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Cement paste microporosity analysis: a comparison of different experimental techniques

Analiza mikroporowatości zaczynu cementowego: porównanie metod eksperymentalnych

Abstract

Microstructure defines almost all material physical properties of a substance. Thus, its proper identification is essential for the assessment of material durability. Porous materials constitute the vast majority of those applied in civil engineering. The most important parameters describing a porous structure are the specific surface area, the shape and volume of pores and the pore size distribution. There are several methods which provide such results; however, each of them has some drawbacks. The main purpose of this paper is to compare results obtained by means of various methods commonly applied to the investigation of microstructure. These methods are mercury intrusion porosimetry (MIP), low temperature sorption of nitrogen and thermoporometry (TPM). The experimental research is conducted on aluminium oxide, which is characterised by unimodal pore size distribution and hardened cement paste prepared using portland cement (CEM I 42.5R with water-cement ratio equal to 0.5. The results obtained by the above-mentioned methods are thoroughly described and compared in this paper. Each of the presented approaches has some limitations; therefore, in order to receive a reliable description of porous microstructure, one has to apply at least two different experimental methods.

Keywords: porous materials, porous structure, cement paste, mercury intrusion porosimetry, low temperature nitrogen adsorption, thermoporometry

Streszczenie

Wśród materiałów budowlanych przeważającą większość stanowią materiały porowate. Dokładna znajomość mikrostruktury jest kluczowa w ocenie ich wytrzymałości i trwałości. Istnieje wiele metod eksperymentalnych służących do analizy struktur porowatych. W niniejszym opracowaniu porównane zostały następujące techniki: porozymetria rtęciowa (MIP), niskotemperaturowa adsorpcja azotu oraz termoporometria (TPM). Badaniom eksperymentalnym poddano dwa materiały. Pierwszy z nich, tlenek glinu, jest materiałem referencyjnym o unimodalnym rozkładzie porów. Zgodnie z deklaracją producenta dominująca średnica porów wynosi 7.3 nm. Drugim zastosowanym materiałem jest zaczyn cementowy przygotowany na bazie cementu portlandzkiego CEM I 42,5R. Stwardniały zaczyn charakteryzuje się skomplikowanym rozkładem porów. Opisane techniki analizy mikrostruktury są komplementarne. Aby uzyskać wiarygodny opis struktury wewnętrznej materiałów o skomplikowanym rozkładzie porów należy zastosować co najmniej dwie metody badawcze.

Słowa kluczowe: materiały porowate, struktura porowata, zaczyn cementowy, porozymetria rtęciowa, niskotemperaturowa adsorpcja azotu, termoporometria

1. Introduction

Microstructure defines almost all material physical properties of a substance. Thus, its thorough identification is crucial with regard to the proper assessment of its durability and endurance. Most of the materials used in civil engineering are porous. Concrete, probably the most commonly used building material worldwide, is characterised by a highly complex porous microstructure. The porosity of the contact zone between the aggregate and hardened cement paste significantly differs from the structure of the inner mass of cement paste [1]. Moreover various types of pores can occur in hardened cement paste, i.e. closed voids, so-called ink bottle pores and continuous voids. The latter greatly influence the transport properties of concrete. Porous materials are strongly prevalent among those applied in civil engineering. It is crucial to become thoroughly acquainted with the material microstructure in order to understand the formation and potential use of the investigated substance as well as to develop precise prediction models.

Porous material microstructure is defined by parameters such as specific surface area, cumulative pore volume and pore size distribution. Several methods are applied in order to obtain such results. One of these, the mercury intrusion porosimetry (MIP) technique, is commonly acknowledged as the standard method with regard to hardened cement paste. However, due to some limitations, it does not provide a complete insight into its microstructure. MIP enables the investigation of pores in the range of from 3.5 nm to 500 μm [2], when in reality, this technique is usually employed to study macropores[3]. The method is based on the assumption that each pore is connected to the material surface either directly or through larger voids. This results in the underestimation of larger internal pores preceded by narrow channels (ink-bottle pores) [4, 5]. The next applied experimental technique of material microstructure assessment is low temperature nitrogen adsorption [6]. Thus far, many empirical and physical formulas describing sorption data have been introduced, among which, the BET model is the most popular [7]. Although the BET model has been submitted to much criticism, it is widely used to determine the surface area and is recognised as a reference method. It assumes that adsorbate particles do not influence each other but do adsorb on a surface in several layers. However, a similar problem as in the case of MIP arises – due to the diameter of nitrogen particles, they are often excluded from ink-bottle pores, which disturbs the accuracy of results [8]. Additionally, large mesopores correspond to a narrow range of relative pressure, which is why they are often measured with insufficient precision [9]. Thermoporometry (TPM) is another method which enables the investigation of material porosity [10]. This is a relatively new technique based on the fact that liquid in pores freezes at a much lower temperature than bulk liquid. The temperature decrease depends on the size of the saturated pore. This relation is described by the Gibbs-Thomson equation [11]. In TPM, samples of a few milligrams are measured using a calorimeter, which results in a fast and low-cost analysis. Water is a common choice as far as a probe liquid in TPM is concerned; its relatively large heat of fusion leads to high sensitivity of the calorimetry curve. However, it is observed that during pore liquid freezing there exists a non-freezable layer of thickness of up to 2 nm, which can affect the accuracy of results [12]. This paper aims to investigate the porous microstructure of hardened

