



Discussion

Reply to the discussion on, “The use of nitrogen adsorption to assess the microstructure of cement paste” by M.C.G. Juenger and H.M. Jennings[☆]M.C. Garci Juenger^a, H.M. Jennings^{b,*}^a*Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA*^b*Departments of Civil Engineering and Materials Science and Engineering, Northwestern University,
2145 Sheridan Road, Evanston, IL 60208, USA*

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The comments are relevant and bring up some very important issues. We agree that nitrogen surface area is important, as are surface areas measured by all of the available techniques. Only by comparing data from several techniques can we begin to gain a better understanding of the “true” surface area of calcium silicate hydrate (C-S-H). In light of this, the observation that the surface area calculated from the reversible part of the water isotherm is roughly equal to nitrogen surface area is very interesting.

That water vapor sorption has a reversible and an irreversible part is substantiated by the observation that drying shrinkage also has the two components. We have proposed that the nitrogen surface area, or the amount of small pores measured by nitrogen, is directly related with a high degree of confidence to drying shrinkage, indicating that the pores seen by nitrogen are important pores [1]. Because there is an irreversible part of both the water isotherm and drying shrinkage, we believe that this is a strong reason to argue that water does not return to some parts of the structure on resaturation. Indeed, it has been shown [2] that there is a permanent water loss on drying associated with a fundamental change in the structure of C-S-H. This is somewhat contrary to a simple interpretation of the SAXS results, which show that surface area is completely restored on resaturation.

The issue of what is the correct surface area is a complex problem. One of us has proposed a model for C-S-H that quantitatively accounts for the surface area, density, and chemical composition (water content at different relative humidities) of C-S-H [3]. An important point of the model, and one where we disagree with J.J. Beaudoin, is that when the volume of porosity seen by water is compared to that

seen by nitrogen, one must draw the conclusion that nitrogen does not enter all of the porosity [4]. It is excluded from some volume that does not completely collapse on drying. Does this volume bound a surface, or is it an interlayer space that does not completely collapse? To some extent, the answer is philosophical. However, the excluded volume of pores is about 30% on average [3], a value that is large enough to suggest internal porosity. This is a volume inside the globules and the high density C-S-H of the model. Since this internal volume is fundamental to C-S-H formed in cement paste, the conclusion can be reached that cement with a w/c less than 0.36 does not contain enough volume to accommodate all of the C-S-H that can form, and, therefore, complete hydration cannot occur, as is observed. Taylor has stated that explaining this observation is an important consequence of the model for C-S-H [5].

This internal pore volume is subject to a great deal of path-dependent change on drying, as noted by J.J. Beaudoin. This is one of the factors that makes measurement and discussion of surface area so enigmatic. It is important to understand these changes, their relationship to drying methods, and the underlying causes of the changes. The suggestion that short-term oven drying may prove to be an appropriate drying method for surface area studies should be investigated further.

Although much work has been done to investigate a possible chemical reaction between methanol and calcium hydroxide, the results are inconclusive and controversial. Therefore, we disagree that the similarities between the surface area trends measured with and without methanol exchange are coincidental. In fact, the consistency in the data with and without methanol exchange reinforces the idea that methanol is reducing pore collapse.

We thank J.J. Beaudoin and his thoughtful insights and comments on the long-standing subject of cement paste surface area. It is clear that it is a topic that merits more research and discussion. A research direction that may shed

[☆] