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Wang, Tian; Wu, Min

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Pore size distribution of cement based materials determined by dynamic water vapor sorption and low temperature calorimetry

Tian Wang² and Min Wu¹

¹ Department of Engineering, Aarhus University, 8000 Aarhus, Denmark
mnwu@eng.au.dk

² Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark

Abstract. In this work, both dynamic water vapor sorption (DVS) and low temperature calorimetry (LTC) methods were adopted to study the pore size distribution of cement pastes prepared by two types of cements CEM I and CEM III. A model porous material, MCM-41, was also included in order to investigate important aspects of the measurement and the data evaluation approaches. As indirect methods for pore structure characterization, important assumptions involved in the data analysis of both methods were highlighted and discussed. In addition, a special attention was paid to the comparison of the results obtained from the two methods. A careful examination of the bases for the two methods for pore structure characterization revealed that a number of matters could affect the obtained results, including sample preparation, possible influencing factors on the measured results, unsolved factors for data analysis, etc. Consequently, the results obtained from one method might differ significantly from the other. Nevertheless, a certain degree of agreement was still found for the pore size distributions determined by the DVS and the LTC methods, despite of the uncertainties involved in each method. Meanwhile, it was concluded that probably none of the two studied methods could deliver the “true” (actual) pore size distribution information at this stage. To further improve the accuracy of the results obtained from the methods, it was highlighted that emphases should be laid on clarifying relevant assumptions made in both measurement and data analysis.

Keywords: Pore size distribution, Sorption, Low temperature calorimetry, Cement paste

1 Introduction

The importance of pore structure to cement and concrete materials can never be overstressed. Apart from being a main parameter which determines the mechanical properties, it is also a major parameter that influences the durability. As is well known,

long-term durability is highly desirable for large infrastructures. The design lives for bridge and tunnel structures nowadays typically are longer than 100 years. It should be mentioned that a number of durability problems could be linked to the pore systems of cement/concrete including reinforcement corrosion (e.g. due to the transport of chloride ions and CO₂ gas into the materials) and frost damage, etc. Therefore, accurate characterization of the pore structures can help understand various properties of the concerned materials.

In cement based materials, the pore structures can be rather complicated. Different types of pores with different sizes exist. For instance, mixing and casting often entrap air voids and the sizes can reach millimeters [1]. The sizes of deliberately entrained air voids for frost protection are on the order of 50-100 μm [2]. At the nano-micro scale, “capillary pores” exist, which are the remnants of the interstitial spaces between the unhydrated cement grains [3]. Additionally, there are interlayer spaces, or “gel pores” at the nanometric level, i.e. between the primary particles of the hydration products calcium-silicate-hydrates (C-S-H) [4]. Among the different pores, it has been demonstrated that the transport properties of mature cement based materials are dominated by the so-called “mesopores” [5], with the characteristic sizes between 2 and 50 nm according to the IUPAC definition [6].

Because of the paramount importance, considerable efforts have been devoted to understanding the pore structures of cement based materials. The representative characterization methods include, e.g. nitrogen adsorption/desorption (NAD), mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), small angle scattering using X-rays or neutrons and nuclear magnetic resonance (NMR) [7]. A brief discussion of the merits and limitations of the typical methods can be found, e.g. in [7].

In this work, dynamic water vapor sorption (DVS) and low (micro-)temperature calorimetry (LTC) were used to investigate the pore size distribution (PSD) of cement based materials, especially at the nanometric level. Compared with traditional methods, e.g., NAD, MIP and SEM, a major advantage shared by the DVS and LTC methods is that the measurements can be conducted on virgin samples without any pre-drying treatment. This is important, since pre-drying treatment may alter the cement pore structures [8]. Advantages of LTC include also the possibility of using short measurement time and it involves a relatively simple sample preparation procedure [9]. By using the DVS instrument combined with data extrapolation processing, the measurement time for obtaining a sorption isotherm can be shortened to make the overall process more effective [10]. However, it should also be mentioned that both DVS and LTC are indirect methods for pore structure characterization. Special attention has to be paid to the measurement and the data analysis procedures, as a number of factors can affect the final results [7, 10-15]. By including both methods in this work, one intention was to validate if the results obtained from one method can be compared with that from the other. In addition, the comparability of the results may also indicate the accuracy of the two methods to some extent.

