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## Interpretation of Full Sorption-Desorption Isotherms as a Tool for Understanding Concrete Pore Structure

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### ABSTRACT

Sorption isotherms are frequently used to characterize the structure of porous materials such as cement. Their interpretation has been somewhat hindered by the large hysteresis observed between the adsorption and desorption processes. Here we model the hysteresis due to pore blocking, whereby water condensed in small pores prevents propagation of a vapour interface into the pore structure, trapping water condensed in larger pores in a metastable state. The model identifies the adsorption isotherm as more useful in determining the pore size distribution. Additionally, and of particular interest, it provides a way of calculating an additional structural parameter, quantifying the exposure of mesopores (gel pores) to the surrounding atmosphere. This exposure is higher for samples with higher water to cement ratio, suggesting that it is mediated by capillary pores. The model also allows calculation of the connectivity of the pore structure, although the intertwined influences of exposure and connectivity make the latter difficult to interpret.

### INTRODUCTION

The measurement of sorbed mass as a function of the partial pressure of the sorbate has long been used to gain information about the structure of porous materials (Pierce 1953; Shull 1948). In particular, adsorption data at low partial pressure are used to calculate internal surface area (Emmett and Brunauer 1937; Harkins and Jura 1944). One difficulty of this approach is that significant hysteresis may be observed in the measured quantity of water in the pores when increasing and decreasing humidity. This hysteresis has caused some confusion in the study of the pore structure of cement. Physical changes in the cement structure have been identified as one cause (Feldman and Sereda 1968; Jennings 2000), but these are expected to be significant only if the cement is dried below 20% relative humidity (Jennings 2008), leaving the bulk of the hysteresis at higher humidity unexplained. The retention of condensed water in a metastable state in large pores located behind smaller pores (Espinosa and Franke 2006; Quenard and Sallee 1992), and the effect of disjoining pressure and

discreteness in the smallest pores (Bažant and Bazant 2012), have also been identified as contributing to the hysteresis. Disentangling each of these effects requires an accurate understanding of each process, including a mathematical model. Here we present a model of the hysteresis caused by pore blocking.

## SORPTION MODEL

**Adsorption.** We consider both the adsorption of water on the internal surfaces, and the filling of pores through capillary condensation. Surface adsorption is treated by the Langmuir equation (Langmuir 1917):

$$\theta = \frac{\alpha h}{1 + \alpha h}, \quad (1)$$

where  $\theta$  is the proportion of the surface that is covered by water molecules,  $h$  is the relative humidity, and  $\alpha$  is a constant related to the energy of adsorption. The adsorbed mass is then directly proportional to  $\theta$ .

Capillary condensation in a pore occurs when the humidity is sufficiently high that the free energy cost of filling the pore is outweighed by the decrease in water surface energy that results from condensing water and forming a curved meniscus. Assuming the system can attain thermodynamic equilibrium, capillary condensation occurs at a humidity given by the Kelvin equation (Feldman and Sereda 1968):

$$\ln h = -\frac{2\gamma v}{rkT}. \quad (2)$$

Here  $\gamma$  is the surface tension of water,  $v$  is the molecular volume,  $k$  is the Boltzmann constant and  $T$  is temperature.  $r$  is the radius of curvature of the meniscus separating the condensed water from the vapour: if the meniscus lies perpendicular to the axis of a cylindrical pore and water perfectly wets the pore wall, then  $r$  is the effective radius of the pore. The thickness of the adsorbed layer must be subtracted from the physical radius of the pore, in order to obtain the effective radius for use in the Kelvin equation.

Of course, the complexity of the pore structure of concrete means that we cannot assume that every pore is cylindrical and fills through the propagation of a meniscus along its axis at the equilibrium filling humidity. An alternative assumption, still applicable to cylindrical pores, is that filling instead occurs in the radial direction, beginning at the adsorbed layer on the pore wall and proceeding inwards. In this case, filling requires not only that the filled state is at lower free energy than the empty, but that increasing the thickness of the adsorbed layer on the pore wall monotonically decreases free energy (Celestini 1997). In this case, the relationship between radius and filling humidity is (Cohan 1938)

$$\ln h = -\frac{\gamma v}{rkT}$$

Since the humidity at which a pore will fill depends primarily on its radius  $r$ , which we can think of as a measure of the volume to surface area ratio in the case of non-cylindrical pores, we can relate these quantities using the general relation

$$\ln h = -\frac{f\gamma v}{rkT}, \quad (3)$$

where  $f$  is a parameter related to the shape of the pore and the presence or absence of full neighbouring pores to nucleate condensation. We adopt the simple approximation that  $f$  varies from 1 at 0% relative humidity, when there are no full pores, to 2 at 100% relative humidity, when all the mesopores of concrete are full.

