



Freezing and thawing porous media: experimental study with a dielectric capacitive method

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Abstract

A capacitive sensor-based apparatus has been used to study the ice/water phase change in consolidated porous media subjected to freezing and thawing. This technique relies on the dielectric properties of water, ice, air, and the mineral substrate in the radio-frequency range. It gives directly the freezing and thawing temperature depressions and indirectly provides an estimation of pore size distribution through the Gibbs–Thomson relation. It also holds good promise for evaluating the amount of liquid water in frozen porous media by combining drying and freezing tests. *To cite this article: T. Fen-Chong, A. Fabbri, C. R. Mecanique 333 (2005).*

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Résumé

Étude du gel et dégel des milieux poreux par un capteur capacitif. À l'aide d'un dispositif de sonde capacitive, on étudie le changement de phase eau/glace dans des milieux poreux consolidés soumis au gel et dégel. Cette technique exploite les propriétés diélectriques de l'eau, de la glace, de l'air, et du substrat minéral dans la gamme des fréquences radio. Elle permet d'obtenir directement les abaissements des températures de solidification et de fusion et indirectement la distribution des tailles de pores via la relation de Gibbs–Thomson. Elle devrait aussi fournir un moyen d'évaluer la teneur en eau liquide dans un milieu poreux en combinant un test en séchage et en gel. *Pour citer cet article : T. Fen-Chong, A. Fabbri, C. R. Mecanique 333 (2005).*

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1. Introduction

Water freezing temperature depression in porous media is a well-known and established phenomenon commonly attributed to intermolecular surface forces, pore water impurity, or supercooling [1–3]. This can result in a serious civil engineering or geotechnical durability problem, as reviewed in [3]. That is why the amount of liquid water in (partially) frozen porous media has been investigated by nuclear magnetic resonance [4], differential scanning calorimetry [5], acoustic approach [6], or time domain reflectometry [7], on loosely bonded porous media like silty, clayey soils, or silica glass powders. Low temperature calorimetry was also applied to cementitious materials in [8–11]. This Note presents the use of a spectroscopic-like dielectric capacitive method for studying the ice/water phase change in cohesive porous media such as stones, cement pastes, concrete, or fused glass beads. The experimental set-up, calibration, and use for studying the drying (air/water phase change) of similar materials have been described in [12].

2. Dielectric capacitive method

2.1. Basic measurement principle

The capacitive method consists in measuring the electric capacitance of a sample in the radio-frequency range. The sample is inserted between two plane and circular stainless steel electrodes as sketched out in Fig. 1. These are connected in parallel to a 30–50 MHz oscillator circuit, which forms an oscillating circuit. The experimental apparatus delivers a reduced resonant frequency that depends on the sample capacitance. A plane capacitance is proportional to its real dielectric constant. As a partially frozen porous material is composed of liquid water, ice, and the solid mineral substrate, its dielectric constant depends on the dielectric constant and volume fraction of each phase. Accordingly, any variation of the liquid water content by ice/water phase change gives rise to capacitance change, as explained below.

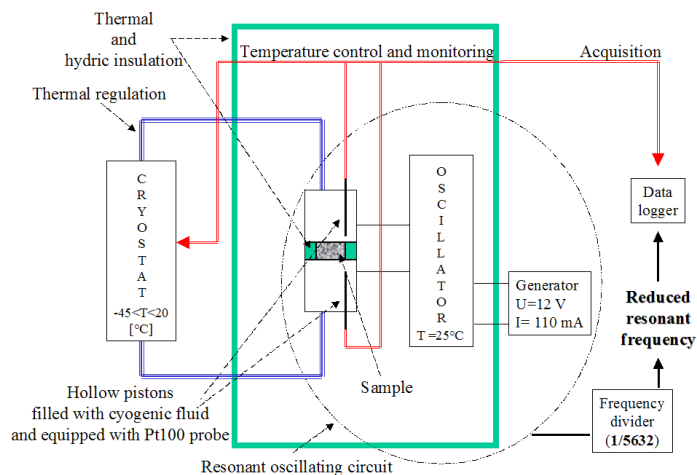


Fig. 1. Schematic diagram of the capacitive sensor-based apparatus. The oscillator was implementing a frequency divider in order to reach a low frequency range (in the order of several kHz) before outputting the resonant frequency to the data logger device. Galden PFPE HT200 from Solvay Solexis company is used as cryogenic fluid for its low static dielectric constant (about 2 at 20 °C).

