

Paper III

**Influence of frost damage and sample preconditioning in
studying the porosity of cement based materials using low
temperature calorimetry**

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Influence of frost damage and sample preconditioning on the porosity characterization of cement based materials using low temperature calorimetry

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Abstract

Low temperature calorimetry (LTC) can be used to study the meso-porosity of cement based materials. The influence of frost damage on the meso-porosity determination by LTC was investigated using a model material MCM-41 and two types of cement pastes by conducting repeated cycles of freezing and melting measurements. The results indicate that the pressure generated during freezing and melting measurements has little impact on the pore structure of the powder MCM-41 samples. As for the studied cylinder samples of cement pastes, frost damage probably takes place and it changes the pore connectivity while it has limited effects on changing the interior size distribution of the meso-pores. The analysis of the freezing and melting behavior of the pore liquid of cement based materials is complicated by the presence of ions. The freezing and melting behavior of the pore solution of cement paste samples preconditioned in either a small amount or a big amount of saturated limewater was compared. The results suggest that either the preconditioning in a big amount of limewater does not change the ionic concentration of the pore solution very much or the possible leaching of ions from cement hydrates during the preconditioning has limited influence on the freezing and melting behavior of the pore solution in the studied cement paste samples.

Keywords: Cement paste, calorimetry, freezing and thawing, frost damage, thermoporometry, cryoporometry.

1. Introduction

The freezing point of water or melting point of ice confined in pores is lower than that of bulk water or ice and the magnitude of the freezing/melting point depression depends on the size of the pores in which the freezing/melting takes place [1]. Cement based materials have a rather complicated pore system, whose pore sizes can range from nanometer to millimeter [2, 3]. Due to the confinement of pores with different sizes, water present in the pores of cement based materials freezes at different temperatures when the materials are exposed to low temperature environments. The freezing behavior of the water and/or the melting behavior of the ice confined in the pores can be used to study some important properties of the materials, e.g., the freeze/thaw durability [4, 5] and the porosity [6, 7].

Low temperature (micro-)calorimetry (LTC), which is also known as thermoporometry and sometimes is referred to as thermoporosimetry or cryoporometry [8], can be used to characterize the porosity of cement based materials. The basic concept of LTC is that the freezing process of water is an exothermic process and the melting process of ice is an endothermic process. During a measurement, the LTC instrument (calorimeter) records the heat flow of the sample at different testing temperatures. Based on the measured heat flow and using the heat of fusion for the confined water/ice, the ice content in the freezing or the melting process can be calculated. The volume of the ice formed/melted under different temperatures in a sense indicates the pore information of the sample under the testing. By introducing proper assumptions, thermodynamic studies demonstrate that there is a unique equation showing the correspondence between the phase transition temperature of the water/ice confined in pores and the curvature of its solid-liquid interface [1, 9]. The quantitative relation of the freezing/melting temperature and the pore size can be determined by adopting appropriate values for the thermodynamic parameters of the water/ice confined in the pores. LTC is an indirect method to determine porosity and special attention should be given to the measurements and the analysis of the measured data. More related discussions about using LTC to characterize cement based materials can be found, e.g., in [8, 10, 11].

Compared with traditional methods developed for porosity characterization, e.g., nitrogen adsorption/desorption (NAD), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM), a major advantage of using LTC to characterize cement based materials is that the measurements can be conducted on virgin samples without any pre-drying treatment [7, 12–15]. This is important because the drying treatment often results in an apparent alteration of the pore structure under consideration for cement based materials [13, 14, 16]. Meanwhile, it should be mentioned that due to the fact that water in very small pores does not freeze and the freezing/melting point depression of water/ice in big pores is too small. Thus, the pores that can be

studied by LTC are limited mainly to those with radii between about 2 nm to about 40 or 50 nm [7, 17]. Water in larger pores is monitored, but the resolution is too limited to allow for determination of the actual pore size.

For water saturated porous materials, frost damage may potentially take place as the pore water freezes, especially when water in very small pores freezes [18]. The frost damage may change the pore structure of the studied materials to a certain extent. Considerable studies have been conducted to study the frost damage in cement based materials, e.g., see [19–25]. Several different mechanisms have been proposed, including the hydraulic pressure theory [20], the crystallization pressure theory [23], the closed container theory [25], etc. Even though disagreement exists with respect to the exact cause(s) of frost damage, it can be concluded that the probability of frost damage to take place is high in cement based materials with a high degree of saturation, especially when the materials are exposed to very low temperatures, e.g., in LTC measurements. Using LTC to characterize a pore size distribution, it has been explained theoretically that the pores under consideration should be fully saturated [6, 26]. An experimental study [11] has demonstrated the impact of non-fully saturated pores on the pore size determination. Thus, in practice, the samples in LTC studies are often treated with vacuum saturation with the aim to fully saturate all the accessible pores before calorimetric measurements. That is, the frost damage would be highly probable for the vacuum saturated samples of cement based materials during LTC measurements, as the lowest temperature during the measurements can be down to $-80\text{ }^{\circ}\text{C}$ or even lower to ensure all the freezable pore water can freeze [5]. In a LTC study conducted by Johannesson [5], the elastic moduli of the vacuum saturated concrete samples were measured before and after a cycle of freezing and melting measurement. The results showed that even for some of air-entrained samples, the elastic moduli decrease considerably after a cycle, indicating that the concrete samples possibly have been damaged during the measurement. Although LTC has been applied to study cement based materials for several decades, the impact of the frost damage on the porosity determination is not fully clear. Thus, one aim of the present work is to further explore the impact of frost damage on the porosity determination of cement based materials by LTC.

