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Effect of temperature on porosity of concrete for nuclear-safety structures

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Abstract

Structure changes of the cement gels of concrete PENLY and TEMELIN are carried out under the influence of the heat load in the temperature range 25–910°C. These changes are studied in the region of micro- and mesopores using the methods of physical adsorption of nitrogen and the mercury porosimetry. It was found out that the volume and surface of pores increase up to a temperature of 500°C approx., corresponding to the decomposition of $Ca(OH)_2$ on CaO. At the further increase of temperature, the volume and surface of pores decrease, so that the dependence of characteristics of pore space on temperature is approximately parabolic. The causes of this phenomenon are discussed.

Keywords: Microstructure; Pore size distribution; Thermal analysis; High temperatures

1. Introduction

Porous structure and volume of pores (so-called texture) influence considerably the physical and mechanical properties of a material [1]. This texture is not constant in time. It is being changed both, under the influence of internal parameters (e.g., as a result of hydration processes), and also under the influence of external conditions, in which material occurs (temperature, moisture, aggressive substances); and also by changes of these conditions.

In case of so-called extra-projects disasters of nuclear power plants, the high-temperature effect on the concrete buildings quality has a fundamental importance. Therefore, the change of concrete PENLY and TEMELIN texture in the dependence on the temperature change, ranging from 25°C to 910°C, is studied in this article. This dependence is studied on the cement gel of concrete samples, because the decisive processes and changes proceed exactly in the gel.

Both types of concrete are formed on the basis of Portland cement and have approximately the same water coefficient (PENLY — 0.43 and TEMELIN — 0.45). These facts are only similar: concrete TEMELIN belongs to the class B 40, while concrete PENLY is prepared as the so-called the high-strength concrete (the uniaxial compression strength is bigger than 60 MPa) [2].

The porous structure of the hardened cement paste, as well as its chemical and mineralogical composition, is a very important property, because it influences considerably such properties as resistance against physical and chemical factors, heat resistance, tension, and heat conductivity. These properties are undoubtedly fundamental for materials such as concrete.

2. Material composition

All projected studies will be carried out on two concrete types: concrete used for the construction of containment NPP TEMELIN (T) (in the Czech Republic) and concrete PENLY (P). The composition of the concrete mixtures for production of 1 m^3 of ready material is shown in Table 1. Mineral composition of the cements (% by weight) is shown in Table 2.

3. Differential thermal analysis

Results of DTA (Fig. 1) show the loss in free water content on the endotherm with maximum at 90°C for TEMELIN and at 95°C for PENLY. The endotherm at about

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Table 1
Composition of the concrete mixtures for production of 1 m^3 of ready material

Component	PENLY (kg)	TEMELIN (kg)
Cement	290 (CPA)	499 (42.5R)
Water	131	215
SiO_2	30	–
$CaCO_3$	105	–
Resin	10.62	–
Retarder	1.7	–
Plasticizer	–	2.8
Aggregates	831 (0–5)	705 (0–4)
	287 (5–12.5)	460 (8–16)
	752 (12.5–25)	527 (16–32)

490°C (T) and at about 485°C (P) belongs to the effect of decomposition (dehydration reaction) $Ca(OH)_2$:

$$Ca(OH)_2 \rightarrow CaO + H_2O \tag{1}$$

The endotherm at about 820°C for both materials indicates the decomposition of calcium carbonate:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2}$$

4. Experiment

Mercury porosimeter is predominantly used for the study of the porous structure of building materials. A measured sample, approximately 0.5 cm^3 big, is destroyed during the measurement [3]. This reality complicates substantially the evaluation of changes in porograms of such heterogeneous materials like the cement gels of concrete samples.

Table 2
Quantitative composition of cements (% by weight)

Sample	CP 52.5 France	CEM I 42.5 Mokra
Phase clinker composition		
C_3S	53.7	68.5
C_2S	26.7	11.6
C_3A	4.4	7.4
C_4AF	14.8	11.5
C_{free}	0.4	1.0
Total	100.0	100.0
C_3S_{eq}	55.4	72.7
C_2S_{eq}	25.4	8.4
Components fraction in cement		
Clinker	97.0	95.0
Gypsum	2.9	3.5
Fly ash	0.1	1.3
Slag	Trace	0.2
Total	100.0	100.0
Components fraction without gypsum		
Clinker	99.9	98.4
Fly ash	0.1	1.4
Slag	Trace	0.2
Total	100.0	100.0

