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A novel method to predict internal relative humidity in cementitious materials by ^{1}H NMR

Zhangli Hu[a,b,*], Mateusz Wyrzykowski[b], Karen Scrivener[a], Pietro Lura[b,c]

[a] Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland
[b] Concrete/Construction Chemistry Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf CH-8600, Switzerland
[c] Institute for Building Materials, ETH Zurich, Zurich CH-8092, Switzerland

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ABSTRACT

In sealed cementitious materials, the internal relative humidity (RH) decrease is mainly due to the water activity depression caused by menisci formation in partially-saturated pores. This process can be conveniently described with the evolution of the Kelvin radius. To obtain the Kelvin radius, a novel method based on the evolution of pore volumes quantified by ^{1}H nuclear magnetic resonance (NMR) and mercury intrusion porosimetry (MIP) was developed. This approach was validated against experimental results for cementitious materials with a range of water to cement ratios from 0.30 to 0.46. A comparison between the Kelvin radius calculated with this approach with a previously published method using data obtained from MIP and chemical shrinkage was presented. A sensitivity analysis for the new prediction method was performed using a bootstrapping technique.

1. Introduction

1.1. Objectives

Autogenous shrinkage is one of the major causes of early-age cracking in high performance concrete (HPC) [1]. In hydrating cementitious materials, chemical shrinkage takes place due to the fact that the volume occupied by the products of the hydration reaction is smaller than that of the reactants. Before setting, when concrete is still plastic, chemical shrinkage causes a bulk volume reduction without the buildup of stress [2]. After setting, the solids form a solid skeleton and chemical shrinkage leads to desaturation of pores within the microstructure. Due to formation of capillary menisci at the pore fluid-vapor interfaces, capillary tension in the pore fluid and compression in the solid skeleton develop. At the same time, the development of the menisci leads to a decrease of the internal relative humidity (RH), so-called self-desiccation [3,4]. The compression of the skeleton caused by the action of the capillary pressure induces autogenous shrinkage. Since autogenous shrinkage in concrete members is invariably restrained, the resulting buildup of tensile stresses may lead to the formation of micro- and macro-cracks.

Changes of pressure exerted on the skeleton by the pore fluid can be linked with the internal RH decrease in the pores as expressed by the Kelvin-Laplace equation [5]. Thus, knowing the internal RH evolution is key in understanding the development of autogenous shrinkage and finding more reliable ways to estimate the risk of cracking and ultimately prevent cracking. Relatively simple and accurate methods for measuring internal RH evolution due to self-desiccation in cement-based materials, e.g., employing capacitive water activity sensors [4], have been employed since several years. As long as the RH can be directly measured, the microstructural mechanisms behind its evolution [3,4] still lack sufficient experimental validation. This is an objective of the present paper, where it is shown that the RH evolution can be indeed predicted based solely on microstructural data. Further, predicting the RH evolution based solely on the microstructural data and on the evolution of the hydration degree can constitute a basis for extending the application of microstructural models of hydration to the macroscopic level, where deformations are considered.

This paper aims to evaluate and predict the evolution of the internal RH in cementitious materials with different water-to-cement ratios (w/c) based on the knowledge of the pore size distribution and its evolution due to hydration. Hua et al. [6] showed that the Kelvin radius, the key

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* Corresponding author.
E-mail address: zhangli.hu@epfl.ch (Z. Hu).

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parameter to calculate the internal RH with the Kelvin equation (see Section 1.2), can be estimated based on the pore size distribution as determined with mercury intrusion porosimetry (MIP). This approach was extended to account for the adsorbed water and validated with RH measurements by Chen et al. [7]. A limitation of this approach is that the amount of empty porosity is obtained from chemical shrinkage experiments, which are out of necessity performed on water-saturated samples, while the internal RH evolution is measured on sealed, self-desiccating samples.

To overcome this limitation, in the present work the volume of pores filled with pore solution is obtained by ^{1}H nuclear magnetic resonance (NMR) measurements on sealed samples, and then combined with MIP for estimating the Kelvin radius. The predictions are compared to measurements of RH evolution in autogenous conditions (self-desiccation). In addition, a sensitivity analysis regarding the effect on the internal RH predictions of different parameters, including contact angle of mercury (assumed for the calculation of pore sizes) and cut-off radii (assumed as a size boundary between the capillary and gel pores), was presented. Further, a study on the propagation of uncertainty from experimentally-determined data used as input for modelling (MIP, NMR and RH depression due to ions present in the pore solution) on the model predictions of the overall RH evolution was carried out.

