

Water Isotherms, Shrinkage and Creep of Cement Paste: Hypotheses, Models and Experiments

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ABSTRACT

Cement paste has a complex mesoscale structure, and small changes in its pore network potentially causing large variation in measurements such as the water isotherm (also nitrogen). We deconvolute the water isotherm with the help of advanced computational techniques, hypotheses, and a re-examination of published data. The pore system is divided into four different categories, each containing water with its own physical properties. By viewing the highly interdependent roles of water in each of the pore categories as a system, new insights are gained regarding possible mechanisms that control drying shrinkage and creep, and experimental strategies for verification.

BACKGROUND

While it is widely accepted that mobile and evaporable water can be divided into several distinct pore categories, (i.e. interlayer, gel, capillary), each of which plays an identifiable role that controls properties, there remains significant confusion. Over the years a standard approach to characterizing porous solids, analysis of sorption isotherms, has been applied to cement paste without widely accepted interpretation. The goal, however, of translating information from the water isotherm to a deep understanding of microstructure has not been realized in spite of many decades of research effort. Some of the reasons for this include:

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1. Isotherms have a strong dependence on adsorbate: For example BET surface area using nitrogen varies from 20 – 60 m²/g while using water gives about 200 m²/g. This paper will only discuss the water isotherm.
2. The shape of the isotherm depends strongly on specimen preparation. The BET surface area for nitrogen is strongly dependent on method of drying. The water isotherm has an unusual hysteresis at relative pressures below 50%, and the shape of this hysteresis depends on specimen preparation.
3. Drying shrinkage strain exhibits a very unusual hysteresis referred to as the “upside down” behavior (Jennings) and there is no relaxation of the bulk sample due to an unstable meniscus.

To address these issues we analyze each pore category with the goal of identifying specific roles and influences on drying shrinkage, and implications for creep. These categories are dictated by the huge range of pore size in cement paste, ranging from sub nanometer to micron, or a span of 10⁴, and noting that the physics of water in different size pores depends on size. It is also noteworthy that all of the categories are already discussed in the literature, and we propose here only to consider them together in a new way. The pore system in C-S-H gel, the glue that contains all of the smallest pores in cement paste, has been divided into several categories, depending on size, but separated by physical properties of contained water and dissolved ions, and discussed relationships to drying shrinkage and creep. Specifically the role of the small gel pore, or the pore spaces where the particles contact each other, are of particular interest. These categories are shown in Fig. 1.

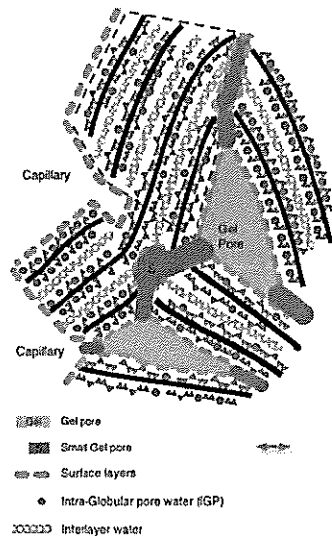


Fig. 1. Schematic of nanometer-scale calcium-silicate-hydrate (C-S-H) gel structure, and associated locations for water. Red triangles are the silicate tetrahedra within the silicate chains, thick black lines are calcium oxide layers within the solid C-S-H. With the simplification that the water content inside the solid C-S-H particles is constant under most conditions, the model focuses on the water in gel pores, the size and volume of which has been discussed elsewhere. There are three identifiable pore types outside the solid C-S-H: 1) Small open spaces between particles (gel pores), 2) defect regions where solid C-S-H particles come into imperfect contact (small gel pores), and 3) much larger capillary pores. Arrow is one nm.

THE PARTICLES AND CONTAINED WATER

We here treat the water inside of the particles separately, with a hypothesis that greatly simplifies the water isotherm. From the perspective of the colloid model there are two types of water within the particles. The hypothesis is that this water (and associated properties of the particles) remains constant as long as the relative pressure outside of the particles is maintained above about 20% (CMI and CCR). The only way of testing this hypothesis (isolating the behavior of the particles of C-S-H independent of the gel pores outside of the particles) is with accurate detailed models. Starting with the model (Pellenq) and Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) an isotherm for the particles can be simulated as shown in Fig 2.

