

ORIGINAL ARTICLE

Deconstructing water sorption isotherms in cement pastes by lattice density functional theory simulations

Yao Zhang^{1,2}  | Han Liu²  | Cheng Zhao^{2,3} | J. Woody Ju² | Mathieu Bauchy² ¹Structural Health Monitoring and Control Key Laboratory of Hebei Province, Shijiazhuang Tiedao University, Shijiazhuang, China²Department of Civil and Environmental Engineering, University of California, Los Angeles, CA, USA³State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, Wuhan, China

Correspondence

Mathieu Bauchy, Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095, USA. Email: bauchy@g.ucla.edu

Funding information

National Natural Science Foundation of China, Grant/Award Number: 51578410 and 1922167; Fundamental Research Funds for the Central Universities, Grant/Award Number: 300102218511; China Scholarship Council

Abstract

The moisture content in cement pastes influences their mechanical properties and durability. However, the complex, multiscale nature of cement pastes makes it challenging to isolate the contributions of each scale to their macroscopic water sorption isotherms. In particular, the contribution of the calcium–silicate–hydrate gel (the binding phase of cement pastes) remains only partially understood. Here, we introduce a density functional theory lattice model describing water sorption in calcium–silicate–hydrate, which properly reproduces experimental water sorption isotherms in cement pastes. Based on this model, we deconstruct the contribution of each pore scale (interlayer spacing, gel pores, and capillary pores) to the total sorption isotherm. We show that, when the relative humidity is below 80%, the calcium–silicate–hydrate gel accounts for more than 90% of the moisture content adsorbed in cement pastes. In turn, we find that the contribution of the interlayer space within the calcium–silicate–hydrate grains is governed by the competition between the rate of interlayer space opening and the increasing propensity for water to fill larger pores upon increasing relative humidity. Overall, our results highlight the key role played by the calcium–silicate–hydrate in governing the sorption isotherms of cement pastes.

KEYWORDS

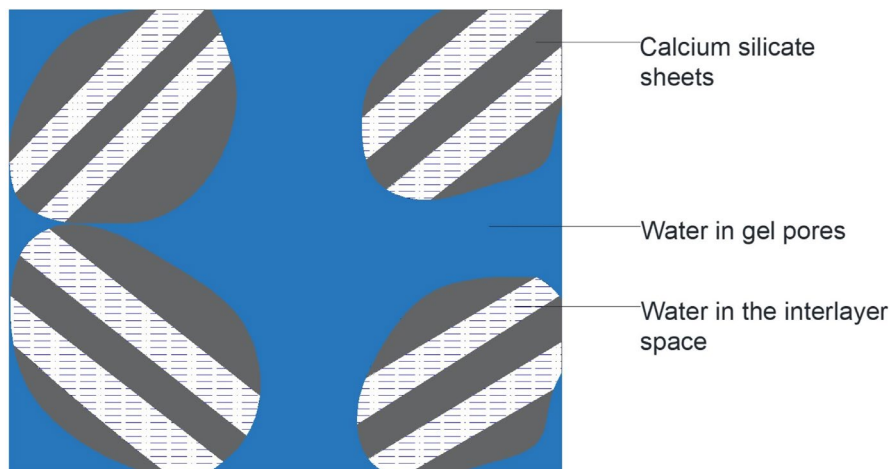
calcium–silicate–hydrate gel, cement paste, density functional theory, water sorption

1 | INTRODUCTION

Water vapor adsorption isotherms are generally used to describe the variation of equilibrium moisture content in cement pastes as a function of relative humidity (RH) under isothermal conditions.¹ Importantly, the adsorbed moisture content in cementitious materials influences their stiffness, shrinkage, and creep.^{2–10} This mainly arises from the fact that the retained moisture alters the surface energy and hydrostatic pressure in pores. Moreover, the moisture content also controls the electrical resistivity and oxygen diffusivity, which, in turn, can both influence the long-term durability of cementitious materials exposed to the complex environment (acid and damp).^{11,12} As a result, the origin, mechanism, and manifestations of water sorption in cementitious materials has attracted some significant attention.^{13–15}

The cement paste presents a complex, heterogeneous, and multiscale structure, wherein calcium–silicate–hydrate (C–S–H) acts as the binding phase.¹⁶ C–S–H can be described as a colloidal gel made of nanometric grains (see Figure 1).^{17–19} The C–S–H grains present a layered structure, wherein water can be present in the interlayer spacing, depending on RH.¹⁷ The presence of water in the interlayer space plays a critical role in governing the microstructure of cement pastes.^{17,18,20–22} Notably, the multiscale nature of cement pastes makes it extremely challenging to decipher the role played by each scale/phase in governing the macroscopic sorption isotherms of cement pastes, which is key to develop a self-consistent global understanding of the mechanism of moisture sorption in cementitious materials.¹ To this end, McDonald studied the characteristics of the pore structure

FIGURE 1 Schematic illustrating the microstructure of the calcium–silicate–hydrate gel [Color figure can be viewed at wileyonlinelibrary.com]



of cement paste at different saturation degrees and showed that cement pastes exhibit two families of pore reservoirs in C–S–H gel, namely: (i) interlayer spacing within the C–S–H grains (around 1 nm) and (ii) gel pores in between the C–S–H grains (around 5 nm).²³ Based on the volume ratio of evaporable water, the fractions of C–S–H sheet porosity (pores in the C–S–H grains) and evaporable porosity (pores can retain evaporable water in C–S–H grains) were estimated to be 47% and 38%, respectively. However, the magnitude of the internal swelling of the cement paste as a function of RH was not accounted for—the magnitude of which being subsequently quantified by Bede et al.²⁴ The linkages between RH-induced swelling and resulting water sorption isotherm were later on discussed by Beaudoin et al.²⁵ and Maruyama.^{8,26} Based on these analyses, it was found that the interlayer basal space in the C–S–H grains is stable from 5% to 40% RH, but collapses at low RH. Despite these useful insights, conventional experimental techniques are intrinsically unable to isolate the respective contributions of each pore scale to the total sorption isotherm of cement pastes as a function of RH.

Theoretical models offer a valuable alternative, a complementary route to access some details of the water sorption mechanism in cement pastes that are invisible to conventional experiments. As a recent illustration of this, Pinson et al. introduced a series of continuum and molecular physics-based models describing water sorption in cement pastes and resulting volume variations.²⁷ It was found that, upon desorption, interlayer water in C–S–H evaporates below around 20% RH, but gradually recondensates throughout the full RH range upon subsequent adsorption. However, the connectivity of pores was not accounted for in this model. To address this point, a general formula was subsequently developed by introducing a simple measure of hierarchical pore connectivity.²⁸ Similar studies were also conducted by Burgh, Jiang, and Huang, wherein the pore size distribution and the contribution of the interlayer C–S–H spacing to the sorption isotherm were empirically described without explicitly considering the detailed micro- and mesoscale structure of

cement pastes.^{29–31} Moreover, atomistic simulations offer an accurate description of water sorption within the C–S–H layers, but, in turn, are intrinsically unable to describe the multiscale structure of cement pastes due to the limited number of atoms they can account for.³² Overall, a unifying model describing accurately describing the role of each pore scale in governing the water sorption behavior of cementitious materials is still lacking.³³

Here, as an alternative route, we introduce a lattice-based density functional theory (DFT) model of water sorption in the C–S–H gel and cement paste. DFT models have previously been applied to describe inhomogeneous and confined fluids.^{34,35} Notably, they have been shown to properly describe fluids adsorption and capillary condensation in various porous solids, for example, silica aerogels, activated carbons, or carbon nanotubes.^{36–39} Specifically, the simple lattice-gas DFT (LDFT) model proposed by Kierlik et al. offers a convenient framework to model the sorption of fluids in disordered mesoporous solids.⁴⁰ Here, we adopt this framework and further expand it by introducing a probability evolution equation that describes the gradual opening of the interlayer spacing in C–S–H upon water adsorption. By Bejaoui's pore model,⁴¹ we demonstrate that our model offers a reasonable description of water sorption in cement pastes. Furthermore, by describing C–S–H gels as random configurations of nanoscale particles, our model allows us to deconstruct the contribution of each pore scale to the total sorption isotherm in cement pastes and, importantly, uniquely isolate the contribution of the C–S–H gel. Overall, we show that, at RH < 80%, the C–S–H gel accounts for more than 90% of the moisture content adsorbed in cement pastes, while the contribution of capillary pores significantly increases at RH > 80%. Based on our model, we also explore the role of the C–S–H gel packing density on the sorption isotherm.

This paper is organized as follows. In Section 2, we first introduce our LDFT model, the C–S–H gel geometrical structure adopted herein, as well as the equation describing the gradual opening of the C–S–H interlayer spacing. Our model

is then validated, and its outcomes are discussed in Section 3. Finally, some conclusions are presented in Section 4.

