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LOW TEMPERATURE DILATATION MEASUREMENTS IN THE SILICATE RESEARCH

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The main application fields of thermal expansion measurements in the silicate research are summarized. Special emphases is given to frost dilatometry, the expansion effect due to water freezing on the low temperature thermal expansion curves of water saturated porous solids.

Thermal expansion measurements have important role in the silicate research. The results of the measurements can be applied as data characterising the behavior of materials (thermal expansion coefficient), or for solving analytical tasks.

Thermal expansion coefficient is usually determined when a new material was synthetized or found e.g. [1-5], in other case when structural materials or composites are exposed to changes of temperature during applications [6-9]. In the field of glass and glaze research there is a continuous demand for development of glasses, glass-ceramics and glazes of certain thermal expansion coefficients. In connection with this developing several methods were proposed for calculating the expected thermal expansion coefficient based on chemical composition data e.g. [10-13].

Linear thermal expansion curves can be used for qualitative and quantitative analysis of ceramic row materials, though their mineral components show different types of dilatation behavior when heating e.g. [14-16].

Low temperature measurements are seldom used although the knowledge of low temperature thermal expansion coefficient is important for both theoretical and practical reasons [17-20]. Low temperature dilatation measurements were used for research of superconductors as well [21-23].

Special application field of low temperature dilatation measurements is the research of porous materials exposed to weather conditions.

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The importance of frost dilatation measurements

In springtime severe damages can be observed in several porous construction materials. The cause of this damage is that the pores in the material were filled with water, and the volume of water might increase by 9.02 % during water-ice transformation. Such volume changes cause extremely high stress inside the pore structure. If stress overtakes a certain level, damage might be created. Considering, that both the construction materials and the water-ice system are very complex systems, it is very difficult to predict the probability of frost damage. Low temperature dilatation measurements on water saturated porous structural materials may contribute to solve this rather difficult problem.

Frost dilatation effect on the low temperature dilatation curve of a water saturated porous, solid material

An illustrative low temperature dilatation curve of water saturated porous material can be seen in Fig. 1. Both the cooling and the heating curves can be divided into three ranges:

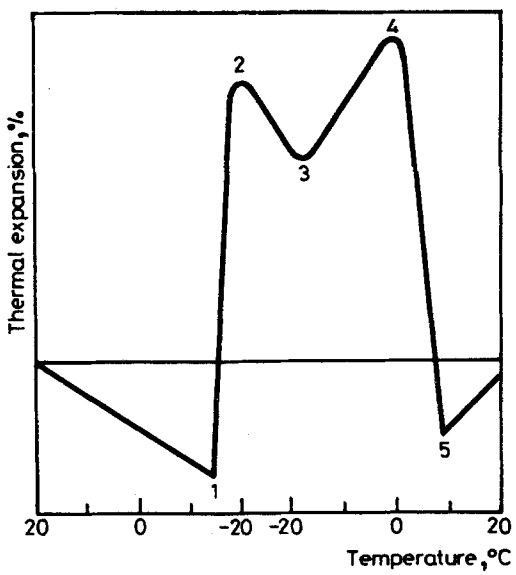

Fig. 1 Illusrative low temperature dilatation curve of a water saturated porous, solid material

– The range from room temperature to temperature No. 1 in the cooling curve and from No. 5 to room temperature in the heating curve. There the dilatation of the matrix material is dominant; thermal expansion values do not depend on wether the body is saturated or not.

– The ranges between No. 1 and 2 and between No. 4 and 5, where the dominant effects are the freezing of water and melting of ice, respectively, which result in relatively great changes in length, detectable in the dilatation curves. During cooling the water-ice transformation occurs at a temperature below 0^{o}. It should be noted that the freezing temperature is influenced by the measuring conditions (i.e. the temperature is usually measured in the vicinity and not inside of the sample, thus the difference between the real temperature of the material and the temperature measured depends on the heating - cooling range); by the pore size distribution and by the supercooling effect. For the same reasons melting temperature registered in the heating curve may be higher than 0^{o}.

The change in length due to freezing is considered as frost dilatation effect. Frost dilatation depends on the saturation coefficient, the water adsorption capacity and the mechanical properties of the sample.

