

HYDROTHERMAL DEGRADATION OF CERAMIC MATERIALS ON THE NATURAL RAW MATERIALS BASE

Part 1: Physical changes

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The paper deals with simulation of long-lasting atmospheric moisture exposure of ceramic materials on the base of natural raw materials. The exposure causes the irreversible volume expansion, recorded by as a relative length deformation. Series of samples from mixtures of clays with dolomite and calcite were prepared and the influence of the changing composition on the deformation was studied. In the following fired bodies based on kaolinic clays were exposed to various hydrothermal conditions, namely two exposure times and two temperatures were used. Correlation between mixtures composition and length changes (deformation) of material was confirmed. Results have shown a strong dependence of the found irreversible deformation on the content of kaolinite and hydrothermal exposure conditions. On the other hand, changes of firing regime didn't have significant influence on the deformations.

INTRODUCTION

Atmospheric water, namely air moisture is an important factor influencing long-lasting stability of ceramic materials. Air moisture causes physical and chemical changes [1, 2]. Effect of moisture on ceramic material produces its expansion; this can cause material defects and its destruction. This expansion is called moisture expansion and could be reversible and irreversible. If it acts as adsorbed moisture that doesn't cause changes in physical and chemical properties of material, then it is called a reversible moisture expansion. But if the penetration of water induces changes in physical and/or chemical properties of material and if water reacts with instable phases of body and causes irreversible changes of mineralogical and chemical composition of body under the normal temperature, then it is called irreversible moisture expansion (IME). IME is simply quantified by the relative deformation $\varepsilon = (\Delta l/l)$, where Δl is prolongation of the body after hydrothermal exposure and l is its original length before hydrothermal exposure. So hereafter we can talk about length changes - about prolongation.

As a reason of length changes can be considered rehydrations of instable phases present in a body [3]. Dilatancy (increase in volume) is caused by water penetrated through pores and bound by chemical bonds. One of the possibilities how to reduce the value of IME is the change of the input raw materials composition, e.g. replacing the part of clay raw materials by raw materials

with high content of CaO - calcite and dolomite. During firing these additives are decomposed and CaO can hydrate or react with CO₂ and thus increase moisture expansion, which is after firing almost irreversible [4]. But reactions with other components appearing in a body during firing (in particular with metakaolinite and spinel phase) are more probable [5].

Reversibility of moisture expansion through biscuit firing was studied. It wasn't succeeding in eliminating the moisture expansion, what was interpreted as a confirmation of chemically bounded moisture [4]. Other way how to regulate moisture expansion is in a prolongation of firing time [6].

The moisture expansion of ceramics resulting from the reaction of the body with the water influences their service lives. Much attention has been paid in recent years to the method of determining the moisture expansion of ceramics. This property is determined by autoclave treatment in a moist atmosphere using the appropriate pressure and duration. The effect of moisture expansion of ceramics under the action of steam at high pressure is explained by the splitting action of the molecular water [7].

Many workers who have investigated the effect of moist atmosphere on fired clay products have made use of autoclave treatments to accelerate the rate of expansion [8]. The possibility of accelerating moisture expansion of clay products by milder treatments, such as bowling water or steam at atmospheric pressure, has received little attention. Other measurements [8] have

confirmed earlier observations that treatment in saturated steam at 100°C accelerates moisture expansion of fired clay products. It has also been found that correlation with a natural expansion is sufficiently good [9].

Moisture attack on ceramic material can be simulated under conditions of elevated temperature and water vapour pressure. This has been utilized for determination of the body moisture expansion, which is a measure of the volume changes of the body in the course of its long-term ageing [7]. Among current test methods there are two methodically different standard tests, whose principle is modelling long-term moisture expansion by simultaneous exposure of material to moisture and elevated temperature and/or pressure. These are the French norm NF 13-302, 1183, and Czech technical norm CSN EN ISO 10545-10 [10, 11]. Both norms for the determination of IME differ mainly in an execution of the hydrothermal exposure. The modified French standard test consists of boiling in autoclave at the increased pressure and temperature (500 kPa, 160°C, 2 hours), Czech standard test prescribes long lasting boiling at the normal pressure (100°C, 24 hours).

