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AGEING OF HISTORICAL CERAMICS

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ABSTRACT
Irreversible moisture expansion of specimens made from porous ceramics of historical fired tiles is analysed here. Irreversible moisture expansion values, which reflect the rate of body ageing, were determined by heating at a temperature of 650 °C for 20 minutes and by repeated dilatometric measurement until a temperature of 700 °C. To evaluate body ageing due to moisture expansion, it is necessary to specify the non-crystalline phase content. The causative factors influencing body ageing can be determined on bodies that have comparable non-crystalline phase content and are of similar chemical and mineralogical composition. Sufficient data set may facilitate a rough estimate of the age of historical ceramics.

KEYWORDS: irreversible moisture expansion, historical ceramics, fired roof tiles, dilatometric measurements, noncrystalline phase

1. INTRODUCTION

Historical ceramics provides a long-lasting document of human activities at a given time and in a given locality. A historical ceramic body consists of a basic material, the so-called matrix, which comprises grains of quartz, feldspar, mica, or possibly a group of other minerals. The distribution of these solid phases is usually heterogeneous. A chaotic system of open pores often forms an additional substantial component of these bodies. The body matrix arises from firing the original plastic body and soil with a certain clay mineral content, or a mixture of these materials with a variable content of implastic components. This implastic part of the source mixture forms the hard matrix of the ceramic body and is usually present as mineral and rock grains. The open pores in the body arise primarily when water dries out of the formed products. Their content and shape change during the firing process. Water condensate in the open pores of the ceramic successively bonds the water and causes ageing of the material.

2. BASIC PROCESSES IN CERAMICS FIRING

Water bonded by physical forces in a ceramic body is released at a temperature up to about 100 °C. Brick material, which is mostly formed from basic illite clay mineral, released physically bonded water up to about 300 °C. However, the dominant process during the heating is dehydroxylation of the clay minerals. This endothermic reaction is accompanied by shrinking of the fired specimen and brings about considerable changes in the clay minerals that are the basic component of ceramics. Chemically bonded water in the illite structure is released in the temperature range 350 - 600 °C, (approx. 22 % by weight) in the dehydroxylation process. Its course is described approximately by the equation:

$$\underset{\text{illite}}{K_{2-x}Al_4(Si_{6+x}Al_{2-x})O_{20}(OH)_4} \rightarrow$$
$$\rightarrow \underset{\text{dehydroxylated illite}}{K_{2-x}Al_4(Si_{6+x}Al_{2-x})O_{22}} + 2H_2O \qquad (1)$$

$$K_{2-x}Al_4(Si_{6+x}Al_{2-x})O_{20}(OH)_4 \rightarrow$$
$$\rightarrow \text{mixture } (K_2O + 3Al_2O_3 + 6SiO_2) + 2H_2O \qquad (2)$$

The crystalline illite structure disintegrates at the same time. Reactive non-crystalline product emerges from illite in the oxidative environment at temperatures above 750 °C; this process is terminated at about 930 °C. An unstable phase, practically non-crystalline, arises from the stable mineral illite phase, and is insufficiently resistant to the long-term action of moisture. Firing of illite at temperatures above about 1050 °C leads to formation a new stable phase of mullite ($Al_6Si_2O_{13}$). The course of these reactions can be considerably influenced by the presence of admixtures. Firing of ceramic mixture with raw natural material produces a relatively homogeneous substance, usually composed of a complex of minerals with high proportion of non-crystalline phase.

This phase is insufficiently stable and enables any water content to be bonded in the structure. The

Table 1 Basic properties of historical fired roof tile material.

