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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

EVOLVED GAS ANALYSIS (EGA) OF BRICK CLAYS

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Abstract

Using a system based on non-dispersive infrared (NDIR) detectors, evolved gas analysis (EGA) was able to identify and quantify the principal volatiles produced by heating powdered samples of UK brick clays. From these results, atmospheric emissions likely to result from brick production can be predicted. In addition, EGA results for extruded brick clay test pieces are significantly different from those of powdered samples. Within an extruded brick clay body, evolved gases are contained within a pore system and evolved gas-solid phase reactions also occur. This EGA study provides further evidence on the nature of firing reactions within brick clay bodies. The qualitative and quantitative influence of heating rate – a key process condition in brick manufacture – on gas release is also outlined.

Keywords: brick clays, EGA

Introduction

The firing of bricks generates a range of gaseous compounds, some in considerable quantities. Identification and quantification of such gas-producing phases in the raw materials for brick manufacture is necessary as environmental legislation increasingly limits both amount and type of gases that can be released into the atmosphere. Those minerals and other constituents of brick raw materials which release gases (e.g. carbonates, sulphides, clay minerals, organic matter and sulphates) are usually key phases with respect to firing characteristics and properties of the end-product, such as degree of vitrification, porosity development, bloating and black coring.

Historically, thermal analysis has been widely used for examining the composition of clay raw materials and also for technological control of the firing process [1]. Of the various techniques available, evolved gas analysis (EGA) has the advan-

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tage that it can both identify [2] and quantify [3, 4] gases released from these key phases. This paper describes the results of an EGA investigation of three typical UK brick clay raw materials and shows that additional data can be obtained from EGA which relate to actual reactions taking place in the brick clay body during firing.

Methods and equipment

The EGA system consisted of a tube furnace linked, in series, to non-dispersive infrared (NDIR) detectors for H_2O, CO_2, CO and SO_2. Volatiles generated by heating the sample were transferred to the detectors by a carrier gas consisting of a 2:1 mixture by volume of N_2 and O_2, and flowing at 300 ml min^{-1}. Variations in evolved volatile content of the carrier gas were continuously monitored against sample temperature on a multi-channel chart recorder. Sample weights were between 100 and 150 mg, and heating rates applied were between 2 and 10°C min^{-1}.

Each of the four NDIR detectors contained two analysis cells capable of measuring up to 1000 and up to 10 000 ppm of the relevant volatile in the carrier gas stream. These cells were calibrated using standard gas mixtures. Calibration was further checked by measuring peak areas for these four volatiles generated by known mechanisms on heating analytical-grade sodium bicarbonate (CO_2 and H_2O; [5]), magnesium oxalate (CO and CO_2; [6]) and sodium dithionate (H_2O and SO_2 [7]).

Due to the variable nature of clay raw materials, three EGA runs were carried out on each sample and the quantitative data in Tables 2–5 represent averages from these. Samples were run in both powdered and extruded form.

Materials

Three UK brick clays were studied from three distinct argillaceous formations: the Etruria Marl, Mercia Mudstone, and Lower Oxford Clay. These together account for approximately two-thirds of UK brick clay production. The three samples formed part of a larger batch that had previously been subject to detailed chemical, mineralogical and physical analysis, particularly in relation to phase compositions produced under variable conditions of firing [8]. Geological, mineralogical and technical background to these samples is given by Ridgeway, Prentice and Dunham [9–11]. Chemical analyses and mineralogical compositions of the three brick clay samples are given in Table 1.

Significant carbonate is present in both the Mercia Mudstone and Lower Oxford Clay, whereas no carbonate was detected in the Etruria Marl. The presence of dolomite in the Mercia Mudstone coincides with a relatively high MgO content. Goethite is present in the Fe_2O_3-rich Etruria Marl but is absent from the other two samples. Detectable pyrite is present only in the Lower Oxford Clay which has a correspondingly high sulphur content; this is the only sample to contain appreciable organic carbon.