All previous studies dealt only with physical changes of ceramic materials, but for understanding of moisture expansion there is very important to study chemical (structural) changes. It is necessary to search the dependence between physical and structural changes in material what turns to be the aim of this paper. In the first part of the paper there is evaluated the influence of the raw materials to physical changes of samples after hydrothermal exposure and the influence of the firing regime and the hydrothermal exposure regime on the physical changes of fired ceramic bodies. Conditions of hydrothermal exposure were derived from standard test's conditions (see above) and were modified. Deformation (length changes) of samples due to hydrothermal exposure was studied. In the second part of the paper structural changes and correlation between physical and structural changes will be analyzed.

EXPERIMENTAL

Raw materials used for the experiment were natural clay raw materials, calcite and dolomite from Czech Republic. Clays were taken from Plzen, Louny, Prague, and Cheb area in the ratio as used for the commercial tile production in Czech Republic. Element characterization was made by X-ray fluorescence spectroscopy. Content of SiO₂ was higher than 50 wt. % for all clay raw materials. Major component of clay raw materials were kaolinite, quartz and feldspar (Na, K).

At first influence of raw materials on the hydrothermal degradation (measured by the length changes) of ceramic materials was studied with an aim to compare the extent of degradation caused by calcite and dolomite. So model mixtures from clay raw materials and from

calcite and dolomite were prepared. The first group of mixtures contained calcite in the range from 0 wt.% to 20 wt.% in the batch and mixtures were marked C0-C20 according to calcite content. The second group of mixtures marked D0-D20 contained from 0 wt.% to 20 wt.% of dolomite in the batch. The third group of mixtures contained a changing ratio of dolomite/calcite and a constant amount of clay raw materials (85 wt.%). These mixtures were marked DxCy, where Dx is dolomite content in the batch and Cy is calcite content in the batch.

For next experiments, which were carried out on fine raw materials, kaolinitic clay raw materials were used. Kaolinitic clay raw materials were from Karlovy Vary, Podbořany and Pilsner deposits and were signed K1-K4. Content of kaolinite in these raw materials was higher than 80 %, additional phases were quartz, feldspar and mica (X-ray phase analysis). Characterization was made by X-ray fluorescence spectroscopy. Content of SiO₂ was higher than 52 % and content of Al₂O₃ was higher than 41 %. Particle size distribution measurements yield median values in the range of 4.5-7.5 µm and mode values in the range of 3.1-7.8 µm for all kaolinitic clays.

After raw materials separation and drying, mixtures were prepared. Then moistening, homogenization and grading were followed. Samples were formed by a laboratory pressing machine (metal form, forming pressure of 40 MPa). The dimension of the samples were 100×20×7 mm³.

Prepared samples were fired in a laboratory furnace under time variable high temperature treatment. For classification of influence of firing conditions on physical changes of samples, five different firing regimes were chosen. Base regime was the commercial "fast-firing" used in industry. Modification of this regime consists in time prolongation of some chosen parts (see Figure 1). Firing regime F1 was the base regime. Firing regime F2 corresponds to the time prolongation of the part A 5 times.

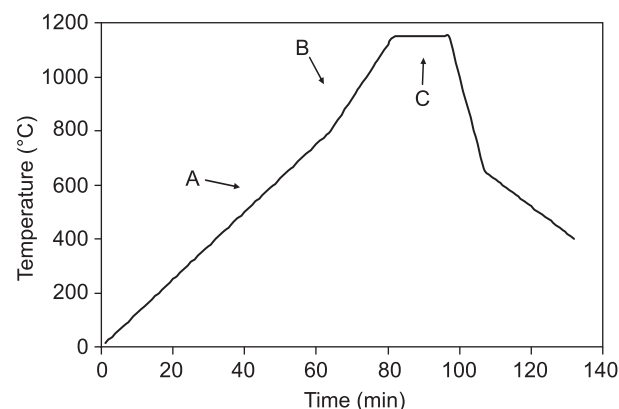


Figure 1. Curve of "fast-firing" regime. This regime was selected as the base one and was marked as F1. The next regimes were obtained by the prolongation of the particular parts (A, B, or C), see Experimental part for details.

