

NUMERICAL MODELLING OF THE WATER ISOTHERMS OF CEMENT PASTE: BRIDGING THE GAP BETWEEN THE CAPILLARY AND C-S-H GEL PORES

M. Zalzale (1), P.J. McDonald (2) K.L. Scrivener (1)

(1) Laboratory of Construction Materials, EPFL, CH-1015 Lausanne, Switzerland

(2) Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

Abstract

Despite the success of lattice Boltzmann models in simulating complex flows in a multitude of porous media, their application to cement paste remains rather limited. The main reasons appear to be the multi-scale nature of the porosity and the uncertain structure of the calcium silicate hydrate. In this work, a lattice Boltzmann effective media approach is extended from isothermal to non-ideal fluids. The liquid and vapour phases are linked by an equation of state and the interfaces between them are tracked automatically. The model allows the definition of multiple independent surface tensions (*i.e.* contact angles) between the fluid, C-S-H and solid phases. The novel part is the characterization of the C-S-H with effective transport and wetting properties. The model is used to calculate the water isotherms of a model cement paste composed of solids, nano-porous C-S-H and micron-sized capillary pores.

1. INTRODUCTION

The water desorption and adsorption isotherms quantify the liquid – vapour – solid interactions. They are obtained by plotting the water content *vs.* the relative humidity (RH) at mass equilibrium and constant temperature. The time to reach mass equilibrium depends on many factors including the specimen thickness and RH gradient and ranges from few months to well over a year [1]. Therefore, most measurements of water sorption isotherms are the results of several-year experiments [1].

Numerical modelling of the water sorption isotherms is a faster alternative but its application has been severely limited by the difficulties of tracking liquid - vapour interfaces in complex geometries. Additionally, the porosity of cement paste spans more than five orders of magnitude making the numerical simulations extremely expensive. These obstacles have restricted most of the research to homogenized models applied to one-dimensional elementary representative volumes [2].

Recently, Zalzale and McDonald [3] used the lattice Boltzmann method to calculate the permeability and water isotherms of model cement pastes. The broad features of the experimental curves were captured but the permeability was overestimated and the simulated

^{a)}Corresponding author. E-mail: m.zalzale@gmail.com

isotherms lacked breadth, mainly due to the absence of nanometre-sized gel pores in the microstructures. To overcome these problems, Zalzale *et al.* [4] included the C-S-H gel pores in permeability simulations by using an effective media approach where the C-S-H is described with effective transport properties. The simulated permeability span the whole range of experimental measurements and the results showed that the degree of capillary water saturation is a very plausible explanation for the large experimental scatter. The results also showed that the role of the weakly-permeable C-S-H, omitted in earlier modelling studies, is critical to determine the permeability at low capillary porosity or low degree of capillary water saturation.

In this work, the lattice Boltzmann effective media approach presented in [4] is extended to include multi-phase non-ideal fluids. The ability of the model is demonstrated by calculating the water isotherms of model cement paste composed of impermeable solid phase, micron-sized pores and nano-porous calcium silicate hydrate treated as effective media with effective transport and wetting properties.

2. METHODS

2.1. Free energy approach

The equilibrium properties of a one-component non-ideal fluid with no solid surfaces can be described by a Landau free energy functional [5, 6, 7]:

$$\Psi = \int_V dV \left[\psi(T, \rho) + \frac{\chi}{2} (\partial_\alpha \rho)^2 \right]. \quad (1)$$

In this case, $\int_V dV \rho$ is the total mass of a fluid of density ρ at temperature T and $\psi(T, \rho)$ is the free energy density of the bulk phase. The second term of the RHS of equation 1 describes the liquid – vapour interfaces and χ is a constant related to the surface tension between the liquid and vapour phases. This free energy can be incorporated in the lattice Boltzmann algorithm via a pressure tensor in the equilibrium functions that contains the equation of state of the fluid [8, 9]. More information about the pressure tensor and the equilibrium functions can be found in [10, 11].

2.2. Wetting dynamics

The contact angle Θ quantifies the wettability of a solid surface by a liquid via the Young’s equation [12]. Hence, the wetting dynamics can be incorporated in the lattice Boltzmann simulations by creating a boundary condition that reproduces Young’s equation in equilibrium [7]. The solid – liquid and solid – vapour surface tensions can be incorporated in the Landau free energy functional by the addition of a surface term [7] so that the total

free energy becomes:

$$\Psi = \int_V dV \left[\psi(\theta, \rho) + \frac{\chi}{2} (\partial_\alpha \rho)^2 \right] + \int_S dS \Phi(\rho_s) \quad (2)$$

where S is the surface bounding V . The surface free energy density $\Phi(\rho_s)$ depends only on the fluid density at the surface ρ_s . Following some assumptions described in [7, 10], the desired contact angle Θ can be imposed in the simulation by calculating the required wetting potential ϕ where $\Phi(\rho_s) = -\phi\rho_s$.