2 | METHODS

2.1 | Lattice density functional theory simulations

The porous C–S–H gel is modeled as a two-dimensional square lattice comprising N_s sites i , wherein each site can be a pore ($\eta_i = 1$) or fully filled with solid ($\eta_i = 0$). In turn, depending on RH, each pore site i can empty ($\tau_i = 0$) or filled with a water molecule ($\tau_i = 1$). In this study, the size of each lattice site is fixed to $3 \times 3 \text{ \AA}$ (i.e., the typical size of a water molecule), so that each lattice size can contain at most one water molecule at a time. This simplification is a consequence of the fact that we are using a square lattice, which prevents us from simulations layers with arbitrary directions. Nevertheless, since our model simply relies on nearest-neighbor interactions, its outcome is rotation-invariant. In addition, the chain model of the pore network³⁰ and individual spherical or cylindrical pore model^{27,28,31} suggest that the orientation of the pores does not significantly influence the sorption curve. Note that the sites filled with solids cannot contain any water molecule, so that $\eta_i = 0$ necessarily implies $\tau_i = 0$. Following Kierlik et al., only nearest-neighbors interactions are considered. Therefore, the Hamiltonian $\mathcal{H}$ of the system can be expressed as^{40,42}:

$$\mathcal{H} = -w_{\text{ff}} \sum_{\langle i,j \rangle} \tau_i \tau_j \eta_i \eta_j - w_{\text{mf}} \sum_{\langle i,j \rangle} [\tau_i \eta_i (1 - \eta_j) + \tau_j \eta_j (1 - \eta_i)] \quad (1)$$

where w_{ff} is the interaction energy between two adjacent water molecules (fluid-fluid interaction) and w_{mf} the interaction energy between a water molecule and an adjacent C–S–H solid surface (matrix-fluid interaction), and where the summation is performed over all the pairs of sites $\langle i,j \rangle$ that are nearest-neighbors (i.e., sharing one edge). For the present lattice geometry, the fluid-fluid interaction energy is given by $w_{\text{ff}} = \mu_{\text{sat}}/2 = k_B T_c$, where μ_{sat} is the chemical potential of water at saturation, k_B the Boltzmann constant, and $T_c = 647 \text{ K}$ is the critical temperature of water.

The degree of hydrophilicity of the solid surface is captured by the following dimensionless parameter:

$$y = w_{\text{mf}}/w_{\text{ff}} \quad (2)$$

We adopt here $y = 1.8$ to simulate the interaction between water and C–S–H following Ref. [32]. In addition, a comparison between the predictions of the present model and molecular simulations from Ref. [32] for nanopores supports the value of y adopted herein, that is, $y = 1.8$ (see Figure S1 in

Supplementary Information). Furthermore, the effect of y on the adsorption of C–S–H gels (wherein the interlayer space is open at RH = 0) is shown in Figure S2 in Supplementary Information. We observe that a higher value of y results in a higher hydrophilic nature for the C–S–H sheets. Meanwhile, C–S–H gels can be filled at a lower RH for a higher value of y . Following Kierlik et al., periodic boundary conditions are imposed in all directions to avoid any spurious finite-size effects arising from the surfaces.⁴⁰

The grand-potential functional $\Omega(\{\rho_i\})$ of the modeled lattice system can be expressed in terms of the ensemble of the average water density at site i $\{\rho_i\}$:

$$\begin{aligned} \Omega(\{\rho_i\}) = & k_B T \sum_i [\rho_i \ln \rho_i + (\eta_i - \rho_i) \ln (\eta_i - \rho_i)] \\ & - w_{\text{mf}} \sum_{\langle i,j \rangle} [\tau_i \eta_i (1 - \eta_j) + \tau_j \eta_j (1 - \eta_i)] \\ & - w_{\text{ff}} \sum_{\langle i,j \rangle} \tau_i \tau_j \eta_i \eta_j - \mu \sum_i \rho_i \end{aligned} \quad (3)$$

where T is the temperature and μ the chemical potential of water—which is given by $\mu = \mu_{\text{sat}} + k_B T \ln RH$. Note that Equation (3) neglects any correlation between the thermal fluctuations of the instantaneous fluid densities, $\eta_i \tau_i - \langle \eta_i \tau_i \rangle$. The equilibrium water density at each site for given T and RH can be obtained by minimizing the grand-potential functional with respect to $\{\rho_i\}$, which yields⁴⁰:

$$\rho_i = \eta_i / [1 + \exp(-\beta v_i^{\text{eff}})] \quad (4)$$

where $\beta = 1/k_B T$ and v_i^{eff} is the effective potential imposed by the nearest neighbors of site i , which is given by:

$$v_i^{\text{eff}} = \mu + w_{\text{ff}} \sum_{\langle i,j \rangle} \rho_j + y (1 - \eta_j) \quad (5)$$

Based on this model, we simulate the adoption isotherm in the porous configuration of interest as follows. We initially impose $\rho_i = 0$ at RH = 0%. We then iteratively increase RH by small increments of 2.5% until RH = 100%. For each step of RH, we then solve Equation (4) in an iterative fashion following Kierlik et al. In detail, we initially start from the equilibrium water densities ρ_i obtained at the previous step of RH. Based on Equation (5), these density values are then used to calculate the effective potential at each site, which, in turn, are used to calculate a new set of water density values. These two steps are iteratively repeated until convergence of obtained, that is, when the variation in the water density values between two steps satisfies $\frac{1}{N_s} \sum_i (\rho_i^{n+1} - \rho_i^n)^2 < 10^{-8}$. Note that LDFT assumes that the water density ranges from 0 to 1.0 under different RH conditions. Based on the simulation by Qiom et al.,¹⁶ the density of the confined water in the interlayer space is around 1.05 g/cm^3 when the calcium silicon

molar ratio is 1.65 which is the average value for calcium silicate hydrate. To consider this effect, the water mass adsorbed in the interlayer space is enlarged by 5% in this paper.

2.2 | C–S–H gel model

We now detail the construction of the two-dimensional lattice configuration (i.e., the ensemble $\{\eta_i\}$) used herein to model the porous structure of C–S–H gels. Several models based on spherical particles have previously been shown to properly capture the mechanical and sorption behaviors of cement pastes.^{33,43–45} Here, following previous studies,^{33,46,47} we model the porous C–S–H gel as an ensemble of circular grains that are packed together so as to achieve selected packing density values (from 60% to 80%). Such a colloidal structure results in the existence of a continuous range of pore sizes and geometries. In the present model, we simply model two-dimensional C–S–H configurations by randomly distributing circular particles (with diameter values that are randomly sampled from 3 to 15 Å with a uniform probability distribution), while ensuring the absence of any overlap in between neighboring grains. In addition to the gel pores forming in between the grains, the model C–S–H lattice presents some layers of pores to model the interlayer spaces within the C–S–H grains (see Figure 2). Previous studies suggested the total porosity of the C–S–H grains to be around 50%,^{23,47–49} while the evaporable water was found to account for about 25-to-37% of the total interlayer water.^{29,30} The number of water layers that can

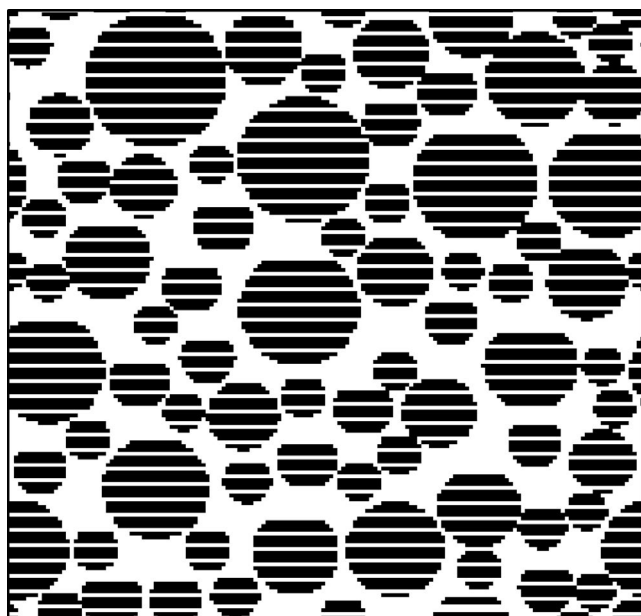


FIGURE 2 Example of lattice configuration used herein to model the porous structure of C–S–H gels (with all the sites being open in the interlayer space). Black pixels indicate solid lattice points, while white pixels indicate pores (i.e., within which water molecules can adsorb)

be adsorbed within the C–S–H particles is largely controlled by the size of the interlayer space, which is smaller than 5 Å (see Figure 1 in Ref. [21]). Since the typical diameter of a water molecule is 3 Å, it is reasonable to assume that only a single layer of water molecules can be accommodated within this space. We impose that a given interlayer space can accommodate only one layer of water molecules. As a simplification, these pore layers are all assumed to be horizontal. Note that, in our model, only the evaporable water is considered, while non-evaporable water (i.e., water remaining at circa 150°C²³) is regarded as being part of the C–S–H solid. In all the C–S–H configurations generated herein, the total lattice size is chosen to be at least five times larger than the size of the largest C–S–H grain present in the structure. This is because the C–S–H grains are here assumed to be randomly distributed, and the size of the simulated system (representative volume element) should be large enough to accommodate a large number of possible configuration, ensure satisfactory statistical average, and, overall, be representative. The fact of imposing that the simulated system is at least five times larger than the size of the largest C–S–H grain ensures that the simulated system can exhibit a large range of C–S–H grains, ranging from small to large grains—to capture the polydisperse nature of the C–S–H gel. We then conduct several independent simulations for statistical averaging purposes. As shown in Figure S3 in the Supplementary Information, we observe the average simulated sorption curve exhibits a convergence when the number of independent simulations exceeds 20. Therefore, 50 independent configurations are considered herein. All the adsorption isotherms presented throughout the present study are obtained by averaging the isotherms computed from 50 distinct (random) C–S–H configurations with constant system size and packing density. It should be noted that, as described below in Section 2.3, the interlayer spaces are not systematically allowed to be filled with water—to account for their transformation from closed- to open-state upon increasing RH.