Age (years)	Specimen (locality)	Material properties			
		E (%)	*OH* (gcm^{-3})	$P_{ap.}$(%)	$d_{ap.}$(gcm^{-3})
200	South Moravia	20.6 ± 1.0	1.710 ± 0.02	35.2 ± 1.2	2.641 ± 0.02
188	Duchcov	15.5 ± 0.2	1.888 ± 0.008	29.3 ± 0.3	2.672 ± 0.02
165	Chotýšany	15.5 ± 1.4	1.847 ± 0.02	28.7 ± 2.1	2.593 ± 0.05
148	Bedřichovice	16.7 ± 0.6	1.842 ± 0.02	30.7 ± 0.9	2.659 ± 0.01
143	Olbramovice	14.9 ± 1.0	1.866 ± 0.02	27.9 ± 1.5	2.593 ± 0.02
101	Opava	8.2 ± 0.5	2.127 ± 0.01	17.5 ± 0.9	2.580 ± 0.02
88	V. Chuchle	21.3 ± 5.0	1.665 ± 0.1	35.1 ± 6.1	2.572 ± 0.08
78	Prague-pantile	13.5 ± 0.4	1.876 ± 0.01	25.4 ± 0.6	2.515 ± 0.007
1	Blížejov	7.5 ± 0.2	2.138 ± 0.01	16.1 ± 0.4	2.547 ± 0.02

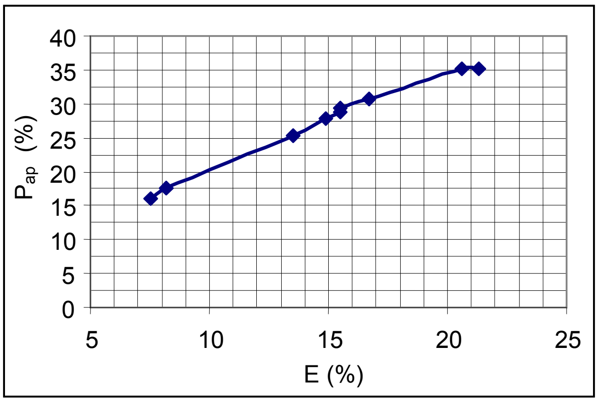


Fig. 1 Apparent porosity P_{ap} of historical roof tile materials and their water absorption *E* relation.

long-term action of moisture causes water to start bonding to the ceramic material (particularly to the non-crystalline phase), which is different from physical bonding. In the case of chemisorptions, the water is afterwards bonded by stronger bonding than in the case of physical bonding. Porosity is one of the basic properties of ceramics. Porosity significantly influences not only its mechanical and thermal properties, but also its resistance to climatic effects. Porosity can be open or closed, and can be characterized by direct measurement, with the use of mercury, or by optical porosimetry. An assessment of water absorption and of apparent porosity also offers adequate information of porosity (Hanykýř and Kutzendörfer, 2008; Kloužková and Hanykýř, 2007; Wilson et al., 2003).

3. LIQUID SATURATION METHODS

According to liquid saturation methods, the bulk density, apparent porosity and apparent density of a ceramic material are assessed by weighing the specimen with accuracy at least 0.01 g (depending on specimen size). The specimen is weighted before boiling in distilled water for 2 hours. Then, the specimen is placed in water for a period of 24 hours. After that, it is reweighed, both under water and in the air (Hanykýř and Kutzendörfer, 2008; Kloužková and Hanykýř, 2007).

Water absorption *E* after firing is equal to the relation of the water weight absorbed into the ceramic material by the open pores to the weight of the fired material. The following formula is used

$$E = (m_w - m_p)100 / m_p , \quad (\%)$$

where m_p is the weight of the fired material dried to a steady weight (g), m_w is the weight of the material saturated by water after wiping it with a wet towel, weighed in the air (g).

Bulk density *OH* is the ratio of the fired material weight to its volume mass, including all open and closed pores. It is calculated by the formula

$$OH = m_p\, d_{H2O} / (m_W - m_{W1}) , \quad (g.cm^{-3})$$

where m_{W1} is the weight of the water-saturated material weighed under water (g), d_{H2O} is the water density at a given temperature, measuring ($g.cm^{-3}$).