The pore liquid in cement based materials is another factor that should be considered in LTC studies. As we know, the pore liquid is not pure water but contains certain ionic species including calcium, sodium, potassium and hydroxide ions, etc. [27]. The presence of ionic species influences the freezing and melting behavior of the pore solution. To minimize the influence of the ions on the data analysis in LTC studies, it has been suggested to use water cured samples. The consideration is that the alkalis could leach out and then the pore liquid becomes dilute [6]. In a study conducted by Sun and Scherer [7], mortar samples ($\sim 20 \times 30 \times 100\text{ mm}$) were stored in a relatively big amount of saturated limewater ($\sim 48\text{ liters}$) for about 6 months; and then it was

suggested that the alkalis would likely to have diffused out during the curing and the pores contained a solution very similar to saturated limewater. Since saturated limewater solution is rather dilute (~ 2 g calcium hydroxide/liter water), they further concluded that the freezing and melting behavior of the pore solution in their mortar samples could be approximated to that of pure water [7]. However, it is noted that due to a relatively big buffering capacity of the cement hydrates as demonstrated in thermodynamic modeling studies, e.g., see [28–30], the ionic concentration in the pore solution of the samples cured in big amount of saturated limewater might not necessarily be significantly changed.

In order to study the relevance of the related arguments above regarding cement pore solution, comparison measurements were performed on cement paste samples of the same recipe but preconditioned either in a small amount or in a big amount of saturated limewater (details see Section 2.1). The heat flow curves of freezing and melting of the samples preconditioned at different conditions were compared. The saturated limewater rather than pure water was used with the purpose to limit the leaching of calcium ions, since the leaching of calcium ions from cement hydrates has been demonstrated to be able to change the porosity of cement based materials to a certain extent [31, 32].

2. Experimental

2.1. Materials preparation

One mono-sized model material MCM-41 and two types of hardened cement pastes were included in this investigation. One aim of including the MCM-41 in this study was to check the instrument stability among different measurements and the homogeneity of the prepared cement paste samples, which will be further explained in Section 2.2.

MCM-41 is a silica based material and the pore structure is in the form of hexagonal arrays of uniform tubular channels of controlled width. The MCM-41 used in this study is a commercial product in powder form produced by Tianjin Chemist Scientific Ltd. The nominal pore diameter provided by the producer is 3.0 nm.

The cement paste samples were prepared by two types of cement, i.e., CEM I 32.5 R and CEM III/B 42.5 N, with the properties and the chemical composition of the cements shown in Table 1. The water-to-cement ratio was 0.4 for all the samples prepared. The fresh paste samples were mixed by a paddle mixer. After mixing, the fresh pastes were cast into cylindrical plastic vials ensuing proper compaction. The dimension of the plastic vials was about $\phi 15 \times 50$ mm. The hardened cement pastes were demoulded after one day of sealed curing at room temperature (about 20 °C) and then placed into slightly bigger plastic flasks ($\sim \phi 25 \times 60$ mm) filled with saturated limewater for curing at room temperature. After about three months, the paste samples

Table 1: Properties and the chemical composition of the two 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

were divided into two groups: the first group was still left curing in the slightly bigger plastic flasks (denoted as preconditioned in a small amount of saturated limewater); and the second group was cured in a big bucket filled with saturated limewater (~ 40 liters) (i.e., denoted as preconditioned in a big amount of saturated limewater) until the date of calorimetric measurements. If it is not specially stated, the paste samples presented in this study are the samples cured in the plastic flasks (preconditioned by curing in a small amount of limewater). By using two types of cement, part of the effect due to cement types on the porosity determination by LTC is expected to be observed.

CEM I and CEM III are designated to denote the hardened cement pastes in the following description.

2.2. Calorimetric measurements

In this study, a Calvet-type scanning calorimeter (SETARAM) was used. The calorimeter was calibrated and operated to work between about 20 °C and about -130 °C. The temperature scanning of a freezing and melting cycle starts at about 20 °C and goes down to about -80 °C and then goes back to about 20 °C again. The cooling and heating rate were set to be 0.1 °C per minute.

For the easy handling of powder samples of the MCM-41 in the calorimeter, a plastic vial was chosen as a sample holder. The MCM-41 powders were placed into cylindrical plastic vials ($\sim \phi 14 \times 48$ mm) up to about half volume of the vials (the

dry weight later determined was about 0.2 g). The size of the plastic vials was chosen to fit the measuring chamber of the calorimeter. To saturate the powder samples held in the plastic vials, they were covered with distilled water and then placed under a reduced pressure (~ 40 mbar) for about 3 hours. After that, the plastic vials with saturated powder samples were put on shelf standing still for about two weeks. The apparent excess bulk water on top of the powders was removed before the calorimetric measurements. A corresponding plastic vial but empty was placed in the reference chamber of the calorimeter to counteract some uncertainties that the plastic vials may experience at low temperatures during the measurements.

The cylinder samples of cement pastes ($\sim \phi 15 \times 45$ mm) were vacuum saturated first and then the apparent water on the surface was wiped off. The paste samples were assumed to be saturated surface dry when placed in the calorimeter. A totally dry paste sample (oven drying at about 105°C until constant weight) with the same dimension as the testing specimen was used as a reference sample. In the investigation, the same reference was used throughout all the tests. One purpose of using the reference sample is to reduce the possible uncertainties of the solid paste during the freezing and melting. More discussions about the influence and the benefits of using such a reference sample in calorimetric measurements can be found in [5, 10]. The total curing time of the cement paste samples was about one year when the calorimetric measurements were performed.

The mass of each tested vacuum saturated sample before and after calorimetric measurements were determined. The relative difference of the mass was less than about 0.15%. That is, there is almost no water loss during the calorimetric measurements. After calorimetric measurements, the samples were subjected to oven-drying at about 105°C till constant weight and then the dry weights of the samples were determined.