cement paste through various experimental methods. Our intention is to compare results obtained by means of mercury intrusion porosimetry (MIP), low temperature sorption of nitrogen and thermoporometry (TPM).

2. Experimental methods

The mercury intrusion porosimetry technique is based on the premise that mercury, a non-wetting liquid, can be forced into pores of solid material only by applying external pressure. The relationship between pressure and the diameter of equivalent cylindrical pore, into which mercury is pressed at a given pressure, is described by the Washburn equation [12]:

$$d = -\frac{4\gamma\cos\theta}{P} \tag{1}$$

where:

P – the external pressure,
d – the pore diameter,
γ – the surface tension,
θ – the contact angle.

The MIP analysis is conducted by means of Micromeritics AutoPore IV9500 apparatus. The investigation is performed on coreshaped samples of a representative volume of cement paste (10 mm in diameter and 15–20 mm in length).

The second method applied is N_2 nitrogen adsorption/desorption. The analysis is performed at the temperature of liquid nitrogen (approx. 77 K) by means of a Micromeritics ASAP 2020 device. Firstly, the sample has to be outgassed. Secondly, consecutive portions of adsorbate are supplied to a crucible containing the specimen and the system is enabled to attain a state of equilibrium. As a result, nitrogen adsorption/desorption isotherms are created. In order to estimate the specific surface area, the BET model is applied in the presented paper. This approach is based on the following expression [13]:

$$\frac{1}{v\left[\left(\frac{p_0}{p}\right)-1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \tag{2}$$

where:

p – the equilibrium pressure,
p_0 – the saturation pressure of the adsorbate,
v – the adsorbate quantity,
v_m – the adsorbate volume, when it covers the adsorbent as a monolayer.

BET theory assumes that gas particles can embed in the surface in several layers, but every layer above the first is characterised by liquid-like properties. Pore size distribution is

determined according to Barrer, Joiyner and Halenda theory (BJH), which is based on the Kelvin equation concerning capillary condensation in mesopores [14]:

$$\ln\left(p/p_s\right)=\frac{-2\gamma w_m \cos\theta}{RTr_c} \tag{3}$$

where:

θ – the surface tension,
w_m – the molar volume,
γ – the contact angle.

The method is acknowledged as a standard method especially in North America. The theory is based on the premise that during capillary condensation (i.e. for relative pressure larger than 0.4), the pressure increase causes a thickness increase of the adsorbate layer located on the pore walls. On the basis of the estimated thickness, the diameter of the equivalent cylindrical pore is determined.

Phase transitions are connected to heat effects. During freezing, energy is released whereas in the case of melting, energy needs to be provided. The measurement of the net heat exchanged with surroundings enables assessment of the progress of any endo or exothermic process. This fact associated with temperature decrease during freezing/thawing in confined space is the foundation of the thermoporometry technique. The relationship between the liquid-solid transition temperature and the interface curvature considering the triple point of a pure substance was introduced by Defay et al. [11]. If one assumes that the chemical potentials of water and ice remain in equilibrium and that pores are of a cylindrical shape, then by applying the Laplace equation describing the mechanical equilibrium at the interface, the following depression temperature formula can be obtained:

$$\Delta T_m=\frac{2T_0\gamma_{sl}}{\rho_l\Delta H_f}\frac{\cos\theta}{r_p-\delta} \tag{3}$$

where:

T_0 – the melting temperature of the bulk state,
γ – the solid/liquid surface tension,
ρ_l – the liquid density,
r_p – the radius of the pore,
δ – the thickness of the unfrozen water film,
θ – the contact angle.

