

DILATOMETRIC ANALYSIS OF CERAMIC ROOF TILES FOR DETERMINING IRREVERSIBLE MOISTURE EXPANSION

MIROSLAV VOKÁČ, ALEXANDRA KLOUŽKOVÁ*, VLADIMÍR HANYKÝŘ*, PETR BOUŠKA

Czech Technical University in Prague, Klokner Institute,
Šolínova 7, 166 08 Prague, Czech Republic

*Institute of Chemical Technology Prague, Department of Glass and Ceramics,
Technická 5, 166 28 Prague, Czech Republic

E-mail: vokac@klok.cvut.cz

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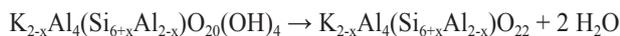
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Porous clay ceramic materials are subject to an ageing process which leads to moisture expansion. The irreversible moisture expansion value is usually determined with the use of time-consuming standard tests that require samples 20 cm in length. An advantage of dilatometric method that samples 2.5 cm in size can be measured. Using this method, we determined the irreversible moisture expansion values of samples of historical roof tiles of various ages. The procedure analyzes the course and the shape of the curves and reveals whether the volume changes result from the moisture expansion process. Rehydrated water is evolved within the interval 150-500°C. In addition, the correlation between the mineralogical composition and the irreversible expansion value has been studied. Materials containing mullite fired at temperatures above 1000°C show low values, while samples with high porosity and containing no mullite fired at temperatures below 1000°C show high values. Material containing gypsum exhibits the opposite effect – the tested fragments shrank, rather than expanded.

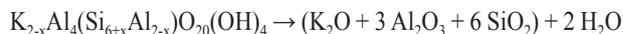
INTRODUCTION

In 1928, Schurecht [1] described crazing of glazed surfaces due to irreversible moisture expansion of ceramics. Nowadays, the use of composite concrete-ceramic floor structures in civil engineering results in occasional failures [2], where moisture expansion is one of the dominant loadings. For this reason, civil engineers and technologists in the ceramics industry need a reliable prediction model and other useful knowledge about this volume change of ceramics.

Ceramic masonry bricks, blocks, roof tiles, etc., are usually made from a raw material in which the predominant clay mineral is illite. The firing process of illite can be described in a simplified manner, as follows. First, the physically bonded water is released in the range 100–350°C. Then, the chemically bonded water that is in hydroxyl form is lost in the temperature range 350-600°C. Dehydroxylation proceeds by the reaction



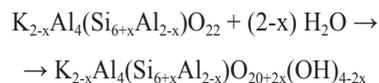
The crystalline octahedral structure of illite is not destroyed by dehydroxylation below a temperature of about 700°C. Above this point, the crystalline structure is destroyed, and non-crystalline fine-grained products are created. We can write the disintegration of illite into non-crystalline oxides as



In an oxidizing atmosphere, the crystalline structure is fully destroyed at a temperature of approx. 930°C. Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) is the first mineral that can be formed from non-crystalline products at temperatures above 1050°C.

The described firing process of pure illite can be significantly influenced by reactive oxides (CaO, SiO_2 , MgO, FeO) in a raw mixture. It is known that the presence of CaO reduces irreversible moisture expansion.

Porous ceramics rehydroxylate in a normal atmosphere with ordinary relative humidity immediately after firing. This is a very slow process and in the case of illite raw is assumed reversed to its firing. So, we can write it as



The potential for rehydroxylation depends on the firing technology (temperature and rate) and on the composition of the raw material. If the maximal firing temperature is in the range 700-1000°C, increased irreversible expansion can occur. The mass gain and irreversible moisture expansion of a porous ceramic occurs as a consequence of its rehydroxylation.

The ageing of porous ceramic by rehydroxylation can be accelerated by curing in an environment with

a high temperature and humidity. There are several standard methods that can be used for determining a conventional irreversible moisture expansion value. The specimens can be treated by boiling them in water for 24 hours (EN 772-19), by steaming them above boiling water for 4 hours (AS/NZS 1156.11:1997), or by high pressure steaming in an autoclave at 180°C for 5 hours (NF P 13-302).

Although the volume change is referred to as irreversible moisture expansion, a ceramic can be restored to the dehydroxylated state immediately after firing by annealing the ceramic to a temperature of 650°C. This effect is utilized for determining the irreversible moisture expansion value in the case of historic samples, or samples taken from structures.