2.3. Effective wetting properties

In this part, we introduce “grey” C-S-H nodes and aim to characterize them with effective wetting properties (the effective transport properties were previously described in [3]). The presence of grey nodes in the lattice Boltzmann simulations creates an additional class of bulk nodes. Thus, the volume term of equation 1, originally including only the fluid nodes, should henceforth include the grey nodes. Moreover, the presence of grey nodes creates additional classes of surfaces. Accordingly, the equation characterizing the wetting properties, $\int_S dS \Phi(\rho_s)$, is extended to:

$$\sum_{\varsigma} \int_{S_{\varsigma}} dS_{\varsigma} \Phi_{\varsigma}(\rho_{\varsigma}) \quad (3)$$

where the sum is over the classes of surfaces ς . In the simplest case, the surfaces are:

$$\varsigma \subset \left\{ \begin{array}{l} \text{fluid over solid nodes} \\ \text{fluid over grey nodes} \\ \text{grey over solid nodes} \end{array} \right\} \quad (4)$$

and each one of them can be characterized with an independent wetting potential and thus an independent contact angle. Lastly, it is assumed that the grey nodes contribute an effective energy to the total free energy through their internal wetting via $\int_{V_{grey}} dV_{grey} \Phi_{grey}(\rho_{grey})$ where $\Phi_{grey}(\rho_{grey})$ characterizes the internal wetting of the grey nodes. The total free energy therefore becomes:

$$\Psi = \int_V dV \left[\psi(\theta, \rho) + \frac{\chi}{2} (\partial_\alpha \rho)^2 \right] + \sum_{\varsigma} \int_{S_{\varsigma}} dS_{\varsigma} \Phi_{\varsigma}(\rho_{\varsigma}) + \int_{V_{grey}} dV_{grey} \Phi_{grey}(\rho_{grey}). \quad (5)$$

3. WATER ISOTHERMS OF THE CAPILLARY AND GEL PORES

The lattice Boltzmann model presented above is demonstrated on a three-dimensional cement paste model microstructure generated with μic [13]. The structure comprises impermeable solids, weakly-permeable C-S-H and capillary pores. It is $30 \times 30 \times 15 \mu m^3$ in size, has a microstructural resolution of $0.5 \mu m$ and a capillary porosity of 9.2%.

To model adsorption and desorption using a lattice Boltzmann algorithm, the model cement paste is put in contact with a *source* of vapour at a controlled relative humidity (RH). All the capillary and gel pores are initially saturated with liquid and the source is initialized to 100% RH. Once the system is equilibrated, the RH of the source is progressively reduced and the system re-equilibrated at each RH step. Afterwards, the RH is progressively increased back to 100%. Finally, the water isotherms are obtained by plotting the average density in the fluid nodes as a function of the relative humidity.

Each C-S-H node was considered a grey node with an internal wetting potential. The fluid – solid wetting potential was set to $\phi_{fluid/solid} = 0.23$ in order to return a liquid – solid contact angle of $\Theta = 30^\circ$. The additional interface wetting potentials were set to $\phi_{fluid/C-S-H} = 0.23$ and $\phi_{C-S-H/solid} = 0.27$ in order to return contact angles of $\Theta_{fluid/C-S-H} = 30^\circ$ and $\Theta_{C-S-H/solid} = 0^\circ$, respectively.

Figure 1 shows the calculated desorption and adsorption isotherms for two different internal wetting potentials of the C-S-H. The mass of adsorbed fluid is normalized by the pore volume. The figure also shows the contribution of each of the two pore networks separately (capillary pores and C-S-H nodes). The calculated water isotherms have two main steps. The first corresponds to the capillary pores and the second to the smaller C-S-H gel pores. The capillary pores start emptying at 100% but the most considerable step happens between 90 and 75% RH. The relative humidities at which the main emptying and filling steps of the C-S-H gel pores occur depend on the internal wetting potential ϕ_{C-S-H} . Figure 1 also shows that, as expected, as ϕ_{C-S-H} is increased, the ability of the C-S-H to retain water during desorption and to attract water during adsorption is also increased.

