Moisture expansion of Ca-rich ceramic body

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Abstract. Calcareous ceramic bodies are typical for historical pottery, e.g. majolica and faience, as well as for contemporary production of ceramic tiles. The amount of the calcium component and the ratio of the other phases together with the firing temperature are responsible for the final properties of the ceramic body. The amount of the calcium component has a fundamental effect on the expansion of the ceramic body after firing and also during long-term usage or eventually during storage. The expansion behaviour is mainly associated with the planarity of the final product which is required in the case of large-format tiles. Expansion of the ceramic body is also related to the long-term stability of historical ceramics, especially glazed ceramic objects. In the case of low-fired porous ceramics moisture expansion of the ceramic body occurs due to a humid environment. It is a process of rehydration/rehydroxylation of unstable non-crystalline residues which remain from clay minerals in the ceramic body after firing. This process can be suppressed with a suitable mineralogical composition of calcareous ceramics. The main aim of this work is to study moisture expansion behaviour of calcareous ceramic bodies with a focus on both historical and contemporary ceramics.

1. Introduction

Natural raw materials used for traditional ceramic production (majolica, faience, utility earthenware, floor and roof tiles, etc.) contain a relatively high proportion of plastic clays. The basic component of clays are various types of clay minerals which are a source of aging when fired to a temperature of approx. 1100 °C, due to residues of clay minerals in dehydroxylated form [1]. The basis of aging process of rehydroxylation is influenced not only by the amount of reactive non-crystalline residues after the decomposition of clay minerals, but also by the second process, which is absolutely essential for this type of ceramic body, i.e. the decomposition of the calcium component. Calcium clays, crushed limestone, chalk, ground shells, marble dust, dolomite, wollastonite, calcium and soda-lime feldspars are the typical sources of calcium component in ceramic body [1, 2]. The temperature range for the decomposition of limestone, which is the most used raw material in our area, is closely related to the particle size and heating rate. Limestone decomposition can take place from 620 °C, while the main part of decomposition occurs in the range of 700–850 °C [1, 3–5]. During further temperature rise reactive calcium oxide is formed as a new crystalline phase. Furthermore, the calcium oxide reacts with metakaolinite to form gehlenite 2CaO.Al₂O₃·SiO₂. Gehlenite as a thermodynamically unstable phase subsequently reacts with excess silica or other components of ceramic body (metakaolinite, spinel, etc.) to form a stable crystalline phase anorthite (CaO·Al₂O₃·2SiO₂) or other products such as secondary wollastonite (CaSiO₃) or diopside (MgCaSi₂O₆) [5–8]. If the new crystalline phases in the form of anorthite, gehlenite and mullite are formed during firing in the correct ratio (firing above 900 °C), it is possible to obtain a ceramic body with a lower value (almost half the value) of moisture expansion than that of a non-calcium ceramic body fired according to the same firing schedule [9–10]. The spontaneous process of rehydroxylation begins immediately after the firing of the ceramic body; in the beginning it is relatively fast, then it gradually slows down. However, it is always a long-term process, and the value of irreversible moisture expansion depends not only on the chemical and mineralogical composition of the raw materials, but also on the overall technological process of production.

The main aim of this work was to prepare a Ca-rich ceramic body with a low value of thermal expansion coefficient (CTE), which will be suitable for large-format tile production. Furthermore,
the aging process of the prepared ceramic body was to be evaluated under the conditions of laboratory hydrothermal loading. A partial goal was focused on determining the source of deterioration of the glaze of historical faience. The aim of the work was to prepare a Ca-containing ceramics body with a low CTE suitable for large-format tiles and to evaluate its aging in the conditions of laboratory hydrothermal loading. The partial goal was to assess the source of damage to the glaze of historical faience.

**Experimental part**

Three model ceramic bodies (marked as 1, 2, 3), a contemporary ceramic body used for the production of tiles (marked as 0) and historical faience shard material (marked as F) were used to investigate the moisture expansion.