2 Important considerations

2.1 Dynamic water vapor sorption (DVS)

When a porous material is placed into an environment, moisture exchange will occur if there is a gradient on the relative humidity (RH) between the material and the environment until the equilibrium condition is established. The relation between the moisture content and the RH is usually referred to as a sorption isotherm, which may be recorded by a DVS instrument. The sorption behavior is closely related to important properties of the concerned material, e.g. the specific surface area and pore size distribution [16].

For the pore size calculation from the DVS measured results, the BJH model [18] may be adopted. The BJH model assumes two types of water in a pore system, i.e. the adsorbed water and the capillary condensed water. However, the sorption measurement itself cannot distinguish between these two types of water and it only measures the total moisture content at a given RH. That is, the thickness of the adsorbed layer of water, or the so-called t -curve, needs to be determined by some complementing approach in order to make the PSD calculation possible. Several t -curves have been proposed for water vapor. In this work, the Hagymassy et al. curve [19] and the J-BET-curve [17] are used for the calculations. Another important assumption which may significantly affect the obtained PSD results is the assumed meniscus curvature during the capillary condensation processes. It is generally agreed that it is $2/r_k$ during desorption process, while both $1/r_k$ and $2/r_k$ have been proposed for absorption process, where r_k is the Kelvin radius [16]. The impact of the different assumptions will be further illustrated in Section 4. Refer to [17] for more details on the calculation.

As an indirect method for pore size characterization, there are quite some limitations and unsolved factors, some of which are summarized in Table 1.

2.2 Low temperature calorimetry (LTC)

LTC is a calorimetric method for pore structure characterization by analyzing the transient heat flow during the phase transition processes. The freezing/melting point of water/ice confined in small pores is lower than that of the bulk state. The magnitude of this freezing/melting temperature depression is closely related to the size of the pores where the phase transition takes place. If a porous material is saturated, the amount of the water confined in the pores can be a measure for the pore volume. Moreover, thermodynamically there is a relation between the freezing/melting temperature of the confined water/ice and the pore sizes. By making some important assumptions, e.g. regarding the surface energies and its geometrical configurations, the pore size corresponding to each freezing/melting temperature can be determined.

To translate the measured heat flow values to PSD results, several steps are needed and important assumptions have to be made, e.g. the thickness of the so-called unfreezable layer. Details of the PSD calculations can be found in [7, 11].

Similar to the DVS method, LTC is also an indirect method for pore size characterization. Typical limitations and unsolved factors of the method are summarized and compared with that for the DVS in Table 1.

Table 1. Matters of consideration of the DVS and the LTC methods for the pore structure characterization of cement based materials.

Item	DVS	LTC
Sample preparation	The samples must be crushed and/or ground into powders, with the consequence that the pore connectivity becomes seriously affected.	Testing samples must be fully saturated. If not, not only the pore volume but also the estimation of the pore sizes will be misinterpreted.
Pore size range	(1) Micropores with radii corresponding to a few water molecule's thickness may not be detected. (2) The upper limit of reliable pore radius that can be analyzed is about 30 nm.	(1) Pores with radii smaller than that of the un-freezable water layer cannot be detected. (2) The upper limit of reliable pore radius that can be analyzed is about 40-50 nm.
Influencing factors on the measured results	(1) The network effect influences the desorption curves. (2) Delayed condensation and possibly advanced absorption affect the absorption curves.	(1) Supercooling and network effect influence the heat flow curves of the freezing processes. (2) Advanced melting affects the heat flow curves of the melting processes.
Factors not fully solved	(1) The thickness of the adsorbed layer. (2) The meniscus curvature during absorption, i.e. $1/r_k$ or $2/r_k$ (r_k is the Kelvin radius). (3) The computation of pore sizes, especially for the micropores. (4) Applicability of the Laplace equation at the nanometric level.	(1) Temperature dependent heat of fusion. (2) The solid-liquid surface tension. (3) The applicability of the thermodynamic parameters at the nanometric level. (4) The thickness of the un-freezable layer, ions effect and thermal lag.
Other issues	(1) The pore structure may change at low RHs. (2) A rather long waiting time for the equilibrium conditions at a RH to be established.	(1) Homogenous nucleation leads to the pore entry radii smaller than about 2.4 nm not distinguishable. (2) Effects due to frost damage.

