Mesoscale Modeling of Sorption Hysteresis

Problem

The measurement of adsorbed water as a function of humidity is used to ascertain the specific surface area and pore size distribution of concrete, particularly during first drying. Although thermodynamically, the adsorbed water content is a unique function of humidity, experiments reveal large, repeatable hysteresis between drying and wetting. This hysteresis is a 60-year-old puzzle, which must be solved in order to predict drying shrinkage, creep and corrosion from first principles. The widespread notion of "pore collapse" has never led to a quantitative theory.

Approach

We adopt the hypothesis that hysteresis results from sorption and desorption in rigid nanopores[1] and develop a theory of "pore blocking" in concrete. We assume a bimodal distribution of pore radii with peaks around 2 nm and 10 nm, inferred from experiments. A pore exposed to the atmosphere will undergo a transition between almost empty (at most a single adsorbed layer) and full at a humidity given by the Kelvin equation, which states that smaller pores empty at lower relative humidities. However, a liquid-filled pore in the interior of a solid cannot empty until a clear (vapor-filled) path through other pores lies between it and the atmosphere. Thus the humidity at which a pore empties is determined by the size of the smallest pore along such a path, and is well below that at which a single large pore would empty. This is effectively the "ink-bottle effect" in a porous network. We calculate water content using a mean field model, accounting for the proportion of pores exposed to the atmosphere without imposing a specific geometrical structure.

Findings

This model can explain experimental adsorption-desorption results. It suggests that, in ground hardened cement paste and also in a 3-mm thick slice of concrete, a large fraction (up to one third) of large pores are directly linked to the atmosphere, and essentially all large pores can be reached by passing through a few small pores (approximately 4) in series.

More

Research presented by M.B. Pinson, a student in the CSHub, in collaboration with Profs. M.Z. Bazant and H.M. Jennings.

Impact

The model quantitatively predicts sorption hysteresis in hardened cement paste. By answering the basic question, "Where is the water?" it paves the way for bottom-up descriptions of diverse phenomena, such as shrinkage, creep and corrosion. The model can also be used to predict sorption/desorption isotherms and infer microstructural information.

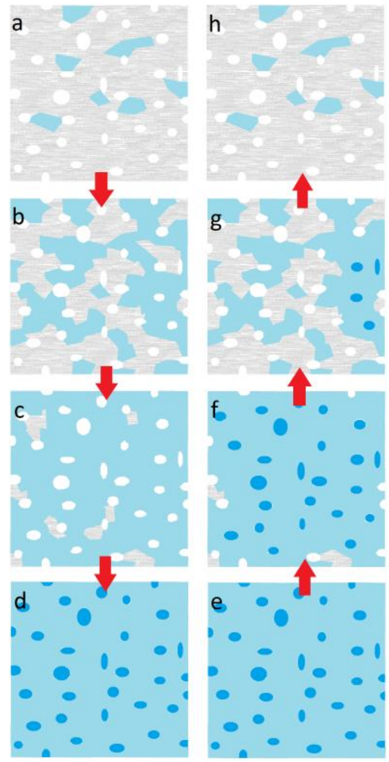
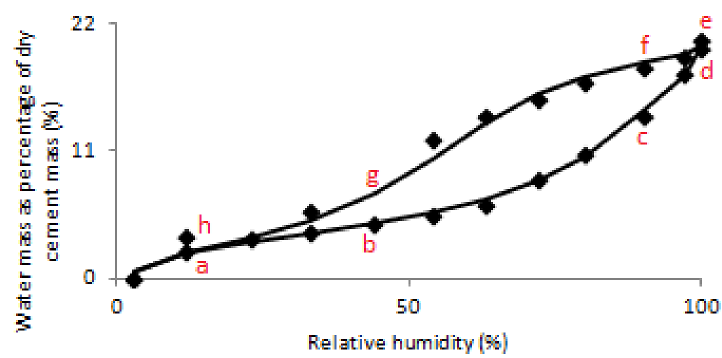


Figure 1: Illustration of sorption (left) and desorption (right) in concrete. The shaded grey area represents material containing small (~2 nm) gel pores, while the white holes represent larger (~10 nm) pores. As humidity is increased (left, *a* to *d*), the smaller pores fill up before the larger. As humidity is decreased (right, *e* to *h*), pores empty at the same humidity at which they were filled only if they are linked to the atmosphere through a path of empty pores. Each configuration corresponds to the letters in the figure below, which compares experimental data[2] for hardened cement paste (points) with the new model (solid curves).



1 M.Z. Bazant, Z.P. Bazant, *J. Mech. Phys. Solids* 60 (2012) 1660.
2 V. Baroghel-Bouny, *Cement Concrete Research* 37 (2007) 414.

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