Firing regime F3 corresponds to the time prolongation of the part B 5 times. Firing regime F4 corresponds to the time prolongation of the part C 5 times. For F5 firing regime all of the referred parts were 5 times prolonged. Maximal temperature for all five regimes of firing was 1150°C. Prolongation of parts of regimes serves for study of influence of the kinetics on the global result. The increase in temperature (in the nearest reasonable) doesn't lead to fundamental changes.

The firing was followed by hydrothermal exposure in autoclave under the variable conditions of temperature and exposure time to compare the influence of the conditions on the final degradation (length changes) of samples. The following regimes were used. A1 - exposure lasts 2 hours at the temperature 80°C, A2 - exposure lasts 2 hours at the temperature 160°C, A3 - exposure lasts 20 hours at the temperature 80°C, and A4 - exposure last 20 hours at the temperature 160°C. Samples were dried in laboratory oven after hydrothermal exposure. Length changes were measured by the mechanical measurements with a precision of 1 µm. The measurement of the samples was repeated after 3 hours, samples were carried in desiccator in the meantime. The measured prolongation served for the further comparison of the influence of the studied parameters to the length changes of the tested materials.

RESULTS

Influence of calcite and dolomite content in ceramic body on length changes were evaluated (Figure 2). If the content of calcite or dolomite is growing (i.e. content of clay raw materials is decreasing) the prolongation of the tested samples show decrease. Samples without calcite or dolomite, i.e. samples prepared only from clay raw materials show the highest deformation, almost three times higher than samples prepared from mixtures of clay raw materials and calcite or dolomite. Samples prepared from mixtures with the lowest content of clay raw materials (highest content of calcite or dolomite) shows the lowest deformation. This is confirmation of negative influence of the clay raw materials content on deformation of material.

On the ground of comparing of influence dolomite and calcite, dolomite/calcite ratio in mixtures was changed in next samples. All samples reached small deformation (Figure 3), because all contained lower amount of clay raw materials (see above). The change of dolomite/calcite ratio in the given range didn't cause significant change of deformation (within 95 % of statistical significance).

Because negative influence of clay raw materials was confirmed, other experiments were focused on influence of clay type on deformation. Four types of kaolinitic clays were used K1-K4. All exposed samples prepared from this clays show relative length changes higher than

0.7×10^{-3} (Figure 4). Differences between the values of deformation assigned for various types of kaolinitic clays are within the range of the standard deviation. Hence, change of kaolinitic clay raw materials doesn't have significant influence on the final values of deformation. Comparing irreversible deformation of kaolinitic clays K1-K4 (Figure 4) with clay raw material (D0, C0 in Figure 2) it is clearly that irreversible deformation of clay raw materials is 2-3 times higher than by kaolinitic clay type. This significant increase can be attributed both to chemical and mineralogical composition and particle size distribution.

The other way how to influence the values of prolongation could be a change of firing regime. Figure 5 shows the irreversible deformation in dependence on regime of firing for A2 hydrothermal exposure. All performed time changes of firing regime don't lead to relevant changes of deformation. Hence, the deformation doesn't markedly depend on the firing regime of samples (firing on the same final temperature).

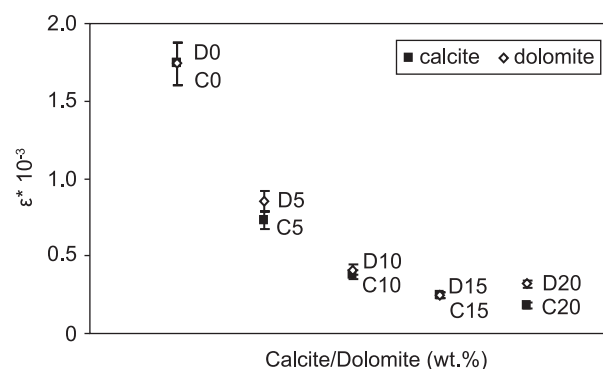


Figure 2. Influence of calcite and dolomite addition into clay raw materials on irreversible length changes. Dx correspond to the addition of x wt.% of dolomite, Cx correspond to the addition of x wt.% of calcite. Error bars means standard deviations obtained from 10 independent samples.

