Thermal analysis of water confined in fully and partially saturated cement paste

Dalia Bednarska^{1,*}, Marcin Koniorczyk¹

¹Lodz University of Technology, Department of Building Physics and Building Materials, Al. Politechniki 6, 90-924 Łódź

Abstract. The main object of the presented research is to apply thermal analysis in order to investigate microstructure of hardened cement paste. The test is conducted by means of differential scanning calorimetry on samples stored in various relative humidity levels as well as the fully saturated ones. The obtained results describe water solidification beginning at several different temperatures, which implies complex nature of cement paste microstructure. The recorded thermograms consist of two main peaks, which clearly indicate the division into capillary and gel pores. Additionally, the thermodynamic properties of actual pore solution confined in cement matrix are investigated. The obtained results indicate ions present in the liquid strongly affects its phase transition temperature as well as amount of ice formed during such the phase change.

1 Introduction

Concrete is one of the most commonly applied composite material in civil engineering. The deep knowledge concerning its microstructure is crucial for accurate modelling and predictions of its properties. Hardened concrete consists of several components such as cement paste, aggregate and interfacial transition zone (ITZ), which vary considerably with regard to microstructure. Apart from several exceptions (e.g. alkali-silica reaction) aggregate is usually considered as the strongest phase of concrete. Additionally, since its porosity is minor and discontinuous it does not contribute to permeability phenomenon and consequently does not limit the material stability. In this regard the cement matrix is a critical component. Its highly complex structure became frequently investigated issue. Hardened cement paste consists of hydration products, among which calcium-silicate hydrate (C-S-H) is the primary one. The C-S-H is a main source of mechanical strength of hardened cement paste, which results in numerous research concerning its microstructure. Powers was one of the first scientists dedicated to this object [1]. He described C-S-H gel as similar to colloid, which is built from globules consisting of three sheets. Within boundaries of this substance, the so-called gel pores are contained. Additionally, the hardened cement matrix includes capillary pores. The resemblance between colloid and C-S-H was also considered by Wittmann [2], who defined the main bonding forces within the gel as simultaneous van der Waals interactions and ionic bonds. Feldman and Sereda assumed that water entering the interlayer space between two adjacent layers of C-S-H reinforces the bonding within the C-S-H itself [3,4]. In the present analysis we would like to adopt the Colloid Model, whose first version was introduced by Jennings in 2000 [5, 6]. He

investigated the C-S-H structure through the analysis of water sorption isotherms determined for hardened cement paste. The model determines the gel as consisting of bricks containing three C-S-H sheets, which are initially separated with water. Apart from capillary pores of sizes larger than 12nm Jennings distinguished several various types of pores and voids within the gel porosity. He defined interlayer spaces between particular C-S-H sheets within the globule. Additionally, due to local remoteness between adjacent layers the so-called intraglobular pores are created (<1nm). Since globules are connected to each other and form bigger clusters the small gel pores are located between particular units (1-3nm). Such clusters also assemble and between them the large gel pores are formed (3-12nm). The Jennings' model also concerns the issue of irreversible shrinkage of based on the described C-S-H gel nanostructure.

The main object of our research is to investigate the complex structure of hardened cement paste by means of thermal analysis. The experiment consists of two stages. Firstly the water sorption isotherm is investigated. Secondly the differential scanning calorimetry (DSC) test is conducted for fully saturated samples as well as those being in equilibrium with air of various relative humidity. The microstructure is analysed based on phase transition temperature and transformed fraction of water confined in particular pores and voids of cement paste. Such an analysis is possible due to the fact that freezing temperature of liquid confined in narrow geometry is decreased comparing to the bulk state. The influence of a pore size on the supercooling is described by means of the well-known Gibbs-Thomson formula [7,8,9]:

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

* Corresponding author: dalia.bednarska@p.lodz.pl

where T_0 is the melting temperature of the bulk state, γ_{sl} is solid/liquid surface tension, ρ_l is the liquid density, r_p is the radius of the pore, δ is the thickness of the unfrozen water film and θ is the contact angle. Additionally, the thermodynamic properties characteristic for actual pore solution confined in cementitious materials are investigated. To that end the artificial pore solution imitating the liquid phase of cement paste is composed. Subsequently it is used to saturated chemically passive porous material and subjected to thermal analysis.

2 Experimental section

2.1 Materials

In the experiment hardened cement paste composed of Portland cement CEM I 42.5N/NA was investigated. The chemical composition of cement powder is presented in Table 1. The applied water-to-cement ratio was equal to 0.5. Cement paste was prepared in hermetic PVC casts and after 28 days since mixing the following specimens were cut out from the central part of the initial one:

- Flattened cylinders (diameter ~ 20 mm and height ~ 3 mm) for sorption isotherm analysis
- Flattened cylinders (diameter ~ 5 mm and height ~ 3 mm) for thermal analysis
- Core-shaped samples (diameter ~ 10 mm and height ~ 20 mm) for Mercury Intrusion Porosimetry

Volumes of each type of samples exceeded the representative elementary volume of cement paste [10].