The above relationship is the so-called Gibbs-Thomson equation. This formula is commonly applied in order to determine the pore size distribution on the basis of the DSC curve [15, 16, 17]. In the literature, numerous variations of the Gibbs-Thompson equation can be found which express pore radius as a function of overcooling temperature. These can be obtained either through the approximation of system parameters [10] or as empirical relationships

which reflect the experimental data [17]. The most important of such relationships is that introduced by Brun [10], which is presented in Table 1.

Table 1. Relationship between pore radius and overcooling temperature introduced by Brun

Freezing	$r_P\,(\mathrm{nm}) = -\dfrac{64.67}{\Delta T} + 0.57$
Melting	$r_P\,(\mathrm{nm}) = -\dfrac{32.33}{\Delta T} + 0.68$

The other commonly applied example is that proposed by Landry [18], who derived it on the basis of experimental data. He also introduced formulas for pore diameter for both freezing and melting (see Table 2).

Table 2. Relationship between pore radius and overcooling temperature introduced by Landry

Freezing	$r_P\,(nm) = -\dfrac{38.558}{\Delta T - 0.1719} + \delta_f$
Melting	$r_P\,(nm) = -\dfrac{19.082}{\Delta T + 0.1207} + \delta_m$

where $\delta_f = 0.04$ nm and $\delta_m = 1.12$ nm.

The differential scanning calorimetry (PerkinElmer DSC 4000) is used to measure the heat released during water solidification.

3. Results

The experimental research was conducted on two kinds of material. Firstly, aluminium oxide was investigated as a material characterised by unimodal size distribution. Secondly, the hardened cement paste as an actual building material is studied.

3.1. Aluminium oxide

The applied material is a porous, amorphous, granular form of aluminium oxide. It is supplied by Norton Chemical Process Products Corp., Akron. According to the producer's declaration, it is characterised by unimodal pore size distribution, specifically, the dominant pore size is 7.3 nm and the porosity is 0.56 ml/g. The chemical composition (% wt) of the material, according to producer's information, is as follows: aluminium oxide (99.7–99.9), silicon dioxide (0.1–0.2), ferric oxide (0.1).

As mentioned in previous sections, the material microstructure was investigated by means of three methods: mercury intrusion porosimetry, low temperature N_2 adsorption/desorption and

thermoporometry with water as a probe liquid. In the case of the MIP technique, the maximum pressure applied to the sample was 400 MPa. The test results are presented in Fig. 1. The pore size distribution and cumulative pore volume imply that the material microstructure actually consists of equivalent pores, the diameters of which are 7.3 nm. Additionally, within the MIP analysis, the following parameters were determined: pore volume was 0.560 ml/g, bulk density was 1.298 g/ml, skeletal density was 4.712 g/ml and the total porosity was 72.5%.

The results obtained by means of the nitrogen adsorption/desorption test are presented in Figs. 2 and 3. The shape of sorption isotherms (Fig. 2) is characteristic for IV type according to IUPAC classification, which is typical for mesoporous adsorbents. The hysteresis loop beginning at $p/p^\circ = 0.65$ can be classified as A type as per de Boer [19], which implies cylindrical pores of relatively constant intersection. The regular sample microstructure is also confirmed by pore size distribution, which is characterised by one visible maximum (see Fig. 3). The specific surface area determined by the BET method was 190 m^2/g, the total pore volume was 0.58 ml/g and the average pore diameter was 7.78 nm.

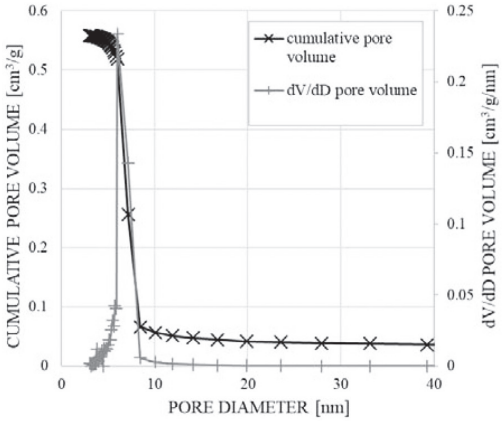

Fig. 1. Pore size distribution and cumulative pore volume of aluminium oxide obtained by the MIP technique