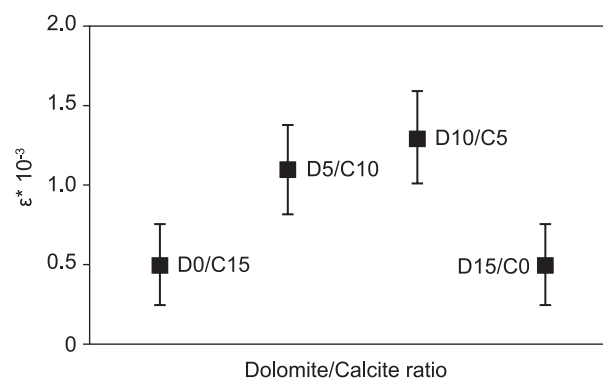


Figure 3. Influence of the replacement of calcite by into clay raw materials on irreversible length changes. Dx/Cy correspond to the addition of x wt.% of dolomite and y wt.% of calcite. Error bars means standard deviations obtained from 10 independent samples.

Figure 6 shows measured values of deformation in dependence on hydrothermal exposure regime. All samples exposed to chosen hydrothermal exposure regimes showed irreversible length changes in dependence on the exposure conditions. Values of deformation are within the range of $0.4-1.2 \times 10^{-3}$. It is evident the lowest values were determined after the exposure by the mildest conditions (80°C , 2 hours). By contrast the highest values of deformation were measured after the hardest conditions (160°C , 20 hours). It is clear harder conditions of hydrothermal exposure lead to the higher degree of deformation.

DISCUSSION

In this work it was carried out a number of experiments searching sources of length changes of ceramic material prepared from natural raw materials. At first influence of raw materials was examined. Samples of

mixtures with different content of clay minerals, calcite and dolomite were prepared. All samples showed irreversible length changes after hydrothermal exposure. Samples prepared from mixtures with higher content of clay raw materials (and with lower content of calcite or dolomite) show substantially higher degree of deformation than other mixtures. With decreasing content of clay raw materials in the body deformation decreased. By the change of calcite/dolomite ratio didn't go to relevant changes of deformation. So from view of raw materials composition correlation between clay raw materials content and deformation of samples is evident. Clay raw materials have negative influence on deformation. No difference between dolomite and calcite addition for found for the final deformation of studied bodies. Amount higher than 10 wt.% doesn't lead to any significant decrease of the deformation. Hence, it seems the Ca and Mg ions are not able to play the role of support of the phase stabilization.

For this reason four types of kaolinitic clays were chosen and their deformations were evaluated. Measured samples achieved almost the same length changes; differences are within the range of standard deviation. Because influence of the type of kaolinitic clay on the length changes wasn't significant all further experiments were carried out just for one kaolinitic clay.

The following study was focused on the high temperature treatment of samples, namely on firing regime. It was carried out by time modification of firing regime, firing time was prolonged, final temperature for all firing regimes was the same. Measured data confirmed, that any time change of firing regime didn't lead to significant changes of deformation of samples. It can be pronounced "fast-firing" regime is created in such way, that any additional modifications in terms of time prolongations would not lead to the significant improvement of properties of the burned samples.

