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Phase transformations during sintering of porcelain stoneware: mineralogical composition and chemico-physical properties of the vitreous phase.

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Porcelain stoneware tile is a ceramic building materials characterized by high technological properties, especially regarding water absorption (<0.5% according to ISO 13006) and durability (chemical and frost resistance) coupled with outstanding aesthetic features. Porcelain stoneware bodies are commonly composed of alkaline feldspars (45-55%), kaolinitic clays (30-40%) and quartz sand (5-20%). More and more often different types of waste, such as glasses, are introduced (up to 5%). The sintering of bodies is accomplished in roller kilns by fast single firing (50-70 min cold to cold, 1200-1230°C of maximum temperature, 5-10 min of soaking time). Investigating transformations involving minerals and the vitreous phase during the sintering process is crucial as the phase composition is one of the main factors affecting the technological properties of porcelain stoneware. In this work, about ninety porcelain stoneware tiles were taken into account to represent different types of batches and products. Bulk chemistry (XRF) and quantitative phase composition (XRD-Rietveld) were determined in order to calculate both the amount of crystalline phases and the chemical and physical properties of the vitreous phase. Moreover, the evolution during the sintering process was followed by laboratory simulation of industrial firing and quenching in the 1100-1200°C range. The sintering process of porcelain stoneware tiles is accompanied by a complex evolution of both chemical and phase composition of the vitreous phase. By increasing the firing temperature, breakdown of clay minerals and feldspars melting give rise, starting from about 1000°C, to mullite and a viscous phase, whose composition does not correspond to the feldspar-quartz eutectics. A further increase leads to progressive dissolution of quartz in the vitreous phase in absence of feldspars. The finished products contain essentially vitreous phase (40-75%wt.) associated with quartz (10-30%wt.), mullite (4-10%wt.) and feldspars (up to 15%wt.). The vitreous phase varies in a wide range of chemical compositions (from “granitic” to “syenitic” with different Na/K and alkali/alkaline earth ratios). Such a vitreous phase plays a key-role in the multistage sintering process, involving: formation of viscous melt, densification by reactive liquid phase sintering, and overfiring, if any, causing density decreasing and eventually bloating.