3 Experimental and data analysis methods

3.1 Materials

Three materials were studied, i.e. one model mesoporous material MCM-41 and two types of hardened cement pastes. The primary purpose of including the model material was to validate relevant aspects of the measurement and the data evaluation approaches.

With the pore structure in the form of hexagonal arrays of uniform tubular channels of controlled width, MCM-41 is often used as a model material in pore structure studies.

The nominal pore diameter of the MCM-41 provided by the producer (Tianjin Chemist Scientific Ltd.) is 3.0 nm and the nominal specific surface area and the total pore volume are reported to be $\geq 800 \text{ m}^2/\text{g}$, $\geq 0.70 \text{ ml/g}$, respectively.

Two types of cements, i.e., CEM I 32.5 R and CEM III/B 42.5 N, were used to prepare the paste samples with a water/cement ratio of 0.4. The properties and the chemical compositions of the cements are shown in Table 2. A paddle mixer was used for the mixing. After that, the fresh pastes were cast into plastic vials ($\phi 15 \times 50 \text{ mm}$) with proper compaction. After one day of sealed curing at room temperature (about 20°C) in the plastic vials, the paste samples were demolded. Then, each paste sample was placed into a bigger self-sealable plastic flask filled with saturated limewater for curing at room temperature until the desired testing ages.

Table 2. Properties and the chemical compositions of the cements used in this study.

		CEM I (CEM I 32.5 R)	CEM III (CEM III/B 42.5 N)
Density	(g/cm^3)	3.06	2.90
Fineness	(cm^2/g)	2905	4635
Water demand	(%)	26.2	32.3
Initial setting time	(min)	185	270
Loss on ignition	(%)	2.1	1.4
SiO ₂	(%)	20.6	29.2
Al ₂ O ₃	(%)	5.6	8.9
Fe ₂ O ₃	(%)	2.4	1.2
CaO	(%)	63.4	48.0
MgO	(%)	1.6	4.8
SO ₃	(%)	2.9	2.6
K ₂ O	(%)	0.7	0.6
Na ₂ O	(%)	0.2	0.2
Cl	(%)	<0.1	<0.1

3.2 DVS measurements

The sample size that can be used in a DVS instrument is relatively small (on the order of milligrams). That is, crushing and/or even grinding of the hardened cement paste samples is needed. After curing for about 6 months, the prepared cylinder paste samples were firstly vacuum saturated with limewater and then the crushing and grinding of the samples was conducted in a carbon dioxide free chamber to avoid carbonation. The RH inside of the chamber was set at 1 (the measured RH was about 0.90-0.95). The sample crushing and grinding was conducted rather quickly (in 30-40 min). Immediately after that, the ground sample powders were placed into plastic flasks containing saturated limewater (for about a week) before the sorption experiments. This procedure was also conducted in the carbon dioxide free chamber.

The measurements were conducted in a climate incubator at 25°C. The RH was generated into the desired proportions by mixing two airflows, i.e. a totally dry (RH = 0) and a totally saturated (RH = 1) air. The proportions of the two flows can be accurately controlled by the flow regulator devices. The duration time of each RH step in the DVS instrument was controlled by setting the mass change ratio against time, dm/dt at 0.002% (of the initial mass). Then an extrapolation procedure was adopted to estimate the moisture content under the equilibrium condition. This is based on the consideration that practically it is almost impossible to wait for the establishment of the exact equilibrium conditions. More details about the instrument and measurement aspects can be found, e.g. in [17].

