STUDY OF SULPHIDES ASSOCIATED WITH DEFECTS: DECOMPOSITION AND EMISSION OF VOLATILE SUBSTANCES

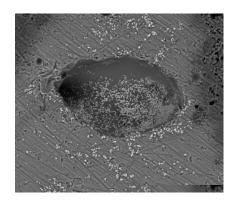
E. Zumaquero, J. Gilabert, E. Díaz, M.P. Gómez-Tena

Ceramic Technology Institute (ITC). Research Association of the Ceramic Industries (AICE)

Universitat Jaume I. Castellón. Spain.

1. ABSTRACT

The high technical and aesthetic demands of ceramic products often make it necessary to carry out a study not only of the physical and chemical properties that the raw materials which are part of ceramic compositions but also a study of the impurities present in these and which will subsequently affect production quality. The maximum concentration of the presence of certain impurities is increasingly restrictive and quality control of raw materials at low concentration levels is essential to avoid defects during the industrial ceramic process.



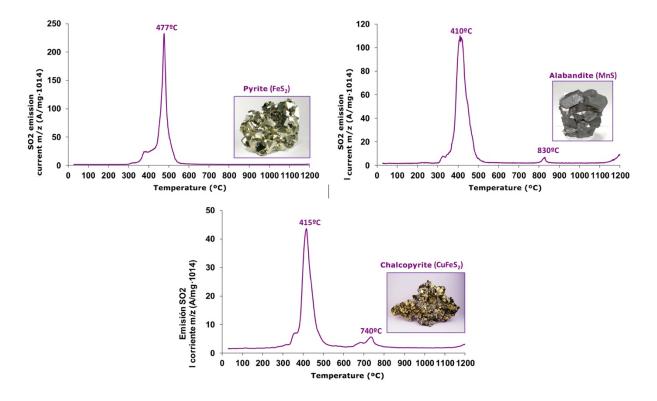
Some of the manufacturing defects may arise from the decomposition of compounds present in the raw materials such as sulphides.

The most common sulphides associated with clays are pyrite, chalcopyrite as well as other sulphides such as manganese sulphide (alabandine). In oxidising conditions, sulphides are unstable, decompose and/or oxidise giving rise to defects which affect the quality of the final product. These defects appear as small bubbles during firing due to gas emissions which can reach the surface of the piece or unwanted colourations.

Usually these minerals appear in very low proportions (lower than 0.5%) and are difficult to detect with other techniques used traditionally to identify crystalline phases such as X-ray diffraction. Other techniques such as x-ray fluorescence allow us to determine the percentage of sulphur in raw materials, but it is difficult to discern whether they are present in the form of sulphide or sulphates when they are in low concentrations, therefore the information it provides us with is insufficient for the study of impurities.

For this reason, a methodology based on linking several analytical techniques, such as thermogravimetry (TG), emission gas analysis (EGA) by Fournier transform infra-red spectroscopy (FTIR) and quadrupole mass spectroscopy (QMS), can be a viable alternative for evaluating thermal decompositions and reactivity associated with these materials with lower detection limits.

The aim of this research paper is to study the thermal behaviour of sulphides present in clay raw materials that are susceptible to generating defects during ceramic processes, using the TG-FTIR-QMS. To do so we have selected the sulphides present in the raw materials (pyrite, chalcopyrite, alabandine...) which have been thermically characterised by studying the decomposition and oxidation processes. Likewise, the emission of sulphur compounds generated during thermal treatment have been studied, observing the significant differences depending on the type of sulphide studied.



According to the results obtained, it is deemed that the TG-FTIR-QMS technique allows studies to be conducted on the impurities present in clay raw materials by identifying the type of sulphide associated with the defect generated in ceramic floor tiles. In this way, this technique opens up a field not just for the study of these minerals but also the interaction they undergo with the rest of the compounds/minerals during the pre-processing of the raw materials, as well as during the firing process.

This project has been co-financed by IVACE and ERDF, within the ERDF Operational Programme of the Valencian Community 2014-2020 in the call for grant applications aimed at Technology Centres in the Valencian Community for R&D projects in cooperation with companies 2017 (IMDEEA/2017/119).

2. ACKNOWLEDGEMENTS



$\langle \langle \rangle \rangle$	UNIÓN EUROPEA Fondo Europeo de Desarrollo Regional
Una mane	ra de hacer Europa

3. **REFERENCE**

- [1] M.P. Gómez-Tena, J. García-Ten, E. Monfort, E. Zumaquero and C. Machi, "Study of sulphur compounds in clays by the TGA-EGA technique;" pp. 914–918 in *11th Int. Conf. Exhib. Eur. Ceram. Soc. 2009.* 2009.
- [2] M.F. Gazulla, M.P. Gómez-Tena, M. Orduña, E. Zumaquero and S. Vicente, "Sulfur Determination in Geological Samples Based on Coupled Analytical Techniques: Electric Furnace-IC and TGA-EGA," *Geostand. geoanalytical Res.*, **33** [1] 71–84 (2008).
- [3] P.S. Thomas, D. Hirschausen, R.E. White, J.P. Guerbois, and A.S. Ray, "Characterisation of the oxidation products of pyrite by thermogravimetric and evolved gas analysis," **72** 769–776 (2003).
- [4] S. Prasad and B.D. Pandey, "Thermoanalytical studies on copper-iron sulphides," 58 625-637 (1999).
- [5] K. Jeridi, A. López-Galindo, M. Setti, and F. Jamoussi, "*The use of Dynamic Evolved Gas Analysis (DEGA) to resolve ceramic defects"*. 2014.
- [6] R. Murphy and D.R. Strongin, "Surface reactivity of pyrite and related sulfides," *Surf. Sci. Rep.*, **64** [1] 1–45 (2009).