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Quantitative determination of pyrite in, ceramic clay raw materials by DTA

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Abstract

The thermal oxidative decomposition in air of 0–1.5 wt% of pyrite added to two traditional powdered clays was investigated by non-isothermal DTA. It emerged that the first step of the exothermic oxidation of pyrite, in the 350–500°C range, partly overlapped the endothermic dehydroxylation of clay minerals, centred at 590°C, and the result was dependent on the pyrite contents. Based on the values of the area of the oxidative peak and of the corresponding oxidation heat, it is possible to calculate quantitatively the amount of pyrite present in the industrial clay bodies and therefore to inform the technicians of the factories so they can avoid the negative effects of reducing reactions that could occur during firing of ceramic raw materials.

Keywords: "Black-core"; Ceramic raw materials; Decomposition; DTA; Pyrite

1. Introduction

Impurities (such as carbon black, organic matter, sulphides, etc.) commonly present in natural clays [1] and other raw materials are responsible for many defects in ceramic products, i.e. tiles and bricks, by acting as reducing agents for iron (III) ions during firing. In the tile industry, reducing substances are responsible for the appearance of the so-called "black core" defect, particularly evident in fast-firing processes. Its formation in clay products has been widely investigated [2, 3], demonstrating that the presence of

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small amounts (generally lower than about 1 wt%) of pyrite (the main sulphide present in ceramic raw materials) can cause "black core", affecting the rate of oxidation of the "core" after it has been formed, while, when carbon was present in the clay sulphur was maintained in the sulphide state and iron was stabilized in low oxidation states.

Therefore, it is of industrial importance to provide a simple technique premitting an accurate evaluation of the amount of pyrite present in clays and in general in raw materials, in order to prevent the above-mentioned harmful reducing reactions. Based on these observations, for a complete knowledge of this type of oxidation processes it is very important to have techniques which will assist in the observation of this phenomenon.

Pyrite is commonly determined in geological samples and ceramic raw materials by means of several methods, such as X-ray diffraction (XRD), combustion, as barium sulphate, etc. Although these methods generally have good sensitivity and precision, some of the sample preparation procedures are complex or time-consuming, and analyses are complicated by inherent analytical difficulties. In particular, preferred crystal orientation, matrix effects, and mineral interferences can adversely affect analyses by XRD. DTA is a potential alternative to quantify minerals [4] and offers a number of advantages over the more conventional methods.

Being particularly interested in the quantification of small amounts of pyrite in ceramic raw materials to prevent the "black core" defect, in this study we explore the possibility of obtaining quantitative information on the oxidative decomposition of small amounts (0.3–1.5 wt%) of pyrite in clay minerals by conventional DTA techniques. This information can be used as a guideline, in particular, for the ceramic tile industry.

2. Background

The oxidative thermal decomposition of pyrite is a complicated process and very difficult to reveal, often involving a series of overlapping reactions. It has been extensively studied by thermal analysis techniques and, over a much wider set of experimental conditions, various mechanisms of reaction have been suggested [4–15] From the four main components identified in the oxidized samples (FeS_2, $FeSO_4$, $Fe_2(SO_4)_3$ and Fe_2O_3) by different analytical techniques, many reactions may be assumed [6].

(a) The simplest reaction pathway involves the direct oxidation of pyrite to hematite, and the formation of Fe_2O_3 (hematite) has been confirmed by petrographic analysis [16] and by XRD [17].

(b) A second pathway involves the formation of hematite by the thermal decomposition of iron(II) sulphate, with a maximum rate of formation at 200°C [16]. $FeSO_4$ commences decomposition above 225°C, and is not detected above 320°C [16], although some workers have reported it present at temperatures of 460–480°C [18].

(c) Another mechanism involves pyrrhotite formation as an intermediate step [19]. Using microprobe analysis and quantitative SEM,the authors of Ref. [19] observed an outer layer of initial oxide, a thick layer of porous oxide and a core of unreacted pyrite.

A small amount of pyrrhotite was present at the interface between the pyrite core and the porous oxide layer. This phase was only observed in the temperature range 530-550°C.