3.3 LTC measurements

The instrument used for this study was a Calvet-type scanning calorimeter (SETARAM). The calorimeter was calibrated and operated to work between 20°C and -130°C. The cooling and heating rate was set to 0.1 °C/min. A freezing and melting cycle consisted the temperature scanning starting from about 20°C and going down to about -80°C and then back to about 20°C again.

For the ease of handling powder MCM-41 samples in the calorimetric measurements, a cylindrical plastic vial was used as a sample holder. The size of the plastic vials ($\phi 14 \times 48$ mm) was chosen to fit the measuring chamber of the calorimeter. The MCM-41 powders were placed into the plastic vials up to about half the volume (the dry weight was about 0.2 g) and then covered with distilled water. In order to saturate the samples, the plastic vials containing powders were placed under a reduced pressure (~40 mbar) for about 3 hours. After that, the apparent excess bulk water on top of the powders was removed and the samples were stored in closed containers for 2-3 weeks before the calorimetric measurements.

For the cement pastes, powder samples were used for the LTC measurements, i.e. to keep the consistence with the sample type as used in the DVS measurements. The prepared cylinder samples (as described in Section 3.1) were used to obtain the powder samples. The crushing and grinding procedure was similar to that for the DVS sample preparation. The water saturation procedure was the same as that for the MCM-41 samples. The total curing time for the paste samples was about one year when the measurements were performed.

4 Results and discussions

The PSD curves calculated from the measured DVS and LTC data are compared in this section. Since the choice of water meniscus curvature during the absorption process is somewhat arguable, i.e., $1/r_k$ or $2/r_k$ (Section 2), both assumptions are included in the comparison. Due to the occurrence of rather significant supercooling in the freezing process of the LTC measurements, the pore size information that can be ob-

tained from the freezing curve is limited, i.e. between about 2.4 nm to about 5-6 nm. Therefore, only the PSD results calculated from the LTC melting curve are presented.

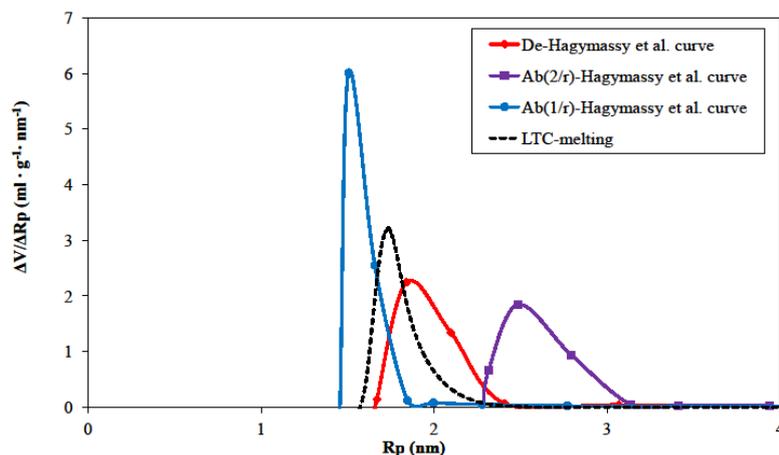


Fig. 1. PSD curves determined from the DVS and LTC methods for the MCM-41. The t-curve used in the sorption PSD calculations is the Hagymassy et al. curve [18]. “De” or “Ab” indicates the desorption or the absorption isotherm is used in the calculation. Ab(1/r) represents that the meniscus curvature during absorption is assumed to be $1/r_k$ and Ab(2/r) represents $2/r_k$.