Apparent porosity P_{ap} is defined as the ratio of the whole open pore volume to the total volume, including all open and closed pores. It is calculated by the formula

$$P_{ap} = (m_w - m_p)100 / (m_w - m_{w1}) . \quad (\%)$$

Apparent density d_{ap} is equal to the ratio of the weight of the fired material to its volume, including the closed pores. It is calculated by the formula

$$d_{ap} = m_p\, d_{H2O} / (m_p - m_{w1}) . \quad (g.cm^{-3})$$

4. PROPERTY ASSESSMENT OF HISTORICAL FIRED TILE MATERIAL

The measured values, characterizing the basic properties of the historical fired tile material, are in presented Table 1. There is a simple, nearly linear relation between the apparent porosity of different historical roof tile materials (Table 1) and their water absorption, see Figure 1. Similarly, with decreasing bulk density of the material there is increasing water absorption, see Figure 2.

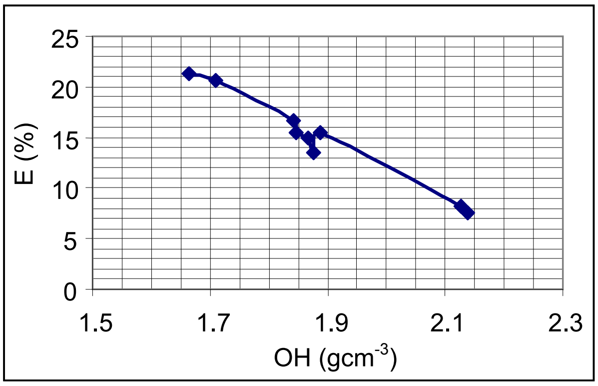


Fig. 2 Relation of water absorption E to the bulk density OH of historical roof tiles.

corresponding to laboratory conditions to a value of 700 °C at a rate of 5 °C per minute). When the specimen is at first heated, the strain-temperature curve is obtained, and at the end of heating the ceramic body is as it was immediately after firing, because the chemisorptive-type water bonds are removed by heating rehydrated ceramics to a temperature above 600 °C. Under this condition, the irreversible moisture expansion is removed. After the dilatometer has been cooled down, heating is performed next time. The difference between the second strain-temperature curve and the first strain-temperature curve is due to the current degree of rehydration, and corresponds to the current irreversible moisture expansion of the specimen

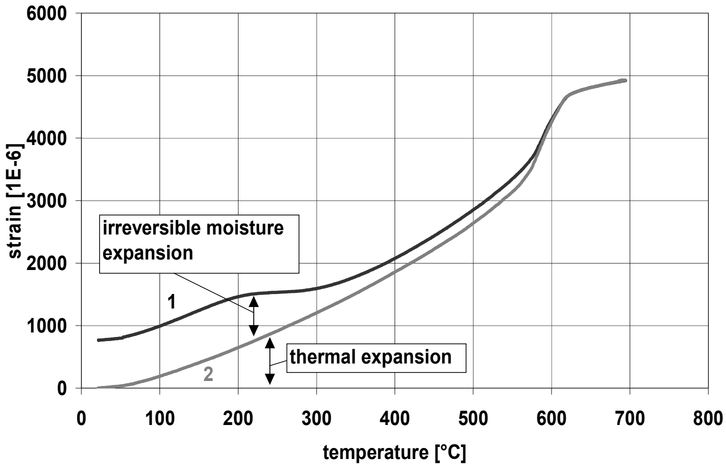


Fig. 3 Strain-temperature relationships on a sample of a 148-year-old roof tile, 1 – the first dilatometric measurement of historical roof tile sample, 2 – the second dilatometric measurement of the same sample.

(Vokáč et al., 2007; Kloužková et al., 2008; Vokáč et al., 2008).

