

# Mineral reactions in thermally treated calcareous clays for brick production

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The commercial production of bricks usually requires firing temperatures in the range of 800-1000 °C. Some raw materials for brick production may contain up to several wt% carbonates. These carbonates thermally decompose in the range of 600-900 °C and subsequently induce the formation of new mineral phases and microporosity. This allows the production of high thermal insulating clay blocks which contribute for an energy efficient building stock, however, the additional release of CO<sub>2</sub> is an unfavorable side effect regarding the overall carbon footprint. Strongly supporting the European Green Deal, Wienerberger AG is striving to find solutions for a reduction of these raw material related process emissions. Therefore, an approach was targeted to find and evaluate additives, which allow lower firing temperatures in the range of decomposition temperatures of carbonates concurrently keeping the physico-technical parameters of the fired products comparable to available products. In this context, it is particularly important that the pure clay-type raw material and its thermal behavior is foremost characterized so that comparisons with clay-additive mixtures can later be made.

Test specimens were extruded, dried, and fired at 620 °C, 700 °C, 760 °C and 880 °C. The mineral phases, chemical composition and thermal behavior of the green body and the fired sherds were determined using PXRD, XRF and TA, respectively. SEM-EDX and EPMA were used for high-resolution images of microstructures and phase identification as well as for identifying mineral reactions.

The results revealed a multitude of processes occurring during the firing process of the investigated calcareous clay. A selection of relevant mineral reactions is listed below:

**(i)** Individual clay minerals were dehydroxylated at 620 °C, while the matrix was visibly molten at a firing temperature of 880 °C (Fig. 1A). Within the reduction core, a higher level of melting was present than at the rim, possibly due to FeO that rather acts as a fluxing agent than Fe<sub>2</sub>O<sub>3</sub> (Fischer 1987).

**(ii)** The beginning of decomposition of carbonates was observed at 620 °C. Decomposing carbonates can react with clay minerals, which leads to a densification of sherds at 600 °C (Fischer 1987). Small dolomite grains displayed an advanced level of decomposition at 700 °C with grains exhibiting a dolomite-type core surrounded by MgO and a Ca-rich shell. This degree of decomposition was also visible within larger dolomite grains at 760 °C. Calcite was also partially decomposed and consisted of a calcite-type core surrounded by a Ca-rich shell. At 880 °C almost all of the carbonate grains had vanished. Remaining MgO or pores with or without carbonate residues were surrounded by a rim of Ca-Mg-Al-silicates due to significant diffusion of Ca and Mg into the matrix (Fig. 1B). PXRD exhibited newly formed gehlenite and akermanite at this temperature.

(iii) Pyrite thermally decomposed between 300-600 °C, gaseous SO<sub>2</sub>-SO<sub>3</sub> was formed (c.f. Schmidt, 1968) and confirmed by evolved gas analysis. The SO<sub>2</sub>-SO<sub>3</sub> gas, however, stayed at most in the sherds and reacted with MgO and CaO of the decomposing carbonates thus forming sulfates (Schmidt 1968). Low concentrations of S were detected in carbonates at 700 °C. The amount of detected S increased with increasing firing temperature. Domains with elevated S contents were formed along the rims of the remaining carbonate grains at 760 °C. At a firing temperature of 880 °C, S could be found in the residues of former carbonates and in the Ca-Mg-Al-silicate reaction rims (Fig. 1B).

(iv) Some Na-rich feldspars exhibited a K-enriched rim at 880 °C (Fig. 1C) due to an exchange of Na<sup>+</sup> for K<sup>+</sup> (Riccardi et al. 1999). Collapsed clay minerals (Riccardi et. al. 1999) and partially collapsed muscovite (Ionescu & Hoeck 2011) can be considered as sources of K<sup>+</sup>.

(v) Some quartz grains were characterized by a rim enriched in Al, Na, K and Fe at 880 °C (Fig. 1C). The interaction of these foreign elements indicates a softening or partially melting of quartz grains (Ionescu & Hoeck 2011).

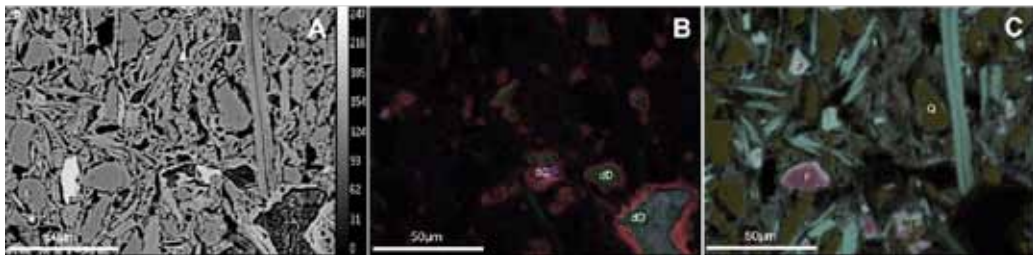


Figure 1. (A) BSE-image of a calcareous clay fired at 880 °C; (B) Stacked element maps of Mg (green), Ca (red) and S (purple); (C) Stacked element maps of Si (yellow), Na (magenta) and K (cyan). Abbreviations: dC decomposed calcite, dD decomposed dolomite, F feldspar, Q quartz.

The outlined observations made are an important basis for firing experiments of clay-additive mixtures. Various mineral reactions were identified, and observations reported in literature were confirmed. The two most significant processes observed in detail are the gradual decomposition of carbonates starting from 620 °C and the melting of the matrix between 760-880 °C. Especially, the role of sulfur during the decomposition of carbonates provides important information for brick producing processes, since the formation of water-soluble sulfates causes severe efflorescence (Schmidt 1961).

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