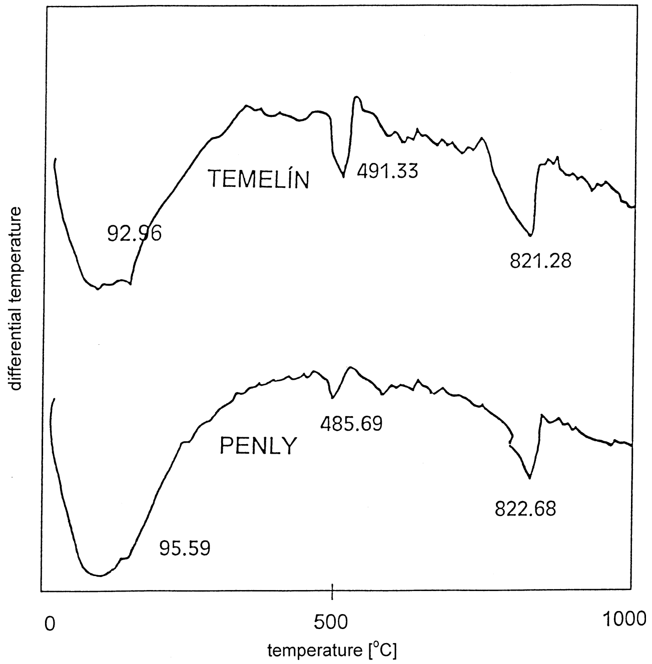

Fig. 1. Differential thermal analysis of PENLY and TEMELIN concretes.

Taking into consideration that the analysis of cement gels pore size distribution of both concrete types shows (see Fig. 2) that the substantial part of the pore space is formed by pores with radius smaller than 50 nm, we aimed to pursue the nanoporosity changes. Moreover, we can expect that pores (cracks) arising as a result of the heat stress will belong, according to their radii, exactly to this micro- and mesopore region.

The porous structure was studied by the methods of physical adsorption of nitrogen. From the adsorption and desorption isotherms, we can determine a distribution of the

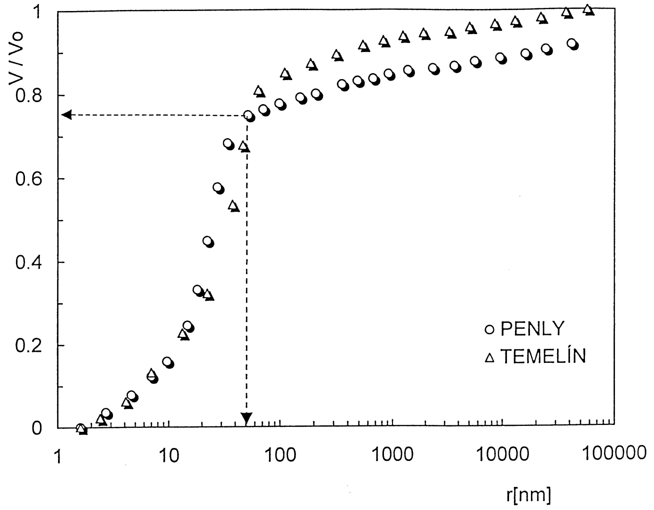

Fig. 2. Dependence of pores volume on pores radii (V_o is the total volume of pores).

specific volume of micro- and mesopores (pores with the radius up to 50 nm). We can also determine, using the method BET, the total specific surface of the pores (for the whole range of the pore radii). The sample is not destroyed at the same time, and therefore, it is possible to pursue an evolution of its porous structure in the dependence on the external condition changes.

The tempering of cement gel samples of both types of concrete was carried out in the high-temperature furnace. The temperature increase proceeded from room temperature up to the final 180°C, lasting 30 min. The samples were left at this temperature for 2 h. After removing, their porous structure was measured. The whole procedure was repeated on the same cement gel samples at the final temperatures 220°C, 380°C, 440°C, 500°C, 700°C, 800°C, and 910°C gradually.

Porosimetric BET measurements were carried out in the Institute of the Processes Fundamentals of Academy of Sciences of the Czech Republic.

5. Discussion

The temperature distribution of the specific volume of micro- and mesopores, and the total specific surface of pores are shown in Figs. 3 and 4. The results indicate that characteristics of pore space depend on temperature that is roughly parabolic, while all the curves reach the extreme at about 500°C.

We explain the increasing parts of curves in a standard way: temperature gradients generate thermostress that leads to the origin of micro-cracks and thus increasing both the volume and surface of pore space.