Using equations 1 and 3, a measured isotherm can be interpreted in terms of a total surface area and a distribution of pore radii.

**Desorption.** The desorption process is more complicated than adsorption. In order to empty a pore of its capillary condensed water, it is necessary that the humidity drop below that at which the full and empty states would be in thermodynamic equilibrium, as given by equation 2. Additionally, one of the following criteria must be fulfilled:

- 1) the pore is in contact with the vapour,
- 2) the humidity is low enough for cavitation (spinodal decomposition) to occur (approximately 35%), or
- 3) the vapour phase is nucleated, such as by a heterogeneous surface.

We neglect the latter processes, and focus on the propagation of the vapour phase through the pore network. The model of desorption should thus be valid in the upper and middle parts of the humidity range. To allow interpretation of sorption at low humidity, the model will need to be extended to account for cavitation (Bazant and Bazant 2012).

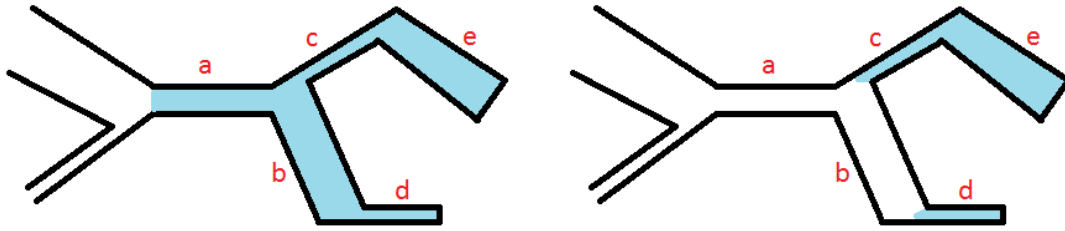
When the humidity to which a sample of cement paste is exposed is increased to 100%, water condenses in all the mesopores. If the humidity is then decreased, some of these pores are already exposed to the vapour, and hence able to empty once equation 2 is satisfied. We define  $Q_0$  to be the fraction of pores that are directly exposed in this manner.

As humidity is further decreased, pores begin to empty. The emptying of pores results in the exposure of additional pores to the vapour phase. We model this process of gradual exposure of pores by relying on two important assumptions. The first is that of a mean field model, that the properties of a particular pore's neighbours (namely their radii, and whether they are exposed to the vapour via another path) are statistically the same as the properties of all pores, independent of the properties of the central pore. The second is that the pore network can be modeled as a network of cylindrical pores of equal length and connectivity, independent of radius. The connectivity  $z$  is defined to be the number of pores exposed to the vapour by emptying a single pore, some of which may already be exposed. The modeled structure is then something like a Bethe lattice with coordination number  $z + 1$  (Stauffer and Aharony 1992).

Using the above assumptions, we define  $q(h)$ , the fraction of pores that would be empty at true thermodynamic equilibrium at a humidity  $h$ , and  $Q$ , the fraction of pores exposed to the vapour phase. These quantities are related through the differential equation

$$\frac{dQ}{dq} = Qz(1-Q) + \frac{dQ}{dq} qz \frac{1-Q}{1-Qq}. \quad (4)$$

The two terms on the right hand side correspond to pores becoming exposed as other pores empty for each of two different reasons. The first term accounts for exposed pores emptying as their emptying humidity is reached, the second term for blocked pores emptying as they are exposed to the vapour. Figure 1 gives a schematic illustration of these two processes. Note that an empty pore means a pore emptied of capillary condensed water: it still contains adsorbed water layers on its walls.