(d) It has been suggested that hematite is formed by the reaction of an iron (III) sulphate species. Two possible routes, either through interaction between unreacted pyrite and sulphate [20, 21], or thermal decomposition of the sulphate [15, 18] have been proposed. Such reactions tend to occur at relatively high temperatures, so that the decomposition of the reported intermediate $Fe_2(SO_4)_3$[20] occurs above 550°C [18].

3. Experimental

3.1. Materials

E.P.K china clay (Hammil & Gillepsie Inc., 225 Broadway, New York 10007, USA) and Bandy Black Clay (H.C. Sapinks, Clay Company Inc., Paris, Tennessee, 38242, USA), both widely used in structural ceramics manufacturing, were selected for this study. Their chemical compositions are shown in Table 1. The ground powders were calcined at 400°C (three hours soaking time) to eliminate organics. TGA and DTA runs and elemental analysis, performed after this treatment, confirmed the absence of organic and sulphide compounds.

Pyrite (Fe, 46.5 wt%, S, 53.3 wt%) sticks (Will Corporation, Rochester, NY, USA) were received as large pellets and ball-milled for five hours using high-sintered alumina grinding media. This resulted in a powder with a particle size less than 40 μm. The powdered pyrite was then mixed with the calcined powders of the two clays in 0, 0.3, 0.6, 0.9 and 1.5 wt% amounts. Each addition was mixed in a twin-shell blender for 60 min.

3.2. Techniques

TG and DTG curves (20-1000°C) were recorded in a static air atmosphere using a Thermal System (Almond, NY 14804, USA) apparatus in the conventional way at

Table 1
Chemical analysis (wt%) of the dried clays

Oxide	E.P.K.	Bandy Black
SiO_2	45.8	61.0
Al_2O_3	38.7	24.5
Fe_2O_3	0.4	1.0
TiO_2	0.3	1.3
CaO	0.1	0.1
MgO	0.1	0.1
Na_2O	0.1	0.4
K_2O	0.2	1.7
L.O.I.	14.2	9.7
Others	0.1	0.2

a heating rate of 10°C min^{-1}. DTA and DDTA curves were recorded in the same non-isothermal conditions using a DTA apparatus made by the same Innovative Thermal System Company. Temperature calibrations were performed using the α–β inversion of quartz, and the cell constant was determined using pure metals and their enthalpy of fusion. Samples were weighed (about 200 mg) directly into the nickel crucibles. Calcined (1000°C) pure kaolin was used as reference material. To increase the measurement sensitivity, the ends of thermocouples were placed in the sample and the reference material.

All the thermal data were collected directly in an interfaced Hatary computer and the exothermic effects of the oxidative thermal decomposition of pyrite were also evaluated.

4. Results and discussion

4.1. Thermal behaviour of clays

Figs. 1 and 2 show the thermal behaviour (TGA and DTA) of the two clays. Some very similar features are present. Firstly, the dehydration typical of clay minerals due to the loss of lattice water [22, 23] is observed at 450–600°C as an endothermic peak in the DTA curves (Fig. 2). The amount of water lost, smaller (13.5 and 9.5 wt% for E.P.K.

