CRYOPOROMETRY CHARACTERIZATION FOR CEMENT BASED MATERIALS

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OBJECTIVES OF THE RESEARCH

Currently, there remain open questions about which pore types in cement hardened pastes form a connected pore network in their own right. The principal goal of this study is to investigate the pore structure and particularly pore connectivity of hardened cement based materials at the nano- and meso- scale (IUPAC definition) mainly using low temperature calorimetry (LTC) and NMR techniques.

MATERIALS AND METHODS

Materials studied in this investigation include a mono-pore-sized reference material MCM-41 with a nominal size of 3 nm, a porous silica glass (SiO_2) with pores of 11 nm, hardened concrete, and cement paste samples.

A Calvet-type scanning calorimeter (SETARAM), which was calibrated and operated to work in the approximate range 20 °C down to -130 °C, was adopted for the LTC studies. For the NMR studies, a ^{1}H Maran Ultra 23 MHz NMR spectrometer with gas-flow controlled Variable Temperature was used. Two NMR techniques were applied: i) cryoporometry, which measures the quantity of liquid present at a given temperature, and ii) relaxometry, which measures relaxation rates of [1]H (T_2), which are strongly dependent on local pore environment. NMR results were obtained on the MCM-41 and SiO_2 model materials, as well as a mature C_2S paste.

RESULTS AND DISCUSSION

(1) LTC studies

The applicability of LTC in the context of pore size determination was first validated using the mono-pore-sized reference material MCM-41. The calculated amount of melted ice as a function of the temperature from the measured heat flow during melting is shown in Fig. 1a. With the numerical relation proposed in [1], the pore diameter (assuming cylindrical pore shape) is calculated to be about 3.4 nm, which is close to the nominal value provided by the producer, i.e., 3.0 nm.
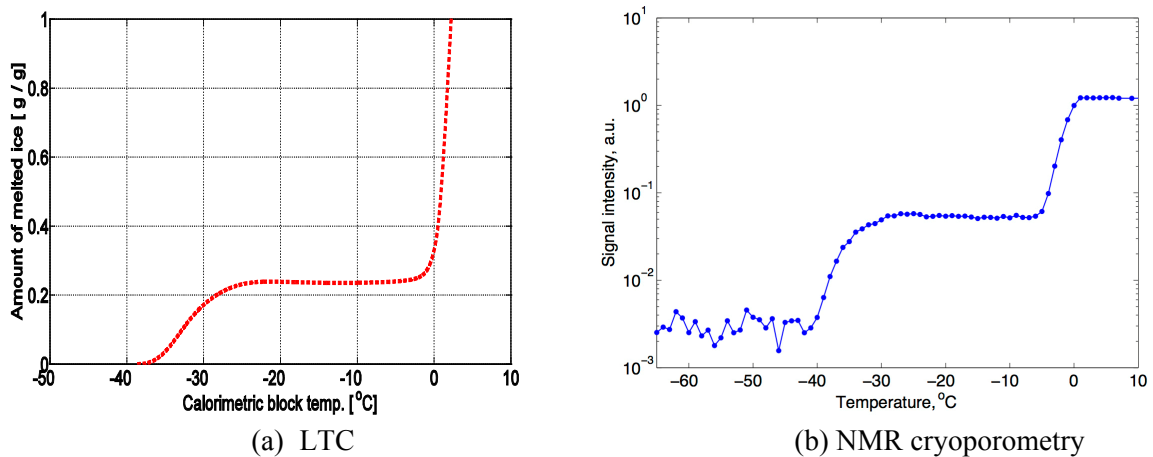

(a) LTC	(b) NMR cryoporometry

Fig. 1: (a) calculated amount of melted ice in the pores of the reference material MCM-41 by LTC; (b) melting curve of water confined in the pores of MCM-41 by NMR cryoporometry.

The impact of frost damage on the porosity determination of cement based materials using LTC was studied. Using cylinder samples of cement pastes, two cycles of freezing and melting measurements were performed on the same sample. The results show that the freezing curves are changed after one cycle of measurement while the melting curves are almost the same. An explanation of the data is that the frost damage takes place in the cement paste in such as way as to change the pore connectivity with limited effect on the interior sizes of the mesopores.