The comparison of the determined PSD curves for the MCM-41 is presented in Fig. 1. The R_{max} corresponding to the peak in the calculated PSD curves, i.e. the most frequently occurring pore size, determined from the LTC melting curve and the desorption isotherm is about 1.7 nm and 1.8 nm, respectively. On the other hand, the R_{max} determined from the absorption isotherm is about 1.4 nm and 2.4 nm using the meniscus curvature of $1/r_k$ and $2/r_k$, respectively. It is generally agreed that a LTC freezing curve indicates pore entry sizes, while a melting curve represents the pore interior size information [7]. Then the PSD curve determined from a LTC melting curve should be compared with that determined from the absorption [6]. However, for the studied MCM-41, the result is that the R_{max} from the LTC melting curve (1.7 nm) differs rather significantly from that obtained from the absorption isotherm, i.e., 1.4 nm (assuming curvature as $1/r_k$) and 2.4 nm (assuming curvature as $2/r_k$). In this case, the R_{max} determined from the LTC melting curve is more close to the value obtained from the desorption isotherm (1.8 nm). Similar conclusions can be obtained by using other t-curves in analyzing the sorption data, indicating the calculated PSD curves for the model material MCM-41 is not very sensitive to the different considered t-curves.

It has been a long debate on which isotherm (desorption or absorption) should be used for the pore size calculation in sorption studies when hysteresis is present. For many years, desorption isotherms were considered to be more thermodynamic stable and therefore, it was thought to be more appropriate to use desorption isotherms to determine the pore size distribution [20]. The drawback of this concept has been demon-

strated by taking the network theory into consideration [21], in which it was concluded that desorption isotherms only reflect the pore entry or neck sizes. It was clearly stated in the IUPAC report [6] that it is impossible to provide unequivocal recommendations in the absence of detailed knowledge about the geometry of the pores under study. However, it seems to be more and more accepted that the calculation using absorption measurements may be more representative for the “true” or pore interior sizes, while the calculation from the desorption isotherms is more related to the network effect (or the pore entry/neck sizes). The results obtained in this study on the MCM-41 seems to support the use of desorption isotherms for interior pore size calculation. However, it should be stressed that this is not conclusive, as many other uncertainties, e.g. the thickness of the un-freezable layer assumed in the LTC analysis [7], may change the picture completely. This is especially true when considering the differences between the R_{\max} values obtained from the desorption and absorption isotherms are not that significant.

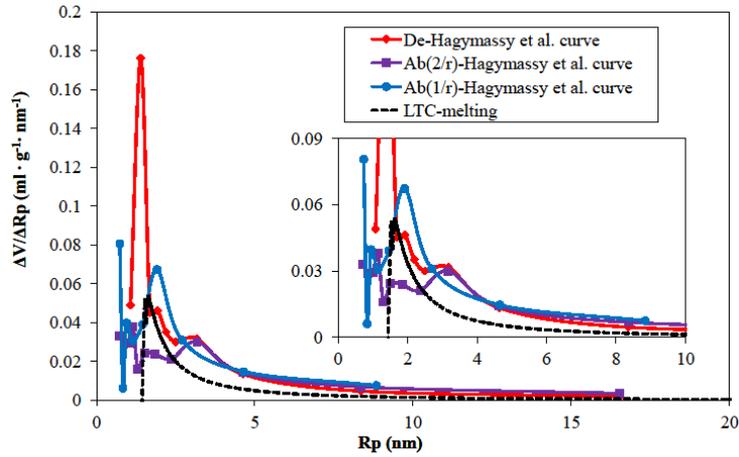


Fig. 2. PSD curves determined from the DVS and LTC methods for the paste CEM I. The t-curve used in the sorption PSD calculations is the Hagymassy et al. curve [18]. “De” or “Ab” indicates the desorption or the absorption isotherm is used in the calculation. Ab(1/r) represents that the meniscus curvature during absorption is assumed to be $1/r_k$ and Ab(2/r) represents $2/r_k$.