In this study, calorimetric measurements were conducted on two different samples of the model material MCM-41 and three different samples of each cement paste. Through the measurements, firstly the stability of the instrument among different measurements can be validated by comparing the measured heat flow curves of the rather homogenous model material MCM-41 (as the tested samples are in powder form and were collected from a rather big batch). The heat flow curves should be quite comparable if the instrument is stable. Secondly, the homogeneity of the prepared cylinder samples of cement pastes can also be checked.

To investigate the influence of the frost damage on the applicability of using LTC to study the meso-porosity, three continuous (repeated) freezing and melting cycles were applied on a sample of the MCM-41 and two continuous cycles were applied on a sample of each cement paste studied. If the heat flow curves of freezing and melting change after each cycle, it may demonstrate the frost damage has an impact on the pore structure of a studied material and hence using the LTC method may not be able

to characterize the original or the “real” porosity accurately.

Calorimetric measurements were performed on cement paste samples of the same recipe preconditioned in a small amount and a big amount of saturated limewater. The influence of the leaching of ions from cement hydrates on the freezing and melting behaviors of the pore solution of the pastes can be studied by comparing the measured heat flow curves of the samples preconditioned at different conditions.

3. Results and discussion

3.1. Instrument stability and sample homogeneity

The measured heat flow curves of two different samples of the model material MCM-41 are shown in Figure 1. There are two distinct peaks on the heat flow curves of melting: one is around about -34 °C and the other is close at about 0 °C. Since the MCM-41 is a mono-sized material, the peak around -34 °C can be assigned to the pore water and the peak close at 0 °C should correspond to the excess bulk water in the samples.

On the heat flow curves of freezing, two groups of peaks have been observed: the first group is around about -10 °C and the second is around about -40 °C. The first group of peaks reflects the characteristics of supercooled water. Bulk water can be cooled down below 0 °C without freezing due to the energetic barrier to nucleation [33]. Supercooling is due to the uncertainties of nucleation, thus it is normally not reproducible [17]. While freezing point depression is caused by the pore confinement and it is reproducible for water freezing in the pores with the same size, which is often called undercooling [17].

For the second group peaks, there are a small peak around about -36 °C and a relatively big one around about -42 °C. The small peak is possibly related to the pore size variation along the channels of the model material MCM-41. This is suggested since studies of desorption isotherms on the same type of materials showed the same type of variations [34] (the desorption process is often considered rather comparable to the freezing process [7]). It is noted that when temperature goes down to about -38 °C, homogeneous nucleation becomes dominant and all the freezable pore water will freeze irrespective of the pore sizes [18, 35, 36]. Thus, the peak around about -42 °C on the freezing curves most likely corresponds to homogeneously nucleated pore water.

Small differences are found on the measured heat flow curves of the two different samples of the model material MCM-41 (Figure 1). That the absolute value of the measured heat flow of sample 2 is somewhat lower than that of sample 1 can be explained by the different baseline (of heat flow) of the two samples. As we know, the heat flow measured by a LTC instrument consists of two parts: (1) the contribution from the heat capacity of the system (including water, ice and the powder MCM-41

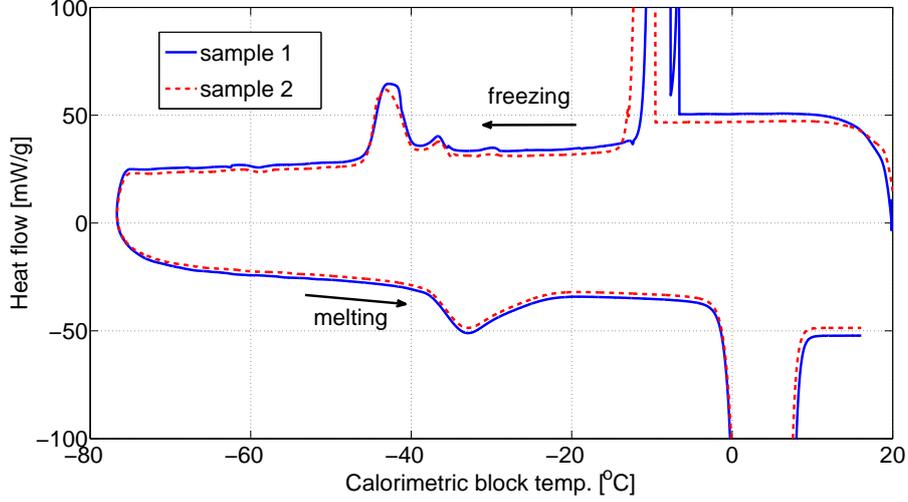


Figure 1: Measured heat flow of two different samples of the model material MCM-41. The heat flow is expressed as milliwatt (mW) per gram of dry material.

sample in this case), i.e., the baseline; and (2) the contribution due to phase transition [5, 10]. The baseline does not reflect any pore volume and should be subtracted in determining the pore volume of the studied material. For the two samples in Figure 1, the baseline of sample 2 is slightly lower than that of sample 1, i.e., due to some higher content of excess bulk water in sample 1. However, the magnitude and the position of the peaks (freezing/melting points) corresponding to the meso-pores are quite comparable for the two measurements, indicating that the pore volume of the two measured samples are comparable. It is, therefore, concluded that the stability of the instrument is satisfactory.

