Research paper

Freezing of fully and partly saturated cement paste

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Abstract: The main purpose of the present paper is to distinguish water located in various types of pores contained within cement paste. The water sorption isotherm is the starting point of the experimental analysis. The investigation was conducted employing the conventional gravimetric method on cement paste composed with w/c=0.5. The investigation was conducted for the following relative humidity values: 11%, 54%, 75%, 84%, 93%, 97% and 100%. Once samples reached the equilibrium water content they were investigated by means of differential scanning calorimetry (DSC), which enabled us to record exothermic peaks corresponding to the crystallization of different water portions. Moreover, we intended to investigate the thermodynamic characteristics of the liquid phase confined within cementitious materials. Hence, the artificial pore solution was prepared. In order to determine the phase transition temperature and the amount of formed ice, the solution was used to saturate silica gel, which is a chemically passive material. Then the thermal analysis was conducted.

Keywords: cement-based materials, freezing, sorption isotherm, thermal analysis

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1. Introduction

Concrete is a material characterized by complex microstructure containing pores ranging from 1 nm to several micrometers. It consists of a skeleton built from aggregates and cementitious matrix, within which pores filled with liquid phase are located. Due to its porous structure concrete subjected to cyclic freezing-thawing action can be severely affected by expanding ice. At a microscopic level concrete is highly heterogeneous material consisting of three main phases: cementitious matrix, aggregate particles, and interfacial transition zone located between them. Since aggregate contains mainly closed pores, within which permeability cannot occur, the cement matrix is the factor limiting the final material stability.

A component, which contributes mostly to the durability and strength of cement paste is calcium silicate hydrate, the so-called C-S-H gel. Its structure develops as a result of a sequence of hydration reactions. In the literature, there have been introduced several important models describing the C-S-H gel structure. Powers was the first researcher, who investigated its morphology [1]. He differentiated gel pores, which were located within the boundaries of the gel. He compared the C-S-H phase to colloids and described its basic building unit, namely a particle consisting of three randomly located layers. A similar idea was developed by Wittman, who described the C-S-H gel as a "xerogel" containing particles affecting each other by van der Waals forces [2]. The approach introduced by Feldman and Sereda [3, 4] is also worth mentioning. According to their theory water penetrating cement paste causes the increase in material strength by generating disjoining pressure, which improves bonds between individual C-S-H particles. Nevertheless, in this paper we would like to pay closer attention to the Colloid Model II (CM II) created and developed by Jennings [5, 6]. The approach was evaluated based on water sorption isotherms of cement paste. Jennings described the single unit of the C-S-H gel as a particle consisting of three layers. Its size equals over 4 nm. Jennings introduced a clear division of voids contained in the cement matrix. First of all, he divided them into capillary and gel pores. The former ones are bigger than approx. 12 nm and are located outside the gel and are created by surplus water, which evaporates. Jennings divided gel pores into several types: large gel pores (LGP), which range from 3 to 12 nm, small gel pores (SGP), from 1 to 3 nm, interlayer spaces located inside the globule between two adjacent C-S-H sheets and intraglobular pores developed.

The main purpose of the present paper is to distinguish water located in various types of pores contained within cement paste. The water sorption isotherm is the starting point of the experimental analysis. The investigation was conducted employing the conventional saturated salt solution method

[7-9] on cement paste composed with w/c=0.5. Once samples reached the equilibrium water content they were investigated by means of differential scanning calorimetry (DSC), which enabled us to record exothermic peaks corresponding to the crystallization of different water portions. Such an analysis is possible due to the fact that the phase transition temperature of liquid confined within a pore is decreased comparing to the bulk liquid. This relation is described by means of the Gibbs-Thompson formula [10, 11]:

$$\Delta T_m = \frac{2T_0\gamma_{sl}}{\rho_l\Delta H_f}\frac{\cos\theta}{r_p-\delta}$$
(1)

where T0 is the melting temperature of the bulk state, γ is solid/liquid surface tension, ρl is the liquid density, rp is the radius of the pore, δ is the thickness of the unfrozen water film and is the contact angle. Moreover, we intended to investigate the thermodynamic characterization of the liquid phase confined within cementitious materials. Hence, the artificial pore solution was prepared. In order to determine the phase transition temperature and the amount of formed ice, the solution was used to saturate silica gel, which is a chemically passive material. Then the thermal analysis was conducted. The next part of the article, called body manuscript, must start from the second page with a new section with 3.30 cm top margin, 2.0 cm bottom, left and right margins..
It should be typed using 12 pt. Times New Roman (TNR) font with 1.5 line spacing, on single-sided A4 sheets and should be divided into numbered (1, 2, etc.) and titled