The samples are also characterised by distinct clay mineral assemblages: (1) kaolinite/illite (Etruria Marl), (2) chlorite/illite (Mercia Mudstone), and (3) illite/kaolinite/chlorite (Oxford Clay). Additionally, 'swelling chlorite' (corrensite) is present in the Mercia Mudstone. A mixed-layer illite-smectite phase may also be present in the Lower Oxford Clay. These results are generally in accordance with published data on the clay mineralogy of these three argillaceous formations [12].

Table 1 Major-element chemistry and mineralogical composition of the three brick clays

	Etruria Marl	Mercia Mudstone	Lower Oxford Clay
SiO_2	58.52	56.11	46.78
Al_2O_3	22.26	11.77	15.88
TiO_2	1.32	0.74	0.79
Fe_2O_3	8.19	4.54	4.66
MnO	0.04	0.007	0.03
MgO	0.81	6.27	1.49
CaO	0.35	5.03	10.21
Na_2O	0.61	0.55	0.38
K_2O	1.58	3.62	2.41
P_2O_5	0.07	0.15	0.15
LOI	7.61	9.85	16.35
Sulphur	0.01	0.03	1.57
Organic carbon	0.007	0.081	2.350
Quartz	****	****	****
K-feldspar	*	**	**
Plagioclase	nd	**	**
Calcite	nd	**	***
Dolomite	nd	*	nd
Gypsum	nd	nd	*
Pyrite	nd	nd	**
Goethite	**	nd	nd
Anatase	*	*	*
Apatite	*	*	*
Kaolinite	****	nd	**
Chlorite	nd	***[1]	**
Illite	***	***	***[2]

**** = >25 wt%
*** = 10–25%
** = 2–10%
* = <2%
nd = not detected
[1] includes corrensite ('swelling chlorite')
[2] includes mixed-layer illite-smectite

EGA results on powdered brick clays

Mercia Mudstone

Water vapour and carbon dioxide were the only volatiles generated in appreciable quantities during heating (Fig. 1). Water vapour is released in two distinct stages, these corresponding to expulsion of adsorbed water (100–150°C) and hydroxyl groups (525°C) from the clay minerals present. Carbon dioxide is released in a single event (750–775°C) which is attributed to carbonate decomposition. (Although, dolomite typically evolves CO_2 in two stages, under certain conditions, i.e. if present in an unconfined sample environment and/or at low concentrations, it gives a single CO_2 evolution peak that is indistinguishable from calcite [4].) Quantities of volatiles corresponding to the individual evolved gas peaks (Fig. 1) are listed in Table 2. The amount of CO_2 evolved is equivalent to a calcite content of 15–16%.

Etruria Marl

Similar to Mercia Mudstone, water vapour and carbon dioxide were the principal volatiles generated by the Etruria Marl during heating (Fig. 2). Three distinct water evolution peaks are apparent. The kaolinite-dominated clay mineral assemblage is associated with a marked hydroxyl water peak (500°C) and a smaller adsorbed water peak (150°C). An intermediate water evolution peak (325°C) is due