A prediction model of irreversible moisture expansion based on steam expansion determined according to AS/NZS 115.11 was presented by McDowall & Birtwistle [3]. They assumed the dependence of expansion ε on time t as $\varepsilon(t) = k_1 + k_2 \ln(t + k_3)$. The same function was used by Pavlovic & Tosic [4] in their work. Zsembery et al. [5] continued measuring McDowall & Birtwistle samples for 35 years, and formulated the expression $\varepsilon(t) = b_1(t)X + b_2(t)X^2$, where X is the steaming expansion. Brooks & Forth [6] performed several measurements on

bricks produced in the United Kingdom, which were sorted into 6 special expansion-age categories, and an appropriate expression was specially developed for each category. This method is difficult to apply for different clays. Finally, Wilson et al. [7] proposed a new expansion law $\varepsilon(t) = a t^{1/4}$, where the kinetic constant a depends on temperature, and is independent of water vapour pressure in all normal environments, i.e. environments with atmospheric humidity only. The exponent $1/4$ is consistent with the theory of fractional single-file diffusion. Further, a modified two-stage power law of mass gain and irreversible expansion was presented [8], where the exponent $1/4$ is applied in both stages.

EXPERIMENTAL

Samples

The phenomenon of irreversible moisture expansion was investigated on historical samples of roof tiles of known age. Of course, the samples were from different places of origin, and consequently were of different chemical and mineralogical composition. For this reason, the samples will be described in greater detail.

The microstructural characteristics derived from hydrostatic measurements are given in Table 1. Water

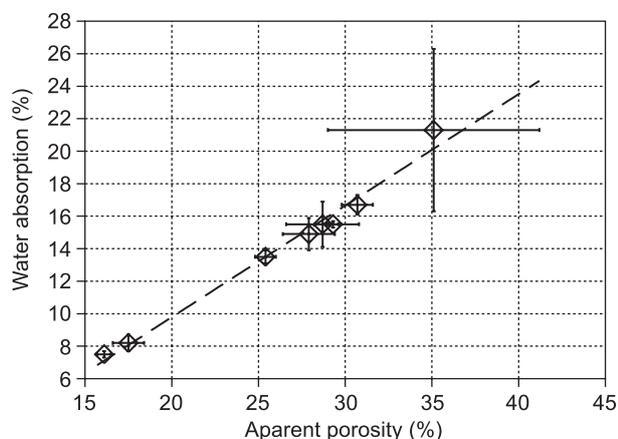


Figure 1. Dependence of water absorption on apparent porosity.

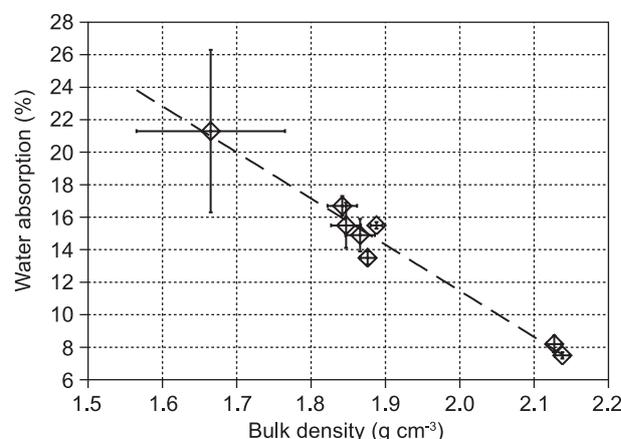


Figure 2. Dependence of water absorption on bulk density.

Table 1. Physical properties of roof tile samples from hydrostatic measurements.

Age (years)	Sample (locality)	Material properties			
		Water absorption WA (%)	Bulk density ρ_b (g/cm ³)	Apparent porosity P_a (%)	Apparent density ρ_a (g/cm ³)
1	Blížešov	7.5 ± 0.2	2.14 ± 0.01	16.1 ± 0.4	2.55 ± 0.02
78	Prague pantile	13.5 ± 0.4	1.88 ± 0.01	25.4 ± 0.6	2.52 ± 0.01
88	Velká Chuchle	21.3 ± 5.0	1.67 ± 0.1	35.1 ± 6.1	2.57 ± 0.08
101	Opava	8.2 ± 0.5	2.13 ± 0.01	17.5 ± 0.9	2.58 ± 0.02
143	Olbramovice	14.9 ± 1.0	1.87 ± 0.02	27.9 ± 1.5	2.59 ± 0.02
148	Bedřichovice	16.7 ± 0.6	1.84 ± 0.02	30.7 ± 0.9	2.66 ± 0.01
165	Chotýšany	15.5 ± 1.4	1.85 ± 0.02	28.7 ± 2.1	2.59 ± 0.05
188	Duchcov	15.5 ± 0.2	1.89 ± 0.01	29.3 ± 0.3	2.67 ± 0.02

Table 2. Mineralogical composition of the crystalline phase.