The comparison of the determined PSD curves for the cement pastes CEM I and CEM III are presented in Fig. 2 and Fig. 3, respectively. Hagymassy et al. t-curve [19] was adopted in the calculations. Compared with the results for the MCM-41, the most important difference is that the magnitude of PSD curve corresponding to R_{\max} obtained from the desorption isotherms are much higher than that obtained from both the absorption isotherm and the LTC melting curve. Similar to that obtained for the MCM-41, the R_{\max} determined from the LTC melting curve (1.7 nm) is more close to that obtained from the desorption isotherm (1.4 nm). In comparison, the values obtained from the absorption isotherm are 1.9 nm (assuming meniscus curvature as $1/r_k$) and 3.2 nm (assuming meniscus curvature as $2/r_k$). In addition, the differences be-

tween the specific values of the R_{\max} , i.e. that determined the LTC melting curve, the desorption isotherm and the absorption isotherm are different when compared with that for the MCM-41. Similar conclusions as drawn for the paste CEM I are also applicable for the paste CEM III, except that there is no dominant peak corresponding to R_{\max} for the paste CEM III when the meniscus curvature during absorption is assumed to be $2/r_k$ (Fig. 3).

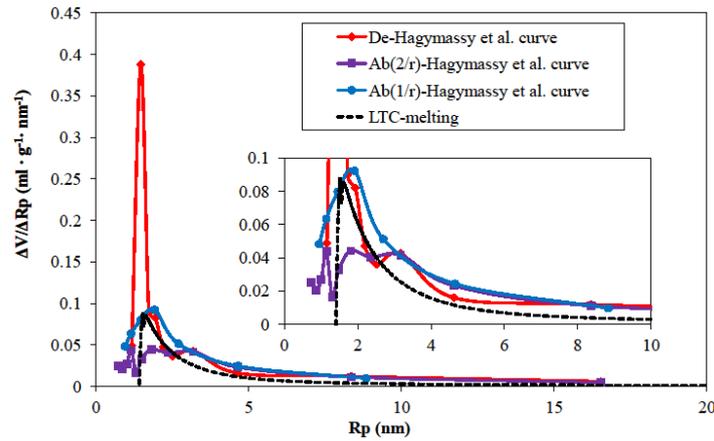


Fig. 3. PSD curves determined from the DVS and LTC methods for the paste CEM III. The t -curve used in the sorption PSD calculations is the Hagymassy et al. curve [18]. “De” or “Ab” indicates the desorption or the absorption isotherm is used in the calculation. Ab($1/r$) represents that the meniscus curvature during absorption is assumed to be $1/r_k$ and Ab($2/r$) represents $2/r_k$.

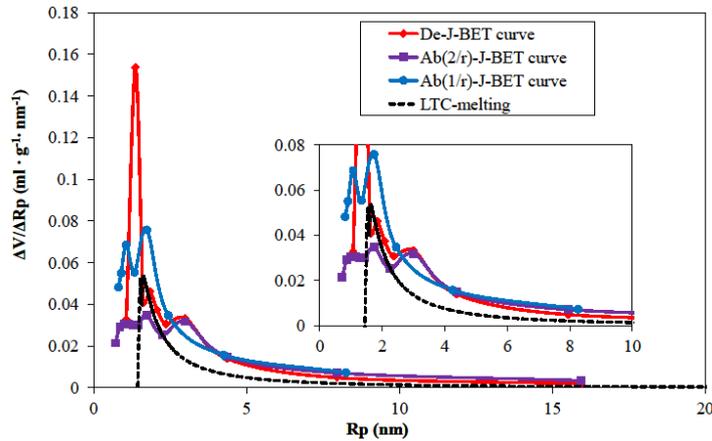


Fig. 4. PSD curves determined from the DVS and LTC method for the paste CEM I. The t -curve used in the sorption PSD calculations is the J-BET curve [16]. “De” or “Ab” indicates the desorption or the absorption isotherm is used in the calculation. Ab($1/r$) represents that the meniscus curvature during absorption is assumed to be $1/r_k$ and Ab($2/r$) represents $2/r_k$.