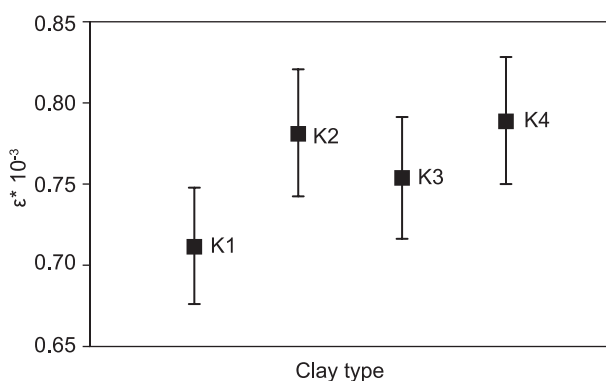


Figure 4. Irreversible deformation in dependence on kaolinitic clay type (see text for the meaning of Kx). Error bars corresponds to standard deviations obtained from 10 independent measurements.

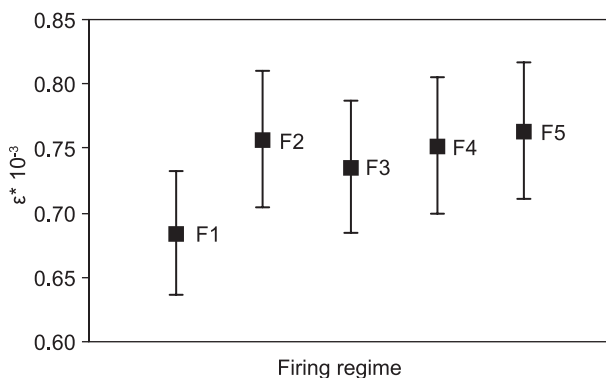


Figure 5. Irreversible deformation in dependence on regime of firing (see text for the meaning of Fx) for A2 hydrothermal exposure. Error bars corresponds to standard deviations obtained from 10 independent measurements.

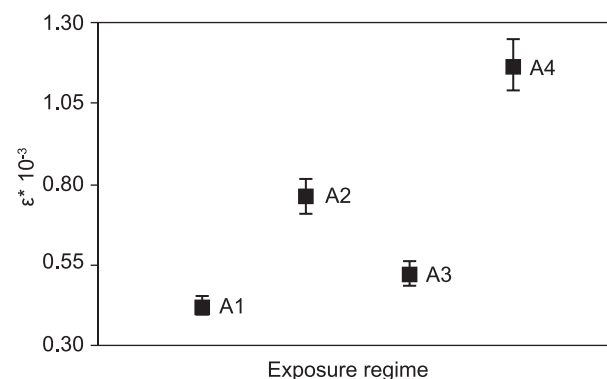


Figure 6. Irreversible deformation changes in dependence on the conditions of hydrothermal exposure. A1 - 80°C , 2 h., A2 - 160°C , 2 h., A3 - 80°C , 20 h., A4 - 160°C , 20 h. Note higher temperature causes larger deformation than the extensive time prolongation. Error bars corresponds to standard deviations obtained from 10 independent measurements.

Influences of hydrothermal exposure conditions on the irreversible deformations were the last performed experiments. They are based on the standard tests but those are modified by both the change of temperature and time of exposure (Figure 6). If hydrothermal exposure conditions are harder, samples also show higher deformation. Both longer exposure times and the increase of temperature support the hydroxylation kinetics and leads to the larger amount of chemically bonded water. Temperature increase decreases the energy barrier of the chemical reaction and therefore it is not surprising that the influence of temperature is significantly higher than the simple prolongation of the exposure times.

CONCLUSIONS

Long-lasting atmospheric moisture exposure on ceramic material was simulated by the hydrothermal treatment of the as fired bodies. Ceramics based on the natural raw materials revealed irreversible volume expansion. For commercial tile ceramics was found length changes (degradation of samples) depended mostly on the amount of clay; the addition of dolomite or/and calcite over 10 wt.% didn't lead to further decrease of the deformation.

The extent of deformation of kaolinit clay ceramics was strongly dependent on the hydrothermal conditions of the exposures. The temperature increase turned to show enhanced influence on the final deformation in comparison with a significant time prolongation. All experiments support the suggestion that the deformation is correlated with bonding of water in a chemical manner. Although irreversible volume changes of ceramic materials are very important phenomenon observed in the macroscopic scale, the understanding of causes points to the microscopic scale where fundamental explanation and relationships should be sought.

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