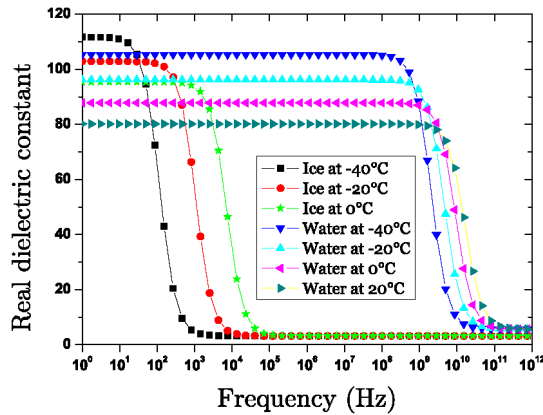


Fig. 2. Frequency dispersion of water and ice real dielectric constants at different temperatures.

2.2. Dielectric properties and ice/water phase change

The use of the capacitive method for freezing conditions relies on the different relaxation times of the electric dipole moments of water molecules in liquid water and in ice Ih. These relaxation times characterize the degree of electric polarisability of liquid water and ice, and thus their real dielectric constants. Fig. 2 shows how the water and ice real dielectric constants vary with frequency and temperature. These curves assume that ice and liquid water dielectric behaviour are well-described by the single relaxation time-based Debye model [13–16]. In particular, our numerical calculation extrapolates the experimental relaxation time data for supercooled water down to -40°C . Under these hypotheses, Fig. 2 reveals that from 1 MHz to 1 GHz the real dielectric constant of ice is equal to its optical value (electronic polarisation) of 3.2 whereas that of liquid water is still equal to its static value (orientation polarisation) between 80 and 105 depending on temperature. In addition to this high ice/water permittivity contrast, experimental tests on dry mineral samples indicate that their real dielectric constants are independent of temperature (between -40°C and 20°C) and close to the optical permittivity of ice: 3.8 for silica constituting home-made fused glass beads, which is in good agreement with data handbook of [17]. The same temperature-independence has been obtained without any sample (air between the electrodes).

3. Experimental tests

Cylindrical cement samples were cored and sawed from their benches. Cylindrical fused silica beads samples come from home-made female moulds that are placed into an oven at 630°C . All were then cleaned up from scraps, dried at 50°C in an oven until their mass becomes constant. Water saturation was always performed with degassed house distilled water at 3 kPa air pressure. For each test, the sample was wrapped in plastic adhesive and weighed just before and after each capacitive test to evaluate the water mass content and to check that no significant water evaporation happened. Freezing and thawing tests were realized between 20 and -40°C by constant steps of between (generally) 1 and 5°C for 20 min.

3.1. Freezing and thawing point depression of cement pastes

Fig. 3 shows the variation of the reduced resonant frequency with temperature during the cooling and heating stages of a CPA-CEM I cement paste. The frequency varies almost linearly with temperature, except in the range of two particular temperatures, around $\simeq -6^{\circ}\text{C}$ and $\simeq -43^{\circ}\text{C}$, where the slope changes significantly. The linear frequency variation is related to the continuous variation of the real dielectric constant of water with temperature,

