



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



Min Wu^{a,*}, Katja Fridh^b, Björn Johannesson^a, Mette Geiker^c

^a Department of Civil Engineering, Technical University of Denmark, Building 118, 2800 Lyngby, Denmark

^b Division of Building Materials, Lund University, Lund, Sweden

^c Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway

ARTICLE INFO

Article history:

Received 8 August 2014

Received in revised form 4 March 2015

Accepted 6 March 2015

Available online 20 March 2015

Keywords:

Cement paste

Calorimetry

Freezing and thawing

Frost damage

Thermoporometry

Cryoporometry

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 explored on a model material MCM-41 and two 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 took place and it changed the pore connectivity while it had limited effect 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.

© 2015 Elsevier B.V. All rights reserved.

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].

Calorimetric methods have been used to study cement based materials for a long time, e.g., see [5,6,8–10]. Low temperature (micro-)calorimetry (LTC), which is also known as thermoporometry and sometimes is referred to as thermoporosimetry or cryoporometry [11], 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 [12,1]. The quantitative relation of the freezing/melting temperature and the pore size can be determined by adopting appropriate values

* Corresponding author. Tel.: +45 45251813.
E-mail address: miwu@byg.dtu.dk (M. Wu).

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 [11,13,14].

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 [7,15–18]. This is important because the drying treatment often results in an apparent alteration of the pore structure under consideration for cement based materials [16,17,19]. 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 [20,7], corresponding mainly to the so-called “meso-pores” (according to the IUPAC¹ definition [21]). Water in larger pores (with radii larger than about 50 nm) is monitored, but the resolution is too limited to allow for determination of the actual pore sizes.

For water saturated porous materials, frost damage may potentially take place as the pore water freezes, especially when water in very small pores freezes [22]. 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 [23–29]. Several different mechanisms have been proposed, including the hydraulic pressure theory [24], the crystallization pressure theory [27], the closed container theory [29], 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 [30,6]. An experimental study [14] 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°C or even lower to ensure all the freezable pore water can freeze [5]. In a LTC study conducted by Johansson [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. [31,32]. 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 ($\sim 20 \times 30 \times 100$ mm) were stored in a relatively big amount of saturated limewater (~ 48 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 [33–35], 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 [36,37].

This work focuses on studying the influence of frost damage and sample preconditioning on the porosity characterization of cement based materials using LTC, by directly comparing the measured heat flow curves of freezing and melting. To derive pore sizes from the measured heat flow curves and further to compare the results obtained using LTC with that obtained using other methods are out the scope of this work. Interested readers can consult, e.g., [13,14], for pore size determination and, e.g., [7,38,39], for the comparison of the results obtained by different methods.

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

¹ International Union of Pure and Applied Chemistry.

Download English Version:

<https://daneshyari.com/en/article/673015>

Download Persian Version:

<https://daneshyari.com/article/673015>

[Daneshyari.com](https://daneshyari.com)