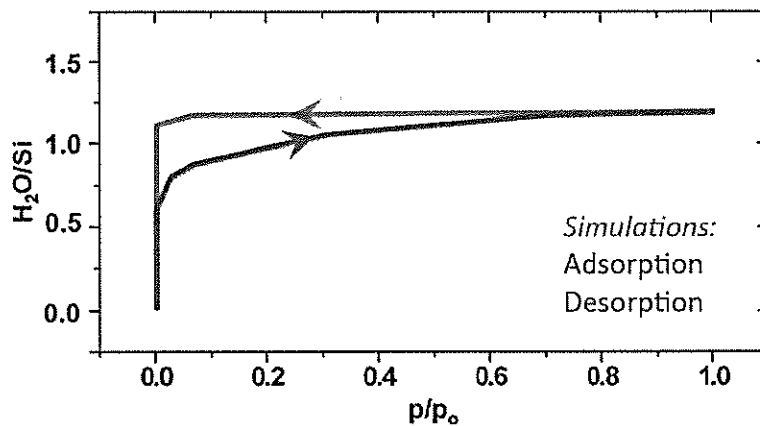


Fig. 2. Simulated isotherms, predicted from atomistic simulations of single C-S-H particles equilibrated sequentially over a range of partial pressures. This desorption/adsorption hysteresis represents loss and gain of intraparticle water from the C-S-H particle, equilibrated initially at 100% RH (i.e., $p/p_0 = 1.0$). This sharp transition in water content upon desorption in predicts a water mass loss of 7%.

As can be seen from this simulation water does not leave the particle until very low relative pressure, and it also only partially re-enters the particle resulting in a low-pressure hysteresis associated only with the particles. This provides an important simplification when interpreting the water isotherm, but it also suggests that if the pores outside of the particles are of interest, the isotherm should be measured on samples that have not been dried below about 20%. Thus we have proposed that one of the obvious unusual features of the water isotherm for cement paste, the low pressure hysteresis, is addressed by assignment to evaporable water inside the particles, which does not leave until very low pressures. Fig 3 shows

isotherms for Vycor glass and cement paste. The dotted arrow in Fig 3, suggests a possible adsorption path from 20% rh. The hypothesis that the particles remain constant during drying and under creep is further discussed below.

THE GEL PORES: TWO CATEGORIES

Two important pore spaces for water are identified in the gel porosity: 1) the irregular spaces created by mis-orientation of contacting particles (small gel pores in Fig 1.) and 2) the pores formed between the packed particles in the LD and HD arrangements. Water in each of these pore spaces has a unique influence on drying shrinkage.

A striking feature of drying shrinkage of cement paste is that, unlike other materials such as Vycor glass, the strain for adsorption is always below(smaller) than for desorption, as shown in Fig 3: we refer to this as the “upside down” behavior. This means that in cement paste, the extra water present during desorption reduces

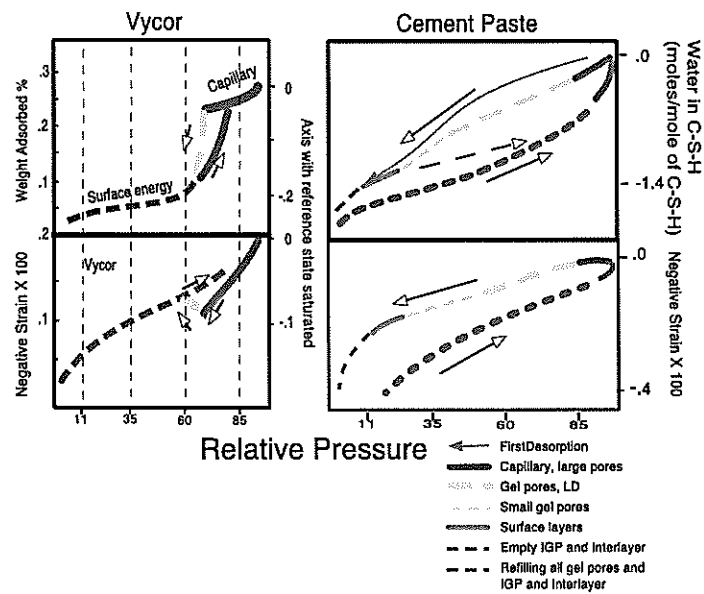


Fig. 3. Water isotherms and strains of Vycor and cement paste. The isotherm for cement paste exhibits a distinct hysteresis over the full relative pressure range. Changes in the packing of particles can be seen between first and second drying. The strain for cement paste is unusually always less on drying (reference is full saturation) than on wetting, referred to here as the “upside down” behavior. There is no evidence of relaxation (reduced strain) when a meniscus becomes unstable, as there is with Vycor glass.