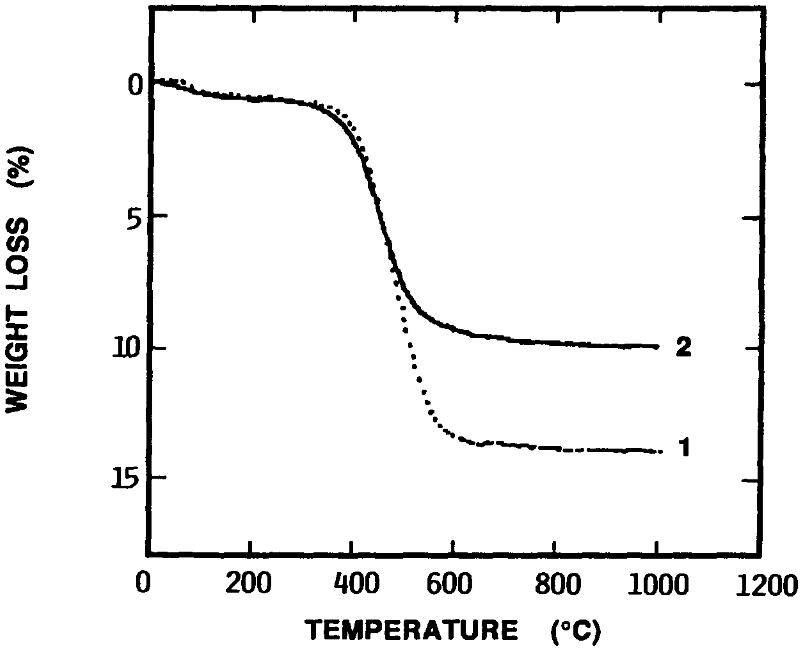

Fig. 1. TGA curves of E.P.K. (1) and Bandy Black (2) clay.

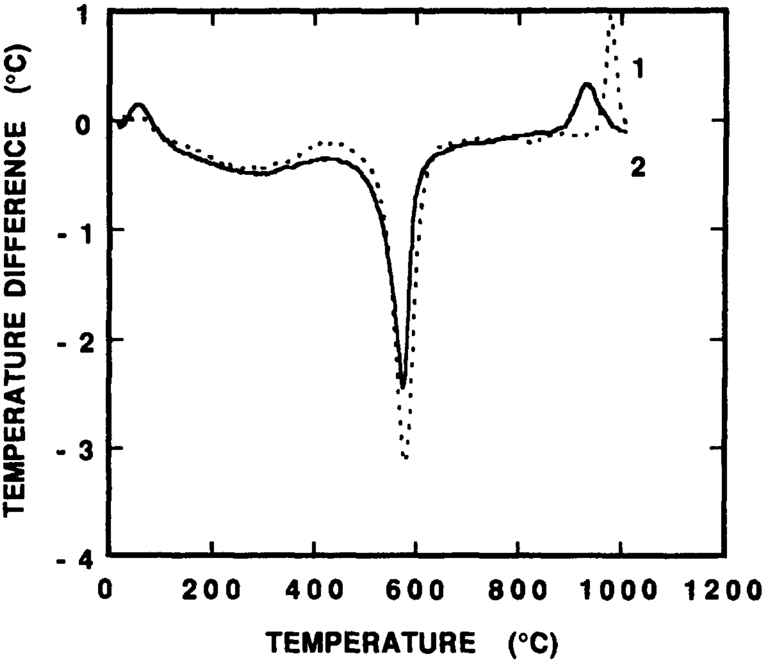

Fig. 2. DTA curves of E.P.K (1) and Bandy Black (2) clay.

and B.B. clays respectively) than the theoretical value (13.96 wt%) for pure kaolinitic minerals, may be due to the variety of clay minerals present in the samples. Secondly, the structural metakaolinite rearrangement is observed at about 980°C, demonstrated by the exothermic peaks due to the typical structural phenomenon occurring within dehydraxylated kaolinitic materials and corresponding to the formation of new ordered phases [24, 25].

4.2. *Thermal behaviour of pyrite*

Literature data are very contradictory on the mechanism of pyrite oxidation because it depends on the type and amount of the investigated pyrite and on the experimental conditions. As previously indicated, the thermo-chemical oxidation of pyrite is characterized by several basic steps and some general statements about oxidation under a dynamic heating regime have recently been suggested (Ref. [5]) and references cited therein). Apart from the specific oxidation mechanism, a total experimental weight loss of 33.5 wt%, corresponding to the complete thermal transformation in air of pyrite into hematite ($2\,FeS_2 + 11/2\,O_2 \rightarrow Fe_2O_3 + 4SO_2$), is measured at all times.