Rapid indicative test of the actual irreversible moisture expansion of ceramic material dried up to constant weight is provided by heating in an electric furnace to a value of 650 °C for a period of 20 minutes. The material is not damaged during after this test. The dilatometric method is another way to determine actual irreversible moisture expansion.

Dilatometric measurements are used to identify linear changes corresponding to the volume changes of ceramic bodies during firing or heating with a constant temperature rate. Dilatometric methods can be used for identifying certain minerals in ceramics or for a quantitative description of processes related to changes in the volume of the material. One of these processes is the ageing of porous ceramics made from mixtures of natural raw materials.

The procedure utilized by the thermal dilatometer is based on accurate continuous measurement of the change in specimen length during a controlled increase in the temperature (from a value

The results of dilatometric measurements carried out on the sample of a 148-year-old roof tile are presented in Figures 3 and 4. The strain-temperature relationships are plotted in Figure 3, where the strains due to thermal expansion and due to moisture expansion, which is a symptom of ageing, can be measured. The derivatives of the strain-temperature relationships obtained numerically are plotted in Figure 4. The peak near a temperature of 573 °C corresponds to a reversible change in the crystalline structure of quartz (rhombohedral ↔ hexagonal) in the sample. The hatched area in Figure 4 is also in accordance with the irreversible moisture expansion value of the fired ceramic roof tile due to its ageing. Figure 4 also shows that the chemisorptive bonds are released in the temperature range from approx.150 °C to 450 °C.

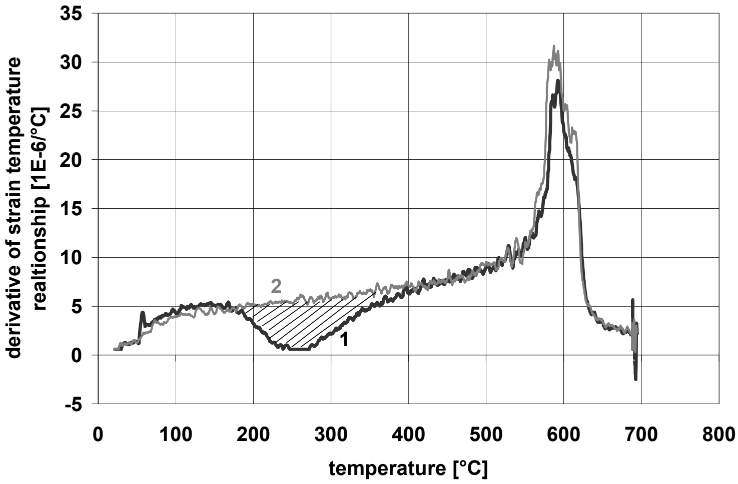


Fig. 4 Derivatives of strain-temperature relationships, 1 – 148-year old roof tile, 2 – the second measurement of the same sample; hatched area corresponds to the irreversible moisture expansion.

Table 2 Loss in weight caused by heating, and actual values of irreversible moisture expansion assessed by the dilatometric method on historical roof tile materials.

Age (years)	Specimen (locality)	Loss in weight Δ m at 650 °C/20 min. (by weight %)	Moisture expansion by dilatometric method A_{irr} (mm/m)
200	South Moravia	1.46	- 1.89
188	Duchcov	0.92	0.77
165	Chotýšany	0.51	0.98
148	Bedřichovice	0.55	0.74
143	Olbramovice	0.49	1.23
101	Opava	0.41	0.38
88	V. Chuchle	3.85	- 0.30
78	Prague- pantile	0.74	1.50
1	Blížejov	0.03	0.04