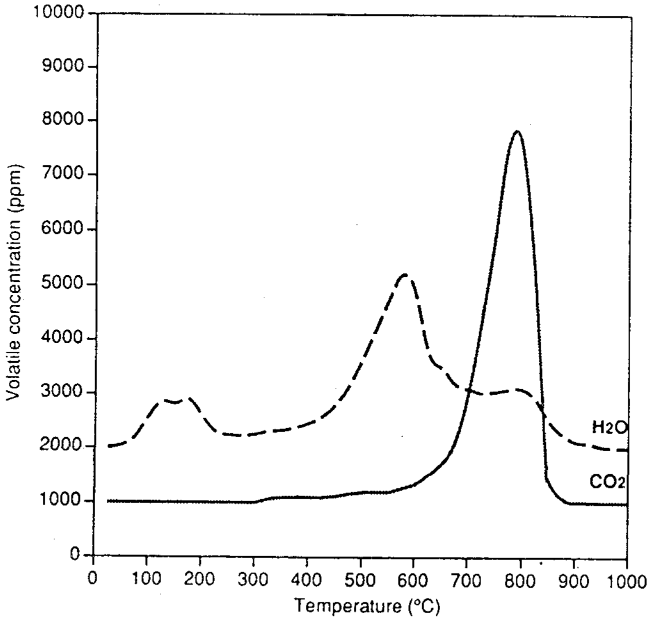

Fig. 1 EGA of powdered Mercia Mudstone. Sample mass 1.5008 g, heating rate 10°C min^{-1}, carrier gas flowrate 600 ml min^{-1}

Table 2 Quantitative EGA data for Mercia Mudstone (wt%)

Adsorbed water	0.33
Hydroxyl water	2.63
Total water	2.98
'Inorganic' carbon dioxide	6.94
Total volatile content	9.92
Equivalent calcite	15.79

to the decomposition of goethite according to the reaction $2FeO(OH) \rightarrow Fe_2O_3+H_2O$. The two-stage CO_2 evolution (325 and 400°C) is probably due to organic matter oxidation. Amounts of volatiles corresponding to individual evolved gas peaks (Fig. 2) are recorded in Table 3.

Lower Oxford Clay

In contrast, a much wider range of volatiles is evolved from the Lower Oxford Clay (Fig. 3). Organic matter oxidation results in two stages of CO_2 evolution (300 and 400°C); corresponding CO evolution peaks signify that oxidative combustion of organic matter to CO_2 is incomplete. The major second peak on the H_2O profile (275°C) and the minor first peak on the SO_2 profile (also at 275°C) represents water generated during organic matter combustion and oxidation of organic-bound sulphur, respectively.

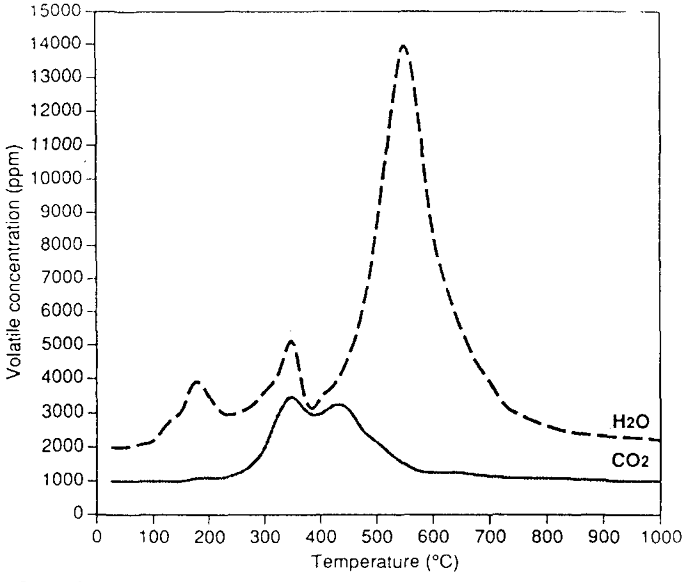

Fig. 2 EGA of powdered Etruria Marl. Sample mass 1.5001 g, heating rate 10°C min^{-1}, carrier gas flowrate 600 ml min^{-1}

Table 3 Quantitative EGA data for Etruria Marl (wt%)

Adsorbed water	0.59
Hydroxyl water [clay minerals]	5.67
Hydroxyl water [goethite]	0.55
Total water content	6.81
'Organic' carbon dioxide	0.34
Total volatile content	7.15
Equivalent goethite	4.55

The second and third SO_2 evolution peaks (425 and 475°C) are due to pyrite oxidation; the two-stage nature of this oxidation probably results from consecutive reactions of the type:

$$FeS_2+O_2 \rightarrow FeS + SO_2 \text{ and } 4FeS+7O_2 \rightarrow 2Fe_2O_3+4SO_2 \text{ [13].}$$

Calcite decomposition is represented by a peak at 775°C on the CO_2 evolution profile. Dehydroxylation of the clay minerals present is represented by an asymmetric, two-stage H_2O profile (400 and 600°C). The initial peak on the H_2O profile is likely to be due both to the loss of adsorbed water from clay minerals and the release of water of crystallization from gypsum (Table 1). Quantitative volatile data for the Lower Oxford Clay sample are given in Table 4.