The oxidative transformation of pyrite into hematite occurs generally in the region 350–700°C, and the corresponding 33.5 wt% weight loss is almost entirely due to the dehydration of clay minerals. For this reason, the analysis of the weight loss of the two clay samples containing small amounts of pyrite is not a suitable method for the

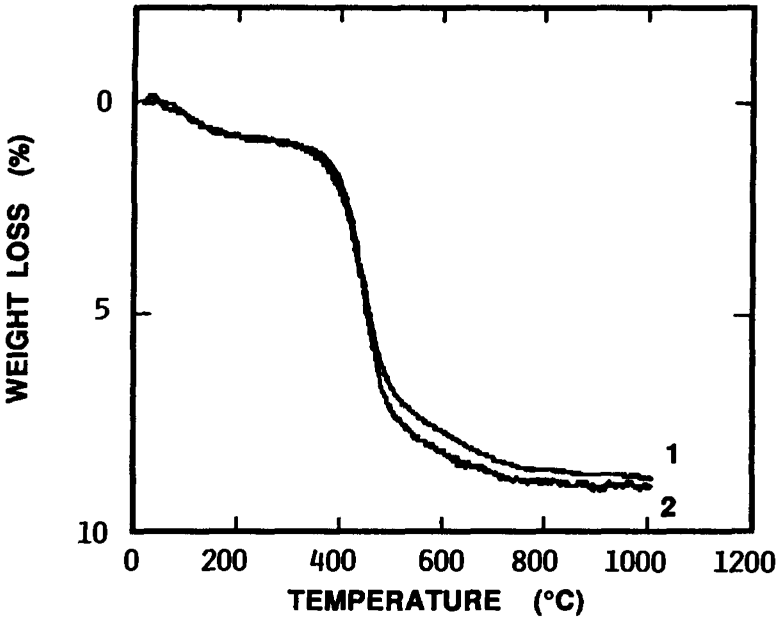

Fig. 3. Representative part of TGA curves of Bandy Black clay containing 0 (1) and 1.5 wt% (2) of pyrite.

evaluation of the sulphide concentration, as shown in Fig. 3. Considering these measurements it is impossible to obtain accurate information about the thermal oxidation of small amounts of pyrite in clay mixtures since the weight changes observed in the presence of 0.3–1.5 wt% pyrite are very small (0.1–0.5 wt%), not clearly attributable, and lie at the limit of the TGA instrumental sensitivity of the equipment available in ceramic factories.

In contrast, using the DTA technique it is possible, by measuring the first step in the oxidation process at 350–500°C, to measure the pyrite concentration in mixtures. The DTA curves (shape and maximum peak position) (Figs. 4 and 5) of the two different clays are very similar to one another, the slight differences observed being due to experimental conditions. In particularte a well-defined exothermic peak is apparent at about 350–500°C, which enlarges proportionally with increasing pyrite content, and partially overlaps with the sharp endothermic events (centred at 590°C) due to the clay dehydration. Although the proximity of the exothermic and endothermic events seems to make the course of the thermal oxidation and evaluating the amount of pyrite in clay mixes very complicated, accurate information can be acquired by concentrating on the first step of the pyrite oxidation process and measuring its area and evolved heat. In Table 2, values of the oxidation heat evaluated in mixtures of the two clays containing different amounts of pyrite are shown. Linear plots, obtained from values of the oxidation heat vs. the amount of pyrite, indicate that they are perfectly co-related, permitting evaluation of the amount of pyrite in the samples. Application of the least-square method to obtain the best straight-line plot from the experimental data