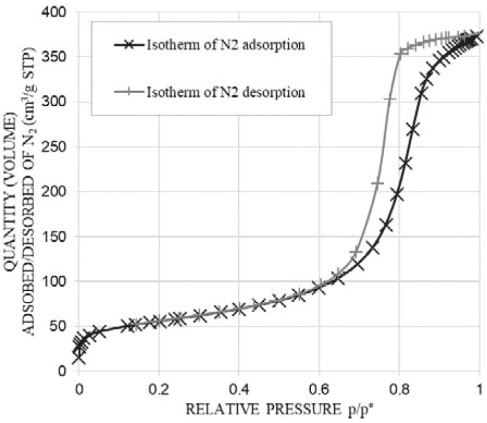

Fig. 2. N_2 adsorption/desorption isotherms determined for aluminium oxide

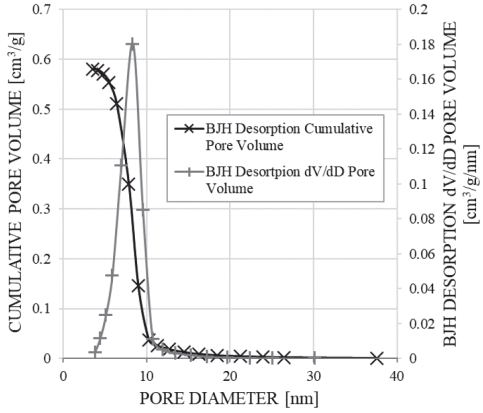

Fig. 3. Pore size distribution and cumulative pore volume of aluminium oxide obtained by low temperature N_2 sorption

The TPM analysis is conducted for DSC scan with slow cooling/heating rate, which is 0.1°C/min. Such a temperature rate allows the sample to remain in a state of thermal equilibrium. The calculations are conducted in accordance with Brun and Landry formulas. The obtained values are compared in Table 3. It is evident that results estimated on the basis of the Landry equation are more thorough in comparison to the producer's data.

Table 3. The average pore diameters of aluminium oxide calculated for the Brun and Landry relationships

	BRUN [nm]	**LANDRY [nm]**
Freezing	11.36	6.10
Melting	9.06	6.86

3.2. Cement paste

Hardened cement paste was the second material under investigation. The material was prepared from the Portland cement CEM I 42.5R with a water to cement ratio of 0.50. Samples were formed in small PVC moulds. After twenty-four hours, they were demoulded and cured for twenty-eight days in a water bath. Two kinds of samples were subsequently cut off from the initial specimens. Small cylinders with diameter 10 mm and height 15 mm were investigated by MIP as well as low temperature N_2 adsorption tests, whereas small discs (5 mm diameter and 3 mm height) were studied using the TPM method. Such dimensions guaranteed the homogenous, representative volume of the examined samples [20]. In the case of each sample, the proper analysis was preceded by the drying process at 30°C until the solid sample mass was obtained. The minimal pore radius possible to be detected by MIP method is 3 nm. Thus, this method enables investigation of both mesopores and macropores. The pore size distributions and cumulative pore volumes are presented in Fig. 4. The obtained results confirm that cement paste has a highly complex structure. As a result of MIP tests, the following sample parameters were determined: pore volume was 0.150 ml/g, bulk density was 1.618 g/ml, skeletal density was 2.120 g/ml and total porosity was 23.7%.

The shape of sorption isotherms obtained by means of low temperature N_2 adsorption (Fig. 5) is typical for mesoporous and macroporous materials. The hysteresis loop begins at a much lower relative pressure for cement paste than for alumina oxide. Such a loop shape implies the presence of ink-bottle pores in hardened cement paste [21]. The BET surface area was 12.510 m^2/g, and the total pore volume was 0.070 ml/g. The cumulative pore volume was nearly two times lower than that determined by the MIP test, which was caused by insufficient estimation of the larger pores (see Fig. 6).

As far as TPM method is concerned, the same experimental procedure as in the case of aluminium oxide was applied. The results according to Brun and Landry equations are presented in Table 4. and in Fig. 7. It can be observed that pore size distributions obtained by two different methods have similar characters. In the case of hardened cement paste, results determined according to Landry's formula are more consistent with those from the MIP test.