2.3 | Evolution equation of open sites in the interlayer space

Interlayer spaces may be dry or partially filled with non-evaporable water at RH = 0 but can accommodate some water molecules when they expand with increasing RH.^{50–53} In the following, we detail the model introduced herein to describe the RH-dependent opening of the C–S–H interlayer pores that is experimentally suggested.^{26,54,55} Note that, although initial cracks and sample conditioning also can influence water adsorption in cementitious phases,^{56,57} such second-order effects are here neglected for simplicity. In detail, the opening of C–S–H interlayer space upon increasing RH has been attributed to the increase in disjoining pressure or hydration pressure.^{8,58} However, such pore opening effects

cannot be described in conventional LDFT models relying on a fixed solid configuration lattice. To address this point, we introduce here an additional equation describing the probability of interlayer pore spaces to open as a function of RH. In analogy with analytical two-states models describing the formation/breakage of interatomic constraints as a function of temperature,^{59–61} we model the opening probability p as:

$$p = p_0 + [1 - \exp(-\zeta \cdot \text{RH})]^m \quad (6)$$

where p_0 is the fraction of pores initially open at $\text{RH} = 0\%$, $\zeta \cdot \text{RH}$ is a linear function capturing the contribution of the increasing disjoining pressure upon increasing RH, $1/\zeta$ is related to the critical RH value at which the pores tend to open, and $m = \nu \cdot t_{\text{obs}}$ is the product of the frequency of pore opening attempt ν and observation time t_{obs} . Note that the term m captures the width of RH values over which pore opening occurs, namely, $m \rightarrow \infty$ would yield a Heaviside step function wherein pore opening suddenly occurs at a critical RH value $1/\zeta$, while lower m values yield a smoother transition. Effects of parameters m and ζ on the adsorption of C–S–H gels are displayed in Figures S4 and S5 in the Supplementary Information. From these two figures, we observe that the parameter m dominates the opening evolution of the interlayer spaces with RH, whereas ζ governs the number of pores that can be open. Although no experimental data regarding the fraction of open pores as a function of RH are presently available, the probability of RH-induced pore opening (i.e., in addition to the pores that are already open at $\text{RH} = 0\%$) can be compared with RH-induced swelling data obtained for C–S–H and cement pastes based on basal spacing or macroscopic deformation measurements.⁵³ Overall, we find that the values $\zeta = 1.3$ and $m = 2.0$ yield a probability of pore opening that is in good agreement with experimental data from Refs. [26, 52, 53] (see Figure 3). We also adopt $p_0 = 10\%$ following data from Ref. [53].

Note that our approach is different from that of Pinson et al.²⁷ In their paper, the BET and Kelvin equations were employed to calculate the isotherm sorption curves of surface, gel pores, and capillary pores in the cement paste. Thereafter, the amount of adsorbed water by interlayer space was obtained from the experimental data after removing the other contributions mentioned above. Then, the relation between shrinkage or expansion and desorption or adsorption of interlayer space was discussed. The discussion indicates that the deformation correlates well with the isotherm sorption of interlayer space. Here, our approach is different since we explicitly model the variation in basal space C–S–H as a function of relative humidity (RH) based on a probability evolution equation that describes the gradual opening of the interlayer spacing in C–S–H. This allows us to capture the contribution of the pore in the C–S–H gel, including gel pores and interlayer spaces, which is not easily accessible experimentally.

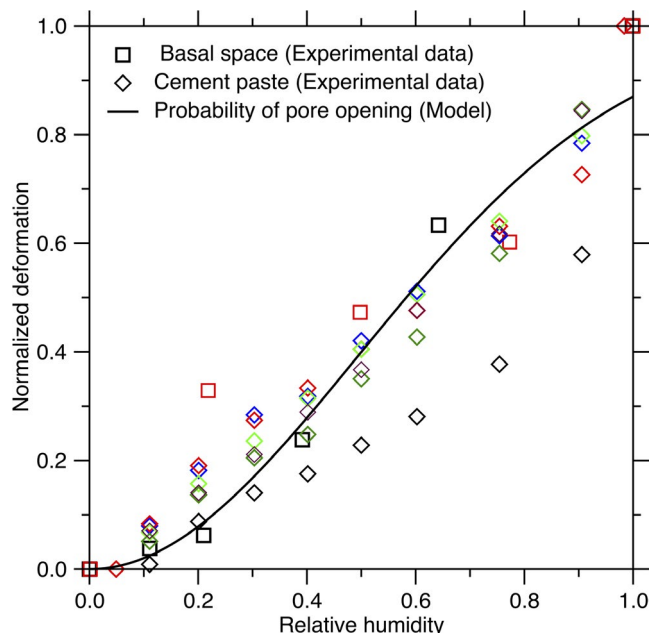


FIGURE 3 Probability of C–S–H interlayer pore opening (given by Equation 6) as a function of relative humidity (RH). The data are compared with relative deformation experimental data based on C–S–H basal spacing^{52,53} and macroscopic cement paste swelling measurements as a function of RH²⁶ [Color figure can be viewed at wileyonlinelibrary.com]

2.4 | Volume fractions of capillary pores and hydration products

Since directly simulating water sorption in cement pastes using LDFT is unrealistic due to the multiscale nature of cementitious systems, we independently compute the contribution of each scale to the total adsorption isotherm. This requires us to model the volumetric fractions of (i) each family of pore and (ii) each phase in the cement paste. To this end, we first adopt Bejaoui's model, which offers an expression of the maximum hydration degree (α_h) in terms of the water-to-cement ratio (w/c , mass basis)⁴¹:

$$\alpha_h = 0.239 + 0.745 \tanh [3.62 (w/c - 0.095)] \quad (7)$$

We then rely on the improved Power's model to estimate the volume fraction of the hydration product (f_{hy}) and capillary pores (f_{cap}). It has been suggested that the volume fraction of portlandite (C–H) (f_{CH}) is larger by 20-to-25% than that of the hydration product (f_{hy}).^{51,62,63} Based on these observations and extant studies,^{64–66} the following expression is obtained:

$$f_{\text{hy}} = \frac{0.68\alpha_h}{0.32 + w/c}, f_{\text{cap}} = \frac{(w/c - 0.36)\alpha_h}{0.32 + w/c}, f_{\text{CSH}} = \frac{0.19\alpha_h}{0.32 + w/c} \quad (8)$$

where $\alpha_h = f_{\text{hy}} + f_{\text{cap}}$ and the volumetric fraction of the C–S–H gel is obtained from $f_{\text{CSH}} = f_{\text{hy}} - f_{\text{CH}}$. Finally, we express the

volumetric fractions of high-density (HD) and low-density (LD) C–S–H (f_{HD} and f_{LD} , respectively) in terms of the ratio of the mass of LD C–S–H with respect to the total mass of C–S–H (M_r)⁶⁷:

$$M_r = 3.017(w/c)\alpha_h + 1.347\alpha_h + 0.538 \quad (9)$$

$$f_{LD} = \frac{f_{CSH}}{1 + \frac{1-M_r}{M_r} \left(\frac{\rho_{LD}}{\rho_{HD}} \right)}, f_{HD} = \frac{f_{CSH}}{1 + \frac{1-M_r}{M_r} \left(\frac{\rho_{HD}}{\rho_{LD}} \right)} \quad (10)$$

where the dry densities of HD and LD C–S–H are taken as $\rho_{HD} = 1750\text{g/cm}^3$ and $\rho_{LD} = 1440\text{g/cm}^3$, respectively.⁶² All these equations allow us to estimate the volumetric fractions of each family of pores in the cement paste.

3 | RESULTS AND DISCUSSION

3.1 | Validation by comparison with experimental data of cement paste

We first validate our modeling approach by comparing the adsorption isothermal predicted for a cement paste with available experimental data—since the sorption isotherm of the sole C–S–H gel is not easily accessible experimentally. Here, the adsorption isotherm of the cement paste is divided into two parts: (i) the contribution of the inter-layer spacing and (ii) the contribution of gel and capillary pores. The total adsorption isotherm can then be determined through the summation of these two parts, which is illustrated in Figure 4. To assess the ability of our lattice density functional theory simulations to offer a realistic description of water sorption in cementitious materials, we use as reference two sets of experimental data obtained by Bahafid et al.⁶⁸ and Jennings et al.,⁶⁹ as described in the following.