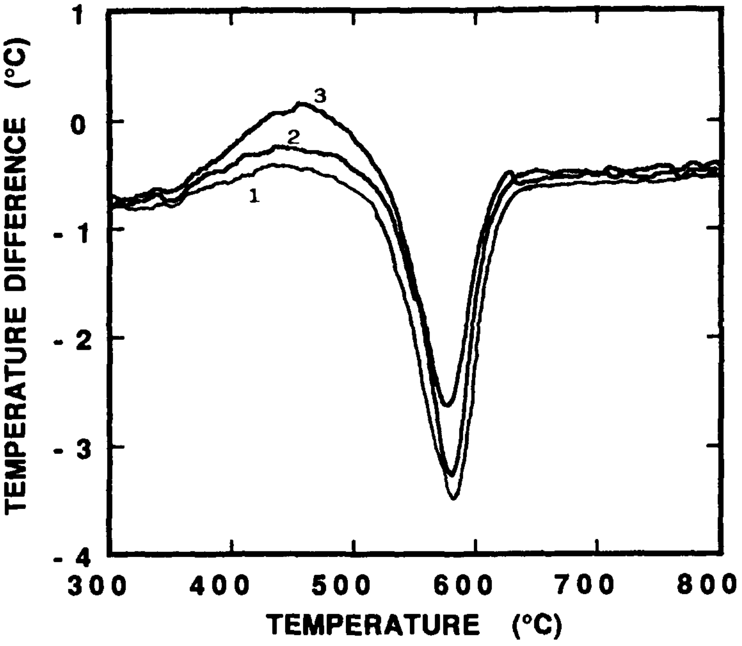

Fig. 4. Representative part of DTA curves of E.P.K. clay containing 0 (1), 0.6 (2), and 1.5 (3) wt% of pyrite.

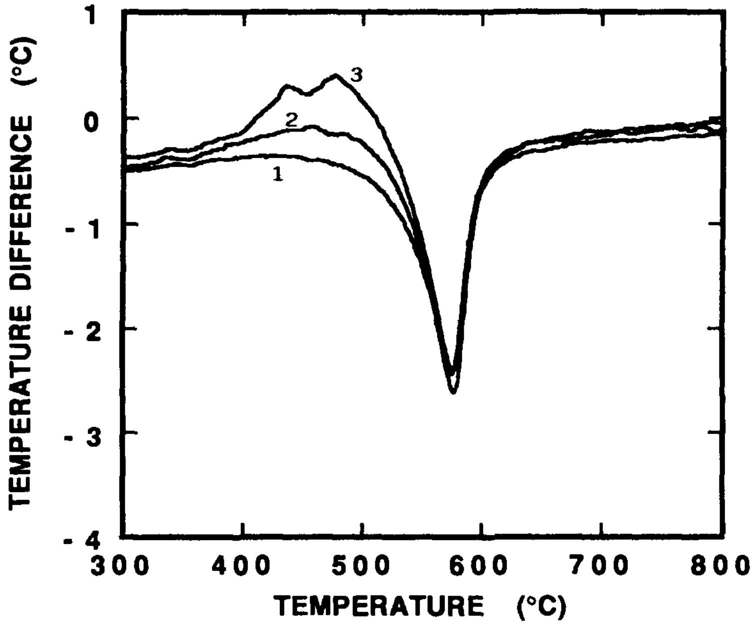

Fig. 5. Representative part of DTA curves of Bandy Black clay containing 0 (1), 0.6 (2), and 1.5 (3) wt% of pyrite.

Table 2
Calculated values of heat of oxidation of mixtures of two clays containing different amount of pyrite

Amount of pyrite/ wt%	Heat/(cal g^{-1} of sample)	
	E.P.K.	Bandy Black
0.3	1.9	2.2
0.6	4.0	4.5
0.9	6.0	7.0
1.5	10.8	10.2

shows that the values regress well to give the linear equations $Y = 7.2\ X$ and $Y = 6.9\ X$ for E.P.K. and Bandy Black clay respectively.

5. Conclusions

Thermo-analytical methods, used for the study of combustion and oxidation processes, can only give partial information about the course of an industrial oxidation process due to the impossibility of reproducing industrial heating conditions with instruments requiring very small amounts of sample.

Even in the presence of this restriction, DTA appears to have a great deal of potential for determining small amounts of pyrite in powdered ceramic raw materials containing clay minerals as prevalent components. The measurement can be carried out very easily, providing important information on the possible defects in ceramic pieces during fast-firing processes.

When heated in air, small amounts of pyrite or sulphides in clays undergo decomposition accompanied by oxidation; this produces exothermic effects in the 350–500°C temperature range. With this study, we demonstrated that proper use of the DTA technique can be favourably applied to solve this industrial problem. The peak area and oxidation heat values, corresponding to the first step of the sulphide oxidation process in the temperature range 350–500°C, calcuated from DTA measurements, appear appropriate parameters for the quantitative determination of small amounts of pyrite in a clay sample and in an industrial ceramic body.

Based on this information, it is possible to avoid the negative effects of reduction reactions which can occur during the firing of ceramic raw materials.

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