Table 4. The average pore diameters of cement paste calculated for Brun and Landry relationships

	BRUN [nm]	LANDRY [nm]
Freezing	34.75	38.46
Melting	32.49	39.07

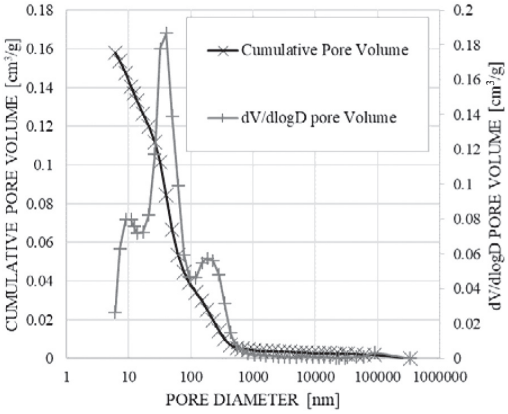

Fig. 4. Pore size distribution and cumulative pore volume of cement paste obtained by the MIP technique

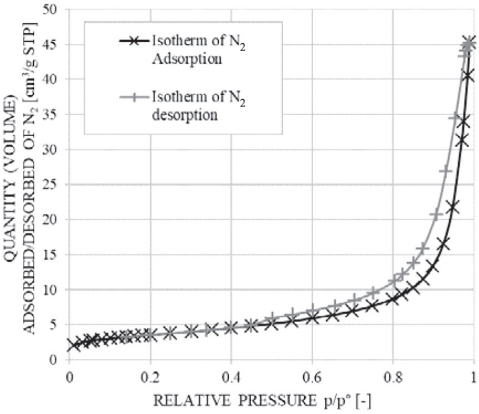

Fig. 5. N_2 adsorption/desorption isotherms determined for cement paste

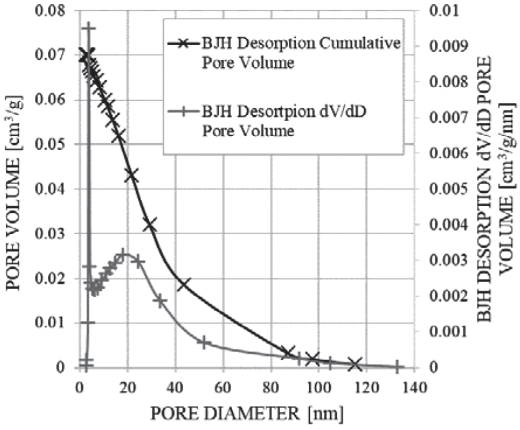

Fig. 6. Pore size distribution and cumulative pore volume of cement paste obtained by low temperature N_2 sorption

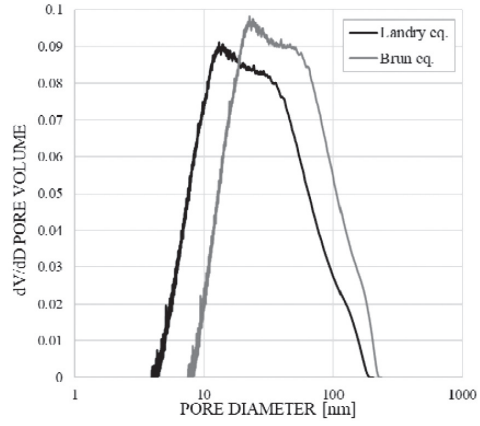

Fig. 7. Pore size distribution obtained by the thermoporometry technique

4. Conclusions

The main purpose of the paper is to compare various methods used in microstructure analysis. The analysis is performed on two kinds of samples. The first is silica alumina, which consists of equivalent pores. The second material, hardened cement paste, is characterised

by complex pore distribution. Since such materials are characterised by a highly complex pore size distribution, a thorough examination of its structure is a challenging task. Each of the presented experimental methods have some drawbacks. For instance, before MIP or nitrogen sorption, samples need to be completely dried. Such a treatment can influence specimen microstructure. High temperature or moisture transport can induce strain and thus produce some micro-cracks, which change the initial pore size distribution. In the case of thermoporometry, a sample has to be fully saturated with a probe liquid and therefore problems connected to deterioration caused by sample preparation are reduced.