In detail, the cement paste model considered herein has a size of (i) $10 \times 10 \text{ nm}^2$ (for the C–S–H sheets) and (ii) $400 \times 400 \text{ nm}^2$ (for the gel and capillary pores)—see Figure 4. We first consider the experimental data from Bahafid et al. (paste A).⁶⁸ The cement paste considered therein was obtained with a water-to-cement ratio (w/c) of 0.44 and was aged for 4 months. The measured pore size distribution is shown in Figure 5A. These data are fitted by a log-normal probability distribution given by $P(d) = \frac{1}{\sqrt{2\pi\sigma d}} \exp \left[-\frac{1}{2\sigma^2} (\ln(d) - \mu)^2 \right]$, where μ and σ are the location and the shape parameters of the distribution, respectively, and d is the pore size). The fit yields some μ and σ values of (i) 4.0 and 1.6 nm for gel pores and (ii) 10 and 16 nm for capillary pores, respectively. As shown in Figure 5A, this function offers a good representation of the experimental pore size distribution and, hence, is used as input for the LDFT simulations. We now focus on the data obtained by Jennings et al. (paste B).⁶⁹ The cement paste considered therein was obtained with a water-to-cement ratio of 0.45, which yields a hydration degree (α_h) of 0.85. Based on the equations above (Equations 7–10), the volume fraction of the gel and capillary pores are estimated to be 21% and 17.5%, respectively. The measured adsorption isotherms are fitted to obtain the pore size distribution (by relying on a log-normal distribution), which yields μ and σ values of (i) 2.4 and 4.0 nm for gel pores and (ii) 8.0 and 10 nm for capillary pores, respectively.

The sorption isotherms predicted by our LDFT simulations are shown in Figure 5B. As expected, we find that the adsorption isotherm predicted for paste B is slightly shifted toward lower RH as compared to that of paste A, which echoes the fact that the pore size distribution of paste B is centered around smaller pore sizes than paste A (see Figure 5A). This agrees with the fact that, based on Kelvin's theory, small pores are filled at lower RH.²⁷ This confirms that our simulations are able to capture the effect of the slightly different pore size distributions in the two cement pastes considered herein. Importantly, in both cases, we observe a very

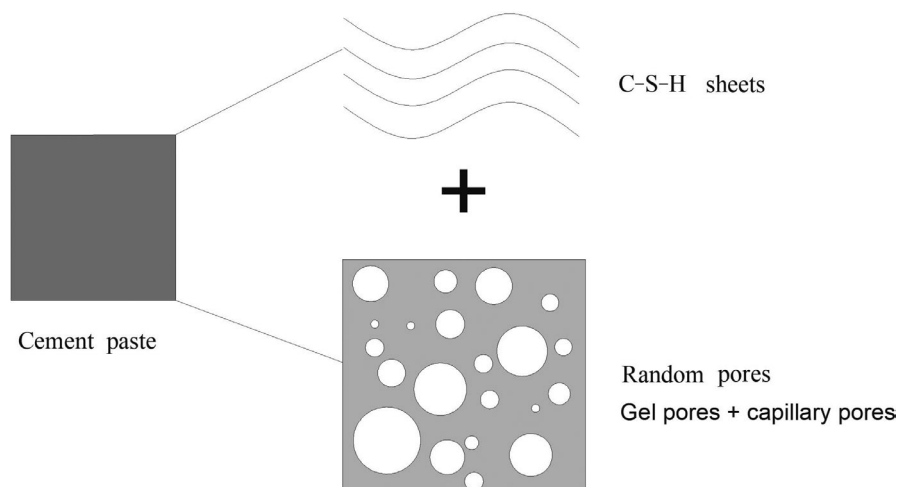


FIGURE 4 Schematic diagram illustrating the separation of the sorption isotherm of a cement paste into the contributions of the C–S–H interlayer spacing and gel/capillary pores

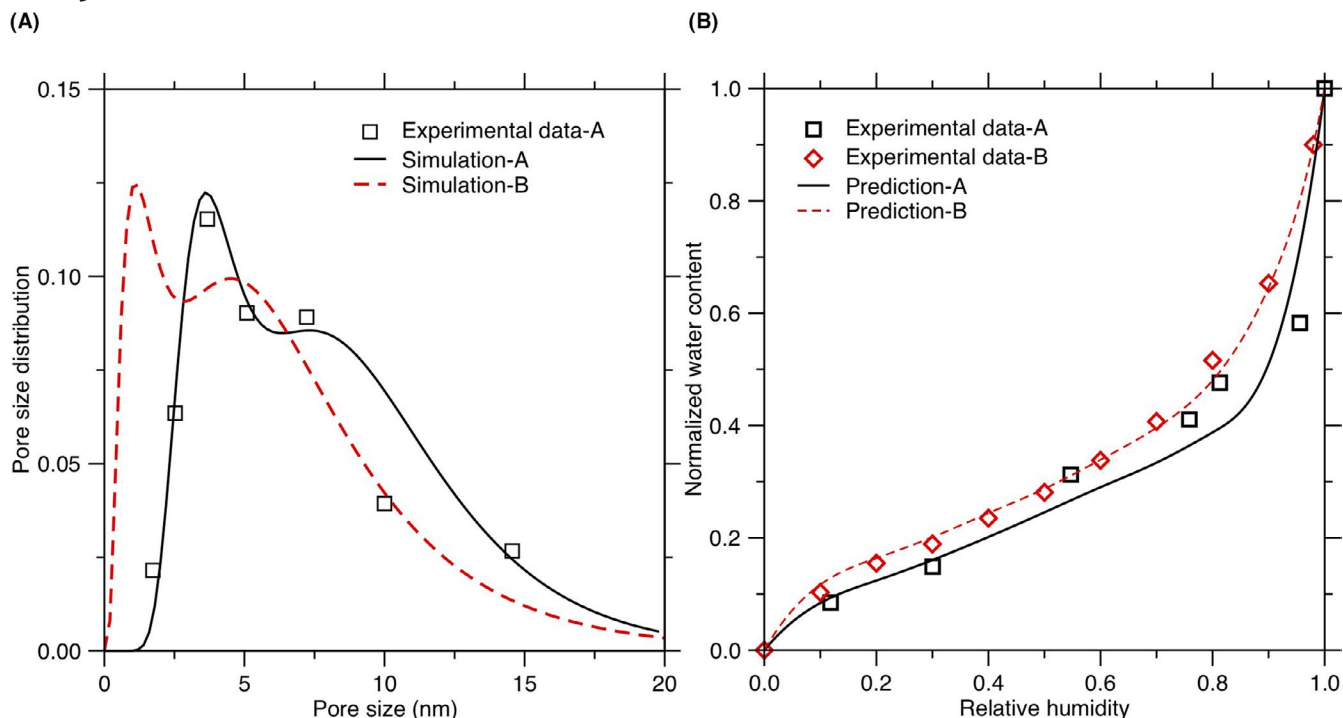


FIGURE 5 Experimental and predicted (A) pore size distributions and (B) adsorption isotherms in two cement pastes from Refs. [68, 69] (Paste A) and [69] (Paste B) [Color figure can be viewed at wileyonlinelibrary.com]

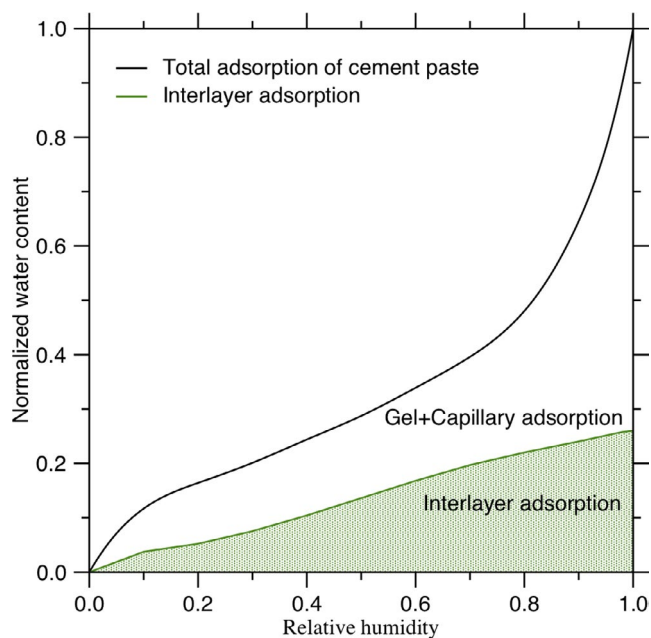


FIGURE 6 Contributions of interlayer space and gel pore +capillary pore to the adsorption of cement paste. The normalized water content is the ratio of the adsorbed water at different relative humidity conditions to the maximum adsorbed amount of cement paste (i.e., at RH = 1) [Color figure can be viewed at wileyonlinelibrary.com]

good agreement between simulation and experimental data, over the entire range of RH values. Overall, these results offer confidence in the ability of our LDFT simulation to offer a realistic description of water sorption in cement pastes.

The adsorption data from the second test are now further used to investigate the contribution of different pore types to the total adsorption of cement paste. The simulated results are presented in Figure 6. From this figure, we observe that the water adsorbed in the interlayer space accounts for about 40%-50% of the total water for RH values ranging from 0.1 to 0.7. However, this proportion decreases gradually with increasing RH. Specifically, we find that, at RH = 1, the interlayer space contributes to only about 26% of the total adsorbed water. In turn, the contribution of the capillary and gel pores to the total adsorbed water increases with increasing RH (see Figure 6). This arises from the fact that, in general, the large gel and capillary pore are filled at higher RH than those present in the interlayer space.