Sample (locality)	Content of crystalline phase (wt.%)								
	quartz	K-feldspar ¹⁾	Na-Ca feldspar ²⁾	calcite	crystalobalite	hematite	rutile	gypsum	mullite
Blížešov	45-55	5-10 (m)	5-10 (a), 10-20 (an)	–	1	2	–	–	5-10
Prague-pantile	60-70	5-10 (o)	20-25 (l)	–	–	2-4	1	–	–
Velká Chuchle	45-55	20-30 (m)	10-15 (l)	3-5 ³⁾	–	2	1	6-8 ³⁾	–
Opava	60-70	5-10 (m)	20-25 (an)	–	–	2-4	–	–	4-6
Olbramovice	76	23	–	–	–	1/	–	–	–
Bedřichovice	45-55	35-45 (m)	5-10 (l)	–	–	1/2 ⁴⁾	1	–	–
Chotýšany	50-60	15-20 (m) 5-10 (o) 5-10 (ak)	–	–	–	2	–	–	–

Notes:

¹⁾ K-feldspar: (o) – orthoclase, (m) – microcline, (ak) – anorthoclase

²⁾ Na-Ca feldspar: (a) – albite calciane, (l) – labradorite, (an) – anorthite

³⁾ Probably of a secondary origin during the life of a roof structure.

⁴⁾ Magnetite

Table 3. Chemical composition of samples of roof tiles.

Sample (locality)	Content (wt.%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Others
Blížešov	65.22	22.75	5.16	0.98	0.93	1.09	2.55	0.93	0.38
Prague-pantile	71.40	15.40	4.87	0.85	2.64	1.21	3.12	0.23	0.28
Velká Chuchle	69.21	9.50	3.53	0.76	10.10	1.59	2.31	0.82	2.18
Opava	76.33	12.70	4.18	0.80	1.48	1.03	2.55	0.65	0.28
Olbramovice	75.67	13.20	4.71	0.91	0.62	0.94	2.57	0.83	0.55
Bedřichovice	72.83	14.60	3.87	0.71	0.63	0.87	4.59	1.38	0.52
Chotýšany	72.71	14.50	4.79	0.78	0.63	1.24	3.48	1.39	0.48
Duchcov	66.71	18.92	5.37	0.87	1.90	1.38	2.98	1.38	0.49

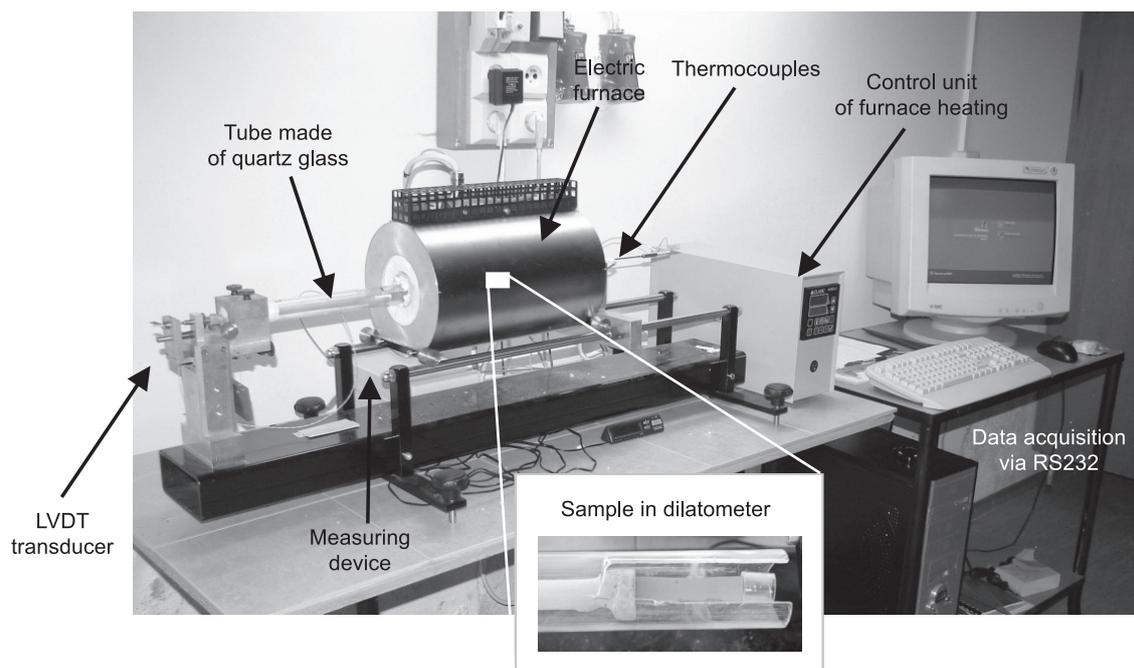


Figure 3. Thermal dilatometer utilised for determining irreversible moisture expansion.

