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Discussion

A discussion of the paper "A multi-technique investigation of the nanoporosity of cement paste" by Hamlin M. Jennings, Jeffrey J. Thomas, Julia S. Gevrenov, Georgios Constantinides and Franz-Josef Ulm ☆

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The authors have used three innovative techniques to investigate the nanoporosity of cement paste. The arguments presented are based on a proposed quantitative colloidal model of C–S–H. The paper is generally of high quality. There are however some contentious issues that merit discussion.

Roper is cited (in Ref. [15]) as reporting the first equilibrium (length and weight change) drying shrinkage measurements for cement paste. In fact, the original water sorption length change isotherm data obtained under fully equilibrium conditions were published by Feldman and Sereda in 1964 [1,2]. This work included detailed length versus weight change curves with some similarities to the data provided by Jennings et al. Important differences, however, occur at humidities below 7% RH. There are large irreversible length changes in the region of partial pressure, $0<p/p_s<0.07$. Rewetting and second drying followed by additional cycling results in very large length change differences after each cycle due likely to a continuous structural collapse process [3]. There is, in effect, considerable hysteresis at the low humidity end of the curves. Therefore the statement that "all of the differences between first and second drying occur above 33% RH" and the size of the pores taking part in the 'emptying' process is questionable.

The authors unfortunately did not obtain equilibrium drying data below 7% RH. Further their use of specimens with least dimension of 5 mm is problematic. Equilibrium times for cement paste at low humidities range from several weeks to several months for specimens about 1 mm thick. The specimens that were used are likely not fully equilibrated and the resultant behavior may be influenced by moisture gradients. Further significant length change can occur when the weight change is minimal i.e. weight change can give a false notion of equilibrium with respect to length change.

Another contentious issue is the existence of any significant number of pores a few nanometers (e.g. 1–3 nm) in diameter in pastes prepared at $w/c=0.50$. Helium atoms can penetrate virtually all the pore space in these systems. Pore volumes obtained using helium as a 'nanoprobe' are (at this w/c ratio) equivalent to those obtained using other displacement fluids e.g. methanol [4], the implication being that nanopores in this size range and in any significant number are probably not present. The C–S–H interlayer region (having about a 1.1 nm separation distance),of course, can not be considered as pore space. In addition, the 5 nm globules forming the fractal regions of the proposed colloidal model of C–S–H, would necessarily be limited to being composed of C–S–H with only 2 or 3 layers. This is doubtful.

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