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

Chemical composition (%mass)	
Ignition loss	2.8
Insoluble residue	0.46
SO ₃	2.76
chloride content (Cl ⁻)	0.066
Na ₂ O	0.18
MgO	1.45
CaO	63.89
SiO ₂	19.96
Al ₂ O ₃	5.21
Fe ₂ O ₃	2.68
CaO free	1.87

The basic microstructural analysis was carried on by means of Mercury Intrusion Porosimetry (MIP) technique, which is considered as the reference one for

cement-based materials. However, the MIP test gives information about some model of an internal structure of cementitious matrix. The technique measures the pore entry sizes, which indicates that larger pores accessible by narrow channels are underestimated. Moreover, the results of microstructural analysis performed on cement mortars cannot be directly exploited for concrete analysis due to, i.e., existence of the interfacial transition zone (ITZ) between cement paste and aggregate. Nevertheless, the MIP test gives some general insight into cement matrix. The technique is based on the fact that mercury, which is a non-wetting liquid, is forced into the pores of a solid porous body by applying an external pressure. Sizes of equivalent cylindrical pores, which are currently filled at a specific pressure are estimated based on the Washburn equation [11]. MIP experiment is conducted by means of Micromeritics AutoPore IV9500 apparatus, with the range of the measuring pore diameters from about 6nm to 100 μ m. The pore size distribution is presented in Figure 1. The obtained results constitute the mean value of three samples. The investigated material is characterized by a complex structure with pores ranging from 6nm to approx. 600nm with dominant pore diameter of 34.5nm.

Fig. 1. Pore size distribution and cumulative pore volume detected by mercury intrusion porosimetry for hardened cement paste with $w/c=0.5$.

2.2 Methods

2.2.1 Sorption Isotherm

Water sorption isotherm describes the relationship between equilibrium moisture content and relative humidity. Among many experimental techniques we chose the conventional and simple saturated salt solution technique (SSS) [32]. The investigated samples have to be stored along with saturated solution of an inorganic salt inside an airtight container. The solution maintains stable relative humidity level, which value depends on a type of a salt. Samples are held in dessicator until they obtain the equilibrium state, which has to be confirmed by the

gravimetric measurements. In the experiment we applied the following salts: LiCl (11%), Mg(NO₃)₂ (54%), NaCl (75%), KCl (93%), K₂SO₄ (98%). To obtain the relative humidity of 100% in one of dessicators samples were stored above water. It was assumed that if two consecutive mass measurements differ less than 0.05% than samples reached the equilibrium state. Both dry and fully saturated samples was investigated in SSS method, which led to determination of both adsorption and desorption branch of isotherm. Before the test samples were dried in mild conditions and subsequently part of them was entirely saturated for desorption.

2.2.2 Differential Scanning Calorimetry

Samples containing equilibrium moisture content were subsequently investigated by means of thermal analysis, mainly the differential scanning calorimetry (DSC). Every phase transition is connected to heat exchange, hence the fraction transformed during particular process can be assess based on measuring the realised or consumed energy. In the DSC calorimeter two samples of similar heat capacity are inserted simultaneously into the furnace, the analysed one and the reference one. The latter one should not undergo any transition within applied temperature program. The measurements were conducted in Perkin Elmer DSC 4000 equipped with a cooling device in the atmosphere of nitrogen. As analysed sample the cement paste cylinder stored at particular RH was used, whereas on the reference side we put equivalent mass of dry sand. The temperature program consisted of cooling down to -65 °C with cooling rate 0.5°C /min. Such a slow cooling rate was applied in order to avoid kinetic effects and provide thermal equilibrium of an analysed sample. Further analysis was conducted on DSC curve which depicts the relation between heat flux and temperature or time. The amount of transformed fraction was estimated according to the formula[15,16]:

$$\frac{dm}{dt} = \frac{1}{\Delta H_f} \frac{dQ}{dt} \quad (3)$$

where ΔH_f is the heat of fusion given by the equation [9]:

$$\Delta H_f = 334.1 + 2.119(T - T_0) - 0.00783(T - T_0)^2, \quad [J/g] \quad (4)$$

where T_0 is the melting point of bulk ice (273.15K).

3 Results

3.1 Sorption isotherm

The determined sorption isotherm corresponds to the average of five samples, see Fig. 2.