**Experimental methods**

Chemical compositions of powder samples were evaluated using a fully automatic sequential XRF spectrometer ARL 9400 XP (Thermo ARL, Switzerland). The X-ray fluorescence method was used for semi-quantitative and qualitative element analysis of up to 83 elements of the periodic table (B-C-O-U) in the range from ppm to 100 %. The spectrometer is suitable for measurement of powders, solid materials, thin films and fluids and is equipped with a Rh tube, a 4kW generator, 4 collimators, 6 crystals (AX 20, TLAP, PET, Ge 111, LiF 200, LiF 220) and 2 detectors – proportional and scintillation. The data obtained were evaluated by the software Uniquant 4.

Mineralogical compositions were identified by X-ray diffractometer PANanalytical X’Pert PRO (PANanalytical, The Netherlands) equipped with a Cu lamp and 1D detector PIXCEL with variable divergence and detected aperture. Measured data were evaluated by the software X’Pert HighScore Plus 3.0 with a reference sample database.

Mineralogical composition of ceramic bodies was also investigated using attenuated total reflectance (ATR) method with multi-reflecting diamond crystal (Nicolet iS50 spectrometer). Data were collected by an Omnic software in the range between 1800 and 400 cm\(^{-1}\) with the spectral resolution 4 cm\(^{-1}\).

The thermal expansion of the ceramic bodies was measured by LINSEIS L75 HS 1600C PT dilatometer. The heating rate was 5 °C min\(^{-1}\) up to 700 °C with 8 min dwell at the final temperature in helium and air flow. The data obtained were evaluated by the software Linseis Platinum Evaluation V1.0.90. Measurements were carried out on samples before and after hydrothermal loading. Fired compact samples of ceramic bodies were exposed to hydrothermal loading in a laboratory autoclave A/650/20 (Ceramic Instruments, Italy). The autoclave is built according to PED standards with a maximum pressure of 20.0 bar (2000 kPa), a manometer with a range of 0.25 bar (2.5 MPa) and an operating temperature of 230 °C.

Powder samples of ceramic bodies were measured also by simultaneous thermal analyses STA PT 1600/1750 °C HiRes (Linseis, Germany) in TG-DTA mode in a temperature range 25–1200 °C with a heating rate 10 °C min\(^{-1}\) in helium flow. The measured sample was placed in a platinum crucible. The released gasses, mainly CO\(_2\) a H\(_2\)O, were analysed by ThermoStar™ GSD320 (Pfeiffer Vacuum, Austria) mass spectrometer. Evaluation of measured data was performed using Linseis Evaluation software.

2. **Results and Discussion**

Model ceramic bodies (1, 2 and 3) were developed to study the dehydroxylation/rehydroxylation process of the Al\(_2\)O\(_3\)-SiO\(_2\)-CaO ceramic system. Ratios of the raw components were based on previous research of historical (F) and contemporary (0) Ca-rich ceramic bodies. Raw materials were combined in order to achieve a suitable mineralogical composition in the resulting model systems, which shows a delay in the area of small length changes during firing. Samples of model mixtures were fired at different final temperatures. The work was focused on the behaviour of model samples during temperature load and the formation of new phases in the ceramic body during firing. A combination of several analytical methods, mainly simultaneous thermal analysis (STA), X-Ray diffraction (XRD) and infrared spectroscopy by attenuated total reflection (ATR), was used for the study.
Chemical composition of the studied ceramic bodies is shown in Figure 1 in the form of a PCA biplot, where the red lines are directives of the rising contents of main oxides. The chemical composition of the ceramic mixtures are presented also in the form of a ternary diagram (right hand side on the top) and in the bottom the Al$_2$O$_3$-SiO$_2$-CaO phase diagram is shown. Quartz and anorthite (calcium feldspar) were identified using XRD as the main mineralogical components. Diopside was identified in the historical faience sample (F) and wollastonite in the model sample (3) with a higher proportion of calcium component, which is presented in Figure 2.
Figure 2 X-ray patterns of ceramic bodies (A) and two details of X-Ray patterns in the range of 25–29 °2θ (B) and 29–42 °2θ (C)