2. Materials and methods

2.1. Cement paste

The investigated samples were prepared using Portland cement CEM I 42.5N-NA with w/c=0.5. For the chemical composition of cement powder see Table 1. After mixing liquid cement paste was put into small PVC bottles and after 28 days appropriate samples were cut out from its central part. We investigated two types of samples: core-shaped ones of volume equal to approx. 30 mm3, which were used in the mercury intrusion porosimetry (MIP) test. The second, small cylindrical samples of approx. height 3 mm and diameter 5 mm were examined by means of thermal analysis (DSC). In each case, the sample volume exceeded the representative elementary volume of cement paste [12]. Each sample was vacuum-dried at 30 ºC until a mass stabilization prior to the test.

Table 1. Chemical composition of CEM I 42.5 N/NA.

Chemical composition (%mass)	
Ignition loss	2.8
Insoluble residue	0.46
SO_3	2.76
chloride content (Cl^-)	0.066
Na_2O	0.18
MgO	1.45
CaO	63.89
SiO_2	19.96
Al_2O_3	5.21
Fe_2O_3	2.68
CaO free	1.87

2.2. Sorption isotherm

Sorption isotherm is a relation between the equilibrium water content and relative humidity of air surrounding a considered sample. It was determined by means of the conventional gravimetric method, in which a saturated solution of particular inorganic salts are used [7-9]. The idea of the method relies on storing samples inside airtight desiccator together with a solution, which provides a particular RH level depending on a type of salt. In our analysis the following salts were used (provided RH level is contained in brackets):

- LiCl (11%),
- Mg(NO3)2 (54%),
- NaCl (75%),
- KCl (84%),
- KNO2 (93%),
- K2SO4 (97%).

Additionally in one of the desiccators, we used distilled water, which provided RH≈100%. All of the tested samples reached the thermodynamic equilibrium with ambient ait after approx. 3 months. Then they were tested by means of differential scanning calorimetry.

2.3. Differential scanning calorimetry

DSC is a technique, which belongs to thermal analysis methods. The experiment consists in subjecting a sample to a thermal program during which its heat response is recorded. The test was conducted in Perkin Elmer DSC 4000 Calorimeter in the atmosphere of nitrogen (of 99.999% purity, provided by Linde Gas). During the test two samples are simultaneously inserted into DSC furnace – the tested one and the reference one. The latter should be characterized by the same specific heat as the tested one, but it should not undergo any transition during the temperature program. Hence, dry sand was used as a reference. Both samples were put into aluminum crucibles of 50 μL and tightly sealed before the test. Once the samples stored in each desiccator obtained the thermodynamic equilibrium, they were tested in DSC. In order to provide thermal equilibrium between a sample and environment, the temperature program consisted of slow cooling realized with temperature rate equal to 0.5ºC/min. The analyzed cooling step was preceded by an auxiliary cooling step, which provided the existence of ice nuclei within the pore solution. The cooling-heating procedure was thoroughly described in [13].

Thermograms, which constitute the relations between heat flux and temperature or time are the results of DSC analysis. In order to integrate exothermic or endothermic peak, one has to define the baseline, which is a theoretical line, which would be recorded if no transition occurred. In this research, we applied the method introduced by Michaelsen and Dahms [14]. Integration of thermograms peak enables one to determine the amount of increasing ice according to the formula [15]:

(2)
$$\frac{dm}{dt} = \frac{1}{\Delta H_f} \frac{dQ}{dt}$$

where ΔH_f is the heat of fusion given by the equation [15]:

(3)
$$\Delta H_f = 334.1 + 2.119\left(T - T_0\right) - 0.00783\left(T - T_0\right)^2, \quad \left[J/g\right]$$

T_0 corresponds to the melting point of bulk ice (273.15K).