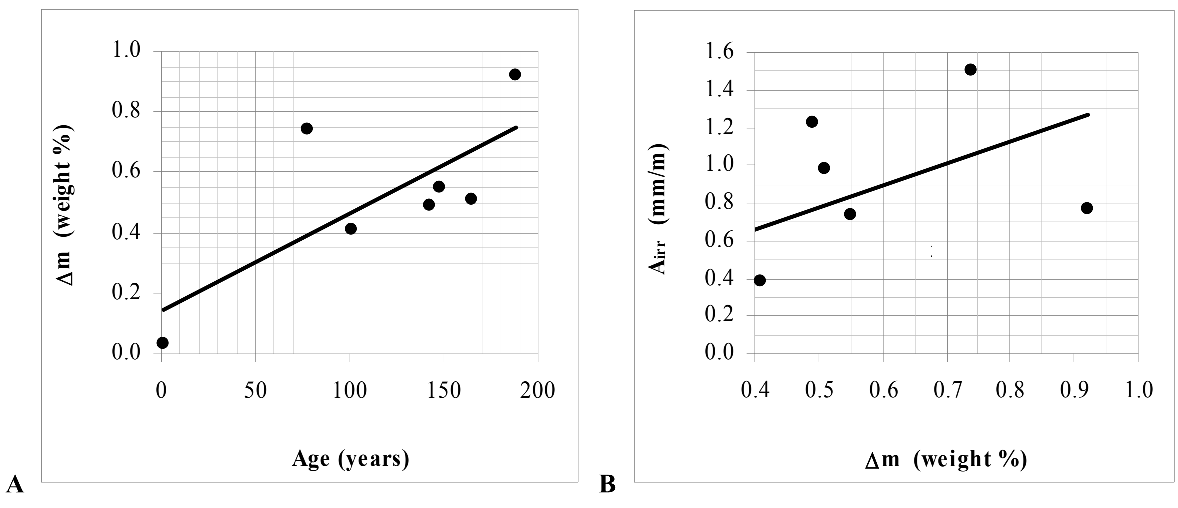


Fig. 5A Relation between the loss in weight caused by material heating Δm (at 650 °C/20 min.) and the age of roof tiles (specimens from South Moravia and from Velká Chuchle are not presented due to their different mineralogical composition),

5B Relation between actual irreversible moisture expansion A_{irr} and loss in weight Δm (650 °C/20 min.).

Table 3 Chemical composition of historical fired roof tile materials (by XRF).

Sample (locality)	Content (by weight %)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Sum
South Moravia	65.35	16.41	4.27	0.82	**6.20**	2.19	2.70	1.50	99.44
Duchcov	66.71	18.92	5.37	0.87	1.90	1.38	2.98	1.38	99.51
Chotýšany	72.71	14.50	4.79	0.78	0.63	1.24	3.48	1.39	99.52
Bedřichovice	72.83	14.60	3.87	0.71	0.63	0.87	4.59	1.38	99.48
Olbramovice	75.67	13.20	4.71	0.91	0.62	0.94	2.57	0.83	99.45
Opava	76.33	12.70	4.18	0.80	1.48	1.03	2.55	0.65	99.72
V. Chuchle	69.21	9.50	3.53	0.76	**10.10**	1.59	2.31	0.82	97.82
Prague-pantile	71.40	15.40	4.87	0.85	2.64	1.21	3.12	0.23	99.72
Blížejov	65.22	22.75	5.16	0.98	0.94	1.09	2.55	0.93	99.62

Table 4 Chemical composition of additives to historical fired roof tile materials.

Sample (loc.)	P_2O_5	SO_3	Cl	V_2O_5	Cr_2O_3	MnO	Co_3O_4	CuO	ZnO	Ga_2O_3
South Moravia	0.11	0.14	0.01	0.02	0.01	0.08	0.005	0.003	0.003	0.002
Duchcov	0.12	0.07		0.02	0.01	0.09	0.007	0.003	0.003	0.003
Chotýšany	0.04		0.04	0.02		0.07		0.02	0.01	
Bedřichovice	0.04		0.04	0.02		0.10		0.02	0.01	
Olbramovice	0.04	0.03	0.05	0.03		0.03		0.02	0.01	
Opava	0.04		0.04	0.02		0.04		0.02	0.01	
V.Chuchle	0.04	**1.72**	0.05	0.02		0.06		0.02		
Prague-pantile	0.04		0.04	0.02		0.05		0.03		
Blížejov	0.08			0.02	0.02	0.08	0.006			

Table 4 Chemical composition of additives to historical fired roof tile materials - continued.