The ratio of anorthite was studied on fired model samples and it was found that the highest amount of anorthite was formed in the model sample (2) and the lowest in the sample (0), in which anorthite is supplemented by a higher proportion of mullite (see the detail of the X-ray pattern in Figure 2B). In the sample (0) also a trace amount of gehlenite was identified. In terms of mineralogical composition, model mixture (2) is the most resistant to deformation during the second part of firing (the area of small length change approx. 950–1160 °C). The resistance to deformation of model sample (2) was confirmed by dilatometric measurements in the temperature range 25–1200 °C (shown in Figure 4). Both anorthite and wollastonite were formed after firing in model sample (3), in which a higher content of CaO was identified by XRF (approx. 20 wt%). Diopside was identified as a main mineral in the historical sample (F). Furthermore, a small amount of gehlenite was determined in the mineralogical composition of historical sample.
Figure 3 shows the measured ATR spectra of model and real ceramic samples, in which the main bands of identified minerals (1079, 796, 777, 694 cm$^{-1}$ - quartz; 912 cm$^{-1}$ - gehlenite; 571 and 942 cm$^{-1}$ - anorthite; 955 cm$^{-1}$ - diopside, 967 cm$^{-1}$ - wollastonite) are indicated. The position of the Si-O vibration in the 1000–900 cm$^{-1}$ region was characteristic for calcium minerals (gehlenite, anorthite, diopside, wollastonite). It was proved that IR spectroscopy could be used for identification of particular Ca-minerals. Decomposition of carbonates and CO$_2$ release from the raw model mixtures during firing process was studied by STA and MS. The DTA curves of all three model systems shows a similar course of carbonate decomposition in the temperature range 630–850 °C that corresponds to the CO$_2$ release identified by MS, because the particle size distribution of the Ca-rich raw material used was similar in all cases (Table 1).

Table 1 DTA parameters of model ceramic bodies

|   | $T_{\text{onset}}$ (°C) | $T_{\text{offset}}$ (°C) | $T_{\text{min}}$ (°C) | Area (μVs mg$^{-1}$) |
|---|-----------------------|-------------------------|----------------------|-------------------|
| 0 | 631.7                 | 738.8                   | 715.5                | 15.74             |
| 1 | 654.1                 | 758.4                   | 740.9                | 25.06             |
| 2 | 659.5                 | 757.7                   | 742.1                | 23.68             |
| 3 | 654.7                 | 855.7                   | 781.0                | 56.87             |
A combination of several subsequent processes occurs during the firing of Ca-rich ceramic bodies. In the temperature range 700–850 °C different processes are involved (still ongoing dehydroxylation of clay minerals and onset of mica dehydroxylation, carbonate decomposition, and onset of gehlenite crystallization). The expansion of the ceramic body takes place in this temperature interval. Initial sintering and significant shrinkage occur above 850 °C. The area of small length changes (approx. 950–1160 °C) is characterised by crystallization of stable phases of anorthite and mullite. Shrinkage of the body is interrupted in the region of small length changes in the case of predominant anorthite phase (sample 1 and 2), which is shown in Figure 4. A significant increase in the volume of the model sample (3) is due to the crystallization of gehlenite and wollastonite. On the other hand, no noticeable interruption of shrinkage is detected in sample (0), in which the crystallization of mullite is dominant. The course of the firing process with regard to the formation of new phases was observed in sample (2). It was proved that with increasing firing temperature, there is a gradual increase in the anorthite content in the ceramic body. Model samples of the model mixture (2) were fired at different final temperatures (900, 950, 1000, 1050, 1100, 1150 and 1200 °C) using similar firing schedules, and part of the samples were subsequently exposed to hydrothermal aging. Dilatometric curves of samples before and after hydrothermal aging were measured and compared. Values of moisture expansion were obtained. The model samples fired at 900, 950 and 1000 °C contained residual metaclays, which rehydroxylated due to hydrothermal treatment (4.69 mm m⁻¹, 3.71 mm m⁻¹ and 0.37 mm m⁻¹, respectively). This effect compensates the presence of anorthite. The amount of anorthite phase increases with increasing firing temperature. Samples fired at 1050 °C and higher contain a sufficient amount of anorthite which led to a significant inhibition of the aging process of the Ca-rich body. The mineralogical composition of the historical sample (F) was different, and it was proved that the faience body caused the crazing of the glaze.

3. Conclusion
A Ca-rich ceramic body exhibiting favourable behaviour in the regions of small length changes (approx. 950–1160 °C) and is suitable for the production of large-format tiles, was prepared. In the case of
historical Ca-body, the effect of irreversible moisture expansion on the development of glaze defects was proved.

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