The measured heat flow curves of three different samples of cement pastes CEM I and CEM III are presented in Figure 2 and Figure 3, respectively. For both pastes, the first peak on the heat flow curves of freezing (observing from high to low temperatures) is believed to mainly correspond to supercooled water. Since the saturated surface dry paste samples were used in the calorimetric measurements (indicating almost no excess bulk water), the first peak is mainly contributed by the water in big pores, in which the freezing point depression of the confined water is very small, and partly contributed by the pore water with corresponding freezing point higher than that of the supercooled water. That is, the first peak on the heat flow curves of freezing mainly reflects the uncertainties of supercooling and indicates little about pore (entry) size information. The peak on the heat flow curves of freezing starting around -40 °C, similar to what has been discussed for the MCM-41, corresponds to homogeneously nucleated pore

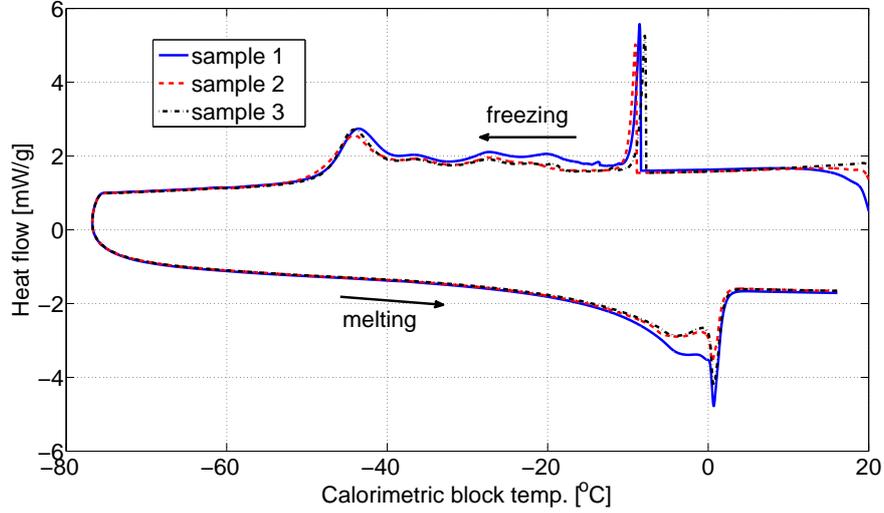


Figure 2: Measured heat flow of three different samples of the cement paste CEM I. The heat flow is expressed as milliwatt (mW) per gram of dry material.

water. On the heat flow curves of melting of the paste CEM I (observing from low to high temperatures), there are one plateau-like peak starting around -6 °C and a peak starting around 0 °C, which is extended to higher temperatures for several degrees; while on the heat flow curves of melting of the paste CEM III, besides the peak at about 0 °C, there is another peak around the temperature of about -8 °C. The peaks found on the heat flow curves of melting of the studied cement paste samples below 0 °C are contributed by the water/ice in the small pores (mainly nanometric pores) and the peak starting around about 0 °C mainly correspond to the water/ice in big pores with small temperature depression.

As can be observed from Figure 2 and Figure 3, the heat flow curves of two measured samples (sample 2 and 3) for both pastes are quite comparable except the first peak on the freezing curves. As for the model material MCM-41, the first peak is mainly related to supercooling and supercooling is normally not reproducible. For both cement pastes, the heat flow curves of sample 1 have peaks at similar locations (temperatures), but differ in magnitude of heat flow from that of the other two samples to a certain extent. One possible explanation could be an inhomogeneity of the prepared samples.

Based on the small differences as observed between the results of the measurements on the different samples of the model material MCM-41 and the relatively comparable results on the two different samples of each studied paste, it is assumed that the stability of the instrument is satisfactory. The measured differences of the cement pastes are concluded to be mainly attributed to the inhomogeneity of the prepared samples.

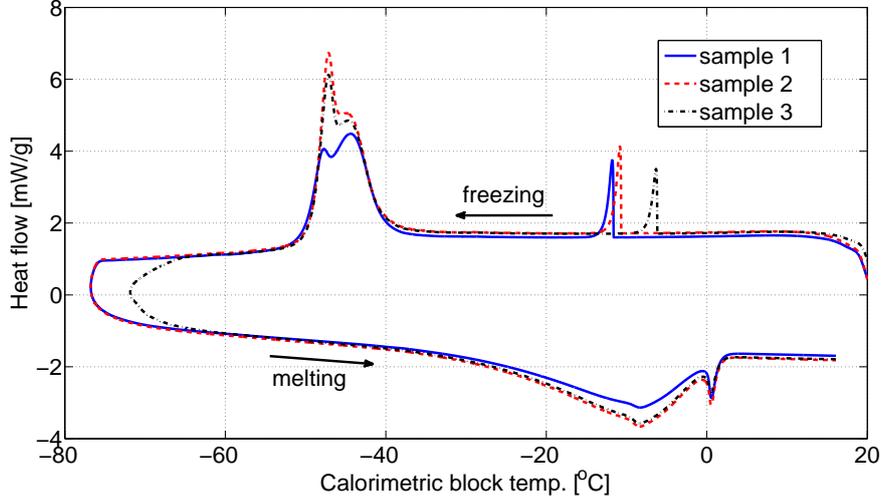


Figure 3: Measured heat flow of three different samples of the cement paste CEM III. The heat flow is expressed as milliwatt (mW) per gram of dry material.

3.2. Impact of frost damage on heat flow curves

In LTC studies, it is normally assumed that the freezing curves (after the first nucleation which is often related to supercooling) is controlled by the connectivity of a pore system, or rather the pore entry or neck sizes (assuming that the freezing process is initiated by heterogeneous nucleation followed by progressive penetration); while the melting is controlled by the pore interior sizes [7, 8, 11, 18].

3.2.1. Model material MCM-41

The measured heat flow curves of three continuous freezing and melting cycles on a sample of the model material MCM-41 is shown in Figure 4.