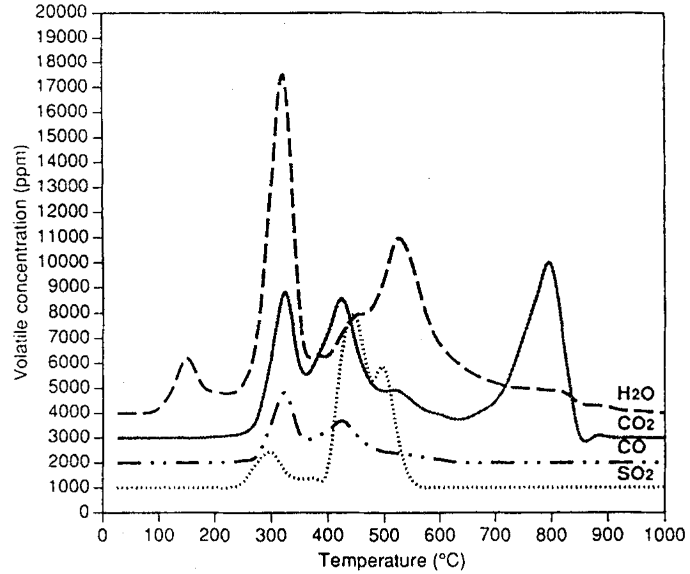

Fig. 3 EGA of powdered Lower Oxford Clay. Sample mass 1.5024 g, heating rate 10°C min^{-1}, carrier gas flowrate 600 ml min^{-1}

Table 4 Quantitative EGA data for Lower Oxford Clay powder sample (wt%)

Adsorbed water	0.73
'Organic' water	2.96
Hydroxyl water	4.34
Total water content	8.03
'Inorganic' sulphur dioxide	1.18
'Organic' sulphur dioxide	0.17
Total sulphur dioxide content	1.35
'Organic' carbon monoxide	1.34
'Organic' carbon dioxide	9.26
'Inorganic' carbon dioxide	6.98
Total carbon dioxide	16.24
Total volatile content	26.97
Equivalent calcite	15.88
Equivalent pyrite	1.11
Organic sulphur	0.08
Organic carbon	3.09

EGA results on extruded test piece of Lower Oxford Clay

EGA analyses of powdered samples of brick clays can thus provide information on the nature and quantities of gases released during heating and help identify those minerals responsible for individual firing reactions such as dehydroxylation, oxidation, decomposition etc. However, 'open system' conditions existing during evolved gas analysis of a loose powder in an oxidizing environment, where product gases are rapidly removed from the sample, are not analogous to the 'real' situation within a brick clay body where constituent minerals are tightly packed and a pore system is present. Within a brick clay body, even if firing takes place in an oxidizing environment, access of oxygen to some mineral particles will be restricted and product gases may be confined within the pore system – and subsequently react with the solid phase. A number of solid phase-gas phase reactions have been reported previously. Heller-Kallai *et al.* [14] and Mackenzie *et al.* [15] noted the acid, reactive nature of water vapour evolved from clay minerals and its ability to etch calcite. Also, Taylor [16] suggested that sulphur dioxide evolved from pyrite oxidation undergoes a displacement reaction with carbonate minerals resulting in sulphate formation and the release of carbon dioxide.

In order to investigate evolved gas release under conditions which simulated a 'real' firing situation, EGA was carried out on portions of an extruded test piece formed from the Lower Oxford Clay sample. This sample was chosen as it evolved both the widest range of volatiles on heating and showed the largest volatile content. The test piece was produced using the procedure described by Bain and Highley [17]. Portions of the test piece were first heated at a 'fast' rate (10°C min^{-1}) to provide a direct comparison with the powder sample. To approach the 'slow' firing rates used in brick manufacture, portions of the test piece were also heated at 2°C min^{-1} – the lowest heating rate possible using the present experimental configuration.