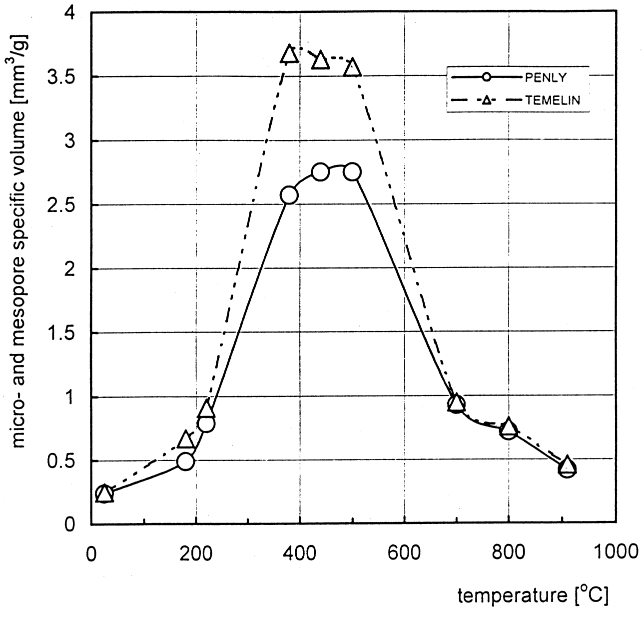

Fig. 3. Dependence of micro- and mesopore specific volume on temperature.

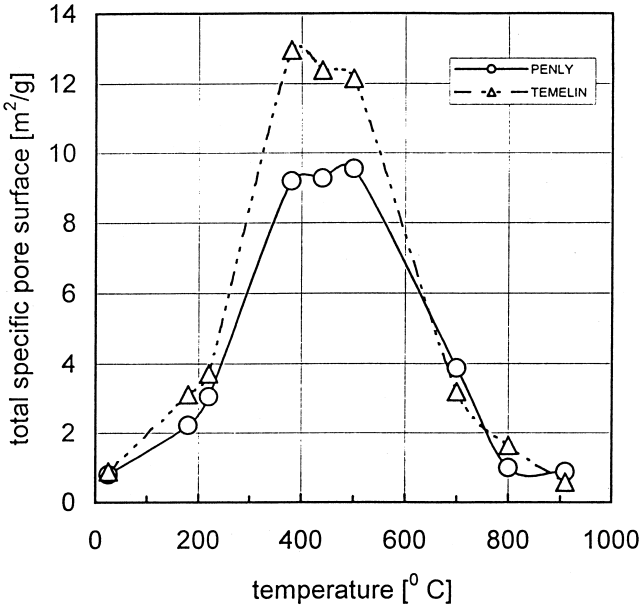

Fig. 4. Dependence of total specific pore surface on temperature.

We presume that there exists the causal relation between decomposition of $Ca(OH)_2$ on CaO (see Eq. (1)), whose temperature corresponds to the extremes of dependencies in Figs. 3 and 4 and the consequent decreasing of pore space. During the endotherm reaction (1), the chemically bound water releases (and consequently evaporates) on the one hand, and the crystals of $Ca(OH)_2$ with characteristic dimension 10^{-6} m are replaced with the crystals CaO with a characteristic dimension 10^{-9} m on the other hand. These changes evidently launch three types of simultaneous reactions being in progress:

1. Chemical reactions,
2. Phase transformations,
3. Sintering process.

CaO, due to its large surface, reacts with present silicates and hydrates, which leads to the development of new crystals that penetrate into the pores and either decrease them or completely fill them up.

The change of CaO concentration in the cement gel multiphase system leads to various modification transformations, often accompanied by expansion, which decrease the space of pores again.

Finally, the transformation of $Ca(OH)_2$ on CaO is accompanied by an increase of the specific area by several orders, which is energetically very disadvantageous. Therefore, the spontaneous process of sintering, i.e., closing, decreasing and at last vanishing of pores starts to be in progress, so that the surface energy of the porous body might increase. Taking into consideration that impurities (K_2O, Na_2O), which markedly decrease eutectic temperatures, are probably present in materials, we can assume that the sintering process proceeds in the presence of a melt.

All these processes are in the course of increasing temperatures supported, for example, with the transformation of α-quartz to β-quartz at about 570°C (when the specific volume increases by 5% approx.), the decomposition of $CaCO_3$ (see Eq. (2)), when the concentration of CaO further will increase, etc.

Parabolic dependence of characteristics of the pore space on the temperature is possible to find from time to time in the literature (see e.g. Refs. [4,5]). The peak of the parabola is, however, found at considerably higher temperatures than at the presumed work (about at 1000°C). The difference of our results is determined by the composition of the studied cements.

Acknowledgments

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