3. Results

3.1. Thermal analysis

The results of the microstructural analysis conducted by means of MIP technique are presented in Fig. 1. The pore size distribution confirms the complex structure of the cement matrix. Pore diameters ranging from 6 nm to app. 600 nm and the dominant pore size equals 34.5 nm. The cumulative pore volume equals 0.16 cm^3/g. Carrying on the examination of MIP test results, Muller and Scrivener [16] introduced the idea of a separation point, which corresponds to the pore size being a boundary between gel and capillary porosities. It is located in the local minimum of derivative pore volume between 10-20 nm. In case of the investigated sample, the separation point equals 13 nm.
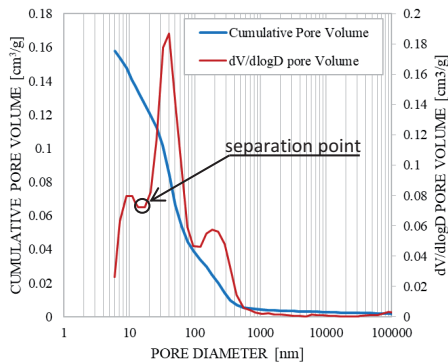

Fig. 1. Pore size distribution and cumulative pore volume of hardened cement paste with w/c=0.5 obtained by means of MIP
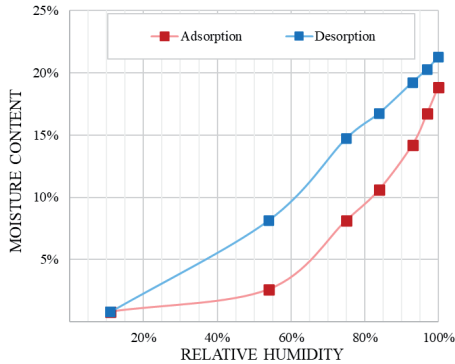
Fig. 2. Sorption isotherms of hardened cement paste with w/c=0.5.

The sorption isotherm obtained by means of saturated salt solutions method for cement paste composed of w/c=0.5 is presented in Fig. 2. It is based on mean values from five specimens and the experiment was conducted at 22ºC±0.1ºC. After drying, samples that underwent the desorption process were entirely saturated with distilled water. Both types of samples, undergoing adsorption and desorption process were placed in the same desiccators. All of the tested samples reached the thermodynamic equilibrium with ambient air after approx. 3 months. The sorption isotherm can be identified with the IV type classified by IUPAC [17], but it does not evince the plateau at its final stage. In case of lower RH, up to 85% values, the isotherm shape is governed by gel porosity [18], whereas above that value the capillary pores have a crucial influence. There is also observed large hysteresis loop, which covers all range of RH values. This results from the presence of ink-bottle type pores within the cement matrix. Moreover, since the liquid phase of cement paste constantly exchanges ions with the skeleton, its chemical composition also enhances the phenomenon of the hysteresis loop. It can be noticed that the hysteresis is the widest in case of middle-ranged RH. This is caused by the fact that for RH≈40-80% the adsorption/desorption process is the slowest, which detains reaching the thermodynamic equilibrium [19]. According to Jennings [5], the hysteresis occurring at low RH values results from irreversible shrinkage of C-S-H layers. After reaching the thermodynamic equilibrium samples were investigated in the DSC analysis.

Thermal analysis was conducted on samples being in thermodynamic equilibrium with air of the following relative humidities: 100%, 97%, 93%, 84%, 75%, 54%, and 11%. The results obtained for RH≈54% and 11% are not presented, because there was not any peak recorded during the temperature program. To provide background for reliable conclusions we also investigated entirely saturated samples, which were immersed in water before the test. The DSC curves recorded for each relative

humidity are presented in Fig. 3. To make the figure easily readable, only thermograms for adsorbing samples are presented. The results constitute the average value of three samples. It is visible that during cooling down to -60 ºC there are two main exothermic peaks. The first one begins rapidly below 0 ºC and the second one below -35 ºC. The former one corresponds to the solidification of water confined within capillary pores, and the latter one – within C-S-H gel. Based on the thermograms we determined the values of ice formed during each transition, see Fig. 4. The dashed line corresponds to samples undergoing the desorption process, whereas the solid line – adsorption process.
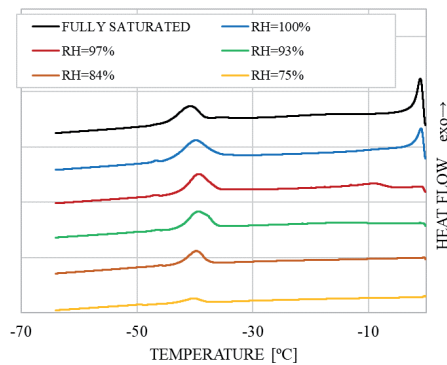