3.2 | Contribution of the adsorption of C–S–H gel

Although using the random-pore model presented in Section 3.1 offers a good prediction of the water sorption isotherms of cement pastes, it does not allow us to isolate the contribution of the C–S–H gel pores to the total sorption isotherm. This arises from the fact that, in this random-pore model, there is no clear boundary between gel and capillary pores. Therefore, to study the water uptake ability of the C–S–H gel (i.e., comprising the interlayer space in the C–S–H grains and the pores between the C–S–H grains) under different RH conditions, we adopted in the following the random-particle

model described in Section 2.2, that is, wherein the structure of the C–S–H gel is explicitly accounted for (see Figure 2). In this model, the diameter of the circular C–S–H grains ranges from 3 to 15 nm.⁴⁶ We adopt a C–S–H gel model of $150 \times 150 \text{ nm}^2$. As an example, a typical C–S–H gel configuration with a packing density of 65% is shown in Figure 7A. This model allows us to deconstruct the total sorption isotherm into the contributions of interlayer spaces, gel pores (i.e., pores between the C–S–H grains), and capillary pores (i.e., the remaining large pores) in the case of the cement paste B (i.e., the second test in Section 3.1).

Figure 7 shows the computed distributions of adsorbed water in a C–S–H gel configuration with a packing density of 65% at RH = 0, 0.4, 0.8, and 1.0. As expected, we observe that, at low RH, water first fills the interlayer space and is adsorbed on the surface of the C–S–H grains, as well as in the smallest pores of the gel (see Figure 7B). At RH = 0.8, we observe that most of the gel pores are fully filled, while only the largest gel pores remain partially empty (see Figure 7C). Finally, at RH = 1.0, all the pores eventually filled with water (see Figure 7D). In addition, we note that only a small fraction of the interlayer space is initially open at RH = 0 (see Figure 7A), while the proportion of open sites gradually increases with increasing RH—so that most of the interlayer space sites are eventually open at RH = 1.0 (see Figure 7D).

Figure 8 shows the contribution of the C–S–H gel to the total water sorption isotherm in the case of the cement paste B (i.e., the second test in Section 3.1). The contributions of the interlayer spacing and gel pores are highlighted in green and blue, respectively. Notably, based on these results, we find that the C–S–H gel accounts for more than 90% of the total sorption isotherm of the cement paste for RH < 0.8. In this regime, the interlayer space contributes to around 50% of the water adsorbed within the C–S–H gel. This highlights the critical role played by the C–S–H gel (including that of the interlayer spacing within the C–S–H grains) in governing the sorption response of cement pastes at moderate RH values. In turn, we find that the contribution of the C–S–H gel to the total isotherm eventually plateaus for RH > 0.8 (see Figure 8), which arises from the fact that, in this regime, nearly all the interlayer and gel pores are already filled with water. Moreover, in this regime, the capillary pores are still gradually filled with water, in agreement with the conclusions from Jennings.⁶⁹ Eventually, we find that, at RH = 1, the C–S–H gel contributes for 60% of the total adsorbed water in the cement paste, wherein about 40% of the C–S–H gel water is presented within the interlayer spacing. While in Ref. [22], the saturation degree of the interlayer spaces was found to increase with RH (see Figure 6 in Ref. [22]), which is consistent with the findings presented in our paper, as well as with Refs. [30, 69, 70]

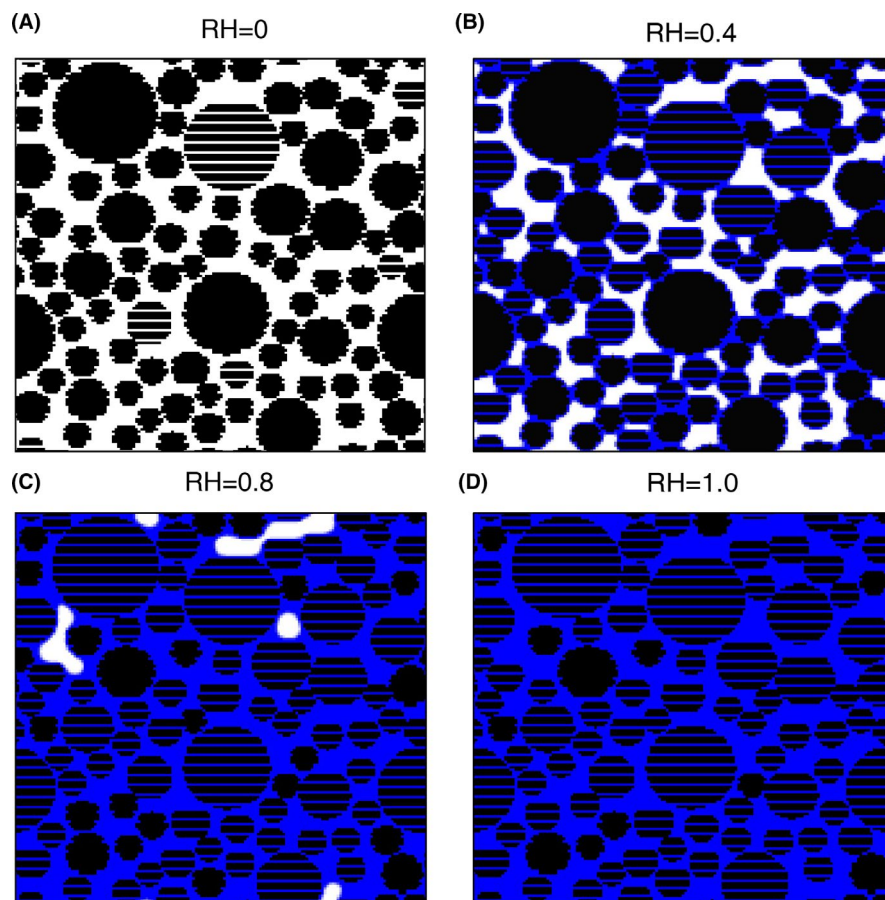


FIGURE 7 Example of C–S–H gel configuration with a packing density of 65% under varying relative humidity (RH). Black pixels indicate solid lattice points, while white pixels indicate pores (i.e., within which water molecules can adsorb). Blue pixels indicate the spatial distribution of adsorbed water at (A) RH = 0, (B) RH = 0.4, (C) RH = 0.8, and (D) RH = 1.0 [Color figure can be viewed at wileyonlinelibrary.com]

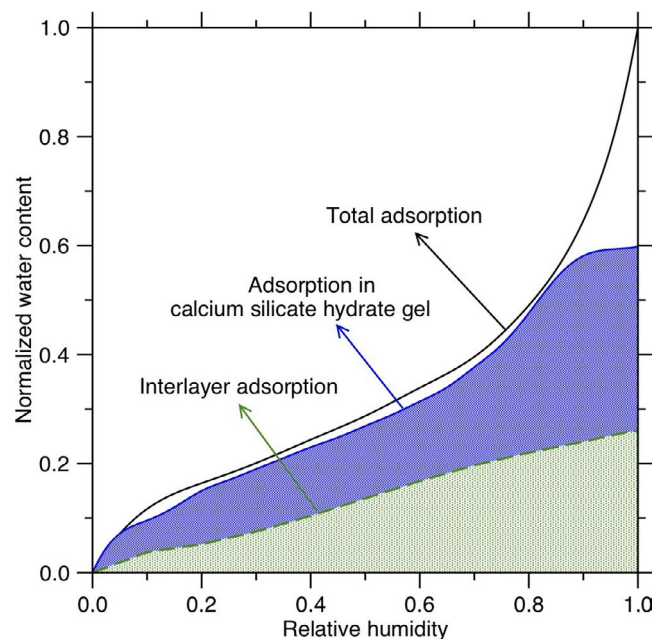


FIGURE 8 Decomposition of the to the total water sorption isotherm of cement paste B (black solid line, see Section 3.1) into the contributions of the C–S–H grain interlayer spacing (green area), C–S–H gel pores (blue area), and larger capillary pores (white area). The normalized water content is the ratio of the adsorbed water at different relative humidity conditions to the maximum adsorbed amount of cement paste (i.e., at RH = 1) [Color figure can be viewed at wileyonlinelibrary.com]

Note that, in Ref. [22] the interlayer water redistribution from the interlayer space to the gel pore (with a total constant amount of water) is mainly induced by heating rather than by variations in RH (see Figure 5 in Ref. [22]). We consider that such temperature effects are outside the scope of our manuscript.