– The ranges between No. 2 and 3 and between No. 3 and 4, in which the thermal expansion is determined by the dilatation properties of both the solid matrix and the ice formed. In the case of silicates thermal expansion coefficient of the ice is one magnitude higher than that of the silicate matrix. Stress caused by the ice during cooling decreases, because the volume of ice decreases with a higher rate, than the volume of the solid matrix. Thus thermal expansion coefficient in these ranges is slightly higher than that of the silicate matrix.

Properties influencing the frost dilatation effect

Saturation coefficient

Frost dilatation can be registered when the saturation coefficient of porous material is between 70-100 %. When saturation coefficient is lower than 70 % no frost dilatation effect can be registered. Between 70 and 100 % of saturation the magnitute of frost dilatation is proportional to the saturation coefficient.

Strength of the matrix material

The characteristics of ceramic materials are developed by firing. Certain properties (i.e. mineral composition, colour, porosity, pore size distribution, strength, etc.) may be influenced by the temperature and the duration of firing applied. Strength of a solid depends on the strength of the solid matrix (strength of poreless state) and its specific pore volume. It may be supposed, that the strength of the solid matrix of ceramic bodies fired applying the same firing conditions is equal and independent of the pore structure of the body. The effect of strength can be shown by measuring the frost dilatation of samples of various pore structure but fired at the same conditions.

It can be seen in Fig. 2, that the strength of the ceramic matrix material is increasing with increasing of the firing temperature at relatively low temperatures. Strength is almost constant in the range of 1100-1180°. At higher temperatures strength decreases with increasing firing temperatures.

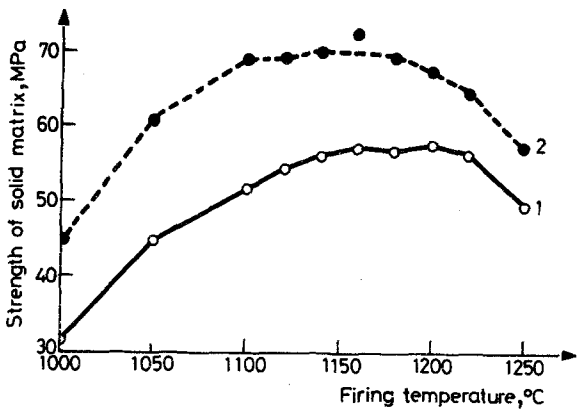

Fig. 2 Strength of solid matrix of a ceramic material *vs.* firing temperature calculated by two different estimation methods

Frost dilatation values of the samples fired at relatively low temperatures are shown in Fig. 3. It can be seen, that increasing of firing temperature results in decrease in frost dilatation, but the frost dilatation effect is influenced by the pore volume as well.

Figure 4 shows frost dilatation of samples fired in the temperature range where maximum strength has been created. Although, porosity varies in a wide range, no change of frost dilatation can be seen.

It can be concluded, when strength of the solid matrix reaches a certain level frost dilatation becomes independent of pore volume i.e. the volume of water which freezes.

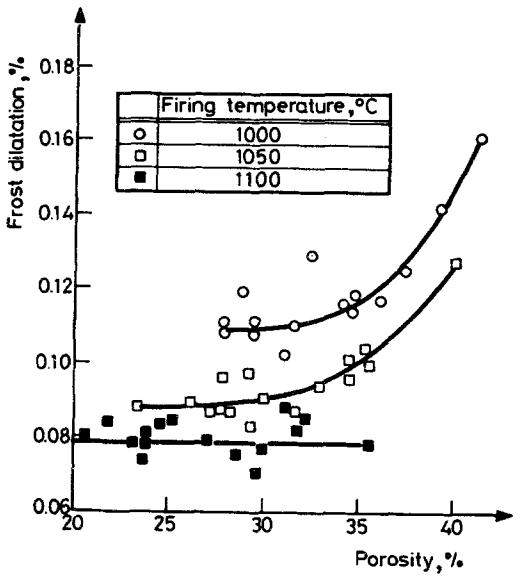

Fig. 3 Frost dilatation *vs.* porosity of ceramic samples fired at relatively low temperatures

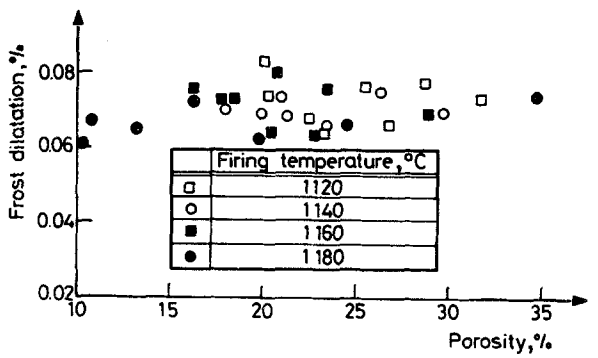

Fig. 4 Porosity dependence of the frost dilatation of ceramic samples having maximum matrix-strength

The effect of pore size distribution

Pore structure of hydrated cement pastes is more complicated than that of ceramics. In Fig. 5 porosity curves of a hydrated Portland cement paste compacted by vibration can be seen in different stages of hydration.