EGA at 'fast' heating rate (10°C min^{-1})

Thermal release profiles of all volatiles (Fig. 4) are significantly different from those given by the powdered sample (Fig. 3). Peaks show much less definition and, generally, can not be attributed with confidence to specific mineral decomposition or oxidation reactions as was the case for the powdered sample. Lower-temperature events were not able to reach equilibrium and consequently overlap with – and become indistinguishable from – higher-temperature events. Total volatiles evolved from the test piece are appreciably lower than from the powder sample (23.31% *vs.* 26.97%, Table 5). All volatiles contribute to this deficit, although it should be noted that the amount of SO_2 evolved from the test piece is less than one-third that evolved from the powder.

Organic matter combustion, as represented by the CO_2 evolution profile, occurs at an approximately constant rate from 400°C (Fig. 4, 'point A'). Nicholson and Ross [18] suggested that organic matter within the inner core of ceramic bodies oxi-

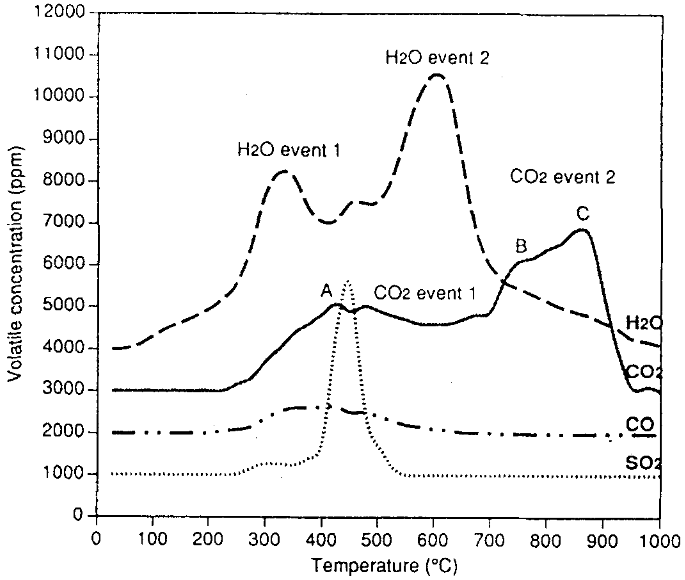

Fig. 4 EGA of extruded test piece of Lower Oxford Clay. Sample mass 1.5056 g, heating rate 10°C min^{-1}, carrier gas flowrate 600 ml min^{-1}

dizes at a steady, time-dependent rate controlled by the inward diffusion of oxygen through the pore system. The main control on rate of organic matter oxidation appears to be the presence of H_2O within the pore system of the test piece, as CO_2 evolution increases markedly following completion of clay dehydroxylation (Fig. 4, 'point B'). Following calcite decomposition (Fig. 4, 'point C'), CO_2 evolution returns to baseline. Inspection of test pieces fired to 600°C at 10°C min^{-1} revealed 'black coring' – consistent with the presence of residual organic matter at high temperature.

Table 5 Quantitative EGA data for Lower Oxford Clay test piece (wt%)

	10°C min^{-1}	2°C min^{-1}	(powder sample)
H_2O event (1)	2.66	3.36	
H_2O event (2)	4.85	4.06	
Total water vapour content	7.51	7.42	(8.03)
Total carbon monoxide	0.65	1.18	(1.34)
CO_2 event (1)	5.84	12.06	
CO_2 event (2)	8.90	6.42	
Total carbon dioxide content	14.75	18.48	(16.24)
Total sulphur dioxide	0.40	0.62	(1.35)
Total volatile content	23.31	27.70	(26.97)

