APPLICATION OF THE EGA TECHNIQUE IN THE CHARACTERISATION OF SULPHUR EMISSIONS OF CLAYS AND CERAMIC COMPOSITIONS

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1. INTRODUCTION

The presence of sulphur in ceramic compositions can be a source of defects in the end product, particularly when sulphur compound decomposition coincides with the glaze sealing temperature. When the sulphur concentration is low, there are chemical analysis methods that allow the sulphur in a sample to be quantified, though they fail to provide information on the type of sulphur. This information, which may be obtained by techniques such as X-ray diffraction (XRD), is of limited usefulness in compositions with very low sulphur contents.

2. OBJECTIVES

The EGA (evolved gas analysis) technique [1] [2] has been used in the present study to characterise sulphur compounds in clays and ceramic compositions. It was sought to determine the sulphur compounds present and their related emissions with a view to establishing which clays could give rise to the most problems in the production process and/or end product as a result of their emission kinetics. The influence of the heating rate on sulphur dioxide emission was also studied.

3. EXPERIMENTAL PROCEDURE

The equipment used for EGA analysis was a Netzsch STA 449C TG-DSC Jupiter instrument coupled to a QMS 403 Aëolos® quadrupole mass spectrometer and a BRUKER TGA-IR Fourier transform (FTIR) infrared spectrometer. Tests were conducted using the following two cycles: 'laboratory' slow cycle: heating rate: 10ºC/min and industrial cycle: heating rate: 25ºC/min, isothermal heating for 6 minutes at peak temperature. In both cases, the peak test temperature was 1150ºC and the tests were conducted in dynamic air atmosphere with a flow rate of 40 ml/min using helium as protection gas with a flow rate of 20 ml/min.

Figure 1. Equipment TG-DSC-QMS-FTIR.

The sulphur emissions of the samples were monitored, recording the signal associated with the mass-to-charge (m/z) ratio of SO_2 in the QMS, that is m/z 64,

and the emission of SO_2 was verified recording the spectra of the samples in the FTIR at different temperatures.

4. RESULTS AND DISCUSSION

4.1. Characterisation of selected clays.

Four samples with a similar sulphur content (about 1200 ppm S), two red-firing clays (A1 and A2), a white-firing clay and composition (A3 and A4) were selected. In the studied samples, sulphur compounds (gypsum) were only detected in samples A2 and A4. Table 1 and figure 2 summarise the results obtained after EGA analysis of the samples.

Reference	T_{Onset} (ºC)	T_{max} (ºC)
A-1	701	822, 1150(*)
A-2	967	1121
A-3	390	458
A-4	1008	1077

(*) Emission still continues at this temperature
Table 1. T_{Onset} and T_{max} of SO_2 emission (slow cycle).

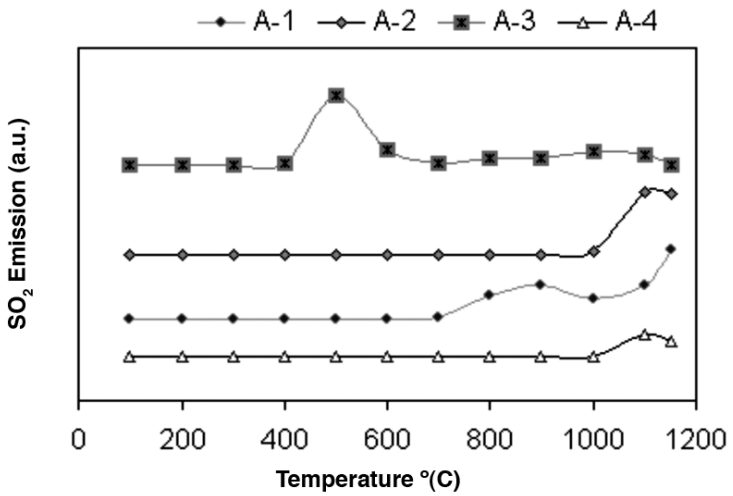

Figure 2. SO_2 emission of the samples.

In view of the emissions of the different samples, and on the basis of the emission kinetics of the different sulphides and sulphates [3], sample A-3 was found to contain sulphides (pyrites), while the other samples contained sulphates. In accordance with the emission kinetics, the sulphates in samples A-2 and A-4 would correspond to calcium and/or magnesium sulphates, while the A-1 sample, in addition to containing these types of sulphate, also seems to contain the more fluxing aluminium sulphate.

4.2. Influence of the cycle used.

When the tests with both cycles (laboratory and industrial) were being conducted, it was observed that, in general, the industrial cycle led to a delayed start of the sulphate emissions [4], while no significant differences were noted in the sulphur dioxide emissions from pyrite decomposition. However, despite the delay, the emissions observed in the industrial cycle were usually larger than in the laboratory cycle and this difference became more noticeable depending on the sample matrix. At low heating rates the matrix is probably able to retain the released SO_2.