The experimental results obtained for aluminium oxide are consistent with data provided by the producer. The material microstructure consists of a framework with one dominant pore diameter, which is proven by nitrogen adsorption as well as the MIP technique. The dominant pore size obtained by the three various methods are in agreement with the producer's declaration. Despite the much more complex microstructure, the results obtained for hardened cement paste by the different methods are also relatively consistent with each other. Each of the presented techniques has some drawbacks. The most important issue which has to be taken into consideration before the choice of a proper experimental method is the range of pore sizes occurring in the sample microstructure. Each of described method presents the highest precision for a limited range of pore sizes. One should be aware that the presented methods are rather complementary. Thus, in order to receive a thorough and exact microstructure description, at least two different experimental methods should be applied.

References

[1] Neville A.M., *Właściwości betonu*, Pearson Education Limited, Kraków 2012.

[2] Giesche H., *Mercury Porosimetry: A General (Practical) Overview*, Particle & Particle Systems Characterization 23(1)/2006, 9–19.

[3] Léon y León C.A., *New perspectives in mercury porosimetry,* Advances in Colloid and Interface Science 76–77/1998, 341–372.

[4] Abell A.B., Willis K.L., Lange D.A., *Mercury Intrusion Porosimetry and Image Analysis of Cement-Based Materials*, Journal of Colloid and Interface Science 211(1)/1999, 39–44.

[5] Moro F., Böhni H., *Ink-Bottle Effect in Mercury Intrusion Porosimetry of Cement-Based Materials*, Journal of Colloid and Interface Science 246(1)/2002, 135–149.

[6] Sing K., *The use of nitrogen adsorption for the characterisation of porous materials*, Colloids and Surfaces A: Physicochemical and Engineering Aspects 187–188/2001, 3–9.

[7] Baroghel-Bouny V., *Water vapour sorption experiments on hardened cementitious materials: Part I: Essential tool for analysis of hygral behaviour and its relation to pore structure*, Cement and Concrete Research 37(3)/2007, 414–437.

[8] Garci Juenger M.C., Jennings H.M., *The Use of nitrogen adsorption to assess the microstructure of cement paste*, Cement and Concrete Research 31/2001, 883–892.

[9] Majda D., Ikonen T., Krupa A., Lehto V.-P., Makowski W., *Application of thermoporometry for characterization of mesoporous silicon: In search for probe liquid aimed at large pores*, Microporous and Mesoporous Materials 264/2018, 1–7.
[10] Brun M., Lallemand A., Quinson J.-F., Eyraud C., *A new method for determination the simultaneous of the size and the shape of pores: the thermoporometry*, Termochimica Acta 21(1)/1977, 59–98.
[11] Defay R., Prigogine I., Bellemans A., Everett D.H., *Surface tension and adsorption*, Wiley, New York 1966.
[12] Ishikiriyama K., Todoki M., Motomura K., *Pore Size Distribution (PSD) Measurements of Silica Gels by Means of Differential Scanning Calorimetry: I. Optimization for Determination of PSD*, Journal of Colloid and Interface Science 171(1)/1995, 92–102.
[13] Brunauer S., Emmett P.H., Teller E., *Adsorption of Gases in Multimolecular Layers*, Journal of the American Chemical Society 60/1938, 309–319.
[14] Barrett E.P., Joyner L.G., Halenda P., *The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms*, Journal of the American Chemical Society 73(1)/1951, 373–380.
[15] Jähnert S., Vaca Chávez F., Schaumann G.E., Schreiber A., Schönhoff M., Findenegg G.H., *Melting and freezing of water in cylindrical silica nanopores*, Physical Chemistry Chemical Physics 39/2008.
[16] Ishikiriyama K., Todoki M., *Evaluation of water in silica pores using differential scanning calorimetry*, Thermochimica Acta 256(2)/1995, 213–226.
[17] Ishikiriyama K., Todoki M., *Pore Size Distribution Measurements of Silica Gels by Means of Differential Scanning Calorimetry: II. Thermoporosimetry*, Journal of Colloid and Interface Science 171(1)/1995, 103–111.
[18] Landry M.R., *Thermoporometry by differential scanning calorimetry: experimental considerations and applications*, Thermochimica Acta 433(1–2)/2005, 27–50.
[19] de Boer J.H., *The Structure and Properties of Porous Materials*, Butterworth, London 1958.
[20] Zhang M.Z., Ye G., van Breugel K., *A numerical-statistical approach to determining the representative elementary volume (REV) of cement paste for measuring diffusivity*, Materiales de Construcción 300(60)/2010, 7–20.
[21] Sarbak Z., *Adsorpcja I Adsorbenty. Teoria i zastosowanie*, UAM Academic Publishing, Poznań 2000.

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