Fig. 3. DSC thermograms obtained for hardened cement paste (w/c=0.5) stored in various relative humidity.
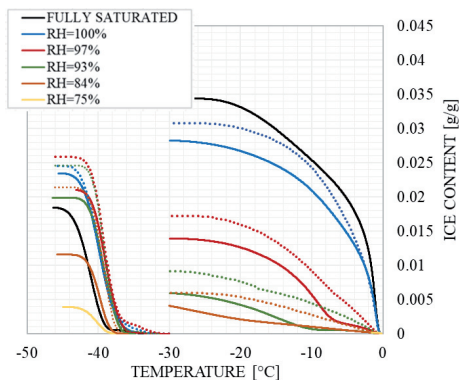

Fig. 4. Ice content determined for hardened cement paste (w/c=0.5) stored in various relative humidity.

The peaks referring to capillary water are predominant only in case of fully saturated samples and those stored above water. For RH≈97% there is a noticeable significant decrease in peak intensity and its main share begins below -5 ºC. For RH≈93% capillary peak is almost undetectable, which is consistent with Powers and Brownyard's statement, that such pores are empty at RH≈85% [20]. The decreasing intensity of the capillary peak is caused by the smaller size of pores occupied by water at lower RH and results from the depression of phase change temperature according to the Gibbs-Thompson formula (1). Jennings described capillary porosity as the one, within which menisci are formed and specified its pores sizes as ranging from ~8nm to 10μm [5], but simultaneously he acclaimed that sometimes also smaller pores can be treated as capillary ones if capillary phenomena even if they are located within the C-S-H gel. A similar tendency as for thermograms is also visible considering the amounts of formed ice for each RH. Considering capillary pores there was formed nearly 0.035 grams of ice per gram of dry sample. The amount of arisen ice decreases along with decreasing RH. For each considered relative humidity the amount of solidified water is larger for samples undergoing desorption process. On the other hand, the peaks corresponding to gel pore water change in a slightly different manner. They are of similar intensity down to RH≈84% and there is observed a huge decrease for RH≈75%, see Fig. 3. The amount of arisen ice ranges from 0.15 to 0.25 g/g for RH≈84% and higher, whereas for RH≈75% only 0.004 g/g of ice was formed. , In each considered relative humidity value more water solidified in samples undergoing desorption process. However, this pore diameter is underestimated due to the chemical composition of the liquid phase confined in the cement matrix. Conducting the thermal analysis one has to remember about the severe limitation of this group of techniques. Namely, the existence of non-frozen layer of liquid covering pore walls. It is reported that such a film remains even in extremely low temperatures [21]. Its thickness is a widely discussed issue nowadays, but generally, scientists report it as 1 to 3 nm wide. The transformed fraction is also affected by ions existing within the liquid phase of cementitious materials, which is thoroughly analysed in the subsequent section. Those phenomena cause that the largest pores of cement matrix, which we are able to investigate by means of thermal analysis are the large gel pores, e.g. pores being located between C-S-H clusters. According to Jennings [6] those voids are saturated at RH ranging from 50% to 85%, which is in agreement with the obtained results – the estimated transformed fraction remains at the almost stable level until RH=84% and for samples stored in lower RH levels diminishes significantly.

3.2. Pore solution

The liquid phase in cement-based materials contains the matrix of ions. Pore solution exchanges ions with cement matrix and its composition depends on the type of cement. Generally, the most concentrated ions existing in the pore solution are OH^-, K^+, and Na^+ [22]. In order to investigate the thermodynamic properties of the actual liquid phase of cement paste, we composed the artificial pore solution containing the mentioned ions. We used deionized water as a solvent and as a source of particular ions the potassium hydroxide and sodium hydroxide were applied. The following concentrations were employed: OH^- - 0.6 mol/l, K^+- 0.5 mol/l, and Na^+- 0.1 mol/l. In order to investigate the behavior of the prepared solution as a pore liquid, we used it to saturate chemically passive porous material with a well-defined pore size distribution, namely silica gel. The entirely saturated material was subsequently investigated by means of DSC technique with the same temperature program as in case of hardened cement paste. In order to draw a direct comparison also silica gel filled with deionized water was studied. The material was provided by Sigma-Aldrich Co. The structural properties of silica gel are as follows:

SG (Sigma Aldrich Co., No. 236845)

- Dominant pore diameter: 11.3 nm,
- Particle size: 250-500 μm,
- Pore volume: 1.15 cm^3 g^{-1},
- Surface area: 300 m^2 g^{-1}.