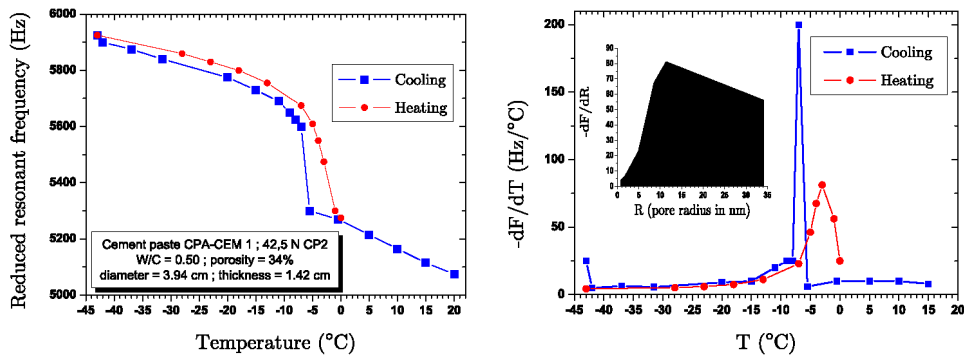


Fig. 3. Freezing and thawing of a water-saturated cement paste.

Table 1

Review of some cement paste freezing temperature as obtained by low-temperature calorimetry. The left-hand side column of this work is related to Fig. 3

Reference	This work	Bager and Sellevold [8]		Béjaoui et al. [10]	Kaufmann [9]
Cement	Ordinary Portland Cement (CPA CEM I)				
W/C Ratio	0.5	0.4		0.5	0.5
Cure	HR 100% until drying or testing				
Drying before testing	70 °C (1 week)	none	HR 11%	none	none
T_{f1} [°C]	-6	none	-9	none	-10
T_{f2} [°C]	none	-25	none	-25	none
T_{f3} [°C]	-43	$T(t) \geq -37$	-43	-43	-40

as shown in Fig. 2. The frequency slope change is due to the progressive water/ice phase change: a first freezing beginning at $\approx -6^\circ\text{C}$ and ending at $\approx -15^\circ\text{C}$, a second freezing at $\approx -43^\circ\text{C}$ on cooling, and ice melting beginning at $\approx -13^\circ\text{C}$ and ending at 0°C on heating.

3.2. Discussion

Table 1 indicates that our freezing temperatures are in good agreement with some other works. The physical origin of these freezing temperatures can be explained as follows.

The transition temperature T^* at which an ice crystal of mean curvature κ^* is in stable equilibrium with neighbouring liquid water, both mechanically (Young–Laplace’s law) and thermodynamically (equality of chemical potentials) is approximated by the Gibbs–Thomson equation [2]:

$$T^* = T_f - \frac{\gamma\kappa^*}{S_f} \tag{1}$$

where $\gamma \approx 0.0409 \text{ J/m}^2$ is the water/ice interface energy and $S_f \approx 1.2 \text{ MJ}/(\text{m}^3 \times \text{K})$ is the entropy of fusion per unit of crystal volume [16]. Since $\kappa^* = \frac{1}{r_1^*} + \frac{1}{r_2^*}$ where $r_{i=1,2}^*$ are the principal curvature radii of the ice/water interface, we classically have

$$\kappa^* = \frac{2}{r^*} \text{ for spherical ice crystal; } \quad \kappa^* = \frac{1}{r^*} \text{ for cylindrical ice crystal} \tag{2}$$

where r^* is the radius of the spherical or cylindrical crystal. It remains now to specify the physical meaning of radius r^* in the context of partially frozen porous media. In-pore ice formation can result from: (i) heterogeneous

nucleation where dispersed nucleating agents in water act as catalyst sites [18,10]; (ii) homogeneous nucleation (although less probable than the previous one); (iii) ice percolation through nanoscopic channel-like pores leading to the sample free surface where heterogeneous nucleation is easier or to already frozen pores [2,10,11]. In the first two mechanisms r^* corresponds to the critical ice spherical embryo radius while in the latter r^* is related to the channel-like pores radii.