saturation was achieved by boiling in water. The same nature of the samples is demonstrated in Figures 1 and 2, where the dependences of water absorption on apparent porosity and on bulk density are plotted. It is shown that the results are close to a linear functions. This follows from the very similar apparent density values.

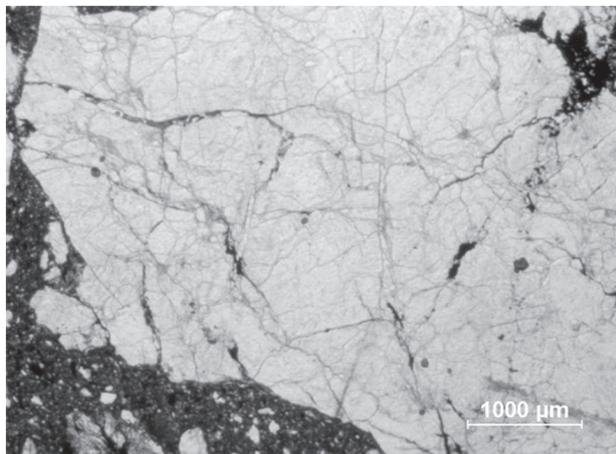


Figure 4. Sample of a roof tile from Bedřichov - cracked quartz grain.

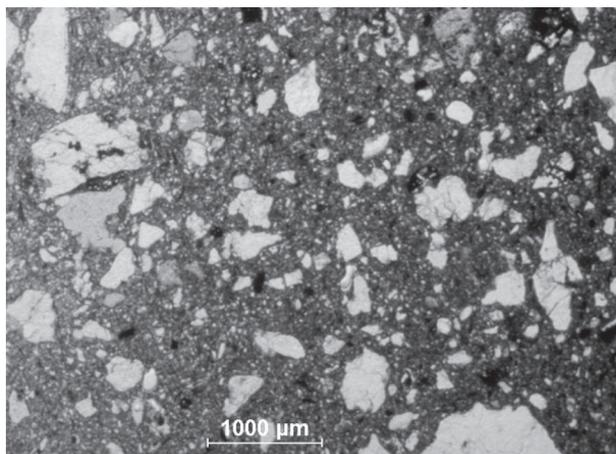


Figure 5. Sample of a roof tile from Bedřichov.

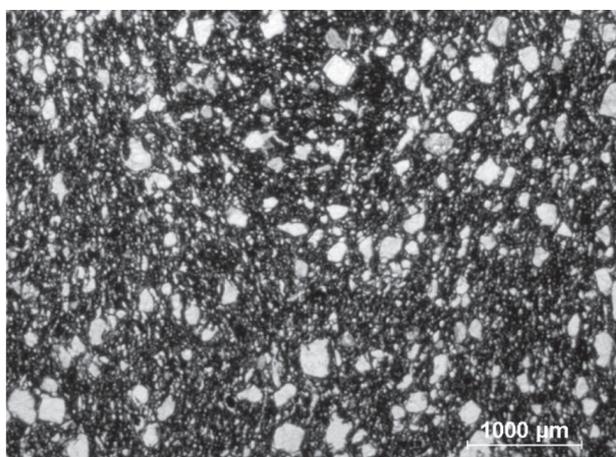


Figure 6. Sample of a roof tile from Opava.

The samples from Velká Chuchle have large standard deviation values, calculated for all material parameters introduced in Table 1. The historical samples of ceramics have properties with a large standard deviation due to significant non-homogeneity corresponding to the technology available when they were produced.

The mineralogical composition was investigated by X-ray diffraction analysis, which offers two options: qualitative analysis and quantitative analysis. Qualitative analysis provides a description of the phase composition, i.e., it identifies all crystalline phases. These results have to be compared with the determined chemical composition. Quantitative analysis provides information about the content. X-ray diffraction analysis was applied to specify the mineralogical analysis together with the polarization microscopy. The estimated mineralogical composition is given in Table 2.