1.2. Background

In moisture-sealed, isothermal conditions, the reduction of internal RH in cementitious systems depends on two major mechanisms: desaturation of pores due to chemical shrinkage and water activity of the pore solution [3,8]:

$$\mathrm{RH} = RH_S \cdot RH_K \tag{1}$$

RH_S (range from 0 to 1) is the RH depression due to water activity in the pore solution. It can be measured directly by water-activity probes on extracted or synthetic pore solution, or approximated using Raoult's Law based on composition of pore solution [3]:

$$RH_S = \frac{n_{H_2O}}{n_{solution}} \tag{2}$$

where $n_{H_2}O$ [mmol/l] and $n_{solution}$ [mmol/l] are the number of moles of water and the total number of moles in the solution (including solute), respectively. Note that this equation is based on an ideal solution (the equilibrium RH relies on the molar fraction of water in the pore solution) [7,8].

RH_K is RH depression due to presence of menisci at the interface of air and pore solution and can be described with the Kelvin-Cohan equation:

$$RH_K = \exp\left(-\frac{2\gamma_w \cos(\theta_w) M_w}{(r_p - t)RT\rho_w}\right) \tag{3}$$

where r_p is the pore radius, $R = 8.314$ [J/mol·K] is the universal gas constant, T [K] is the temperature (293.15 K in this paper), and the other parameters are assumed as for pure water: molar mass $M_w = 0.01802$ [kg/mol], density $\rho_w = 1000$ [kg/m^3], contact angle θ_w assumed to be 0° (perfect wetting), surface tension $\gamma_w = 0.073$ [N/m]. The Kelvin-Cohan equation takes into account the presence of an adsorbed water layer of thickness t [m] on the surface of the pores, which for the case of perfect wetting ($\cos(\theta_w) = 1$) yields the Kelvin radius equal to $(r_p - t)$ [m] [7,9].

For cement pastes, the thickness of the adsorbed layer can be estimated based on an empirical formula proposed by Badmann et al. [10]:

$$t = K_1 - (K_2 \cdot \ln(-\ln(\mathrm{RH}))) \tag{4}$$

With the values of the fit parameters determined in [10] as $K_1 = 0.385$ and $K_2 = 0.189$ that provide the thickness t in [nm]. As shown previously [7], the Kelvin radius turns out to be the key parameter in this calculation. The methods for determining it are described in the following section.

2. Methods for predicting the Kelvin radius

Two different approaches are followed in this paper to obtain the Kelvin radius. The previously-reported method using MIP combined with chemical shrinkage [7] is based on estimating the radius of pores corresponding to the volume of capillary pores *already emptied* of pore solution during hydration at a given hydration stage, following the approach originally proposed by Hua et al. [6]. The second approach is the new method proposed here. NMR combined with MIP is used to estimate the radius of pores corresponding to the volume of capillary pores *still filled* with pore solution at a given hydration stage. A fundamental difference is that, in the former method, the emptied pores were measured in water-saturated conditions (chemical shrinkage measurement), while in the method proposed here the amount of water-filled pores is measured during self-desiccation.

2.1. Method based on chemical shrinkage and MIP

This method (further referred as chemical shrinkage-MIP method) combines chemical shrinkage and MIP by tracing the smallest emptied pore size corresponding to the chemical shrinkage at a given age [6]. Obtaining the emptied pore radius in this way is based on the following assumptions:

1) The volume of pores emptied of water corresponding to the smallest emptied pore size is equal to the volume of mercury intruded in the MIP test through pores larger than that size;
2) The volume of pores emptied by chemical shrinkage and resaturated in the chemical shrinkage test (saturated sample) is the same as the volume of pores emptied by chemical shrinkage in the sealed samples;
3) The pores are emptied of water from largest to smallest sizes during hydration [11];
4) The pores are filled by mercury from largest to smallest during the MIP test, yielding a pore size distribution.

Assumption 1) is a direct basis of the method as proposed in [6]. It has been also shown to yield good predictions of RH evolution in [7]. However, a limitation of this method stems from the incorrect assumption 2).

In fact, the degree of hydration of saturated samples is higher than that of sealed samples at the same age, especially for low w/c [12,13]. Note that the difference between sealed samples and samples in contact with water varies also with the thickness of the latter [7,13–16]. This problem can be corrected by using the degree of hydration instead of the hydration time when combining chemical shrinkage and MIP (Fig. 1(a) and (b)). As long as the evolution of chemical shrinkage in *time* is dependent upon curing regime, it can be assumed that there is always a linear relationship between chemical shrinkage and *hydration degree* independently on the curing conditions, as also evidenced in [12]. A similar method was already mentioned and quantified with one single system in reference [7].

Assumption 3) stems directly from the Kelvin-Laplace equation.

Assumption 4) in fact is equivalent to neglect the so-called ink-bottle effect, i.e. the size distribution of pores would not be affected by the artifact of the MIP method, where large pores are accessed through