An accurate analysis of the measured LTC data is the basis to calculate the pore volume and pore size distribution for a porous material. Two fundamental aspects are crucial in this context, i.e., the baseline calculation of the measured heat flow and the value of the heat of fusion for the water confined in pores. The difficulty of calculating the baseline in an exact manner is due to the continuously changing proportion of ice and water in the sample and the dependency of the heat capacities of water, ice and the concrete skeleton matrix on the temperature. The heat of fusion of the water confined in small pores is another important parameter to be considered in the calculation of the ice content. It should be noted that there is no general agreement on how to obtain the important temperature dependence of the heat of fusion of water confined in small pores. Based on comparison studies, the importance and necessity to adopt a proper method to calculate the baseline and to use an accurate value of the heat of fusion for the pore confined water is emphasized. More details are presented in [2].

A careful examination of the thermodynamics emphasizes that the freezing/melting temperature of the water/ice confined in the non-fully saturated pores is further depressed compared with that in fully saturated pores [3]. The impact of sample saturation on the analysis of the pore volume and the pore size distribution has been demonstrated using experimental data measured on hardened concrete samples conditionally by capillary and vacuum saturation. Using the same calculation method for a concrete mix, the proportion of the calculated pores with smaller radii is higher in the capillary saturated samples than that in the vacuum saturated samples. Fig.2a shows an example of the comparison for a concrete mix. The reason is probably that for the capillary saturated samples, not all of the pores under study are fully saturated during the freezing/melting process and thus the corresponding phase transition temperatures for the water/ice confined in these pores are further depressed, as indicated by the theoretical examination. On this basis, the pore radii are wrongly calculated as we still assume the relation based on full saturation. However, since the relation for non-fully saturated pores is extremely difficult, if it is still possible, to define, it is not appropriate to determine the pore size distribution in LTC studies using non-fully saturated samples.

(a)   (b)
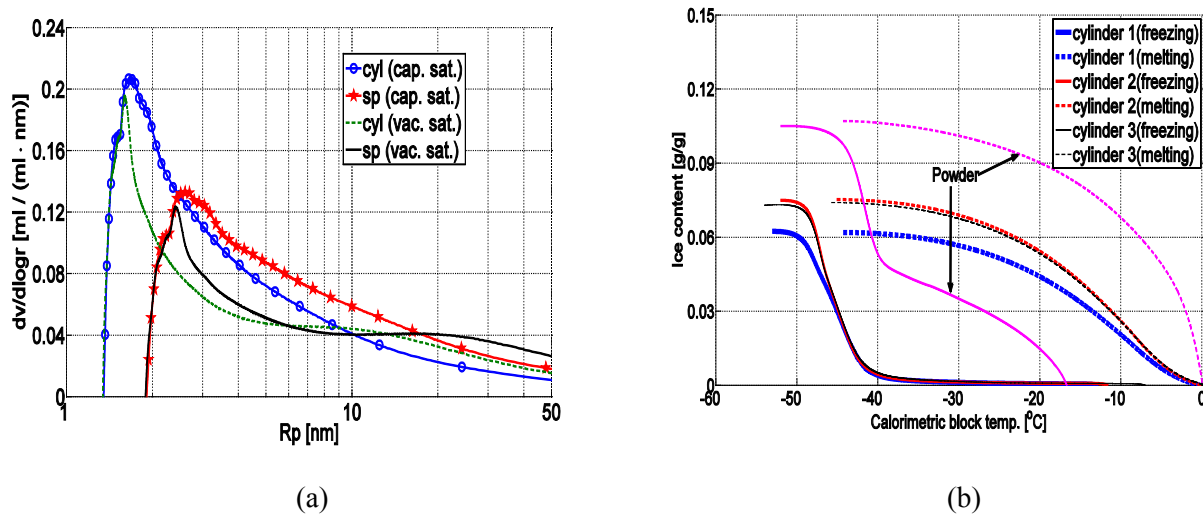
Fig. 2: (a) comparison of the calculated pore size distribution of concrete samples conditioned by capillary or vacuum saturation assuming cylindrical (cyl) or spherical (sp) pore shape; (b) calculated ice content curves for one powder and three cylinder samples of a cement paste CEM III.