Sample (loc.)	Rb_2O	SrO	Y_2O_3	ZrO_2	Nb_2O_5	BaO	Cs_2O	La..Lu	HgO	PbO
South Moravia	0.007	0.02	0.005	0.07		0.05		0.005		
Duchcov	0.01	0.02	0.004	0.04		0.06		0.006	0.01	0.005
Chtotýšany	0.01	0.01		0.05		0.08	0.12			
Bedřichovice	0.02	0.02		0.05		0.12	0.10			
Olbramovice	0.01	0.01		0.08		0.07	0.17			
Opava	0.01	0.01		0.05		0.06				
V. Chuchle		0.03		0.07		0.06	0.11			
Prague-pantile	0.01	0.02		0.05		0.06				
Blížejov	0.01	0.01		0.06	0.006	0.05	0.01			

A comparison of the loss in weight caused by material heating Δm (at 650 °C/20 min.) and the values of irreversible moisture expansion established on historical roof tiles is compared in Table 2. Loss in weight Δ m is almost dependent on the age of the roof tiles, as is clearly shown in Figure 5A. There is also a certain verifiable relation between Δm and irreversible moisture expansion A_{irr}, see in Figure 5B.

It is necessary to know the chemical composition in order to understand the ageing processes of porous ceramic materials. The chemical composition is often assessed by X-ray fluorescence analysis (XRF), when not only the basic chemical components but also the content of minor additives is specified, see Tables 3 and 4.

The qualitative and quantitative mineralogical composition of the crystalline phase of a ceramic material is provided by X-ray diffraction analysis XRD. It is necessary to compare the result of this analysis with the chemical composition of the investigated material. The content of the non-crystalline phases in the ceramic body can be determined by applying an external standard (a quartz standard). Quantitative mineralogical composition of

Table 5 Mineralogical composition of the material of historical roof tile bodies.

Sample	S. Moravia	Duchcov	Chotýšany	Bedřichovice	Olbramovice	Opava	V. Chuchle	Pantile	Blížejov
Mineral	Content (by weight %)								
quartz	35	26	31	27	38	36	31	31	22
K- feldspar	3	5	7	21	11	4	16	3	10
Na-Ca feldspar	3	8	14	4		12	7	12	2
hematite				1	1	2	1	1	
magnetite				1					
rutile				1					
calcite	1						2		
gypsum							4		
mullite						2			2
anorthite	13								
biotite	5								
muscovite	10								
Σ cryst. phase	70	38	52	55	50	56	61	47	36

Table 6 Loss in weight after annealing the roof tile material (650 °C/20 min.), and content of non-crystalline phase.

Content of non-crystalline phase in tile material (from 30 to 45 %)			
Age (years)	Δm (by weight %)	Content of non-cryst. ph. (by weight. %)	Sample
88	3.85	39	V. Chuchle
101	0.41	44	Opava
148	0.55	45	Bedřichovice
200	1.46	30	South Moravia
Content of non-crystalline phase in tile material (from 50 to 64 %)			
1	0.03	64	Blížejov
78	0.74	53	Pantile
143	0.49	50	Olbramovice
165	0.51	48	Chotýšany
188	0.92	62	Duchcov