If we assume that the initial freezing temperature of $T^* \simeq -6^\circ\text{C}$ is due to ice nucleation, then freezing should be initiated from ice spherical germs of radii $r^* \simeq 11.4$ nm, according to (1) and (2). This is possible in CPA-CEM I cement pastes since these are full of micrometric pores in which water is thus supercooled down to $\simeq -6^\circ\text{C}$. Once these large pores are frozen, ice can then propagate through cylindrical channels of radii $r^* \simeq 5.7$ nm to other water-filled pores. This picture is most probable for heterogeneous nucleation (as compared with homogeneous nucleation). According to [10], the second freezing at $T^* \simeq -43^\circ\text{C}$ is due to ice nucleation from spherical embryos of $r^* \simeq 1.6$ nm since the other mechanism would give ice propagation through too much thin cylindrical channels of radii $r^* \simeq 0.8$ nm. Consider now the thawing temperature. Melting begins at $T^* \simeq -13^\circ\text{C}$ and is the greatest at $T^* \simeq -3^\circ\text{C}$: assuming that all channel-like pores are frozen, this means that the ice crystal is also cylindrical so that the corresponding radii of melting are respectively $r^* \simeq 2.6$ nm and $r^* \simeq 11.4$ nm. As the transition temperature given by (1) is the temperature above which ice crystal cannot exist with neighbouring water, these melting radii can provide an estimation of the cement paste pore size distribution. To do so, we calculate the cylindrical pore radius $R = r^*$ by inverting (1) with the thawing temperature as input data [1]: this is illustrated in the inset graph of the right-hand side of Fig. 3.

3.3. Amount of liquid water

Since the ice/water phase transformation cannot be directly quantified by weighing, one has to develop an indirect way for evaluating the relation between the spectroscopic dielectric answer of a sample and the liquid water mass contained in the pores. To do so, the following procedure is adopted. First, capacitive tests are done on progressively dried samples, as described in [12]. This gives a relation between the resonant frequency and the liquid water amount. Then freezing tests are conducted on the same initially saturated sample, thus giving a relation between the resonant frequency and the temperature. Both drying and freezing tests then provide the dependence of the liquid water amount on the temperature by eliminating the resonant frequency parameter. Such data analysis surmises that both the slight difference between the dielectric constants of air (1) and ice (3.2), and the temperature dependence of the water dielectric constant, are of no importance.

This elementary procedure is certainly not suited for complex materials like cement pastes for which the in-pore water contains ions and chemically interacts with the mineral substrate. On the other hand, this may be adequate for simple porous media such as fused glass beads. Fig. 4 shows the variation of the liquid water saturation degree

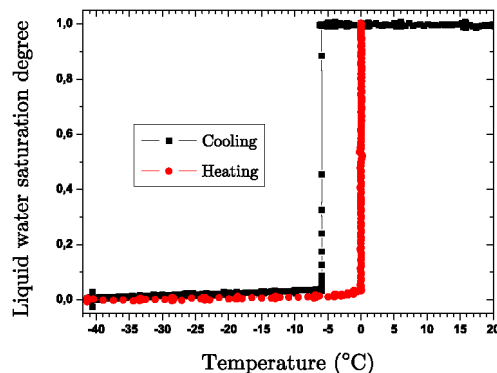


Fig. 4. Freezing and thawing of fused glass beads.

(ratio of liquid water volume over the sample porosity) with temperature for fused glass beads. On cooling the curve slope changes abruptly at -6°C while on heating this happens at 0°C . This indicates that the water-to-ice phase change corresponds to the end of supercooling in deca-micrometric pores. Below these transition temperatures, the liquid water amount changes slightly with temperature, which may be due to residual phase change.

4. Conclusion

The capacitive method is well-suited for determining the freezing and thawing temperature depressions which are of primary concern for cementitious materials use in civil engineering, and for estimating pore size distribution. It also holds good promise for evaluating the amount of liquid water in frozen porous media by combining drying and freezing tests. Further work is now undertaken to improve this determination.

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