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instead of increases shrinkage. This, coupled with the observation that there is almost no evidence for relaxation (expansion) of cement paste at intermediate relative pressures when water is lost from the structure, suggests that there is some sort of overriding expansive pressure: a disjoining pressure.

Disjoining pressure is the origin of swelling in clays such as montmorillonite and certainly must be an important contribution to the "upside down" behavior of cement paste. It is the result of water in tightly confined spaces, and in the case of water hydrophilic surfaces that tend to attract water, it pushes the surfaces apart. The disjoining pressure is defined by:

$$P_{disj} = P_{\text{pore pressure in confined space}} - P_{\text{bulk}}$$

The pore pressure in the bulk is ambient when the pores are saturated. However, for a partially saturated material at higher pressures the pore pressure is dictated by capillary pressure. For a partially saturated material, the bulk pressure is dictated by capillary pressure. Agreement with experiment has been achieved with the following expression for the disjoining pressure in the pores:

$$P_{disj} = -S \left(\frac{e}{\epsilon} \right)$$

where S is a function of the surface tensions between liquid, solid and vapor (always positive), e is the thickness of the adsorbed layer (a function of relative pressure), and ϵ is approximately equal to interatomic distance (~ 0.2 nm). The disjoining pressure increases with relative pressure, interpreted here as the particles being pushed apart as the relative pressure increases. The above equations are simple expressions of an equilibrium state, so what causes the hysteresis? This question has been explored by two modeling approaches.

The first is a thermodynamic approach (discussed in more detail in this conference) that takes into account Langmuir adsorption, and Kelvin condensation. Adsorption and desorption are simulated for a model system with a range of pore sizes, and importantly, during desorption the larger pores in the interior are blocked from completely emptying if they are connected to the surface only through smaller pores. This mechanism is known as pore blocking. During adsorption the pores fill under more or less equilibrium conditions. A schematic of a result is shown in Fig 4. This causes the adsorption branch to be below the desorption branch. Fitting the isotherm produces a model pore system, which characterizes the paste, and provides quantitative parameters that can be used to explore relationships to properties.

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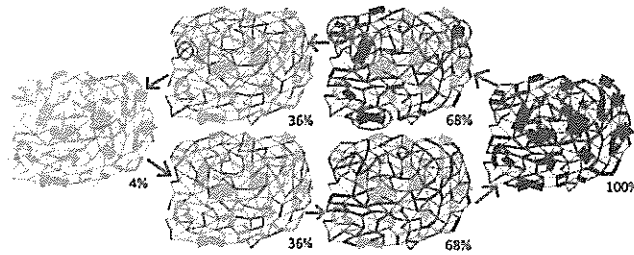


Fig. 4. Schematic illustration of desorption and adsorption of water from a model C-S-H pore system. Blue links represent filled pores, gray links represent mostly empty pores. The width of a link is proportional to pore radius. During desorption (right to left along top figures) some pores remain full below their equilibrium r_h value, due to the absence of a continuous path of empty pores leading to the exterior. Some examples of such pores are circled. During adsorption (left to right along bottom figures) some interior pores do not fill because of pore blocking, resulting in hysteresis.

The second approach combines a model that simulates the structure of packed C-S-H particles (Masoero), with a model that simulates the water in the pore system using a mean field density functional analysis of average density of water in the pore system. During desorption water is emptied but some interior pores remain blocked, while during adsorption the water re-enters all of the pores under more or less equilibrium relative pressures (shown in Fig 5). Again, the hysteresis is captured.

It is important to note that neither of these models (not shown here) captures a low pressure hysteresis. Again, this suggests that the low pressure hysteresis can be assigned to water inside of the particles.

