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Cement and Concrete Research 37 (2007) 1374–1375
Cement and Concrete Research

Discussion

# Reply to discussion of the paper "A multi-technique investigation of the nanoporosity of cement paste"

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Received 18 June 2007; accepted 25 June 2007

We appreciate the insightful comments of Beaudoin and Alizadeh regarding our recent paper [1]. The authors are correct in noting that the water sorption length change isotherms published by Feldman and Sereda in 1964 [2,3] predate the work of Roper [4]. However, Feldman and Sereda reported data for the first rewetting and second drying, whereas Roper was the first to report equilibrium length and weight change data during first drying. Our paper is focused on modeling the irreversible changes that occur on first drying, so Roper's paper was the first relevant publication.

The authors also correctly point out that there are important irreversible length changes that occur below 7% RH, which was the lower limit of our own measurements. The hysteresis at very low RH reported by Feldman and Sereda [2,3] is of scientific importance and is the central theme of a paper now under review [5]. However, concrete in the field rarely experiences such low RH levels, and as has been noted both by Feldman [6], and in our original paper [1], most irreversible shrinkage occurs above 50% RH.

Equilibrium drying of cement paste is indeed very slow. Our specimens were equilibrated for a few weeks at each reported RH level during which both weight and length were monitored, and while true equilibrium was probably not reached the final rates of change were very low. We now have data for specimens equilibrated at various RH levels for over one year, and these results do not change any of the conclusions drawn in our paper. However, there are significant differences between equilibrium (stepwise) drying and drying directly to a very low RH. A major conclusion of the paper under discussion is that most of the irreversible shrinkage of practical importance is associated with changes in the distribution of pores that empty at RH levels above 33%, indeed above 50%. The biggest differences between first and second drying are an apparent decrease in the volume of pores that empty between 85–54% RH (these pores on average are about 10 nm across), and an increase in the volume of the largest (capillary) pores.

Between 33% RH and 7% RH there is no meniscus and thus no direct correlation between the RH and the size of the pores being emptied via the Kelvin equation. The observed weight loss in this RH range is simply attributed to the loss of adsorbed water (See Fig. 6 of [1]). This would generally include both water bound to the outer surface of the C–S–H gel and interlayer water, which is in agreement with the important observation that weight and length changes in this RH range are reversible [1]. While we strongly agree with the authors contention that methanol can access all of the (non-interlayer) pore space, as does helium, (see ref [7]) we disagree that this necessarily implies that pores a few nm in size are not present.

In response to the final comments about C–S–H globules approximately 5 nm in size, we note that while there are chemical and thermodynamic difficulties with the long-term stability of such small particles, there is now a significant amount of direct and indirect evidence for features of this size. In addition to SANS results (e.g. [1,7]), particles of about this size have been observed directly using atomic force microscopy [8].

There is also strong indirect evidence from nanoindentation. The scaling of elasticity with porosity indicates that C–S–H gel obeys the laws of granular mechanics [9]. The experimental data suggest that a stable mechanical packing of particles cannot

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DOI of original article: 10.1016/j.cemconres.2007.06.010.

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doi:10.1016/j.cemconres.2007.06.011

be achieved with a porosity greater than ~50%, which is a hallmark of percolation threshold in granular agglomerate networks [10]. Given typical nanoindentation depths of 100–200 nm, the size of the nanoparticles whose composite response is sensed by nanoindentation, must be at least one order of magnitude smaller than depth; thus providing indirect evidence of a C–S–H globule size in the single digit nanometer range. Furthermore, the experimentally obtained ratio of hardness to uniaxial compression strength for cementitious materials ($H/\sigma_0 \approx 30–60$) deviates significantly from the expected theoretical value for frictionless plastic materials ($H/\sigma_0 \approx 2.7–3$) suggesting that C–S–H strength is driven by internal friction (pressure sensitivity) and the number of interparticle contact forces, further reinforcing its nanogranular nature [11 and cited Refs.]. Indeed the classic experiments of Sereda et al. [12] showing that pressed compacts of "bottle hydrated" cement have essentially the same mechanical properties as those found in hydrated paste were the first to show directly the importance of surface forces on mechanical properties. All this evidence is in favor of surface forces over volume forces and, therefore, a colloidal/nanogranular microstructure for C–S–H.

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