**Figure 1. A schematic diagram illustrating two reasons a pore can empty during the desorption process. Between the left and right sections, the humidity was decreased below the value at which pore a, already exposed to the vapour, empties. Pore b empties immediately on being exposed to the vapour, as the humidity is already below the value at which emptying becomes thermodynamically favourable. Pores c and d remain full due to local thermodynamics, while pore e remains full since it is not in contact with the vapour.**

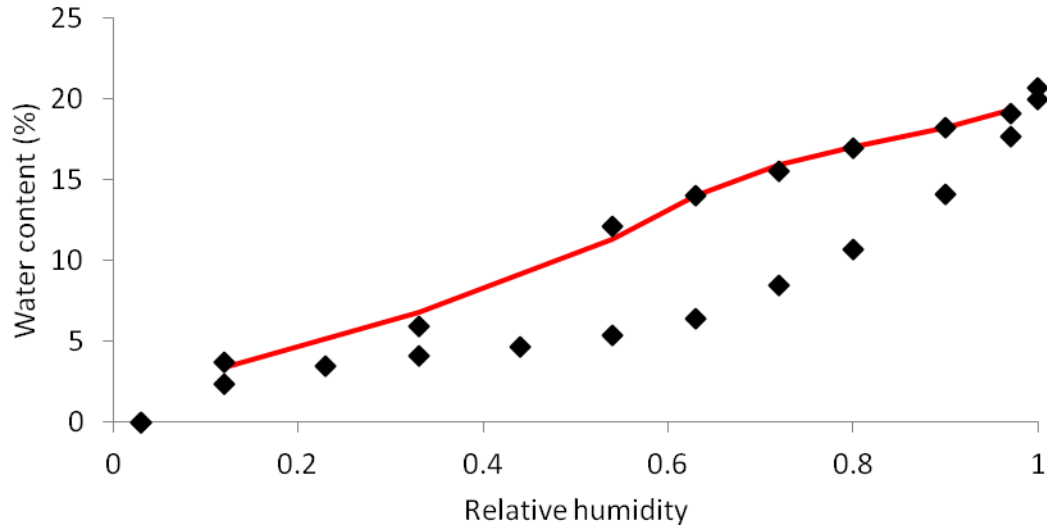
Equation 4, with the initial condition  $Q(q=0) = Q_0$ , can be solved numerically. The product  $Qq$  is the proportion of pores that are actually empty. Since  $q$  depends on humidity, as described by equation 2, the solution  $Q(q)$  allows calculation of the quantity of adsorbed water as a function of humidity.

**Application to experimental data.** We applied the model described in this section to published adsorption and desorption isotherms for concrete and hardened cement paste samples. After calculating the pore size distribution using the adsorption isotherm, we used a least squares fit to find the value of  $Q_0$  and  $z$  for each sample. Since many factors, such as the curing and drying procedures and humidity control, can influence sorption measurements, comparisons between different experiments from a single set are most useful. Here we focus on a recent set of experiments (Baroghel-Bouny 2007) on concrete and cement with a range of water to cement ratios (W/C).