Even allowing for the fact that organic matter oxidation contributes to the amount of CO_2 evolved above 700°C (Fig 4. point B), the amount of CO_2 evolved in 'CO_2 event 2' is less than that resulting from calcite dissociation in the powder sample (Fig. 3). This observation, and the fact that the amount of SO_2 evolved from the test piece is much lower than from the powder sample, are evidence for an SO_2 displacement reaction with calcite, e.g. by the mechanism $SO_2+1/2O_2+CaCO_3 \rightarrow CaSO_4+CO_2$ suggested by Taylor *et al.* [16]. Such a reaction 'captures' SO_2 within the test piece, and releases CO_2 from carbonate minerals below their temperatures of decomposition. X-ray diffraction (XRD) analysis carried out on separate portions of the test piece fired at 200°C intervals over the relevant temperature range provided independent confirmation of $CaSO_4$ formation by the above mechanism (Fig. 6, bottom).

The EGA data obtained at this heating rate are shown schematically together with mineralogical results and 'vitrification' curves in Fig. 6.

EGA at 'slow' heating rate (2°C min^{-1})

The EGA profiles for the test piece at this 'slow' heating rate are better defined (Fig. 5). Total evolved volatiles are, in fact, slightly higher than for the powder

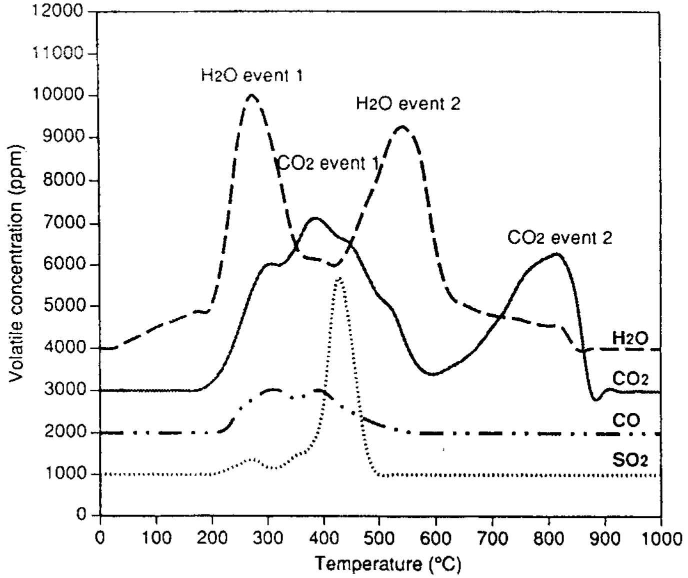

Fig. 5 EGA of extruded test piece of Lower Oxford Clay. Sample mass 1.5035 g, heating rate 2°C min^{-1}, carrier gas flowrate 150 ml min^{-1}

sample (27.70% *vs*. 26.97%, Table 5). Water vapour and carbon dioxide evolution are characterised by a distinct antipathetic relationship, as has been observed previously by Beardmore and Ford [19]. At a heating rate of 2°C min^{-1}, the CO_2 profile consists of two components which can again be attributed (cf. powder sample) to organic matter- and calcite-generated CO_2, respectively. The slower heating rate and lower levels of water vapour within the pore system are likely to improve oxygen availability within the clay body. Maximum organic matter combustion (Fig. 5, 'CO_2 event 1') occurs in the interval between the expulsion of adsorbed water from clay minerals / loss of water of crystallization from gypsum ('H_2O event 1') and clay mineral dehydroxylation ('H_2O event 2'). To some extent, CO_2 evolution from calcite may have contributed to 'CO_2 event 1' due either to the SO_2 displacement reaction outlined above or, possibly, due to etching of calcite by water vapour as noted by Heller-Kallai *et al.* [14] and Mackenzie *et al.* [15]. At this slower heating rate more SO_2 is released from the pore system (Table 5) suggesting that the amount of $CaSO_4$ formed is correspondingly less.