The impact of sample crushing on the detected porosity of hardened cement pastes by LTC was studied by using powder and cylinder samples. Two types of cements were used to prepare the pastes. The difference between the powder and cylinder samples was compared by the calculated ice content curves, total pore volumes and pore size distribution curves. For the studied cement pastes, denoted as CEM I and CEM III, the calculated ice content curves of freezing of the powder sample differ from that of the cylinder samples, especially for the paste CEM III. It indicates that sample crushing changes the pore connectivity. One important feature between the powder sample and the cylinder samples of the paste CEM III is that the

determined maximum ice content in the powder sample is much higher than that in the cylinder samples. The relatively difference is about 40-50%, which is shown in Fig.2b. However, the marked difference is not found from the comparison of the paste CEM I. That is, the sample crushing could possibly result into more pores detected by LTC depending on the (porosity) properties of the studied paste. Concerning the marked difference between the calculated pore volume of the powder and the cylinder samples of the paste CEM III, one possible explanation could be due to the "isolated" pores (either totally isolated or "isolated" by small pore entries) which cannot be not fully filled with water in the cylinder samples during saturation. After crushing, the initially non-fully saturated "isolated" pores can be saturated. Consequently, more pores are detected in the powder sample. The argument about the "isolated" pores is supported by the results of gravimetric measurements on cylinder samples and the DVS measurements on powder samples.

(2) NMR studies

In order to benchmark the above results, we performed NMR cryoporometry on the reference material MCM-41. As shown in Fig. 1a and 1b, both LTC and NMR cryoporometry give similar results in the melting behavior at low temperature. The step at 0 °C is due to bulk water melting. We go further and couple cryoporometry with relaxometry, which involves recording the whole CPMG decay at each temperature step. After performing an Inverse Laplace Transform (ILT) of the data, the T_2 distributions against temperature are shown as a contour plot in Fig.3a.
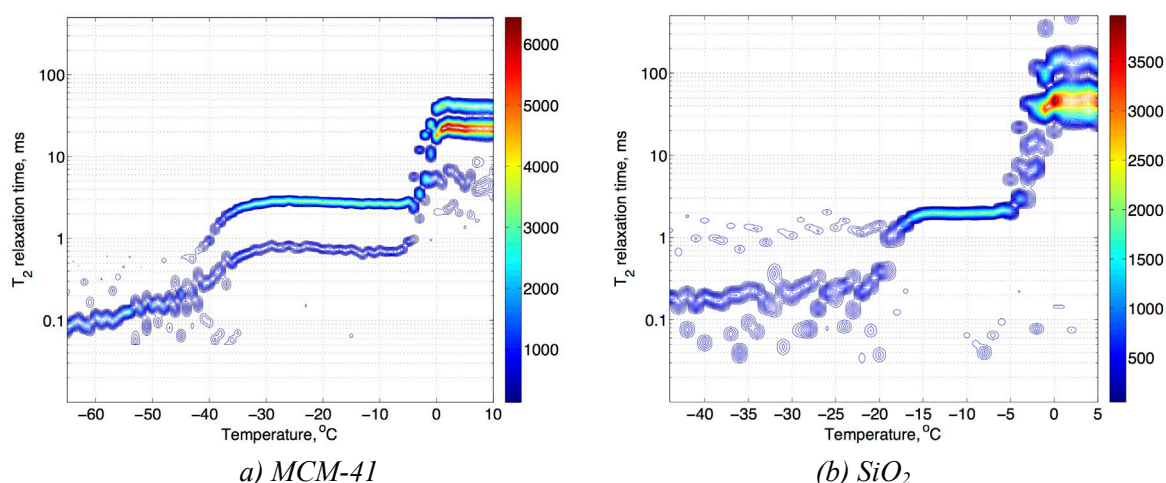

a) MCM-41   *(b) SiO$_2$*

Fig. 3: Coupled cryoporometry and relaxometry on: (a) MCM-41 (3 nm), (b) SiO$_2$ (11 nm) saturated with water on melting.

