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Dielectric capacity, liquid water content, and pore structure of thawing–freezing materials

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Abstract

A capacitive sensor-based experimental approach is worked out to study the ice/water phase change in cohesive porous media subject to freezing and thawing. This technique relies upon the dielectric properties of liquid water, ice, air, and mineral substrate in the radio-frequency range. A semi-empirical method based upon the Lichtenecker model and combining drying and freezing tests provides an accurate estimation of the liquid water content versus the temperature in freezing cement pastes. This estimation is further analysed with the help of thermoporometry concepts in order to characterize the pore size distribution and the specific surface area. The results range in the same order of magnitude as those assessed from gravimetric sorption/desorption isotherms.

Keywords: Porous media; Freezing; Thawing; Dielectric; Capacitive method; Supercooling; Liquid water amount; Pore size distribution; Specific surface; Sorption/desorption isotherm; Cement

1. Introduction

Damage induced by frost action upon concrete structures is a source of main concern in cold climates (Pigeon, 1984; Dash et al., 1995). Contrary to an obvious possible explanation, damage in concrete cannot originate from only the expansion undergone by liquid water when transforming to ice: sample expansion is still observed in cement pastes saturated with benzene, whose density increases with solidification (Beaudoin and MacInnis, 1974). Actually, confined liquid water within a porous material submitted to frost action does not simultaneously freeze at the same temperature. This is commonly attributed to the interaction between water and pore surfaces, water impurity, or supercooling (Scherer, 1993; Dash et al., 1995). As a consequence, an initially water-saturated porous material remains filled by both ice and liquid water down to at least -80 °C (Jehng et al., 1996). Nowadays, the mechanical response of a porous

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material is credited to result from the combination of the liquid–solid expansion, the transport of unfrozen liquid water through the porous network, and the presence of air voids (Wang et al., 1996). A poromechanics-based approach has been recently worked out to understand and quantify the phenomena both at the pore scale (Coussy and Fen-Chong, 2005) and at the material scale (Coussy, 2005). Whatever the approach carried out, the freezing/thawing curve, that is the saturation degree of unfrozen water versus temperature, turns out to be the key curve governing the mechanical behaviour of porous materials upon frost action. That is why the liquid water content as a function of the temperature has been investigated in partially frozen porous media by nuclear magnetic resonance (Watanabe and Mizoguchi, 2002), differential scanning calorimetry (Kozlowski, 2003a,b), acoustic approach (Thimus et al., 1991), or time domain reflectometry (Spaans and Baker, 1995), on loosely bonded porous media like silty, clayey soils, or silica glass powders.

Freezing of cement based materials is usually studied with low temperature calorimetry (Bager and Sellevold, 1986). However, temperature calorimetry applies only to millimetric specimens which in addition are often crushed. Tests on non-crushed heterogeneous materials, like mortar and concrete exhibiting centimetric aggregates, remain difficult to perform using this technique. For such materials requiring larger samples, the dielectric method (Tran and Dupas, 1988) is more appropriate, while being less expensive. This article explores a spectroscopic-like dielectric capacitive method and analyses the results it provides on the ice/liquid water transform in cohesive porous materials such as cement pastes.

2. Dielectric capacitive method

2.1. Principle and experimental apparatus

The dielectric relaxation time τ of liquid water is much smaller than the one related to ice crystal (respectively 10^{-10} s and 10^{-5} s). As a consequence, for an electrical field lying in the radio-frequency range 10–100 MHz, the dielectric constant of liquid water is still equal to its static value, that is between 80 and 100, whereas the permittivity of ice is equal to its optical value which is close to 3. Fig. 1 shows the real dielectric constants ε of liquid water and ice against the frequency f of the exciting electrical field for various values of the temperature θ (in °C). These curves assume that the dielectric behaviour of ice and liquid water are well-described by the single relaxation time-based Debye model (Cole and Cole, 1941; Ellison et al., 1996; Kaatze, 1997):

$$\varepsilon(f,\theta)=\Re e\left(\varepsilon_{\rightarrow\infty}+\frac{\varepsilon_{\rightarrow\infty}(\theta)-\varepsilon_{\rightarrow\infty}}{1+j2\pi f\tau}\right) \tag{1}$$

where $\varepsilon_{\rightarrow\infty}$ is the limit permittivity for f going to infinity, while $\varepsilon_{\rightarrow 0}$ the static permittivity and $j^2=-1$. In addition to the high ice/liquid water dielectric constant contrast, experimental tests on air and dry mineral samples also indicate that the real dielectric constants of the latter are close to the optical dielectric constant of ice; 1 for air, and between 3 and 10 for mineral materials. Hence, any change in the liquid water content, due to solidification/melting or condensation/evaporation, within a porous medium will significantly affect the overall material dielectric constant. Accordingly, the measurement of the latter leads to an indirect assessment of the current liquid water content.

The capacitive method consists in measuring the dielectric constant through the electric capacitance C of a sample submitted to an electrical field in the above mentioned radio-frequency range. Actually

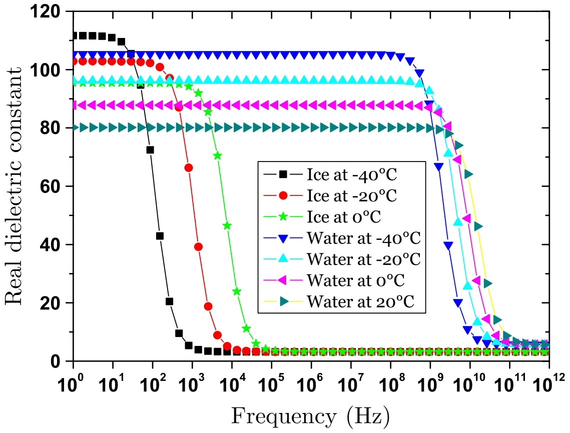

Fig. 1. Frequency dispersion of water and ice real dielectric constants at different temperatures.