The mullite in the mineralogical component of the sample from Opava indicates that the firing temperature was above approx. 1000°C in this case.

Microscopic methods are used for determining the mineralogical composition and also for estimating the technological process of raw material preparation and the forming method. The sample from Bedřichov is very heterogeneous. Figure 4 shows an extensive network of cracks on the quartz grain, which probably originate in the cooling stage after firing. A second microspecimen of this material is shown in Figure 5, and demonstrates the very heterogeneous microstructure of this sample. The sample from Opava (Figure 6) is more fine-grained and more homogeneous.

The chemical composition shown in Table 3 was determined by X-ray fluorescence analysis. The chemical compositions of the samples are very similar, but the sample from Velká Chuchle has a very high content of CaO and other admixtures.

Thermal dilatometric method

The dilatometric method utilises a thermal dilatometer, see Figure 3, with the precise displacement measurement by LVDT transducer. The usual length of a specimen is 35 mm. The proposed testing method consists of several stages (Figure 7), which are described below.

The 1st annealing is performed with a specimen taken from a masonry structure and heated at 105°C to constant mass. The temperature is raised from laboratory temperature to 685°C at a rate of 5°C/min. This is followed by a period of time at the maximum temperature. The strain-temperature relationship measured during annealing is affected by thermal expansion and by contraction due to the elimination of chemisorption in this stage.

The 2nd annealing is performed on the already annealed sample. The strain-temperature relationship is affected only by temperature expansion. The period of

time after the first annealing should not be greater than 24 hours. The period of time is usually as long as is needed to cool down the dilatometer.

After that, the accelerated rehydroxylating test is performed, i.e., boiling in water, steaming or high pressure steaming in an autoclave (according to the given standard). Then the physically bonded water is removed from the sample by heating at 105 °C to constant mass.

The 3rd annealing is the final stage. The measured relationship is affected by thermal expansion and also by an exactly controlled degree of moisture expansion. In this way, the conventional moisture expansion value can be determined.

The strain-temperature relationships in Figure 7 are plotted in such a way that the end points at 685°C are identical, because the same temperature and the same degree of rehydroxylation occur at this moment. The difference between the first and second annealing

in the dilatometer is due to the release of chemisorbed water from the ceramic body, and is equal to the nature irreversible moisture expansion of the historical sample. Similarly, the difference between the third measurement and the second measurement is equal to the irreversible expansion due to the accelerating test.

Once the strain-temperature relationships are numerically differentiated, we can easily estimate the temperature range in which chemically bonded water

Table 4. Nature irreversible moisture expansion determined by dilatometric measurement.

Sample (locality)	Irreversible moisture expansion (µm/m)	Standard deviation (µm/m)
Blížejov	39	8
Prague-pantile	1501	124
Velká Chuchle	-304	475
Opava	383	308
Olbramovice	1084	35
Bedřichovice	736	348
Chotýšany	983	316
Duchcov	724	96

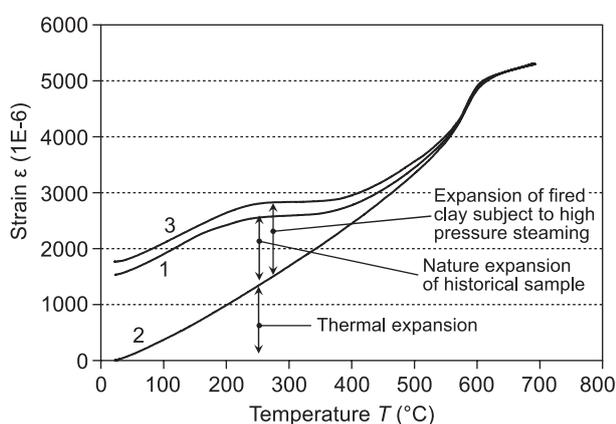


Figure 7. Strain-temperature relationships measured using a dilatometer on a sample from Prague-pantile (1 - first measurement on a historical sample, 2 - second measurement on the same sample, 3 - third measurement on the sample subjected to an accelerating test by high pressure steaming at 180°C).