In the case of MCM-41, there are three distinct regions. Below circa -40 °C, there is a single, low intensity peak with T_2 about 100 µs that gently increases with temperature. From -40 °C to 0 °C there are two peaks. One has T_2 about 700 µs, the other about 3000 µs. The one with longer T_2 is about 10 times more intense than the other and we assign this to water melted in the pores. Above 0 °C, there are two, possibly three peaks with T_2 values of the order of tens of ms. One is clearly bulk water and another is probably water on exterior particle surfaces and between powder grains in exchange with pore water as has been suggested by Mitchell et al. for cyclohexane in [4]. This leaves the low intensity peak in the intermediate size regime to explain. There are various possibilities. First, it may be an artifact of the ILT. However, varying the regularization parameter does not cause the peaks to merge. Second, it may be water or hydroxyls on the pore surfaces. However, for this to be the case we would expect an intensity ratio nearer 2 or 3 to 1, rather than 10 to 1. In addition, it raises the question why the surface layer and bulk pore magnetization do not rapidly exchange average to a single T_2. Finally, it could be water in another, smaller pore reservoir, but no other authors report such a reservoir in MCM-41. Hence we cannot explain this peak at present. Figure 3b shows the same experiment performed on the SiO$_2$ glass. In this case, the results are very much as expected with similar explanation to MCM-41, save that there is no additional intermediate peak. Notwithstanding the difficulties in fully explaining the MCM-41 results, these experiments illustrate how the coupled cryoporometry/relaxometry technique can reveal additional information about pore structure, compared to conventional techniques.

We applied the same above techniques to a 1.5-year old C_2S paste sample. There are 3 peaks at ambient temperature as shown in Fig. 4. As demonstrated in previous studies, the shortest, medium and the longest T_2 times correspond to water in the C–S–H interlayer, gel pores, and capillary pores respectively.

Below 0 °C, or possibly just below that, we see just two peaks. One possibility is that the water in the largest interhydrate pore spaces is completely frozen with a very short T_2 and is not seen. The remaining peaks are unfrozen water in the much smaller gel pore and interlayer spaces. The gel pores are thought to be of the order of 3 nm. Hence, from the SiO_2 materials, we expect this water to freeze at about -30 °C to -40 °C. Interestingly, there is a significant step in the relative intensities of the two peaks in this temperature range. Above -40 °C, the longer T_2 component (larger pores) is dominant, below this temperature the shorter T_2 component (smaller spaces) is dominant. However, the interlayer spaces are extremely small and the distinction between frozen water, surface adsorbed water and mobile water is not well made. Hence, further work is required to fully interpret these results. In passing, however, we note that simulation work by others in the Nanocem consortium is examining the role (if any) in NMR relaxation of surface hydroxyls in model SiO_2 and C-S-H analogue (tobermorite) materials. There are clear differences, which may yet explain some of the more subtle differences in the results between C_2S and SiO_2 presented here, such as the fact that in one case the T_2 is strongly temperature dependent, in the other it is not and that in one case we see one peak per pore type, in the other two peaks.
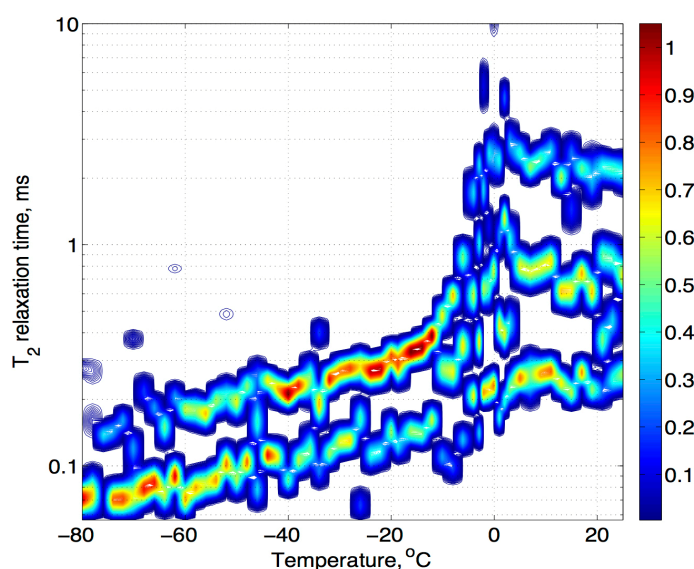

Fig. 4: Coupled NMR cryoporometry and relaxometry on C_2S paste sample on melting.

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