To evaluate the sensitivity of the PSD calculations from sorption data to the assumed t-curves for the cement pastes, the J-BET curve [17] was also used in the calculations. The comparison of the calculated results are presented in Fig. 4 and Fig. 5. By using the J-BET curve, the peak corresponding to R_{\max} for the paste CEM I becomes less pronounced compared with that obtained using the Hagymassy t-curve. For the paste CEM III, the peak corresponding to R_{\max} becomes more well defined compared with that using the Hagymassy et al. t-curve. Other main features of the results obtained using Hagymassy et al. t-curve as discussed above are also applicable to the results obtained using the J-BET t-curve.

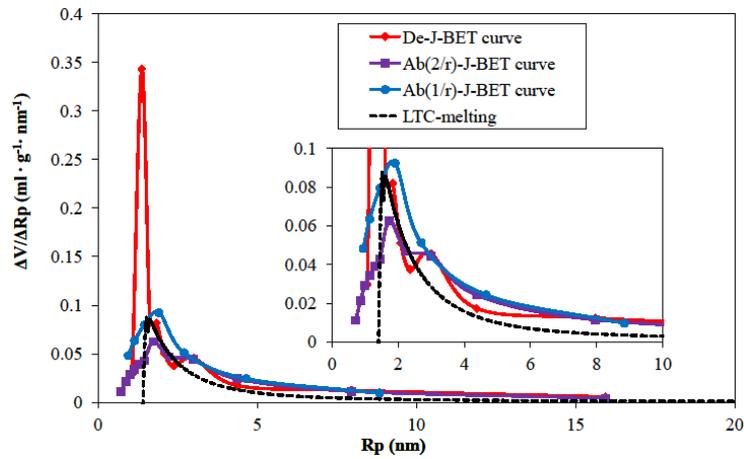


Fig. 5. PSD curves determined from the DVS and LTC method for the paste CEM III. The t-curve used in the sorption PSD calculations is the J-BET curve [16]. “De” or “Ab” indicates the desorption or the absorption isotherm is used in the calculation. Ab(1/r) represents that the meniscus curvature during absorption is assumed to be $1/r_k$ and Ab(2/r) represents $2/r_k$.

Due to the limitations of currently available techniques in pore size characterization, the exact values of the “true” (actual) pore sizes of a concerned material cannot be obtained. By using different measurement techniques, e.g. DVS and the LTC as adopted here, a fitting parameter may be used, e.g. the thickness of the un-freezable layer. Such a fitting parameter can be used to match the pore size distributions obtained from the two separate methods. However, due to the unsolved factors in sorption studies, e.g. the assumed meniscus curvature during the absorption, it may make the adjustment of the thickness of the un-freezable layer little meaning. That is, it is somewhat difficult to make the pore sizes determined by the two methods absolutely fit even for a simple model material (such as the MCM-41). For cement based materials, the pore systems are much more complicated than that of model materials and more unsolved factors come into the picture (Table 1). Of this reason, it becomes even more challenging to make the PSD results determined by the two methods to agree by using parameter fitting only.

5 Conclusions

The current work tried to study the pore size distributions of hardened cement pastes using both DVS and LTC methods. As indirect methods for pore size characterization, it was discussed that a number of matters can affect the obtained results including sample preparation, possible influencing factors on the measured results, unsolved factors for data analysis, etc. Consequently, the results obtained may only be semi-quantitative and remain valuable mainly for comparison purposes.

Nevertheless, a certain degree of agreement was still found for the pore size distributions determined by the two methods, despite of the un-certainties involved in each method. Meanwhile, it should be stressed that probably none of the two studied methods could deliver the “true” (actual) pore size distribution information based on existing knowledge. To further improve the accuracy of the results, emphases should be laid on clarifying relevant assumptions made in both measurement and data analysis for the concerned methods.

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