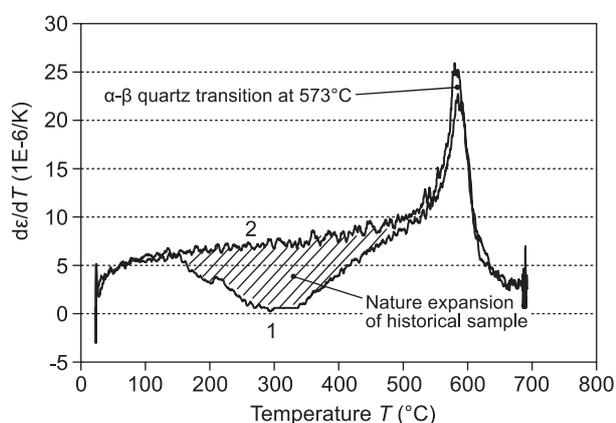


Figure 8. Derivatives of strain-temperature relationships on sample from Prague-pantile (1 - first measurement on a historical sample, 2 - second measurement on the same sample).

is removed from the ceramic body. The derivatives are plotted in Figure 8, where the hatched area indicates to the irreversible moisture expansion. Although we cannot assume a perfect thermal steady state, the transition point of quartz at 573°C can be identified, as well as the coefficient of thermal expansion.

RESULTS AND DISCUSSION

There were a total of 6 samples for dilation measurement from each locality. A typical result with evident presence of rehydroxylation is the result for Chotýšany sample. Figure 9 shows dilation curves (the first and second annealing) and the derivatives are plotted in Figure 10.

However, the curves measured on the samples from Opava display no significant differences between the first annealing and the second annealing in the dilatometer (Figures 11 and 12), and therefore this ceramic expands minimally. This was as expected, because the Opava sample was fired at a temperature higher than 1000°C, cf. mullite in the mineralogical composition (Table 2).

However, anomalous curves were obtained when measuring the specimens from Velká Chuchle (Figures 13 and 14). Here, the dilatation curves indicate that this fired clay shrinks rather than expands.

The mean values of the nature irreversible expansions together with standard deviations are shown in Table 4. It was mentioned above that the samples from Velká Chuchle expanded when annealed in the dilatometer. Also, the standard deviations calculated from the individual results reflect the available historical technologies. A sufficient standard deviation was achieved in the case of like-nowadays fired clays from

Blížejev, Prague-pantile, Olbramovice and Duchcov.

Figures 8 and 10 show that the chemically bonded water starts releasing from a ceramic body above 150°C and is completely removed at a temperature of 550°C. This temperature range depends on the amount of re-hydroxylation. In case of higher irreversible expansion, the range is wider, and vice versa. If the sample is subjected to a gravimetric thermal analysis test (GTA) and to a differential thermal analysis test (DTA), together with a water vapour sensor, similar results are obtained, as presented in Figure 15. The water vapour begins to

increase at approx. 150°C, and above 500°C the output from this sensor is practically constant. Of course, the mass decreases with temperature because of the release of water from the ceramic body. There is also an endothermic reaction at a temperature of 573°C, i.e., the transition in quartz. The physically bonded water also causes cooling of the specimen at the beginning of the test.

In addition, we have performed a long-term measurement of irreversible moisture expansion on selected samples 200 mm in length. The expansion was measured

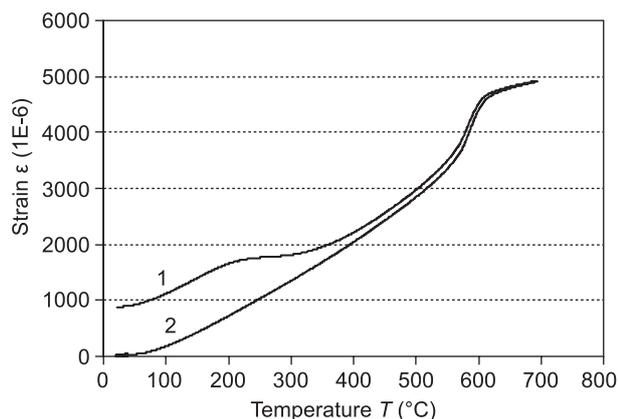


Figure 9. Strain-temperature relationships - Chotýšany.

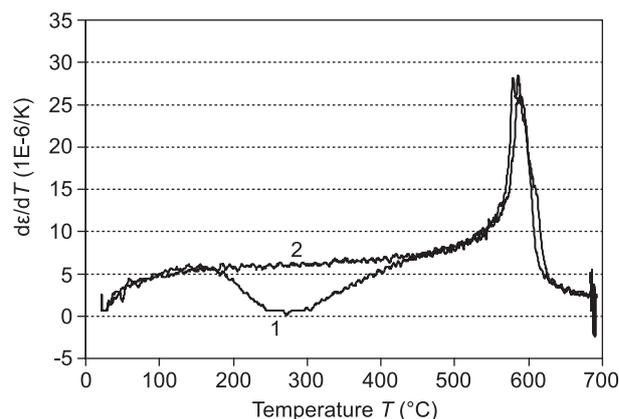


Figure 10. Derivatives of dilation curves - Chotýšany.

