Describing the influence of temperature on water retention using van Genuchten equation

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ABSTRACT

A simple, analytical model was proposed to account for the effect of moderate temperature on water retention in cement-based materials. The model takes advantage of the simplicity and flexibility of van Genuchten equation. It was first calibrated using experimental results taken from literature and then successfully validated on other results. The presented model provides a valuable tool for the description of water transport in unsaturated cementitious materials submitted to moderate temperatures (up to 85 °C).

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1. Introduction

In unsaturated conditions, the durability of reinforced concrete structures is greatly influenced by moisture content: firstly because the presence of water in the pores significantly impacts transport and also secondly because the lack of water can inhibit chemical reactions. Concrete delayed deformations such as creep and drying shrinkage, that can induce cracking, are also driven by moisture exchange with the environment. The description of unsaturated water transport is then the first step in the durability assessment of concrete structures in contact with the atmosphere.

In the framework of radioactive waste management, the concrete structures would undergo concomitant heating and drying. In the French design, the maximal temperature is not expected to exceed 80 °C. Temperature is known to impact water transport in two distinct ways; firstly water transport is thermo-activated [1–9]: the higher the temperature, the faster the transport. Secondly, temperature also impacts water retention: the amount of water retained at equilibrium decreases when temperature is increased [5,9–14]. This reduction is generally attributed to the variation of water properties (density and surface tension) [15] as well as the coarsening of the pore structure generated by ettringite dissolution and C-S-H alteration [16]. It was alternatively suggested that the so-called 'thermal desorption' might be the main phenomenon at work [13,17]. Because adsorption is an exothermic process, increasing temperature tends to shift balance towards

the endothermic reaction (that is to say desorption). As a consequence adsorbed water is released. This effect can be described using Clausius–Clapeyron equation [18]:

$$q_{st}(w) = -R \frac{\partial \ln(p_v)}{\partial \left(\frac{1}{T}\right)}\bigg|_w \tag{1}$$

where:

- R is the universal gas constant (8.3145 J/mol/K),
- p_v vapor pressure (Pa) at equilibrium with the water content w at the absolute temperature T (K),
- w water content (by mass) at equilibrium with the vapor pressure p_v at the temperature T,
- q_{st} isosteric energy (J/mol).

The isosteric energy q_{st} can be evaluated using two isotherms obtained at two different temperatures [17]. Integrating Eq. (1), one can easily assess the isotherm at any arbitrary temperature T using Eq. (1):

$$h(w,T) = h(w,T_0) \frac{p_{vs}(T_0)}{p_{vs}(T)} \exp\left[q_{st}(w) \frac{T-T_0}{RTT_0}\right] \tag{2}$$

where:

- $h(w,T)$ is the relative humidity at equilibrium with the water content w for the temperature T,
- T_0 temperature at which the isotherm is known (ambient temperature),
- $p_{vs}(T)$ saturated vapor pressure (Pa) for the temperature T.

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This approach implicitly does not account for the alteration of concrete microstructure induced by temperature. However, it successfully reproduced results obtained using concretes [17]. This method is quite simple but some computations are required and the results may not be immediately useable: some supplementary fitting operations may be necessary before proceeding to transport simulations [9,19]. A straightforward equation describing explicitly the influence of temperature on the desorption isotherm would be far easier to use. To this end, Bažant and Thonguthai [20,21] used the ASME steam tables to propose the following Eq. (2) to evaluate the isotherm at high temperature:

$$w(h, \theta) = (w_{sat}h)^{\frac{1}{\beta(\theta)}} \text{ with } \beta(\theta) = 1.04 - \frac{(\theta + 10)^2}{781.9 + (\theta + 10)^2} \quad (3)$$

with:

• w_{sat} water content at saturation ($h = 1$),
• θ temperature in °C.

This equation has been extensively used to simulate the behavior of concrete exposed to fire [22–24]. When this equation is compared to recent experimental data in the temperature range 20–80 °C (Fig. 1), high discrepancy between modeled and experimental values is evident. The main reason for this, is that the model was intended to be used on a large temperature range (from ambient temperature up to the triple point). Furthermore, it was constructed in the late seventies without experimental results to be compared with.

Many other equations and models were alternatively proposed for different biological materials [25–30] and for activated carbons [31–34]. Unfortunately all these equations are not suitable for cement-based materials either because they describe type II or III isotherms (for non-porous solids whereas most cement-based materials exhibit type IV isotherm) or because the equations are much too complicated (or involve too many parameters) to be easy to use. It was then the purpose of this study to propose a straightforward analytical formula that can be used to evaluate explicitly the desorption isotherm for any moderate temperature.

