

Characterization of traditional sanitary-ware glazes using classical and unconventional analytical methods

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Sanitary-glazes are technological materials that play a crucial role in the aesthetic quality and durability of the final ceramic product and they are generally constituted by a dominant amorphous phase in which other crystalline phases (such as zircon, diopside and wollastonite) may be dispersed as to provide opacity and give a thermal shrinkage tallying with that of the ceramic bulk [1,2,3].

Two series of glazes have been produced from different combination of the same raw materials (quartz, feldspar, kaolinite, calcite, zircon, etc) and designed to allow one to get insight into network-forming and network-modifying species and have been studied with different analytical techniques.

Fusibility test and hot-stage microscope observations show the influence of even low differences in the starting chemical compositions on the transformation temperature and flowability exhibits a direct and inverse correlation with CaO and SiO₂ content, respectively. A "network ratio" N.R. (expressed by the ratio between forming and modifying species) has been defined for all samples in order to emphasize the relationship of starting composition and rheological temperatures (e.g. sintering temperature) using clustering analysis approach.

Each raw glaze has been also casted in cylinder and 2D-slabs and fired using an industrial cycle with a peak temperature of 1200°C. Cylindrical samples have been used for X-ray and thermal expansion measurements whereas 2-D slabs for electron microprobe analysis, scanning electron microscope pictures and micro-tomography images.

X-ray powder diffraction measurements coupled with chemical micro-analysis show that glass is the most abundant phase (from 87 to 93 wt.%) and that zircon and quartz are still present after firing cycle (from 5-10 to 0-4 wt.%). Processed backscattered electron images show that zircon is uniformly dispersed without aggregation or evidence of zircon crystal growth; we are developing a strategy for zircon quantification using backscattered electron images referred to the new results of Rietveld method and chemical micro-analyses. X-ray synchrotron radiation micro-tomography performed at the SYRMEP beamline of the Elettra synchrotron (Trieste, Italy) allows a quantification of glaze porosity (15% by volume) and shows that voids are prevalently not interconnected and with size up to 50 μ m. Clustering analysis applied to glass transition and softening temperatures obtained from dilatometric test, shows a direct and indirect correlation with SiO₂ and CaO contents, respectively. Finally, the calculated linear thermal expansion of the glass phase of glaze ranges between 6 and 7 x 10-6 °C-1 but we are not able to bring to light the expected dependence on its chemical composition [4] probably because of the low differences in starting compositions.

References.

[1] L. Hupa, R. Bergman, L. Froberg, S. Vane-Tempest, M. Hupa, T. Kronberg, E. Pesonen-Leinonen, A.M. Sjoberg, Chemical resistance and cleanability of glazed surfaces, Surface Science 584 (2005) 113–118.

[2] M.G. Rasteiro, T. Gassman, R. Santos, E. Antunes, Crystalline phase characterization of glass-ceramic glazes, Ceramics International 33 (2007) 345–354.

[3] R. Casasola, J.M. Rincon, M. Romero, Glass-ceramic glazes for ceramic tiles: a review, Journal of Materials Science 47 (2011) 553–582.

[4] A. Fluegel, Thermal Expansion Calculation of Silicate Glasses at 210°C, Based on the Systematic Analysis of Global Database, 2007.