3.3 | Effect of the packing density of the C–S–H gel on the sorption isotherm

Based on the C–S–H model presented in Section 3.2, we now further investigate the effect of the packing density of the C–S–H gel, which has been suggested to play a critical role in governing its sorption behavior.³³ Based on experimental observations,^{51,67} varying gel packing densities ranging from 60% (wherein 64% is typically associated with low-density C–S–H) to 80% (wherein 74% is typically associated with high-density C–S–H) are considered.^{10,71–73}

Figure 9 shows the sorption isotherms of C–S–H gels with varying packing densities as a function of RH. Overall, we observe that the computed sorption isotherms tend to shift toward lower RH values with increasing packing density values. This arises from the fact that C–S–H gels associated with higher packing densities present smaller pores, which, in turn, tend to be filled with water at lower RH. In addition, we note that C–S–H gels presenting higher

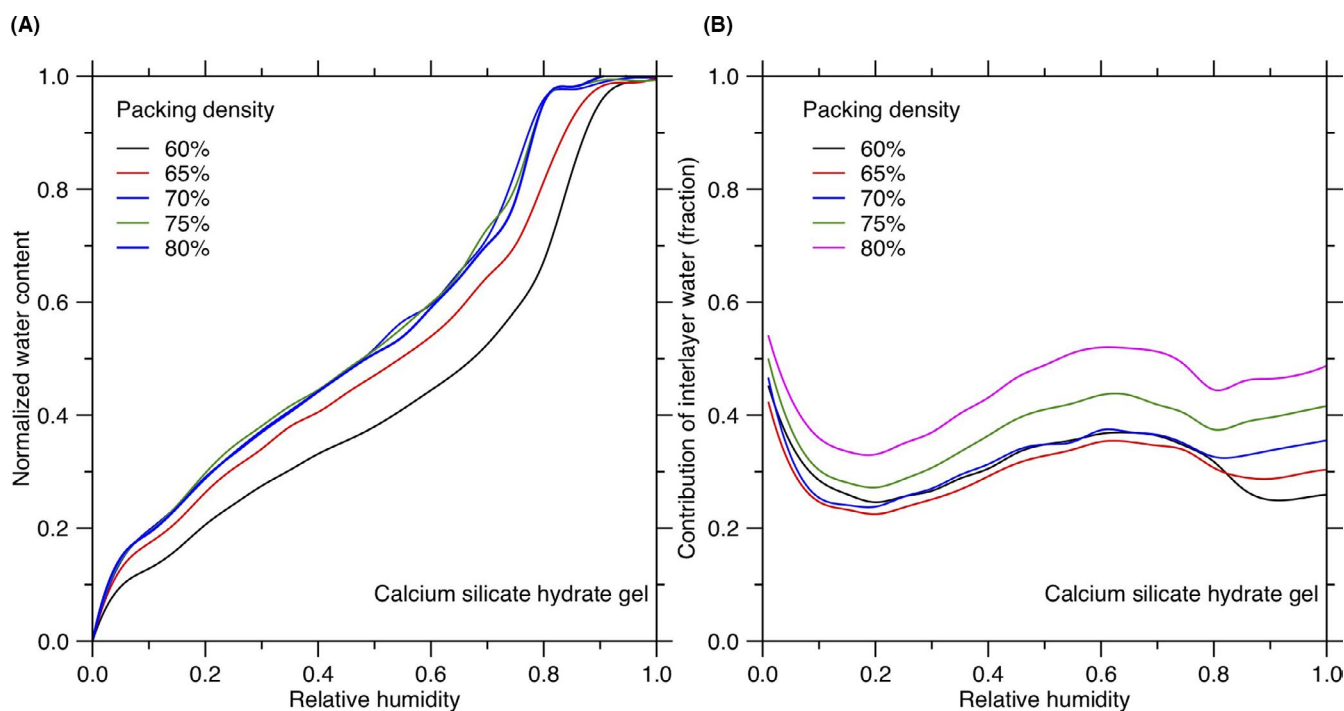


FIGURE 9 Effect of the C–S–H gel packing density on (A) the adsorption isotherm of the C–S–H gel and (B) the contribution (fraction) of interlayer water to the total adsorbed water in the C–S–H gel. The normalized water content is the ratio of the adsorbed water at different relative humidity conditions to the maximum adsorbed amount of C–S–H gel (i.e., at RH = 1) [Color figure can be viewed at wileyonlinelibrary.com]

packing densities are able to achieve a fully saturated state at lower RH than those associated with lower packing densities. Nevertheless, we observe that the sorption isotherm becomes largely independent of the packing density when it exceeds 70% (see Figure 9A).

Figure 9B shows the fraction to which interlayer water contributes to the total adsorbed water in the C–S–H gel. Interestingly, we observe the existence of a systematic, non-monotonic trend. Namely, we observe that the fraction of interlayer water initially decreases for $RH = 0.0$ -to- 0.2 . This can be explained from the fact that, in this regime, the interlayer space that is initially open tends to become filled with water at lower RH than the small pores of the C–S–H gel—so that the relative contribution of the gel pores tends to increase upon increasing RH values. We then observe that the contribution of the fraction of interlayer water increases and exhibits a maximum around $RH = 0.6$. This can be understood from the fact the rate of C–S–H interlayer pore opening is maximum around this RH value, which manifests itself as an inflection point in the probability of C–S–H interlayer pore opening as a function of RH (see Figure 3). Finally, we find that the fraction of interlayer water eventually increases at $RH > 0.9$. This arises from the fact that, in this regime, most of the C–S–H gel pores are already filled with water—so that any incremental sorption of water arises from some residual opening of C–S–H interlayer pores. These results reveal that the contribution of interlayer water is governed by a subtle interplay between (i) the gradual opening of the interlayer spacing opening and (ii) the increasing propensity for larger pores to be filled with water upon increasing relative humidity.

Overall, we find that the contribution of interlayer water increases upon increasing C–S–H gel packing density (see Figure 9B). This arises from the fact that, in turn, the volume fraction of the gel pores (as compared to the total pore volume accessible to water in C–S–H) decreases upon increasing C–S–H gel packing density. Nevertheless, we find that, at moderate RH ($RH < 0.8$), the C–S–H packing density only affects the fraction of interlayer water in a noticeable fashion when the packing density exceeds 70%, whereas, in turn, the fraction of interlayer water hardly depends on the C–S–H packing density otherwise. Overall, these results illustrate that the C–S–H gel packing density does, indeed, affect the contributions of interlayer spaces and gel pores to the total sorption isotherm, albeit to a different extent in varying ranges of RH values.

4 | CONCLUSIONS

In this paper, we introduce a two-dimensional lattice density functional theory framework to predict and deconstruct the water sorption isotherms of cement pastes as a function of

relative humidity. We introduce a new equation to describe the gradual opening of the interlayer spacing upon increasing relative humidity. As the main outcome of the work, this model allows us to isolate the contribution of calcium–silicate–hydrate gel on the total water sorption isotherm of cement pastes, as well as those of the interlayer spacing and gel pores. Based on this analysis, we draw the following conclusions:

1. Despite relying on a simplified model, the sorption isotherms predicted by our lattice-based density functional theory model exhibit an encouraging agreement with experimental sorption data of water sorption in cement paste. This suggests that our model captures the core physical mechanisms governing water sorption in complex, multi-scale porous media. Nevertheless, additional refinements (e.g., considering a 3-dimensional model) would be needed to enhance the quantitative nature of the present simulations.
2. Based on this model, we find that the pores present in the calcium–silicate–hydrate gel (i.e., interlayer spaces and gel pores) account for more than 90% of the total adsorbed water under moderate relative humidity ($RH < 0.8$), which highlights the key role played by the calcium–silicate–hydrate gel in governing the sorption response of cement pastes.
3. The contribution of the interlayer spacing to the total water adsorbed in the C–S–H as a function of relative humidity is non-monotonic and is governed by the competition between the rate of interlayer spacing opening and the increasing propensity for water to fill larger pores upon increasing relative humidity.

However, in general, 2D models cannot capture the real 3-dimensional shape of pores, which can affect water sorption in cement pastes. In addition, a 2D model may also misrepresent sorption hysteresis and the capillary pressure. Nevertheless, 2D models offer a simplified, computationally efficient basis to describe water adsorption in cement pastes under various relative humidity.

ACKNOWLEDGMENTS

The authors acknowledge some financial support from the National Natural Science Foundation of China (51578410), the Fundamental Research Funds for the Central Universities (300102218511), and the funds from the China Scholarship Council. Part of this work was also supported by the National Science Foundation under Grant No. 1922167.