It can be found from Figure 4 that the heat flow curves of freezing and melting after each cycle are almost the same. The similarity between the heat flow curves of melting indicates that the effect of possible frost damage (the pressure generated during the freezing process exerted on the pore walls) probably has no or very limited impact on changing the pore interior sizes of the material MCM-41. As for the heat flow curves of freezing, one may argue that even though the freezing curves are almost the same, it is not easy to judge whether the pore entry sizes (or pore sizes variation along the channels [34]) of the MCM-41 change after each cycle of measurement. The reason for that is most probably that the pore entry sizes are too small. That is, the freezing of the pore water is dominated by homogeneous nucleation, which does not necessarily reflect pore entry sizes. However, the peak around $-36\text{ }^{\circ}\text{C}$ appears at the

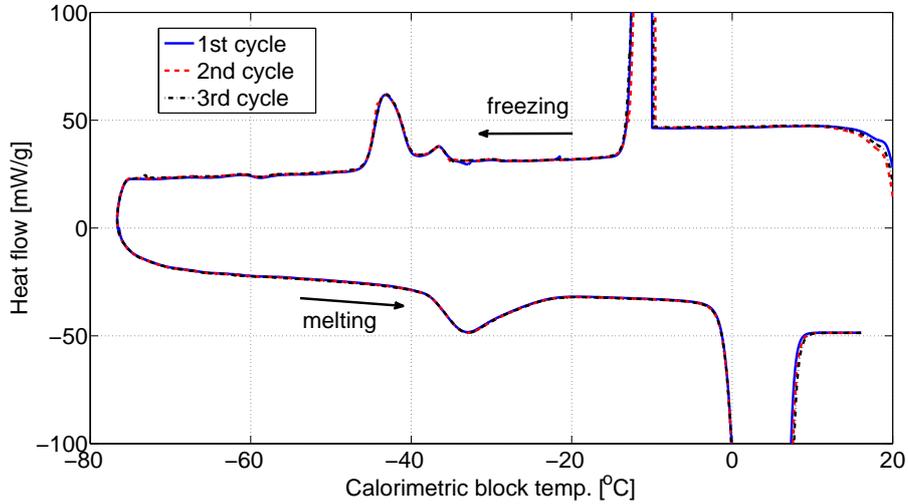


Figure 4: Measured heat flow of three continuous freezing and melting cycles on a sample of the model material MCM-41. The heat flow is expressed as milliwatt (mW) per gram of dry material. The heat flow curves of the three cycles are almost the same.

same temperature with about the same magnitude on the heat flow curves of freezing in all the three measured cycles, which somewhat demonstrates the stability of the pore structure during the three freezing cycles. That is, for the studied powder MCM-41 samples, it is assumed that the ice formed in the pore structure has limited impact on changing the porosity, including both the pore connectivity and the pore interior sizes.

3.2.2. Cement pastes

The measured heat flow curves of two freezing and melting cycles on the same cylinder sample of the cement pastes CEM I and CEM III are presented Figure 5 and Figure 6, respectively.

It can be found that for both pastes, the heat flow curves of freezing change after one cycle of measurement and the change is more evident in low temperature range. It is characterized by the shifting of the peak starting at around $-40\text{ }^{\circ}\text{C}$ (to some higher temperatures). The heat flow curves of melting are almost not affected after one cycle of measurement, except that the magnitude of the peak just above about $0\text{ }^{\circ}\text{C}$ (i.e., mainly corresponds to the water in big pores) decreases.

3.2.2.1. Heat flow curves of freezing. The difference in the heat flow curves of the first and second freezing of the cement paste samples indicates that the pore connectivity probably has been changed, implying that frost damage may have taken place in the tested cylinder samples during the first cycle of measurement. It seems that frost

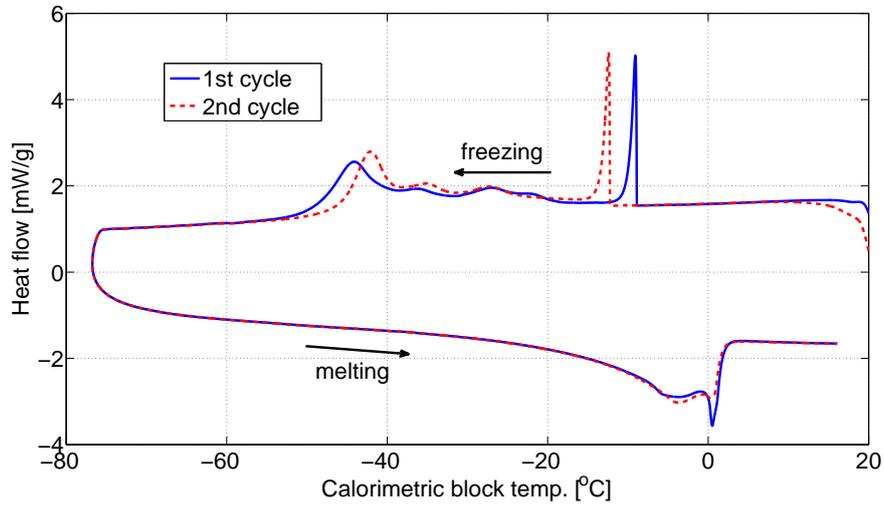


Figure 5: Measured heat flow of two continuous freezing and melting cycles on a same sample of the cement paste CEM I. The heat flow is expressed as milliwatt (mW) per gram of dry material.