Table 5 indicates that the amount of CO_2 released from combustion of organic matter is considerably higher than that released from the powder sample. A possible explanation for this is reaction of H_2O within the pore system with organic matter, e.g. $CO+H_2O \rightarrow CO_2+H_2$ and $C+2H_2O \rightarrow CO_2+2H_2$, the 'water gas reactions' of Beardmore and Ford [19]. This would also explain the lower amounts of CO and H_2O evolved from the test piece compared to the powder sample (Table 5).

Discussion

For a 1 kg brick made from the Lower Oxford Clay, the data in Table 4 indicate that about 270 g gas, including 13.5 g SO_2, could theoretically be released during firing. Processes such as flue-gas desulphurization at the site of brick manufacture ensure that pollutant gases do not escape to the atmosphere, but the present results indicate that careful selection of firing conditions could lead to immobilization of

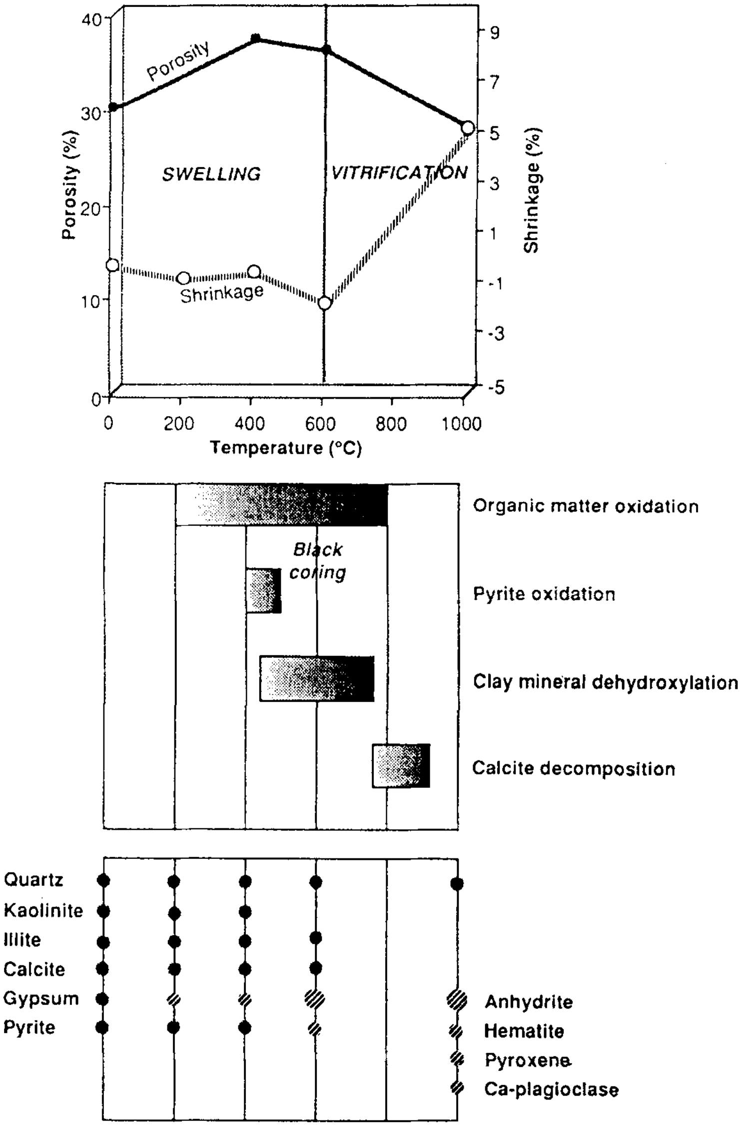

Fig. 6 Summary of EGA results for Lower Oxford Clay heated at 10°C min^{-1} (centre) compared to 'vitrification' curves (top) and mineralogical changes during firing (bottom)

much of the SO_2 generated by sulphide minerals in the brick clay body by reaction with any calcite present.