2. Literature survey

Among the very few published results pertaining to the effect of temperature on water retention in cement-based materials [5,9–16], only the most reliable and relevant ones were retained for this study. All the results related to adsorption [5,11,14] were discarded as well as the work of Wu et al. [15] that unexpectedly showed no significant influence of temperature. The extensive study of Hundt and Kantelberg [10] could not be retained because the 20 °C-results were suspected of being out of equilibrium. Moreover, using saturated salt solutions to maintain RH, Hundt and Kantelberg did not account for the change in RH induced by the temperature increase [35–40]. Eventually, only the results of Ishida et al. [12], Poyet [13], Brue et al. [16] and Drouet et al. [9] were considered in this study (Table 1).

Ishida et al. [12] measured the desorption isotherm of a OPC paste (w/c = 0.50). Limestone powder (15% or 40% by volume) was added to prevent bleeding of the fresh mix. Because the amount of limestone did not appear to influence the resulting isotherm, no distinction was made between the two mixes. After water cure, the specimens were put in a climatic chamber in which the RH was sequentially decreased. Three temperatures were tested: 20, 40 and 60 °C.

Using the desiccator method [41], Poyet [13] measured the first desorption isotherm of a mature high-performance concrete (CEM I, w/c = 0.43) at 30 °C and 80 °C. The use of different desiccators simultaneously allowed to acquire the desorption isotherm over the whole RH range in a reasonable time (a few years). Alternatively Brue et al. [16] used a climatic chamber to subject specimens to decreasing RH-steps at constant temperature and evaluate the desorption isotherm. Two high-performance concretes were used: the first (CEM I, w/c = 0.43) was of the same formulation as that of Poyet [13] and the second one was prepared with CEM V/A (56% OPC + 22% slag + 22% fly ash) and w/c = 0.39. Three temperatures were tested: 20, 50 and 80 °C.

More recently, Drouet et al. [9] characterized the first desorption isotherm of four hardened cement pastes (w/c = 0.40) made with four different binders: (1) CEM I (OPC), (2) CEM II/A (75% OPC + 25% limestone filler), (3) CEM V/A (56% OPC + 22% slag + 22% fly ash) and (4) a low-alkalinity cement (LAC) (37.5% OPC + 30% fly ash + 32.5% silica fume). Three temperatures were tested: 20, 50 and 80 °C.

3. Model calibration

It was decided to use the equation proposed by van Genuchten [42] because it has been broadly used to simulate the unsaturated flow in porous media [43–50]. It is a simple equation with only two parameters that has proven great flexibility in fitting experimental results. van Genuchten's equation writes:

$$S(P) = \left[1 + \left(\frac{P}{P_0}\right)^{\frac{1}{1-m}}\right]^{-m} \quad (4)$$

where:

• S is the saturation index
• m and P_0 two empirical parameters.

P_0 is a (positive) pressure (Pa) similar to the bubbling pressure of the Brooks and Corey model [51]. m is a positive and a dimensional parameter related to the pore-size distribution. For cement-based materials m

(a) Model proposed by Bažant and Thonguthai   (b) Experimental results of Drouet et al. [9]
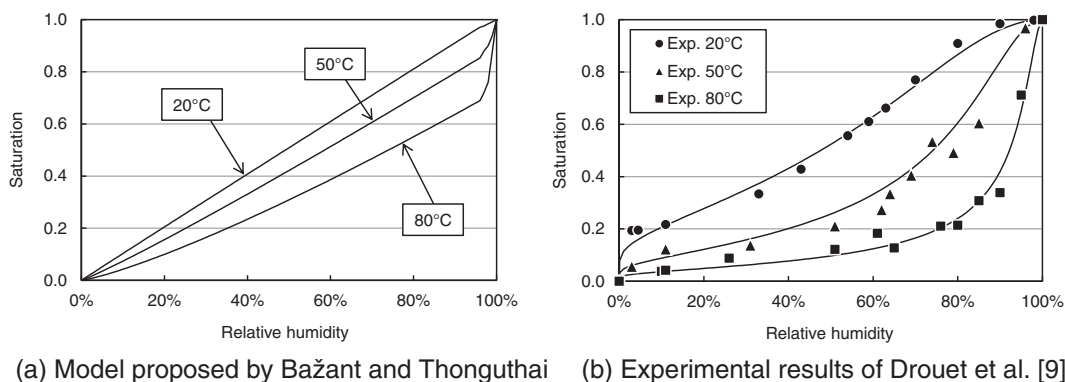
Fig. 1. Desorption isotherm between 20 and 80 °C (a) estimated using the approach proposed by Bažant and Thonguthai [20,21] and (b) experimental results (CEM I paste, w/c = 0.40) [9].