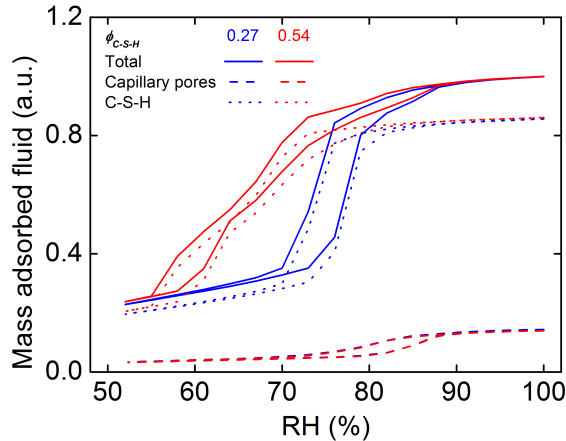


Figure 1: Model water isotherms of the capillary and gel pores of cement paste. The mass of adsorbed fluid is normalized the pore volume (capillary pores and C-S-H nodes). The internal wetting potential of the C-S-H is $\phi_{C-S-H} = 0.27$ or $\phi_{C-S-H} = 0.54$.

4. CONCLUSIONS

A lattice Boltzmann model was developed which allows successful:

- Description of the fluid with an equation of state and an implicit tracking of the liquid – vapour interfaces.
- Description of the fluid / solid boundaries with a wetting potential that defines the contact angle.
- Introduction of grey C-S-H nodes with *effective* transport and wetting properties. The internal wetting potential ϕ_{grey} is linked with the water isotherms of the C-S-H grey nodes. This wetting potential could ultimately be mathematically linked with a characteristic pore size.
- Description of the interactions that arise following the introduction of grey nodes: the fluid / grey and the grey / solid boundaries are characterized with wetting potentials that define the corresponding contact angles.

The model was tested and used to calculate the water isotherms of a 3D model cement paste. The results show:

- Water isotherms with two main steps: the first corresponding to the capillary pores and the second to the C-S-H gel pores.

Finally, the calculated water isotherms will be compared with experimental data in future work.

5. ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Union (FP7 / 2007-2013 grant 264448) and the UK EPSRC (grant EP/H033343/1).

REFERENCES

- [1] V. Baroghel-Bouny, Water vapour sorption experiments on hardened cementitious materials: Part i: essential tool for analysis of hygral behaviour and its relation to pore structure, *Cement and Concrete Research* 37 (2007) 414–437.
- [2] V. Baroghel-Bouny, M. Thiery, X. Wang, Modelling of isothermal coupled moisture - ion transport in cementitious materials, *Cement and Concrete Research* 41 (2011) 828–841.
- [3] M. Zalzale, P. J. McDonald, Lattice boltzmann simulations of the permeability and capillary adsorption of cement model microstructures, *Cement and Concrete Research* 42 (2012) 1601–1610.
- [4] M. Zalzale, P. J. McDonald, K. L. Scrivener, A 3d lattice boltzmann effective media study: understanding the role of c-s-h and water saturation on the permeability of cement paste, *Modelling and Simulation in Materials Science and Engineering* 21 (2013) 085016.

- [5] M. R. Swift, E. Orlandini, W. R. Osborn, J. M. Yeomans, Lattice boltzmann simulations of liquid-gas and binary fluid systems, *Physical Review E* 54 (1996) 5041–5052.
- [6] C. M. Pooley, H. Kusumaatmaja, J. M. Yeomans, Contact line dynamics in binary lattice boltzmann simulations, *Physical Review E* 78 (2008) 056709.
- [7] A. J. Briant, P. Papatzacos, J. M. Yeomans, Lattice boltzmann simulations of contact line motion in a liquid-gas system, *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* 360 (2002) 485–495.
- [8] A. Briant, A. Wagner, J. Yeomans, Lattice boltzmann simulations of contact line motion. i. liquid-gas systems, *Physical Review E* 69 (2004) 031602.
- [9] A. J. Wagner, C. M. Pooley, Interface width and bulk stability: Requirements for the simulation of deeply quenched liquid-gas systems, *Physical Review E* 76 (2007) 045702.
- [10] M. Zalzale, Water dynamics in cement paste: insights from lattice boltzmann modelling, Ph.D. thesis, Ecole Polytechnique Federale de Lausanne, thesis number 6292 (2014).
- [11] C. M. Pooley, K. Furtado, Eliminating spurious velocities in the free-energy lattice boltzmann method, *Physical Review E* 77 (2008) 046702.
- [12] T. Young, An essay on the cohesion of fluids, *Philosophical Transactions of the Royal Society of London* (1805) 65–87.
- [13] S. Bishnoi, K. L. Scrivener, *mic*: A new platform for modelling the hydration of cements, *Cement and Concrete Research* 39 (2009) 266–274.