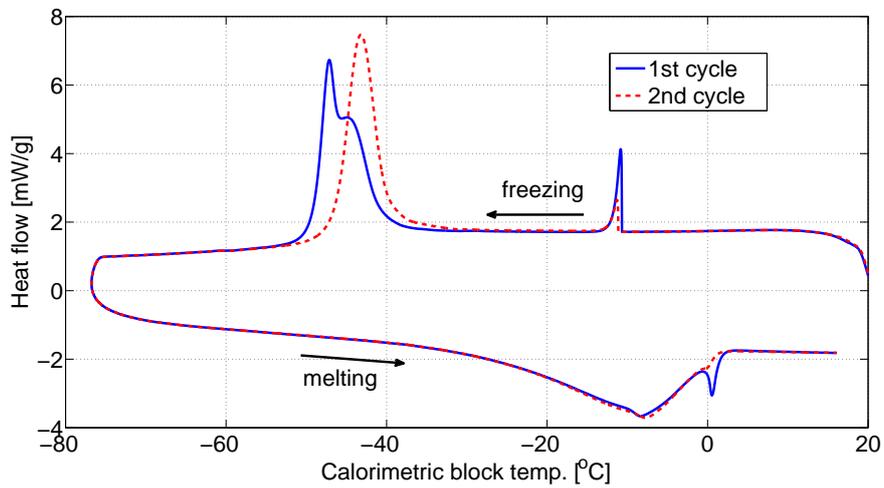


Figure 6: Measured heat flow of two continuous freezing and melting cycles on a same sample of the cement paste CEM III. The heat flow is expressed as milliwatt (mW) per gram of dry material.

damage increases the connectivity of the pore system, i.e., more pores are penetrable by ice at a certain undercooling.

The increased connectivity of the pores in the cement pastes is reflected by the relatively higher heat flow curves of freezing in the second cycle compared with that of the first cycle between the temperature from the point that the first peak finishes down till about $-40\text{ }^{\circ}\text{C}$ (see Figure 5 and Figure 6). As discussed earlier, the first peak mainly corresponds to supercooled water in big pores (in which water has small temperature depression) and the peak starting at about $-40\text{ }^{\circ}\text{C}$ is due to the homogeneously nucleated water, both of which do not necessarily reflect the pore entry sizes or the connectivity of the pore system. Thus, it is difficult to judge whether the shifting of the peak starting at around $-40\text{ }^{\circ}\text{C}$ on the heat flow curves of freezing indicates the change of the pore connectivity. However, the magnitude of the peak starting at about $-40\text{ }^{\circ}\text{C}$ can to some extent indicate the connectivity of the studied cement pastes. If the magnitude of the peak decreases after one cycle of measurement, it means that the volume of the pores in which water homogeneously nucleated decreases. The decreased volume of the (homogeneously nucleated) pores implies more pores are penetrable by the ice at higher temperatures after one cycle of measurement, which then indicates an increase of the pore connectivity. A careful evaluation (Figure 5 and Figure 6) does show that the magnitude of the peak starting at about $-40\text{ }^{\circ}\text{C}$ on the heat flow curves of freezing of the second cycle slightly decreases compared with that of the first cycle.

3.2.2.2. Heat flow curves of melting. The decreased magnitude of the peak just above about $0\text{ }^{\circ}\text{C}$ in the heat flow curves of melting during the second cycle of the studied cement paste samples indicates that the amount of the water in relatively big pores decreases. Moreover, a close check in the curves of melting of the second cycle (Figure 5 and Figure 6) indicates a slight increase of the small pore volume compared with that of the first cycle, reflected by slightly higher (in absolute value) heat flow curves than that of the first cycle at the temperatures lower than about $0\text{ }^{\circ}\text{C}$. Two possible explanations could be proposed accounting for the observations.

The first explanation could be that frost damage in cement paste samples during the first cycle of measurement, e.g., in the form of micro-cracking [23, 37], can make some of the initially water inaccessible pores (e.g., as characterized by homogeneously nucleation in the freezing) accessible. When the first cycle of measurement is completed, some of the newly opened non-fully saturated pores, e.g., with relatively small pore sizes, can suck water from big pores through capillary suction, resulting in the observed changes in the heat flow curves.

This explanation is somewhat supported by the slightly decreased volume of the homogeneously nucleated pores (corresponding to the magnitude of the peak starting at about $-40\text{ }^{\circ}\text{C}$) as observed on the heat flow curves of freezing of the second cycle compared with that of the first cycle. Following the explanation, the slight difference

between the heat flow curves of melting of the two cycles at the temperatures lower than about 0 °C (i.e., corresponding to volume of meso-pores) is not due to that the frost damage enlarges some of the small pores but that some initially homogeneously nucleated pores are opened up by the frost damage. The argument about the pore enlargement can be somewhat validated by considering that if the pore enlargement is relevant, then the small pores are more prone to be enlarged since the pressure generated during freezing in small pores is higher than that in big pores [23, 37], meaning that the volume of small pores should decrease. However, the decrease of the volume of small pores is not observed by comparing the heat flow curves of melting of the second cycle with the first cycle (Figure 5 and Figure 6).

The above explanation may be challenged by taking the cryogenic suction into consideration. Cryogenic suction, or cryosuction, is the effect of water from neighboring pores or from the surroundings being drawn towards ice crystals already created in the pore system during freezing process [18, 38–41]. If some water in the big pores are sucked into small pores which are opened by frost damage during the first cycle as argued above, then the big pores are not fully saturated during the second cycle of measurement. Following the concept of cryogenic suction, water in small pores could be drawn into the non-fully saturated big pores when ice forms in the big pores (during the second cycle). Consequently, the ice in the big pores might not decrease significantly. However, the heat flow curves of melting of the second cycle indicate that the amount of ice melted in the big pores (the peak just above about 0 °C) is smaller compared with that of the first cycle, especially for CEM III (see Figure 5 and Figure 6). The exact reasons are not clear, but it is suspected that it may be related to the very small amount of ice in the big pores of the studied cement pastes during the second cycle of measurement (which is indicated by the peak just above about 0 °C on the heat flow curves of melting). That is because for water to be able to be drawn into the big pores by cryogenic suction, ice should present in the big pores as a freezing front at the connecting points of big and small pores [18, 39, 42]. If there is only a very small amount of ice presented in a big pore, it is possible that the water in a small pore (which is connected to the big pore) can not be drawn into the big pore due to the lack of a freezing front.