Fig. 2. Sorption isotherm determined for cement paste of $w/c=0.5$.

The sorption isotherm shape resembles the IV type according to the classification introduced by the International Union of Pure and Applied Chemistry [17]. Such a case is typical for meso and microporous materials. The isotherm contains significant hysteresis loop in the whole range of RH, which is typical for cement-based materials. This is a complex phenomenon, which is caused by many factors, but one of its main reasons is the well-known “ink-bottle effect”, which indicates that cement matrix contain numerous pores, which are accessible by narrow channels. Additionally according to Jennings the adsorbate diffusion is the slowest in the middle values of relative humidity [19,20], which even extends hysteresis in this range. Moreover various curvatures of liquid-gas interface during adsorption and desorption process also enlarge the detected hysteresis[18]. Generally in case of hardened cement paste the isotherm shape is influenced mainly by capillary porosity in higher RHs and by gel porosity and interlayer spaced in lower RH values. According to Jennings the boundary between those two zones lies around 85%[6].

3.2 Thermal analysis

Thermal analysis was conducted on fully saturated samples as well as those stored in RH≈100%, 97%, 93%, 84%, 75%. The recorded thermograms indicate two main peaks, which correspond to separate transitions, namely to crystallization of water confined in capillary and gel porosity. The obtained DSC curves and the transformed fractions for particular RH are presented in Fig. 3 and Fig. 4 respectively.

Fig. 3. Thermograms recorded for cement paste samples undergoing the adsorption process stored in particular relative humidity levels.

Fig. 4. The amounts of ice formed during particular transitions. The dashed line corresponds to desorption, the solid line to adsorption process.

2.2.1 Capillary porosity

Capillary pores are formed in space, which was previously occupied by water and they are reflected by the first group of peaks arising right below zero. However, the peak is dominant only for fully saturated samples and those stored above water, which is also visible by the transformed fraction. The amounts of ice formed for those specimens range from 0.028 to 0.034 grams of ice per gram of a sample. Considering the next $RH \approx 93\%$ the released energy and hence the peak is significantly lower and shifted towards cooler temperature, whereas for lower RHs the peak is virtually negligible. This observation is in accord with the conclusions drawn by Powers and Brownyard that capillary pores are becoming empty at $RH \approx 85\%$ [21]. Jennings described capillary pores as those larger than 12nm. However forming a clear boundary between gel and capillary pores is a demanding task, because meniscus can sometimes appear also in the zone of C-S-H gel [6].

2.2.1 Gel porosity

The next group of peaks, which corresponds to gel porosity begins below -30°C , Fig. 3. Those peaks are of similar height down to $RH \approx 84\%$ and the one recorded for $RH \approx 75\%$ is significantly lower. This tendency is clearly visible considering the fraction transformed during the transition. The amount of ice formed within samples stored in 84% (desorption) and higher relative humidity values fluctuate between 0.020 and 0.025 g/g, whereas in case of samples undergoing adsorption at 75% it is only approx. 0.004 g/g. As mentioned above the Jennings' Model defines four different kinds of pores within the gel porosity, namely large gel pores, small gel pores, interlayer spaces and intraglobular pores. Carrying on 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 [9]. 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 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 [20] 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 almost stable level until $RH = 84\%$ and for samples stored in lower RH levels diminishes significantly.

3.3 Pore solution

Liquid phase in cement-based materials is sometimes considered as pure water, which can be severe oversimplification. Pore solution exchanges ions with cement matrix and its composition depends on type of cement. Generally the most concentrated ions existing in pore solution are OH^- , K^+ , Na^+ [22]. In order to investigate thermodynamic properties of actual liquid phase of cement paste we composed the artificial pore solution containing 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: K^+ - $0.5 \frac{\text{mol}}{\text{l}}$, Na^+ - $0.1 \frac{\text{mol}}{\text{l}}$, OH^- - $0.6 \frac{\text{mol}}{\text{l}}$. In order to investigate the behaviour of the prepared solution as a pore liquid we used it to saturate chemically passive porous material with 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 structure 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 $\text{cm}^3 \text{g}^{-1}$,
- Surface area: 300 $\text{m}^2 \text{g}^{-1}$.

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) $w/c=0.5$.

Fig. 6. The ice contents determined for pore solution and pure water saturating silica gel.

The temperature difference was analysed 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 non-frozen film is enlarged in cement based materials.

4 Conclusions

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, whereas the second one begins around -30°C and corresponds to the gel porosity. The results remain fairly consistent with the 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 composition of liquid filling pores of hardened cement paste. The amount of formed ice within such solution is significantly lower than in case of water. Hence, the pore solution confined in cement matrix should not be treated as pure water.

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