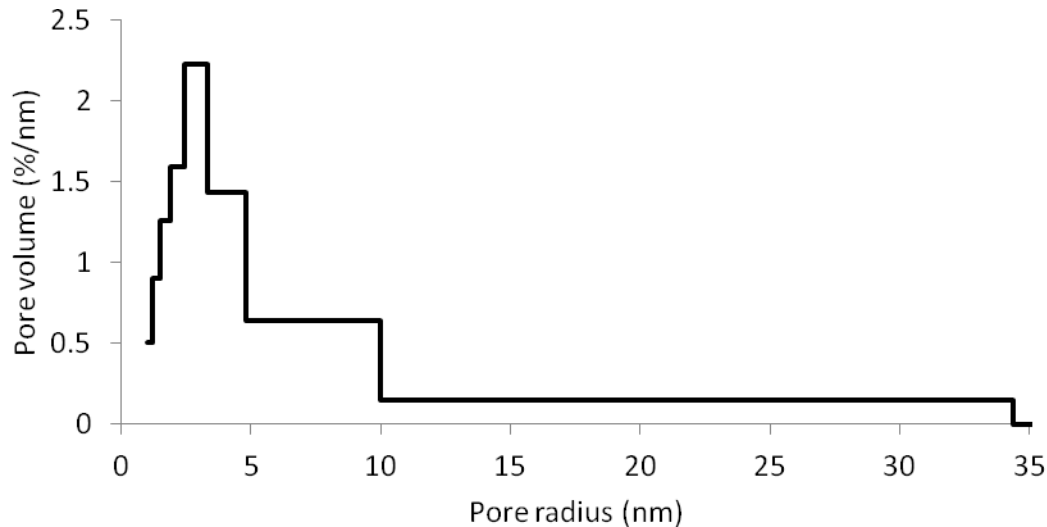
## RESULTS AND DISCUSSION

A typical example of the comparison between experimental results and the best fit of the model is shown in figure 2. The experimental adsorption isotherm is used to

determine the pore size distribution, which is shown in figure 3, while the mean field model of pore blocking is fit to the experimental desorption isotherm to determine  $Q_0$  and  $z$ . The hardened cement paste sample had W/C of 0.45 (Baroghel-Bouny 2007).



**Figure 2. Water content as a function of relative humidity. Points are experimental (Baroghel-Bouny 2007). The experimental adsorption data are used as a direct input to determine the pore size distribution. The red line is the prediction of the percolation model of this work, with two parameters  $Q_0$  and  $z$ .**

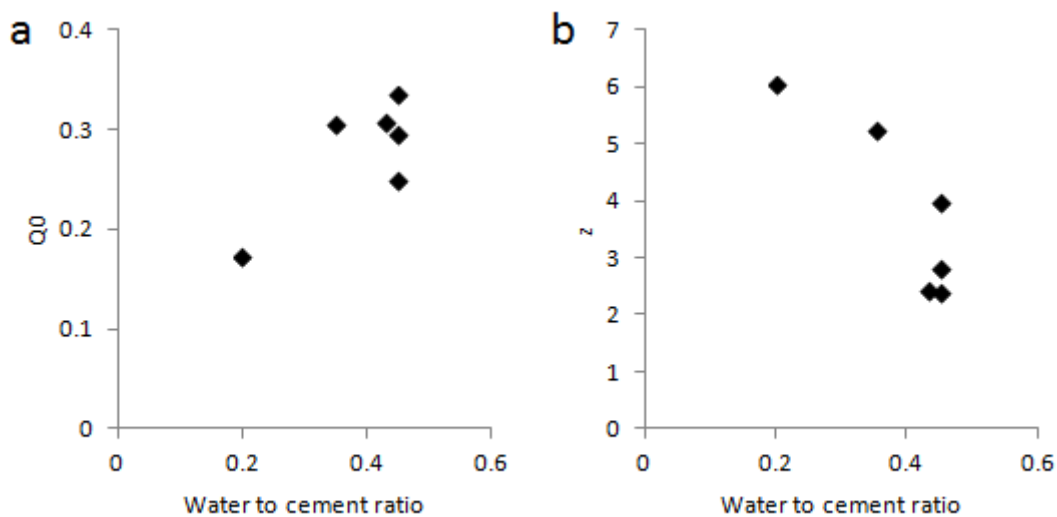


**Figure 3. Volume of pores as a function of pore radius, based on the interpretation of experimental adsorption data (Baroghel-Bouny 2007).**

Figure 4a shows calculated values of  $Q_0$  as a function of W/C. In general,  $Q_0$  increases as W/C increases. This agrees with what may be expected: higher W/C

leads to a greater quantity of capillary pores (Powers 1958). This provides more large pores that will be empty on desorption even at very high humidity, which increases the probability that a mesopore in the cement structure is in contact with the vapour.

Figure 4b shows  $z$  as a function of W/C:  $z$  decreases as W/C increases. This does not necessarily imply that a sample with higher W/C has lower connectivity. Instead, it is likely to be a result of the variation of  $Q_0$ . Higher  $Q_0$  means that more of a particular pore's neighbours are already exposed before that pore empties, decreasing the apparent value of  $z$  even if true connectivity is the same. The model takes this into account, but only through a mean field method. The mean field method will be insufficient if there is substantial geometric dependence of exposure to the vapour, as can be expected if this exposure is mediated by capillary pores.