The second possible explanation is that frost damage takes place and generates micro-cracks during the first cycle of measurement. The micro-cracks have small widths and are connected to big pores (e.g., air voids), directly or indirectly. After the first cycle of measurement, the micro-cracks can suck water from big pores. The consequence is that the magnitude of the measured heat flow corresponding to big pores (above about 0 °C) decreases and that corresponding to small pores (lower than about 0 °C) increases. The key of this explanation is that the generated micro-cracks must have small widths and must be connected to the big pores directly or indirectly. However, the

second explanation cannot explain the slightly decreased volume of the homogeneously nucleated pores (corresponding to the magnitude of the peak starting at about $-40\text{ }^{\circ}\text{C}$) as observed on the heat flow curves of freezing of the second cycle compared with that of the first cycle.

The first explanation assumes that the slight increase of small pore volume is due to existing small pores in the samples (initially isolated but opened up by the frost damage); while the second explanation assumes that frost damage creates some micro-cracks which are detected as small pores during the second cycle of measurement. The first explanation may be more reasonable considering the comparison of the heat flow curves of both freezing and melting of the two measured cycles.

3.2.2.3. Influence of frost damage on pore size distribution. If frost damage takes place in cement paste samples during freezing and melting measurements, an immediate question is that whether LTC can still characterize the original or the “real” porosity of the materials. By looking at the relatively stable heat flow curves of melting of the two cycles below the temperature of about $0\text{ }^{\circ}\text{C}$ from Figure 5 and Figure 6, it indicates that the pore (interior) size distribution (of meso-pores) is not affected to any significant degree by frost damage.

One may argue that the change of pore structure due to frost damage would have taken place during the first freezing cycle, meaning both the first and second melting measurement do not give the “real” pore size distribution. It is reasonable to consider that if the meso-pore walls of cement paste samples are not strong enough to withstand the stress generated during the measurements, the heating flow curves of melting should be shifted to higher temperatures after each cycle of measurement, e.g., as observed for some gel materials [43, 44]. This is because as long as water exists and freezes in small meso-pores, the stress generated is in the similar order. If the pore walls cannot sustain during the first cycle, they would probably also not be able to sustain during the following cycles. However, this is not the case for the studied cement paste samples. That is, the slight increase of pore volume indicated by the heat flow curve of melting of the second cycle for the cement pastes is not due to that the existing meso-pores are enlarged by frost damage. But, it is perhaps due to that the changing of some of the previous homogeneously nucleated pores slightly increases the volume of pores which is not detectable during the first cycle, since LTC can only detect pores filled with water. If the cement paste samples are free of non-penetrable pores, it may be reasonable to assume that the heat flow curves of melting of several cycles are quite comparable.

It has been revealed that a pore system with small pore entries or necks is very susceptible to frost damage. That is because the pressure generated on the pore walls during freezing in this type of pore system is very high [23]. Thus, for the studied cement paste samples, the frost damage may take place when the temperature goes down to low temperatures and the water in small pore necks freezes. The relevance of

this argument is somewhat validated by looking at the heat flow curves of freezing of the two cycles (Figure 5 and Figure 6): the main difference is below the temperature of about -30 °C. However, the relatively stable heat flow curves of melting in two consecutive cycles of measurements as obtained for the studied cement pastes may indicate that the interior sizes of the meso-pores of cement pastes may be not affected by frost damage.

Some cryoporometry studies, e.g., [45, 46], compared ice content curves of the freezing and melting between big integral and crushed samples of a same material. The results showed that the freezing curves (i.e., pore connectivity) are different while the melting curves (i.e., pore interior sizes) remain about the same, which are somewhat comparable to the results obtained in this study. That is, the effect of frost damage in cement pastes may be, to some extent, comparable to crushing big integral samples.

To sum it up, the very similar heat flow curves of freezing and melting of the MCM-41 indicate that the pressure generated during freezing has little impact on the pore structure of the powder model material. By studying the heat flow curves of freezing and melting of cement pastes, it is concluded that the frost damage probably takes place in the studied cylinder samples and it changes the pore connectivity while it has limited effect on changing the interior size distribution of the meso-pores.

3.3. Influence of sample preconditioning on freezing and melting behaviors of cement pore solution

The measured heat flow curves of the cement paste samples with the same recipe preconditioned in a small amount and a big amount of saturated limewater for CEM I and CEM III are compared in Figure 7 and Figure 8, respectively. The freezing/melting points of the peaks corresponding to pores are almost the same for the samples of each paste preconditioned in both a small amount and a big amount of saturated limewater (except the first peak on the freezing curves, which is related to supercooling and it reflects uncertainties of heterogeneous nucleation, as explained earlier), indicating that the preconditioning in different amount of limewater may not affect the freezing and melting behavior of the pore solution very much. Meanwhile, it can be found from Figure 7 that the magnitude of the peaks corresponding to pores especially on the freezing curves for the paste samples preconditioned at different conditions are also comparable (the comparability in Figure 8 is lower, which will be explained in the next paragraph). That is, if the argument given by Sun and Scherer [7] is relevant, i.e., the freezing and melting behaviors of the pore solution in cement samples cured in a big amount of limewater for a relatively long time can be approximated to that of pure water, then the approximation may be also applicable for cement samples cured in a small amount of limewater. Obviously, further study is needed to clarify the ionic concentrations in the pore solution of the paste samples preconditioned under the different conditions.