The DSC curves determined during both tests are presented in Fig.5. Additionally, the amount of formed ice was estimated, see Fig. 6.
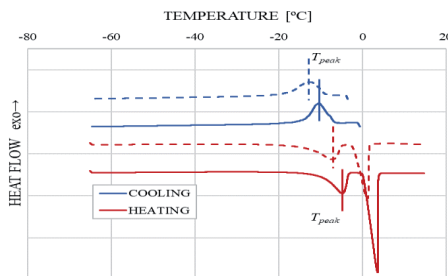

Fig. 5. Thermograms recorded for silica gel saturated with the prepared solution (solid line) and water (dotted line).
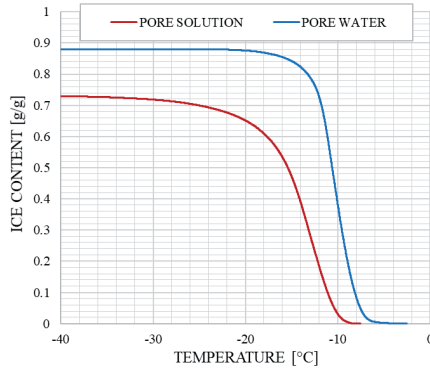
Fig. 6. The ice contents determined for pore solution and pure water saturating silica gel.

The temperature difference was analyzed by comparing melting temperatures of bulk ice for particular liquids. The recorded thermograms imply that the ions contained in bulk water decrease the phase transition temperature to -2.70 °C. Additionally, the determined transformed fractions during transitions of pore fluids indicate that the amount of ice formed in case of the artificial pore solution is decreased by almost 20%. The obtained results confirm that the thickness of the non-frozen film is enlarged in cement-based materials.

3. Results

The main objective of the conducted research is to investigate the complex microstructure of hardened cement paste by means of differential scanning calorimetry. The DSC curves detected for samples characterized by various moisture contents evince two main peaks. The first one begins immediately below zero and refers to capillary porosity. The second one begins around -35ºC and it was believed that it represented freezing of moisture contained in the larger pores connected with the environment by narrow corridors. However, it can be observed that the amount of moisture freezing around -35 ºC increases with growing relative humidity around RH=84%, which by Kelvin equation refers to the diameters of the gel pores. The content and dimension of capillary and gel pores remain fairly consistent with Jennings' structural model, however, one has to be aware of the limits of thermal

analysis. The smallest pores, which can be investigated by means of differential scanning calorimetry are the large gel pores existing among particular clusters of C-S-H. Such a situation is caused by the non-frozen layer of liquid, which covers pore walls even in very low temperatures. Its thickness is additionally strongly affected by the composition of liquid filling pores of hardened cement paste. The amount of formed ice within such a solution is significantly lower than in case of water. It can suggest that the ions are driven inside the smaller pores during the crystallization process.

Acknowledgments

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Zamarzanie zaczynu cementowego w stanie częściowego nasycenia

1. Wstęp

Materiały cementowe charakteryzują się złożoną strukturą wewnętrzną zawierającą pory o szerokim zakresie średnic. Głównym celem przedstawionych badań jest analiza właściwości termodynamicznych wody zlokalizowanej w poszczególnych obszarach matrycy cementowej. Rozważania oparte są na równaniu Gibbsa-Thompsona [1], które opisuje zależność pomiędzy temperaturą przejścia fazowego płynu, a promieniem wypełnionego pora. Wyniki zinterpretowano wykorzystując model mikrostruktury zaczynu cementowego zaproponowany przez Jenningsa [2].

2. Materiały i metody

Przedmiotem badań jest zaczyn cementowy wykonany z cementu Portlandzkiego CEM I 42.5N-NA o wskaźniku w/c=0.5. Pierwszym etapem analizy eksperymentalnej było wyznaczenie izotermy sorpcji badanego zaczynu. W tym celu zastosowano tradycyjną metodę eksykatorową. Technika polega na kondycjonowaniu próbek w eksykatorach wyposażonych w nasycone roztwory soli nieorganicznych, które zapewniają stabilne warunki wilgotnościowe. W przeprowadzonym badaniu zastosowano następujące wilgotności względne powietrza: 11%, 54%, 75%, 84%, 93%, 97% and 100%. Po osiągnięciu przez próbki stanu równowagi, przeprowadzono analizę termiczną zaczynu za pomocą różnicowej kalorymetrii skaningowej. Dodatkowo zbadano również próbki będące w stanie pełnego nasycenia.