**Figure 4. (a)  $Q_0$  and (b)  $z$  calculated by applying the model of this paper to experimental results (Baroghel-Bouny 2007), as a function of water to cement ratio.**

## CONCLUSIONS AND APPLICATIONS

The method outlined here allows additional information to be obtained from sorption isotherms than was previously possible. In addition to the pore size distribution, the method quantifies the exposure of pores to the surroundings (a quantity associated with capillary pore abundance), and the connectivity of the mesopore network. These pieces of information will be of considerable use to the prediction of the properties of a concrete sample. For instance, drying shrinkage behavior is dependent on forces in the mesopores, which depend on pore size and water content (Collins and Sanjayan 2000). Also, permeability is higher for concrete with higher porosity, larger pores and greater pore connectivity (Marsh et al. 1985). The method presented here thus allows the comparison of the suitability of different concretes to a particular application.

## REFERENCES

- Baroghel-Bouny, V. (2007). "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(3), 414–437.
- Bazant, M. Z., and Bažant, Z. P. (2012). "Theory of sorption hysteresis in nanoporous solids: Part II Molecular condensation." *Journal of the Mechanics and Physics of Solids*, 60(9), 1660–1675.
- Bažant, Z. P., and Bazant, M. Z. (2012). "Theory of sorption hysteresis in nanoporous solids: Part I." *Journal of the Mechanics and Physics of Solids*, 60(9), 1644–1659.
- Celestini, F. (1997). "Capillary condensation within nanopores of various geometries." *Physics Letters A*, 228(1-2), 84–90.
- Cohan, L. H. (1938). "Sorption hysteresis and the vapor pressure of concave surfaces." *Journal of the American Chemical Society*, 60(2), 433–435.
- Collins, F., and Sanjayan, J. G. (2000). "Effect of pore size distribution on drying shrinking of alkali-activated slag concrete." *Cement and Concrete Research*, 30(9), 1401–1406.
- Emmett, P. H., and Brunauer, S. (1937). "The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts." *Journal of the American Chemical Society*, 59(8), 1553–1564.
- Espinosa, R. M., and Franke, L. (2006). "Inkbottle Pore-Method: Prediction of hygroscopic water content in hardened cement paste at variable climatic conditions." *Cement and Concrete Research*, 36(10), 1954–1968.
- Feldman, R. F., and Sereda, P. J. (1968). "A model for hydrated Portland cement paste as deduced from sorption-length change and mechanical properties." *Matériaux et Construction*, 1(6), 509–520.
- Harkins, W. D., and Jura, G. (1944). "Surfaces of Solids. XIII. A Vapor Adsorption Method for the Determination of the Area of a Solid without the Assumption of a Molecular Area, and the Areas Occupied by Nitrogen and Other Molecules on the Surface of a Solid." *Journal of the American Chemical Society*, 66(8), 1366–1373.
- Jennings, H. M. (2000). "A model for the microstructure of calcium silicate hydrate in cement paste." *Cement and Concrete Research*, 30(1), 101–116.
- Jennings, H. M. (2008). "Refinements to colloid model of C-S-H in cement: CM-II." *Cement and Concrete Research*, 38(3), 275–289.



- Langmuir, I. (1917). "The constitution and fundamental properties of solids and liquids. Part I. Solids." *Journal of the Franklin Institute*, 38(11), 2221–2295.
- Marsh, B. K., Day, R. L., and Bonner, D. G. (1985). "Pore structure characteristics affecting the permeability of cement paste containing fly ash." *Cement and Concrete Research*, 15(6), 1027–1038.
- Pierce, C. (1953). "Computation of pore sizes from physical adsorption data." *The Journal of Physical Chemistry*, 57(2), 149–152.
- Powers, T. (1958). "Structure and physical properties of hardened Portland cement paste." *Journal of the American Ceramic Society*, 41(1), 1–6.
- Quenard, D., and Sallee, H. (1992). "Water vapour adsorption and transfer in cement-based materials: a network simulation." *Materials and Structures*, 25(9), 515–522.
- Shull, C. G. (1948). "The determination of pore size distribution from gas adsorption data." *Journal of the American Chemical Society*, 70(4), 1405–1410.
- Stauffer, D., and Aharony, A. (1992). *Introduction to Percolation Theory*. Taylor & Francis, Washington, DC.