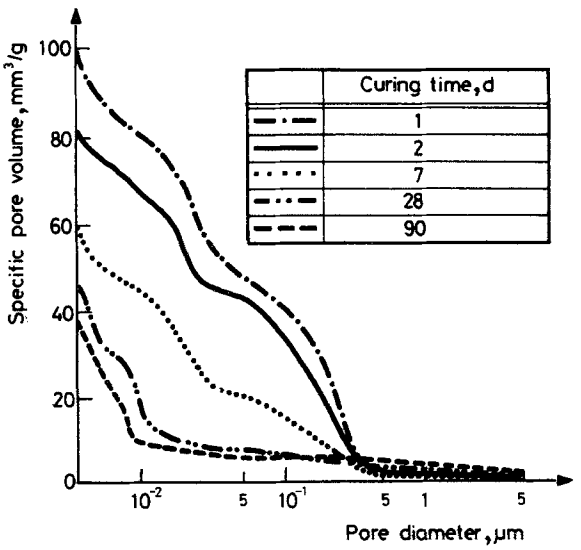

Fig. 5 Cumulative porosity curves of a hydrated Portland cement paste at different stages of hydration

In the course of hydration process several transformations and reactions occur in the cement paste which leads to setting. During hydration porosity decreases and strength of the silicate matrix increases, so both processes contribute to the considerable increase in strength of the whole material. Ranges of macropores (*a*) and mesopores (*b*) can be well distinguished in the curves. It can also be seen that the specific pore volume decreases with curing time, mainly due to the decrease in the number of macropores, but there is a sligth decrease in the number and median pore size of mesopores as well.

According to the pore structure two separated expansion effects can be seen on the low temperature dilatation curves (Fig. 6). Frost dilatation effect decreases with increasing curing time i. e. decreasing pore volumes, but the effect corresponding to the freezing of water filling mesopores decreases rapidly though the volume of mesopores changes only slightly. This

phenomenon is in accordance with the role of strength as it is mentioned above.

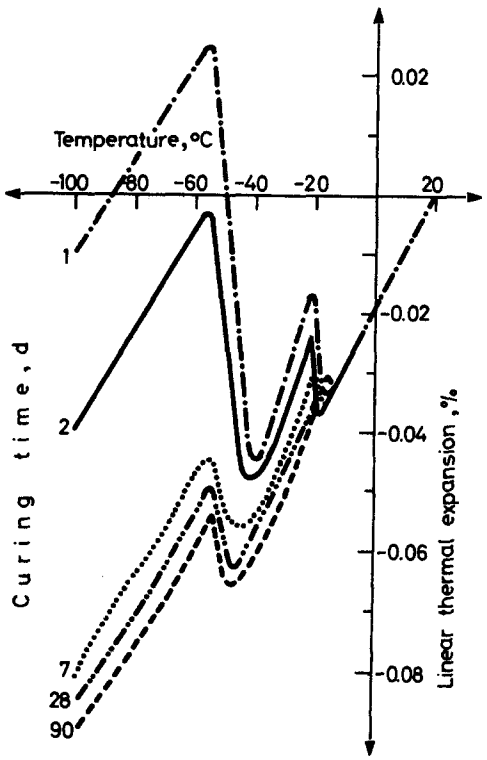

Fig. 6 Low temperature dilatation curves of a hydrated Portland cement paste at different stages of hydration

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Zusammenfassung — Es werden die Hauptanwendungsgebiete von thermischen Expansionsmessungen in der Silikatforschung zusammengefaßt. Besonderes Augenmerk wurde der Frostdilatometrie geschenkt, dem Expansionseffekt durch das Gefrieren von Wasser bei thermischen Expansionskurven wassergesättigter poröser Feststoffe im unteren Temperaturbereich.