ORCID

Yao Zhang  <https://orcid.org/0000-0002-8104-7665>

Han Liu  <https://orcid.org/0000-0002-4899-9998>

Mathieu Bauchy  <https://orcid.org/0000-0003-4600-0631>

REFERENCES

- Babaei S, Seetharam SC, Muehlich U, Dizier A, Steenackers G, Craeye B. A multiscale framework to estimate water sorption isotherms for OPC-based materials. *Cement Concr Compos.* 2020;105:103415. <https://doi.org/10.1016/j.cemconcomp.2019.103415>
- Mills RH. Effects of sorbed water in dimension, compressive strength and swelling pressure of hardened cement paste. *Highway Res Board Special Rep.* 1966;90:84–111.
- Coussy O, Dangla P, Lassabatère T, Baroghel-Bouny V. The equivalent pore pressure and the swelling and shrinkage of cement-based materials. *Mat Struct.* 2004;37(1):15–20. <https://doi.org/10.1007/BF02481623>
- Morshedifard A, Masoumi S, Qomi MJA. Nanoscale origins of creep in calcium silicate hydrates. *Nat Commun.* 2018;9(1):1785. <https://doi.org/10.1038/s41467-018-04174-z>
- Bazant ZP, Donmez A, Masoero E, Aghdam SR. Interaction of concrete creep, shrinkage and swelling with water, hydration, and damage: nano-macro-chemo. *CONCREEP 10*. Vol. 2015. Vienna: American Society of Civil Engineers; 2015. p. 1–12. <https://doi.org/10.1061/9780784479346.001>
- Benboudjema F, Meftah F, Torrenti JM. Interaction between drying, shrinkage, creep and cracking phenomena in concrete. *Eng Struct.* 2005;27(2):239–50. <https://doi.org/10.1016/j.engstruct.2004.09.012>
- Thomas JJ, Allen AJ, Jennings HM. Structural changes to the calcium-silicate-hydrate gel phase of hydrated cement with age, drying, and resaturation. *J Am Ceram Soc.* 2008;91(10):3362–9. <https://doi.org/10.1111/j.1551-2916.2008.02636.x>
- Maruyama I. Origin of drying shrinkage of hardened cement paste: hydration pressure. *ACT.* 2010;8(2):187–200. <https://doi.org/10.3151/jact.8.187>
- Babaei M, Castel A. Water vapor sorption isotherms, pore structure, and moisture transport characteristics of alkali-activated and Portland cement-based binders. *Cem Concr Res.* 2018;113:99–120. <https://doi.org/10.1016/j.cemconres.2018.07.006>
- Jennings HM. Refinements to colloid model of C-S-H in cement: CM-II. *Cem Concr Res.* 2008;38(3):275–89. <https://doi.org/10.1016/j.cemconres.2007.10.006>
- Zeng Y. Modeling of chloride diffusion in hetero-structured concretes by finite element method. *Cement Concr Compos.* 2007;29(7):559–65. <https://doi.org/10.1016/j.cemconcomp.2007.04.003>
- Chen Q, Ma R, Li H, Jiang Z, Zhu H, Yan Z. Effect of chloride attack on the bonded concrete system repaired by UHPC. *Constr Build Mater.* 2021;272:121971. <https://doi.org/10.1016/j.conbuildmat.2020.121971>
- Castro J, Keiser L, Golias M, Weiss J. Absorption and desorption properties of fine lightweight aggregate for application to internally cured concrete mixtures. *Cement Concr Compos.* 2011;33(10):1001–8. <https://doi.org/10.1016/j.cemconcomp.2011.07.006>
- Van den Heede P, Gruyaert E, De Belie N. Transport properties of high-volume fly ash concrete: capillary water sorption, water sorption under vacuum and gas permeability. *Cement Concr Compos.* 2010;32(10):749–56. <https://doi.org/10.1016/j.cemconcomp.2010.08.006>
- Ožbolt J, Oršanić F, Balabanić G. Modeling influence of hysteretic moisture behavior on distribution of chlorides in concrete. *Cement Concr Compos.* 2016;67:73–84. <https://doi.org/10.1016/j.cemconcomp.2016.01.004>
- Qomi MJA, Bauchy M, Ulm F-J, Pellenq RJ-M. Anomalous composition-dependent dynamics of nanoconfined water in the interlayer of disordered calcium-silicates. *J Chem Phys.* 2014;140(5):054515. <https://doi.org/10.1063/1.4864118>
- Papatzani S, Paine K, Calabria-Holley J. A comprehensive review of the models on the nanostructure of calcium silicate hydrates. *Constr Build Mater.* 2015;74:219–34. <https://doi.org/10.1016/j.conbuildmat.2014.10.029>
- Allen AJ, Thomas JJ, Jennings HM. Composition and density of nanoscale calcium-silicate-hydrate in cement. *Nat Mater.* 2007;6(4):311–6. <https://doi.org/10.1038/nmat1871>
- Zhang Y, Chen Q, Ju JW, Bauchy M. Effects of high temperature on the mechanical behavior of calcium silicate hydrate under uniaxial tension and compression. *Int J Damage Mech.* 2021;105678952199187. <https://doi.org/10.1177/1056789521991873>
- Abdolhosseini Qomi MJ, Krakowiak KJ, Bauchy M, Stewart KL, Shahsavari R, Jagannathan D, et al. Combinatorial molecular optimization of cement hydrates. *Nat Commun.* 2014;5:4960. <https://doi.org/10.1038/ncomms5960>
- Zhang Y, Zhou Q, Ju JW, Bauchy M. New insights into the mechanism governing the elasticity of calcium silicate hydrate gels exposed to high temperature: a molecular dynamics study. *Cem Concr Res.* 2021;141:106333. <https://doi.org/10.1016/j.cemconres.2020.106333>
- Wyrzykowski M, McDonald PJ, Scrivener KL, Lura P. Water redistribution within the microstructure of cementitious materials due to temperature changes studied with 1H NMR. *J Phys Chem C.* 2017;121(50):27950–62. <https://doi.org/10.1021/acs.jpcc.7b08141>
- McDonald PJ, Rodin V, Valori A. Characterisation of intra- and inter-C-S-H gel pore water in white cement based on an analysis of NMR signal amplitudes as a function of water content. *Cem Concr Res.* 2010;40(12):1656–63. <https://doi.org/10.1016/j.cemconres.2010.08.003>
- Bede A, Scurtu A, Ardelean I. NMR relaxation of molecules confined inside the cement paste pores under partially saturated conditions. *Cem Concr Res.* 2016;89:56–62. <https://doi.org/10.1016/j.cemconres.2016.07.012>
- Beaudoin JJ, Raki L, Alizadeh R, Mitchell L. Dimensional change and elastic behavior of layered silicates and Portland cement paste. *Cem Concr Compos.* 2010;32(1):25–33. <https://doi.org/10.1016/j.cemconcomp.2009.09.004>
- Maruyama I, Igarashi G, Nishioka Y. Bimodal behavior of C-S-H interpreted from short-term length change and water vapor sorption isotherms of hardened cement paste. *Cem Concr Res.* 2015;73:158–68. <https://doi.org/10.1016/j.cemconres.2015.03.010>
- Pinson MB, Masoero E, Bonnaud PA, Manzano H, Ji Q, Yip S, et al. Hysteresis from multiscale porosity: modeling watersorption and shrinkage in cement paste. *Phys Rev Appl.* 2015;3(6):064009. <https://doi.org/10.1103/PhysRevApplied.3.064009>
- Pinson MB, Zhou T, Jennings HM, Bazant MZ. Inferring pore connectivity from sorption hysteresis in multiscale porous media. *J Colloid Interface Sci.* 2018;532:118–27. <https://doi.org/10.1016/j.jcis.2018.07.095>
- de Burgh JM, Foster SJ, Valipour HR. Prediction of water vapor sorption isotherms and microstructure of hardened Portland