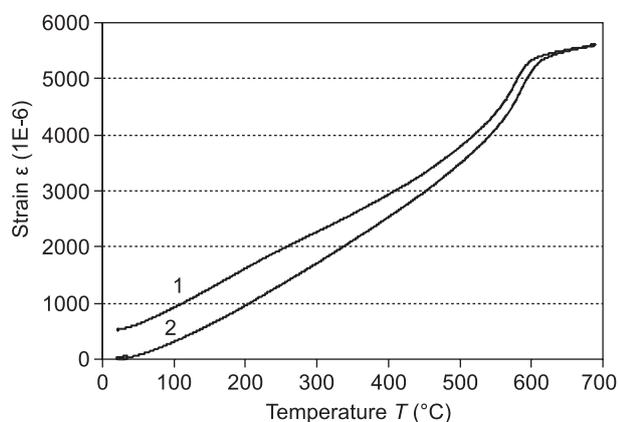


Figure 11. Strain-temperature relationships - Opava.

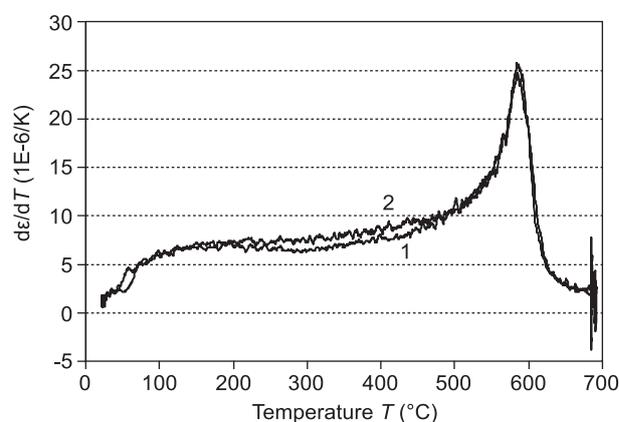


Figure 12. Derivatives of dilation curves - Opava.

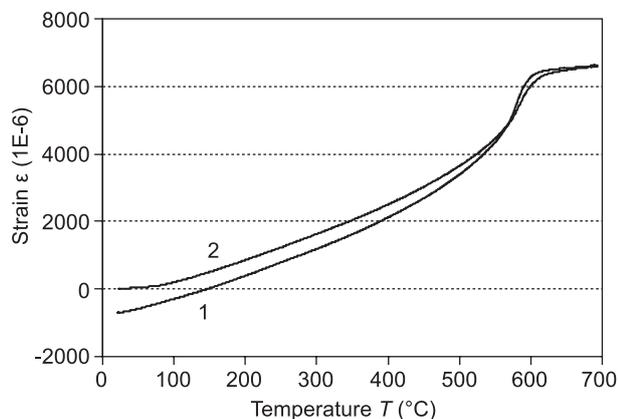


Figure 13. Strain-temperature relationships - Velká Chuchle.

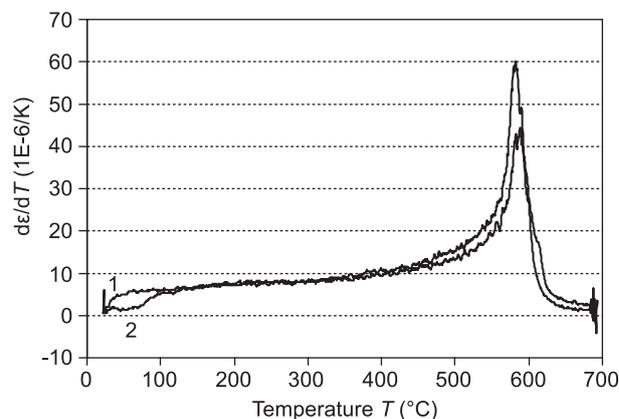


Figure 14. Derivatives of dilation curves - Velká Chuchle.

continuously by LVDT transducers in a stable environment with temperature $18 \pm 1^\circ\text{C}$ and relative humidity $70 \pm 2\%$, see Figure 16. The specimens were first annealed to 650°C for 4 hours, in order to induce a state corresponding to that immediately after firing. The measured expansion is plotted in Figure 17. The magnitudes of the displacements are in proportion to the irreversible expansions shown in Table 4.