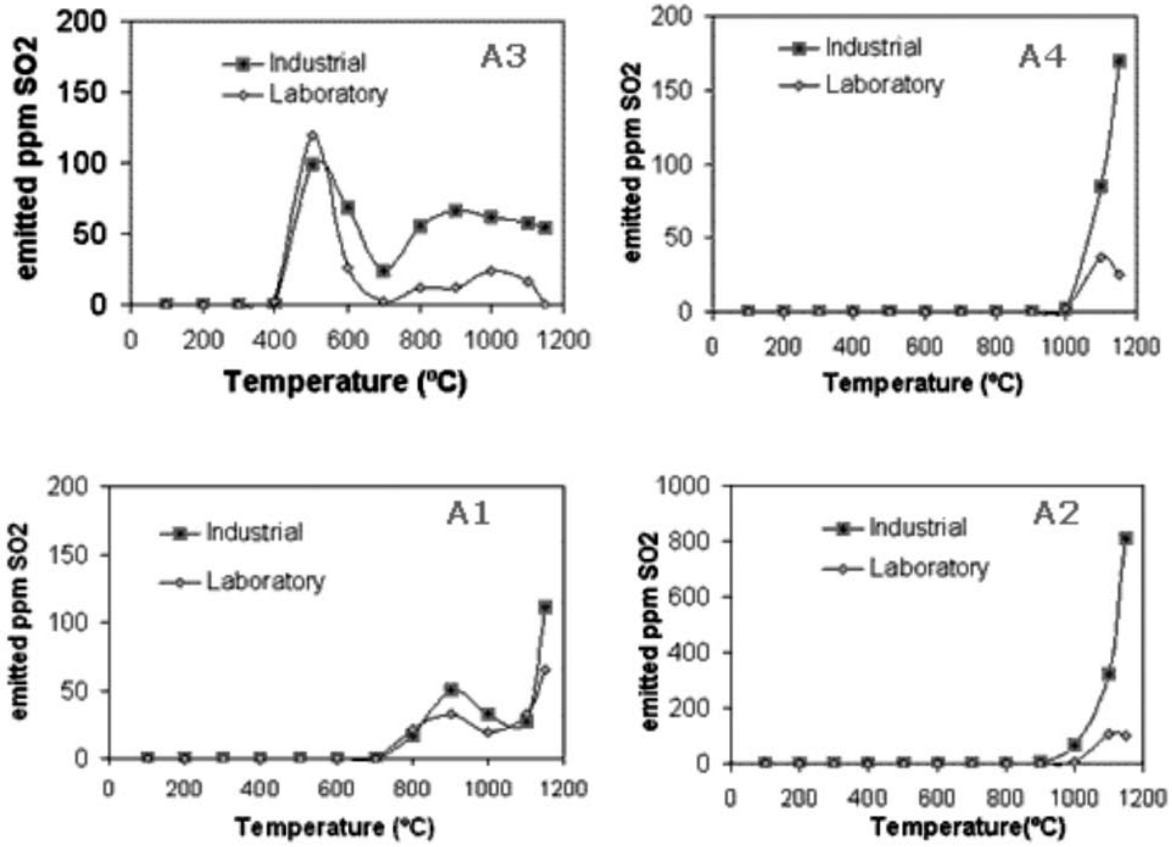

Figure 3.

5. CONCLUSIONS

- The EGA technique is very useful for characterising sulphur emissions during a firing cycle and, therefore, for the mineralogical characterisation of clay raw materials.
- It is possible to determine the raw materials whose mineralogy causes sulphur dioxide emission at temperatures near or above those at which glaze sealing occurs, and thus are more liable to produce manufacturing defects.

- Slow test cycles are useful for the mineralogical characterisation of the sample; however, the possibility of simulating industrial cycles allows information to be obtained regarding industrial emissions on a laboratory scale.

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REFERENCES

[1] PAULIK, F.: PAULIK, M.; ARNOLD, M.; IINCZEDY, J.; KRISTOF, J.; LANGIER-KUZNIAROWA, A. Simultaneous TG, DTG, DTA and EGA examination of argillaceous rocks. Part 1. *J. Therm. Anal*. 35 1849-1860, 1989

[2] PARSONS, A.J.; INGLETHORPE, S.D.J.; MORGAN, D.J.; DUNHAM, A.C. Evolved gas Analysis (EGA) of brick clays. *J. Therm. Anal*. 48 (1), 49-62, 1997

[3] GÓMEZ, P.; GARCÍA-TEN, J.; MONFORT, E.; ZUMAQUERO, E.; MACHI, C. Study of sulphur compounds in clays by the TGA–EGA technique. 11th International Conference and Exhibition of the European Ceramic Society-ECERS. Krakow, Poland 21-25 June 2009.

[4] GÓMEZ-TENA, M.P.; ZUMAQUERO, E.; MACHI, C.; GARCÍA-TEN, J. Application of the EGA (evolved gas analysis) technique in the study of variables that affect SO_2 emissions during the thermal treatment of ceramic compositions for tiles. 9th Mediterranean Conference on Calorimetry and Thermal Analysis. MEDICTA 2009 Marseille, France 15 - 18 June 2009.