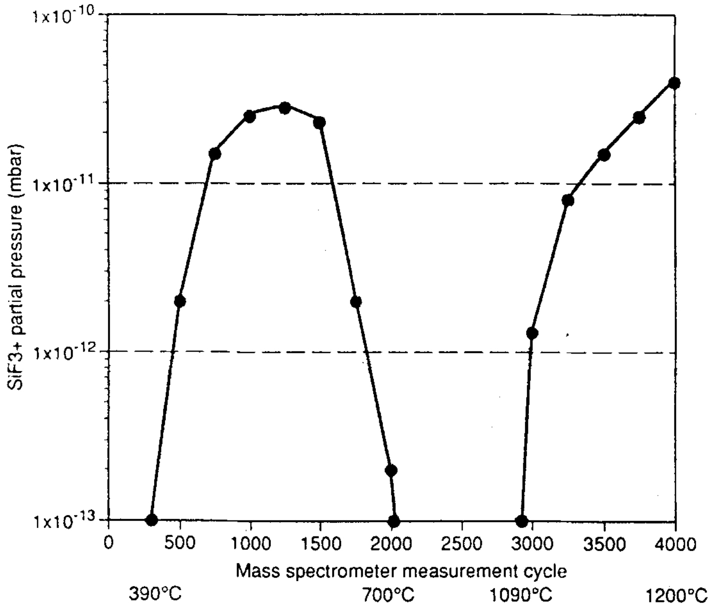

Fig. 7 SiF_3^+ ion evolution profile from coupled TG-MS analysis of Lower Oxford Clay sample. Note non-linear temperature scale

Volatiles other than the four recorded here are released on firing bricks, but an EGA system with greater analytical flexibility would be required to provide data on the complete range of likely pollutants. The environmental problems associated with fluorine emissions from brick plants are well known, and much remedial action has been taken over the last 15 years. Considerable research has been carried out on the effect of variations to firing schedules and varying body composition on extent of fluorine emission [20]. The presence of fine-grained calcite can, for instance, lead to the capture and immobilization of fluorine as CaF_2 [21] – a direct analogy to the results obtained for SO_2 in the present investigation. Fluorine commonly occurs in mica-type minerals where it substitutes for hydroxyl groups; it is usually released from these minerals at temperatures above 800°C, accompanying dehydroxylation [22, 23]. However, preliminary investigation of fluorine release from a sample of the Lower Oxford Clay by mass spectrometry has shown that evolution – as monitored by the SiF_3^+ fragment – takes place over two distinct temperature intervals of 390–700°C and >1090°C (Fig. 7). No explanation can be given for this release pattern at present, but it is apparent that EGA still has a valuable role to play in a number of areas related to brick clay manufacture.

Conclusions

Evolved gas analysis (EGA) of powder samples is able to identify and quantify gases released into the atmosphere from the firing of brick clays. From these results, atmospheric emissions likely to result from brick production can be predicted. The method proved effective at resolving the complex and overlapping reactions often encountered during brick clay firing, detecting individual mineral reactions (loss of water of crystallisation, dehydroxylation, decomposition, oxidation etc.) as discrete evolved gas events.

To some extent, EGA of small-scale, extruded brick clay bodies is able to model a 'real' industrial firing process. Results for the Lower Oxford Clay indicate that water vapour performs a critical role in the firing process. Two distinct types of firing behaviour were observed depending on the rate of heating: (1) For the 'slow' firing of brick clay bodies, an antipathetic relationship develops between water vapour evolution and carbon dioxide release as was noted previously by Beardmore and Ford [19]. Organic matter is able to oxidize completely during a temperature interval when the pore system is effectively free of water vapour. (2) In contrast, during 'fast' firing of brick clay bodies, a high concentration of water vapour is maintained within the pore system inhibiting organic matter oxidation. Carbon dioxide is released at a gradual, constant rate, independent of firing temperature, and residual organic matter may still be present a high temperature causing 'black coring'. It was inferred from EGA and mineralogical data that anhydrite formation takes place during pyrite oxidation by a sulphur dioxide-calcite displacement reaction [16]. Finally, there is evidence from EGA that water vapour and carbon monoxide may be consumed during heating by a water-gas reaction [19], but this was not demonstrated conclusively.

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