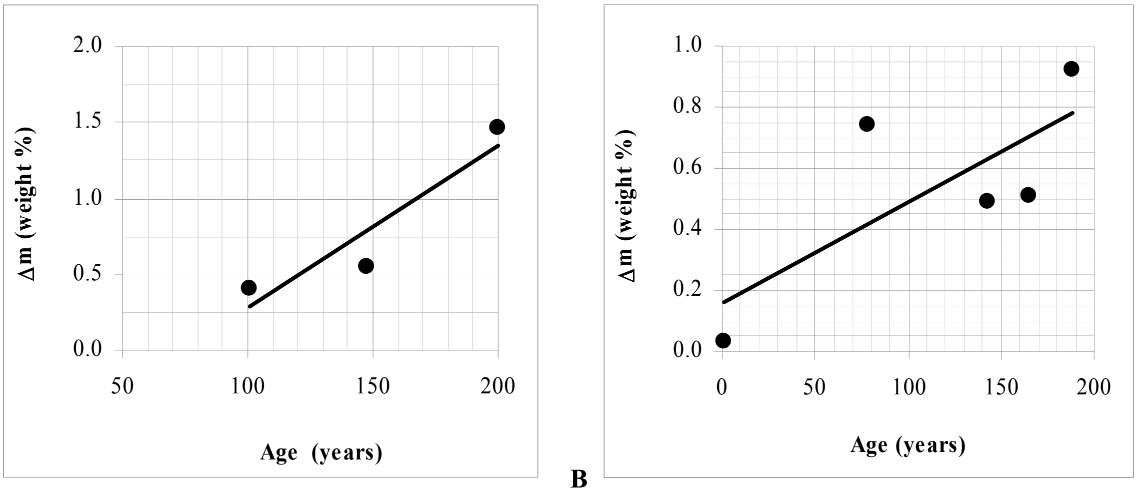
the historical fired roof tile materials was evaluated by Philips X'Pert PRO diffractometer in Bragg-Brentan parafocusing geometry at CuK_{α} radiation (λ = 1.5418 Å, V = 40 kV, I = 30 mA) in the range $2\theta = 5\text{-}70^{\circ}$. The mineralogical quantitative dermination, using quartz standard, and also the assessment of the non-crystalline phase are given in Table 5. This table shows that quartz and feldspar are the prevailing phases. In certain materials (South Moravia and Velká Chuchle), the presence of other minerals was assessed. In other materials (Opava and Blížejov) the presence of mullite was identified. After specifying the approximate content of the non-crystalline phase in the ceramic material and the irreversible moisture expansion values, their relation to the age of the material are presented, see Tables 6, 7 and Figure 6.

5. CONCLUSIONS

The ageing of porous ceramics as a result of irreversible moisture expansion was investigated on a set of specimens taken from historical fired roof tiles. The moisture expansion was determined by

Table 7 Actual irreversible moisture expansion specified by the dilatometric method.

Age (years)	A_{irr} (mm/m)	Content of non-cryst. ph. (by weight %)	Sample
Content of non-crystalline phase in tile material (from 44 to 48 %)			
101	0.38	44	Opava
148	0.74	45	Bedřichovice
165	0.98	48	Chotýšany
Content of non-crystalline phase in tile material (from 53 to 62 %)			
78	1.50	53	Pantile
143	1.23	50	Olbramovice
188	0.77	62	Duchcov



A B

Fig. 6 Relation between loss in weight Δm and age of tile material containing non-crystalline phase in the range:
A - from 30 to 45 % (the specimen from Velká Chuchle is not presented, due to its different mineralogical composition),
B - from 50 to 64 %.

material heating to a temperature of 650 °C for a period of 20 minutes, and by repeating dilatometric measurements up to 700 °C. It was proved that the irreversible moisture expansion values established by heating increase with the age of the material. There is a rather linear relation between the irreversible moisture expansion values and the weight loss values determined by heating. The irregularity of this relation may be explained by the different chemical and mineralogical composition of the materials. The content of non-crystalline phase should be investigated in order to assess the moisture expansion. The behaviour of ceramic materials can be compared only in the case of materials with very similar non-crystalline phase content and with a similar chemical and mineralogical composition. A sufficient quantity of dated specimens should make it possible to estimate the age of historical ceramics.

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