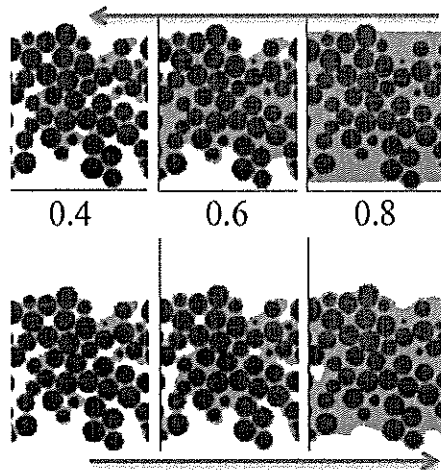


Fig. 5. Cross-sectional snapshots of the simulated particles (black) during desorption and adsorption of water modeled by density functional theory. The important point is that the pores contain more water during desorption than during adsorption.

REVERSIBLE DEFORMATION: UPSIDE DOWN

In the following discussion it is important to note that the reference for strain is saturation. As a consequence, the strain has always a negative value. Both experiment results (isotherm) and the models described above that capture the hysteresis of the water isotherm, clearly show that the water content of the gel pores at any particular relative pressure is higher during desorption than during adsorption, primarily because of pore blocking during desorption.

This increased percentage of full pores, coupled with disjoining pressure that is a direct function of water content in the gel pores, providing a swelling pressure, explains the "upside down" behavior of the strain, compared to Vycor glass. Disjoining pressure first documented for colloids and is responsible for swelling, it must be active in the small gel pores, pushing the particles apart. These contact regions are analogous to grain boundaries and probably represent regions of high energy due to lattice mismatch and very imperfect structure. If the value of disjoining pressure depends on the water content of the adjacent pores, it follows that the pressure will be greater during desorption. In carefully controlled experiments (Beltzung) the disjoining pressure is greater during desorption (almost constant) than during adsorption. During desorption the capillary underpressure, therefore, causes shrinkage with a constant disjoining pressure during desorption, and re-establishing disjoining pressure causes swelling during adsorption when the capillary has not been re-established.

Taking the particle nature of C-S-H to be an important part of its character, there must be significant lattice mismatch at the contact regions, creating the small gel pores. This region is therefore a good candidate for the development of relatively high eigenstress, akin to "microprestress" (Bazant). Combining this structural description of specific regions of water in the pores with poromechanics formulations could allow capturing the shrinkage down to a relative pressure of 50% directly. Below 50% the small gel pores and surface layers only a few molecules thick cause shrinkage by mechanisms other than pore pressure, including surface tension. Below 20% the particles start to empty, which causes them to shrink.

IRREVERSIBLE DEFORMATION

Analysis of neutron scattering experiments (Thomas) has shown that the particles do not change in composition when dried and resaturated, but there is strong evidence for rearrangement of particles during first drying and rewetting. Furthermore, as implied above, the contact regions between the particles is likely to be the point where large deformations, like relative sliding can occur. High positive relative pressures within these small gel pores will assist this process, consistent with the observation that, at constant humidity, creep is highest at high relative pressures.

The region of particle contact has a direct analogy to grain boundaries and therefore to grain boundary sliding in other materials. It is a likely location where stress could be reduced over time (years) with a commensurate reduction in creep under load, or the aging term not associated with increased degree of reaction (Bazant).

CONCLUSIONS

The following conclusions are drawn from models, in consort with hypothesis and experiments.

1. A case has been made that the low pressure hysteresis of the water isotherm is due to water leaving the particles and not reversibly re-entering. This provides an important simplification in that the influence of water on shrinkage and creep is mainly due to gel pores. Subtracting isotherm due to particles may reduce the isotherm to a more conventional form.
2. The high pressure hysteresis is due primarily to pore blocking, with water not able to empty from interior pores when the only channel to the exterior has smaller passages than the pore being emptied.
3. The "upside down" strain on drying and rewetting is due to disjoining pressure that is a direct function of the water content. This prevents deformation on drying. This reduces considerably the deformation on drying.
4. Reversible strain on drying can be modeled by poro-mechanics down to a relative pressure of 50%.
5. Irreversible strain is due to rearrangement of particles and not to deformation of the particles.
6. Aging may be due to an increased bond strength with passage of time where particles touch at the small gel pores. Like grain boundaries this may be a region of high energy – or adopting the terminology of Bazant et al. (Bazant), a region of micro-prestress, that relaxes by local rearrangement with time.

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