3. Wyniki

Dalsza analiza oparta została na termogramach zarejestrowanych w trakcie chłodzenia poszczególnych próbek do temperatury -65$^{\circ}C$ z prędkością 0.5$^{\circ}C/min$, rys. 1.A. Uzyskane wyniki stanowią wartości średnie z trzech pomiarów. W przypadku próbek przechowywanych w powietrzu o wilgotności 11% i 54% nie odnotowano żadnej przemiany. W trakcie chłodzenia pozostałych próbek zarejestrowano dwa, wyraźnie oddzielone, egzotermiczne piki, z których pierwszy rozpoczyna się poniżej 0°C, a drugi w temperaturze ok -35$^{\circ}C$. Pierwszy pik odzwierciedla przemianę fazową wody znajdującej się w porach kapilarnych badanego zaczynu. Jest on dominujący jedynie w przypadku próbek o pełnym nasyceniu oraz przechowywanych nad wodą (*RH*≈100%). Dla *RH*≈97% wydzielone ciepło jest znacznie mniejsze i

główna część przemiany zachodzi w niższej temperaturze (ok. -5℃), natomiast dla wilgotności RH≈93%, 84%, 75% pierwszy pik jest zaniedbywalnie mały. Ta tendencja jest potwierdzona przez zestawienie mas lodu powstałego w trakcie poszczególnych przemian fazowych, rys. 1.B. W porach kapilarnych próbki nasyconej powstało 0,035 grama lodu na gram suchej próbki. Masa lodu znacząco się zmniejsza wraz ze spadkiem wilgotności względnej powietrza, w którym próbki były przechowywane.
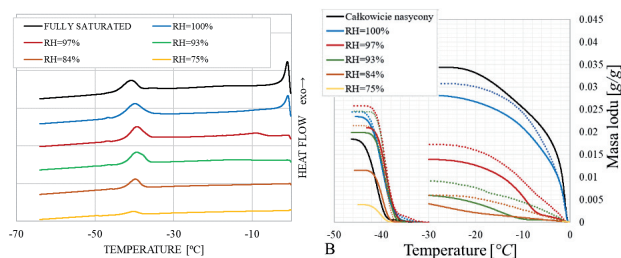
Rys. 1. Termogramy zarejestrowane dla próbek adsorbujących przechowywanych w poszczególnych warunkach wilgotnościowych (A) oraz masy lodu powstałego w trakcie zarejestrowanych przemian fazowych(B). Linia ciągła i przerywana odnoszą się do próbek, w których zachodziła odpowiednio adsorpcja i desorpcja.

Druga zarejestrowana przemiana rozpoczyna się w temperaturze ok. -35℃, która, zgodnie z równaniem Gibbsa-Thompsona [1], odpowiada średnicy porów wynoszącej ok. 5-6nm. Drugi pik odzwierciedla zatem krystalizację wody wypełniającej pory żelowe materiału. Jego intensywność jest na niemal stałym poziomie dla w pełni nasyconych próbek oraz tych, przechowywanych w powietrzu o wilgotności od 84% do 100%.

4. Wnioski

Uzyskane wyniki są zgodne z modelem mikrostruktury matrycy cementowej zaproponowanym przez Jenningsa [2]. W trakcie chłodzenia próbek o zróżnicowanej wilgotności zarejestrowano dwie główne przemiany fazowe wody wypełniającej badany materiał. Pierwsza przemiana (bezpośrednio poniżej 0℃) zachodzi w wodzie kapilarnej, natomiast druga (poniżej 35℃) w porach żelowych. Stosując techniki analizy termicznej należy pamiętać, iż niezamarzająca warstwa cieczy pokrywa ścianki porów nawet w bardzo niskich temperaturach [3]. Dlatego też, zgodnie z podziałem Jenningsa, najmniejsze pory, które można analizować za pomocą kalorymetrii skaningowej to tzw. duże pory żelowe, o średnicy powyżej 5nm. Niemniej jednak, kalorymetria skaningowa jest narzędziem pozwalającym na jakościową ocenę rozkładu wilgoci w próbkach zaczynu cementowego.

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