

A MINERALOGICAL AND PETROLOGICAL APPROACH TO THE CHALLENGE OF THE LARGE CERAMIC SLABS

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The ceramic industry is currently addressing the production of porcelain stoneware tiles towards larger and larger sizes with different thickness. Novel shaping techniques, together with redesigned manufacturing lines, allow to output from 320x160 cm to 480x180 cm (from 5.1 to 8.6 m²) and thickness from 3 mm to 20 mm (from 35 to over 400 kg) each ceramic slab. The driving force of this product and process innovation is twice: gain in efficiency and productivity from highly standardized manufacturing plants (towards the digital factory 4.0) as well as commercial return from value added, versatility (offcuts can be tailored on demand from a single slab) and new application fields (e.g. façades, furniture, alternative to ornamental stones and wood slabs).

On the other hand, the production of such gigantic slabs – matching the standard requirements for porcelain stoneware (water absorption ~0.1% and deviation from planarity <0.5% among others) – is challenging and the control on deformations taking place during firing turns crucial. Indeed, densification of porcelain stoneware occurs by a complex process, entailing partial vitrification, reactive sintering, and viscous flow of the melt in equilibrium with residual minerals (mostly quartz) and newly formed crystalline phases (essentially mullite). The intricate convolution of these phenomena makes porcelain stoneware firing the least known and the hardest to model amongst sintering processes.

What occurs to ceramic tiles during sintering present significant analogies with geological phenomena active, e.g., in granitic melt formation and ascent. Similarities extend to composition, considering that porcelain stoneware consists by 65-75% of feldspars and quartz, in addition to clay minerals (giving rise to a distinctly peraluminous viscous phase). Thus, a mineralogical and petrological approach can be useful to improve the knowledge on the densification mechanisms and the complexity behind the firing of large ceramic slabs.

The evolution of phase amount and chemistry during firing is investigated on ex-situ and quenched samples representative of porcelain stoneware bodies fired with industrial-like schedules. Quantitative phase analysis is performed by XRPD (with internal standard) and Rietveld refinement. The chemical composition of the vitreous phase is calculated by subtracting the contributions of crystalline phases from the bulk composition (determined by XRF-WDS). The melt physical properties at high temperature are estimated by its chemical composition, e.g., using the Giordano *et al.* (2008) model for viscosity.

Industrial firing schedules typically consist of a fast ramp (~40°C min⁻¹) to ~1200°C and some minutes soaking. Feldspars melt quickly (K-feldspar>plagioclase) while quartz is only partially dissolved at the highest temperature. Once formed, mullite is gradually dissolved, though by a decreasing rate, making the melt increasingly peraluminous. The melt viscosity lowers rapidly up to 1200°C, but tends to increase slowly during soaking. These physical and mineralogical features affect both sintering kinetics and tile deformation at high temperature (*pyroplasticity*). In particular, pyroplasticity depends on both the melt viscosity and the amount of crystals suspended in the liquid phase.

Analogously to natural melts (Costa *et al.*, 2009) firing deformation could scale with crystals shape and size distribution, which in turn reflect in a complex way the dissolution rate of mullite and quartz into the melt (buffered by silica oversaturation and strong peraluminous character). Finally, the effect of crystalline and glassy phases on cooling deformation and residual stress is shortly discussed, disclosing a critical issue for the production of large ceramic slabs. (Acknowledgement to IPERCER project).

REFERENCES

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