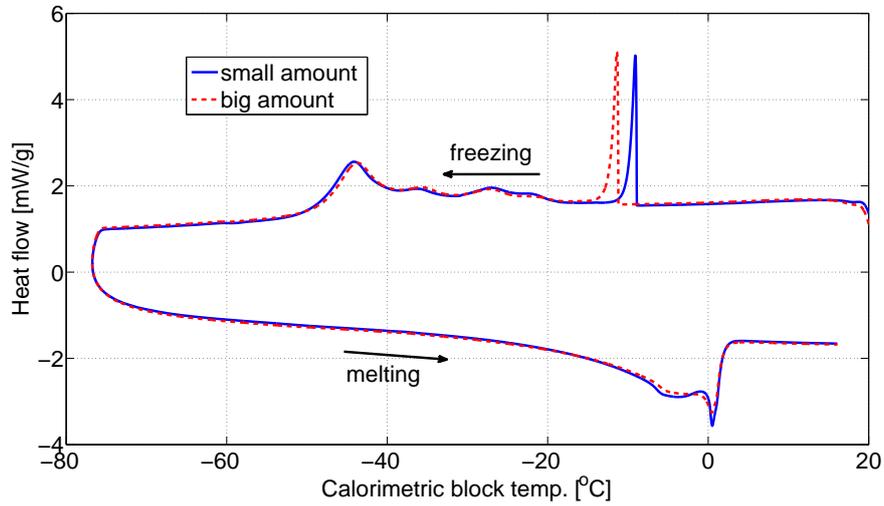


Figure 7: Measured heat flow of samples cured in a small and a big amount of saturated limewater of the cement paste CEM I. The heat flow is expressed as milliwatt (mW) per gram of dry material.

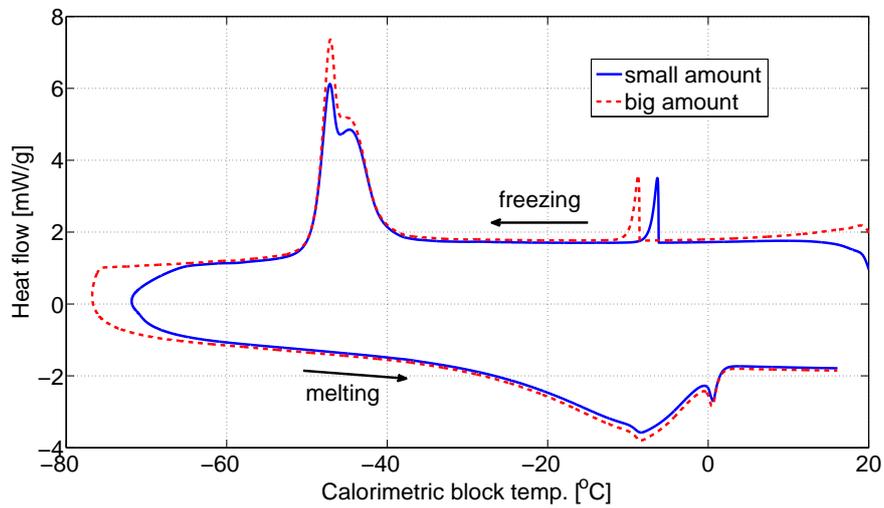


Figure 8: Measured heat flow of samples cured in a small and a big amount of saturated limewater of the cement paste CEM III. The heat flow is expressed as milliwatt (mW) per gram of dry material.

Another concern related to curing cement samples in a big amount of water is that leaching of ions from cement hydrates can possibly increase the porosity. Studies, e.g., [31, 32], have shown the effect of leaching of calcium ions from portlandite and calcium silicate hydrates on the porosity of cement based materials. For the paste CEM III (Figure 8), the heat flow curve is a little bit higher (in terms of absolute value) in the sample preconditioned in a big amount of saturated limewater, which implies somewhat higher porosity. One may argue that the somewhat higher porosity in the sample preconditioned in a big amount of saturated limewater may be related to the leaching of ions. By looking at the difference between the measured heat flow curves of different samples of the same paste CEM III (Figure 3), the difference observed in Figure 8 could also be due to the inhomogeneity of prepared paste samples since the somewhat high porosity is not observed in the paste sample of CEM I preconditioned in a big amount of saturated limewater in the comparison (Figure 7). Nevertheless, to reduce the possibility of leaching changing the porosity, it is probably a better practice to cure cement paste samples in a small amount of saturated limewater rather than in a big amount in LTC studies.

Based on this study, it can be concluded that there is almost no difference on the heat flow curves of freezing and melting between the samples preconditioned in a small amount and a big amount of saturated limewater, indicating that either the preconditioning in a big amount of limewater does not change the concentration of the pore solution very much (e.g., due to the buffering effect of the cement hydrates) or the leaching of ions from cement hydrates has limited influence on the freezing and melting behaviors of the pore solution in the studied cement paste samples.

4. Conclusions

The impact of frost damage on the characterization of the meso-porosity of a model material MCM-41 and two types of cement pastes using LTC were studied by conducting repeated freezing and melting cycles on a same sample of each studied material. The measured results showed that for the model material MCM-41, the heat flow curves of freezing and melting after each cycle were almost the same. For the two cement pastes, the heat flow curves of freezing changed after one cycle of measurement and the change was more evident in the low temperature range. The heat flow curves of melting were almost not affected after one cycle of measurement. The results indicate that the pressure generated during freezing and melting has little impact on the pore structure of the powder MCM-41 samples. As for the studied cylinder paste samples, frost damage potentially takes place and it changes the pore connectivity characteristics while it has limited effects on changing the interior size distribution of the meso-pores.

The freezing and melting behavior of the pore solution of cement paste samples preconditioned in a small amount and a big amount of saturated limewater were compar-

actively studied. The results showed that there is almost no difference in the measured heat flow curves of freezing and melting comparing the samples preconditioned in a small amount and a big amount of saturated limewater. This indicates that either the preconditioning in a big amount of limewater does not change the concentration of the pore solution very much or the leaching of ions from cement hydrates has limited influence on the freezing and melting behavior of the pore solution in the studied cement paste samples.

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