- cement pastes. *Cem Concr Res.* 2016;81:134–50. <https://doi.org/10.1016/j.cemconres.2015.11.009>
30. Jiang Z, Xi Y, Gu X, Huang Q, Zhang W. Modelling of water vapour sorption hysteresis of cement-based materials based on pore size distribution. *Cem Concr Res.* 2019;115:8–19. <https://doi.org/10.1016/j.cemconres.2018.09.015>
31. Huang Q, Jiang Z, Gu X, Zhang W, Guo B. Numerical simulation of moisture transport in concrete based on a pore size distribution model. *Cem Concr Res.* 2015;67:31–43. <https://doi.org/10.1016/j.cemconres.2014.08.003>
32. Bonnaud PA, Ji Q, Coasne B, Pellenq RJ-M, Van Vliet KJ. Thermodynamics of water confined in porous calcium-silicate-hydrates. *Langmuir.* 2012;28(31):11422–32. <https://doi.org/10.1021/la301738p>
33. Zhou T, Ioannidou K, Ulm F-J, Bazant MZ, Pellenq RJ-M. Multiscale poromechanics of wet cement paste. *PNAS.* 2019;116(22):10652. <https://doi.org/10.1073/pnas.1901160116>
34. Malanoski AP, van Swol F. Lattice density functional theory investigation of pore shape effects. I. Adsorption in single nonperiodic pores. *Phys Rev E.* 2002;66(4):041602. <https://doi.org/10.1103/PhysRevE.66.041602>
35. Malanoski AP, van Swol F. Lattice density functional theory investigation of pore shape effects. II. Adsorption in collections of noninterconnected pores. *Phys Rev E.* 2002;66(4):041603. <https://doi.org/10.1103/PhysRevE.66.041603>
36. Detcheverry F, Kierlik E, Rosinberg ML, Tarjus G. Local mean-field study of capillary condensation in silica aerogels. *Phys Rev E.* 2003;68(6):061504. <https://doi.org/10.1103/PhysRevE.68.061504>
37. Landers J, Gor GYU, Neimark AV. Density functional theory methods for characterization of porous materials. *Colloids Surf, A.* 2013;437:3–32. <https://doi.org/10.1016/j.colsurfa.2013.01.007>
38. Miyamoto J, Kanoh H, Kaneko K. The addition of mesoporosity to activated carbon fibers by a simple reactivation process. *Carbon.* 2005;43(43):855–7. <https://doi.org/10.1016/j.carbon.2004.10.049>
39. Jiang J, Sandler SI. Nitrogen adsorption on carbon nanotube bundles: role of the external surface. *Phys Rev B.* 2003;68(24):245412. <https://doi.org/10.1103/PhysRevB.68.245412>
40. Kierlik E, Monson PA, Rosinberg ML, Tarjus G. Adsorption hysteresis and capillary condensation in disordered porous solids: a density functional study. *J Phys: Condens Matter.* 2002;14(40):9295–315. <https://doi.org/10.1088/0953-8984/14/40/319>
41. Bejaoui S, Bary B. Modeling of the link between microstructure and effective diffusivity of cement pastes using a simplified composite model. *Cem Concr Res.* 2007;37(3):469–80. <https://doi.org/10.1016/j.cemconres.2006.06.004>
42. Kierlik E, Monson PA, Rosinberg ML, Sarkisov L, Tarjus G. Capillary condensation in disordered porous materials: hysteresis versus equilibrium behavior. *Phys Rev Lett.* 2001;87(5):055701. <https://doi.org/10.1103/PhysRevLett.87.055701>
43. Liu H, Dong S, Tang L, Krishnan NMA, Sant G, Bauchy M. Effects of polydispersity and disorder on the mechanical properties of hydrated silicate gels. *J Mech Phys Solids.* 2019;122:555–65. <https://doi.org/10.1016/j.jmps.2018.10.003>
44. Masoero E, Del Gado E, Pellenq RJ-M, Ulm F-J, Yip S. Nanostructure and nanomechanics of cement: polydisperse colloidal packing. *Phys Rev Lett.* 2012;109(15):155503. <https://doi.org/10.1103/PhysRevLett.109.155503>
45. Masoero E, Gado ED, Pellenq RJ-M, Yip S, Ulm F-J. Nano-scale mechanics of colloidal C-S-H gels. *Soft Matter.* 2013;10(3):491–9. <https://doi.org/10.1039/C3SM51815A>
46. Masoero E, Del Gado E, Pellenq R-M, Yip S, Ulm F-J. Nano-scale mechanics of colloidal C-S-H gels. *Soft Matter.* 2014;10(3):491–9. <https://doi.org/10.1039/C3SM51815A>
47. Pellenq RJ-M, Damme HV. Why does concrete set?: the nature of cohesion forces in hardened cement-based materials. *MRS Bull.* 2004;29(5):319–23. <https://doi.org/10.1557/mrs2004.97>
48. Pellenq R j-m, Kushima A, Shahsavari R, Van Vliet KJ, Buehler MJ, Yip S, et al. A realistic molecular model of cement hydrates. *PNAS.* 2009;106(38):16102–7. <https://doi.org/10.1073/pnas.0902180106>
49. Richardson IG. The calcium silicate hydrates. *Cem Concr Res.* 2008;38(2):137–58. <https://doi.org/10.1016/j.cemconres.2007.11.005>
50. Rucker-Gramm P, Beddoe RE. Effect of moisture content of concrete on water uptake. *Cem Concr Res.* 2010;40(1):102–8. <https://doi.org/10.1016/j.cemconres.2009.09.001>
51. Jennings HM, Thomas JJ, Gevrenov JS, Constantinides G, Ulm F-J. A multi-technique investigation of the nanoporosity of cement paste. *Cem Concr Res.* 2007;37(3):329–36. <https://doi.org/10.1016/j.cemconres.2006.03.021>
52. Smith RH. Basal spacing hysteresis in CSH(1). *Cem Concr Res.* 1973;3(6):829–32. [https://doi.org/10.1016/0008-8846\(73\)90015-X](https://doi.org/10.1016/0008-8846(73)90015-X)
53. Gutteridge WA, Parrott LJ. A study of the changes in weight, length and interplanar spacing induced by drying and rewetting synthetic CSH (I). *Cem Concr Res.* 1976;6(3):357–66. [https://doi.org/10.1016/0008-8846\(76\)90098-3](https://doi.org/10.1016/0008-8846(76)90098-3)
54. Gartner EM, Kurtis KE, Monteiro PJM. Proposed mechanism of C-S-H growth tested by soft X-ray microscopy. *Cem Concr Res.* 2000;30(5):817–22. [https://doi.org/10.1016/S0008-8846\(00\)00235-0](https://doi.org/10.1016/S0008-8846(00)00235-0)
55. Gartner EM. A proposed mechanism for the growth of C-S-H during the hydration of tricalcium silicate. *Cem Concr Res.* 1997;27(5):665–72. [https://doi.org/10.1016/S0008-8846\(97\)00049-5](https://doi.org/10.1016/S0008-8846(97)00049-5)
56. Wagner C, Villmann B, Slowik V, Mechtcherine V. Capillary absorption of cracked strain-hardening cement-based composites. *Cement Concr Compos.* 2019;97:239–47. <https://doi.org/10.1016/j.cemconcomp.2018.12.017>
57. Castro J, Bentz D, Weiss J. Effect of sample conditioning on the water absorption of concrete. *Cement Concr Compos.* 2011;33(8):805–13. <https://doi.org/10.1016/j.cemconcomp.2011.05.007>
58. Beltzung F, Wittmann FH. Role of disjoining pressure in cement based materials. *Cem Concr Res.* 2005;35(12):2364–70. <https://doi.org/10.1016/j.cemconres.2005.04.004>
59. Mauro JC. Topological constraint theory of glass. *Am Ceram Soc Bull.* 2011;90(4):31–7. <http://search.ebscohost.com/login.aspx?direct=true&db=a9h&AN=60579574&site=ehost-live>
60. Gupta PK, Mauro JC. Composition dependence of glass transition temperature and fragility. I. A topological model incorporating temperature-dependent constraints. *J Chem Phys.* 2009;130(9):094503. <https://doi.org/10.1063/1.3077168>
61. Bauchy M, Micoulaut M. Atomic scale foundation of temperature-dependent bonding constraints in network glasses and liquids. *J Non-Cryst Solids.* 2011;357(14):2530–7. <https://doi.org/10.1016/j.jnoncrsol.2011.03.017>
62. Jennings HM. A model for the microstructure of calcium silicate hydrate in cement paste. *Cem Concr Res.* 2000;30(1):101–16. [https://doi.org/10.1016/S0008-8846\(99\)00209-4](https://doi.org/10.1016/S0008-8846(99)00209-4)
63. Hu C, Han Y, Gao Y, Zhang Y, Li Z. Property investigation of calcium-silicate-hydrate (C-S-H) gel in cementitious composites. *Mater Charact.* 2014;95:129–39. <https://doi.org/10.1016/j.matchar.2014.06.012>

64. Zhang Y, Ju JW, Zhu H, Yan Z. A novel multi-scale model for predicting the thermal damage of hybrid fiber-reinforced concrete. *Int J Damage Mech*. 2020;29(1):19–44. <https://doi.org/10.1177/1056789519831554>
65. Zhang Y, Yan Z, Ju JW, Zhu H, Chen Q. A multi-level micromechanical model for elastic properties of hybrid fiber reinforced concrete. *Constr Build Mater*. 2017;152:804–17. <https://doi.org/10.1016/j.conbuildmat.2017.07.024>
66. Zhang Y, Ju JW, Zhu H, Guo Q, Yan Z. Micromechanics based multi-level model for predicting the coefficients of thermal expansion of hybrid fiber reinforced concrete. *Constr Build Mater*. 2018;190:948–63. <https://doi.org/10.1016/j.conbuildmat.2018.09.030>
67. Tennis PD, Jennings HM. A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes. *Cem Concr Res*. 2000;30(6):855–63. [https://doi.org/10.1016/S0008-8846\(00\)00257-X](https://doi.org/10.1016/S0008-8846(00)00257-X)
68. Bahafid S, Ghabezloo S, Faure P, Duc M, Sulem J. Effect of the hydration temperature on the pore structure of cement paste: experimental investigation and micromechanical modelling. *Cem Concr Res*. 2018;111:1–14. <https://doi.org/10.1016/j.cemconres.2018.06.014>
69. Jennings HM, Kumar A, Sant G. Quantitative discrimination of the nano-pore-structure of cement paste during drying: new insights from water sorption isotherms. *Cem Concr Res*. 2015;76:27–36. <https://doi.org/10.1016/j.cemconres.2015.05.006>
70. Gajewicz AM, Gartner E, Kang K, McDonald PJ, Yermakou V. A ¹H NMR relaxometry investigation of gel-pore drying shrinkage in cement pastes. *Cem Concr Res*. 2016;86:12–9. <https://doi.org/10.1016/j.cemconres.2016.04.013>
71. Vandamme M, Ulm F-J, Fonollosa P. Nanogranular packing of C–S–H at substoichiometric conditions. *Cem Concr Res*. 2010;40(1):14–26. <https://doi.org/10.1016/j.cemconres.2009.09.017>
72. Constantinides G, Ulm F-J. The nanogranular nature of C–S–H. *J Mech Phys Solids*. 2007;55(1):64–90. <https://doi.org/10.1016/j.jmps.2006.06.003>
73. Zhang T, Zhu H, Zhou L, Yan Z. Multi-level micromechanical analysis of elastic properties of ultra-high performance concrete at high temperatures: effects of imperfect interface and inclusion size. *Compos Struct*. 2021;262:113548. <https://doi.org/10.1016/j.compstruct.2021.113548>

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Zhang Y, Liu H, Zhao C, Ju JW, Bauchy M. Deconstructing water sorption isotherms in cement pastes by lattice density functional theory simulations. *J Am Ceram Soc*. 2021;104:4226–4238. <https://doi.org/10.1111/jace.17829>