This measurement reaffirmed the anomalous behavior

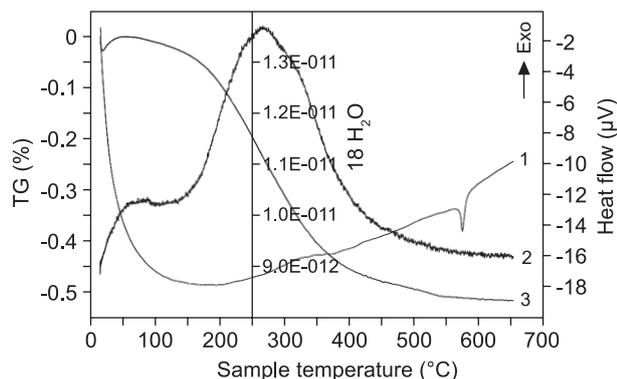


Figure 15. GTA (3) & DTA (1) with a water vapour sensor (2) - Chotýšany.

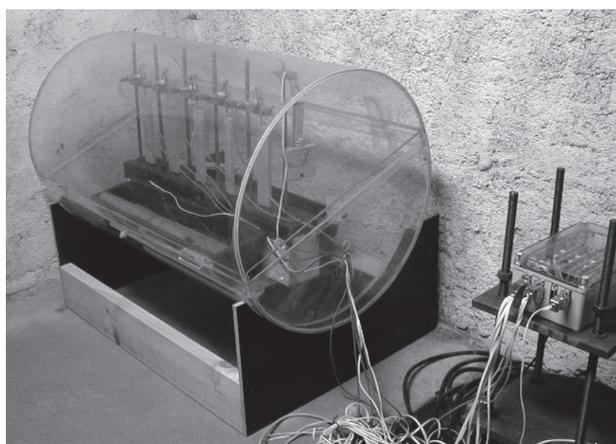


Figure 16. Box for long-time measurement of irreversible moisture expansion.

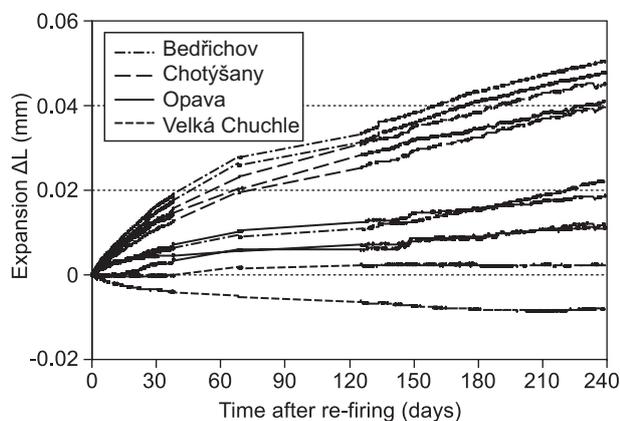


Figure 17. Long-time measurement of irreversible moisture expansion, dependence of the displacements on time.

of the sample from Velká Chuchle - one sample shrinks, while the second sample expands very slightly. This abnormal volume change can be explained by the abnormal chemical and mineralogical composition of this sample. The extremely high content of CaO (Table 3) resulting from calcite and gypsum in mineralogical composition (Table 4) is probably a consequence of secondary effects during its lifetime. It is likely that the chemical processes progress in a different way in this rare case.

CONCLUSIONS

The thermal dilatometric method seems to be appropriate for determining the irreversible moisture expansion of a useful porous ceramic body produced by modern technology. Some historical samples have considerable non-homogeneity, which is reflected in the measured results. It is useful to calculate the derivative of the dilatation curve in order to better evaluate whether the specimen has a higher degree of rehydroxylation. The temperature range in which removal of chemisorbed water takes place can also be better determined from the derivatives. A disadvantage is that the dilatometric measurements are taken in several stages, which is time-consuming, and the results are obtained only after several days of testing.

Rehydroxylation is removed by annealing in the temperature range $150\text{--}550^\circ\text{C}$. This range is narrower if chemisorbed water occurs in smaller amounts. This conclusion was proved by dilatometric measurements and also by GTA and DTA with a water vapour sensor.

An anomalous volume change was discovered in a sample with a very different chemical and mineralogical composition. This sample shrinks, rather than expands. This rare behaviour is probably due to a different chemical reaction in the ceramic body in the course of ageing.

Acknowledgement

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