. In addition, the HF-containing gas stream, which circulates inside the kiln countercurrent to the ceramic tiles, favours CaF_2 formation during preheating.

Acknowledgments

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References

1. W. Strohmenger, ZI Int. 36 [2] (1983) 67-72.
2. H. Kolkmeier, ZI Int. 44[10] (1991) 544-548.
3. J.A.M. Denissen and A.H. Vries, ZI Int. 51[1-2] (1998) 19-26.
4. B. Fabbri, Cerám. Inf. Tecnargilla special issue (1992) 33-36.
5. A. Reymer and J. de Jong, in: Third Euro-Ceramics, edited by P. Durán and J.F. Fernández. (Faenza Editrice Ibérica, 1993) p. 1071-1076.
6. D.A. Brosnan, Am. Ceram. Soc. Bull. 71[12] (1992) 1798-

1802.
7. E. Galán, I. González, A. Miras, I. Carretero, and P. Aparicio, in: J. Zapatero, A.J. Ramón and M. Moya "Integración Ciencia-Tecnología de las arcillas en el contexto tecnológico-social del nuevo milenio" (Sociedad Española de Arcillas], 2000) pp. 59-68.
8. S.J. Chipera and D.L. Bish, Clays Clay Miner. 50[1] (2002) 38-46.
9. E. Monfort, I. Celades, S. Gomar, M.F. Gazulla, H. Adams and J. Tulip, in "VIII World congress on ceramic tile quality volume II" (Cámara Oficial de Comercio, Industria y Navegación, 2004) pp. GI401-GI413.
10. H. Kolkmeier, ZI Int. 32[11] (1979) 670-674.
11. D. Hauck, M. Ruppik, and R. Hilker, in "ZI-Jahrbuch 1992", edited by C. Kokot. (Bauverlag, 1992) pp. 47-73.
12. W. Schlandt, CFI/Ber. DKG 63[1-2] (1986) 71-76.
13. M.F. Gazulla, M.P. Gómez, M.J. Cabrera, and E. Monfort, Téc. Cerám. 243 (1996) 298-302.
14. J. García Ten, E. Monfort and M.F. Gazulla, in XLIII Congreso de la Sociedad Española de Cerámica y Vidrio, November 2003 (Sociedad Española de Cerámica y Vidrio, 2003).
15. M.J. Orts Tarí (Universitat de València, 1991) [Tesis Doctoral].
16. H. Fukuyama, H. Tabata, and K. Nagata, Metall. Mater. Trans. B 34[3] (2003) 307-331.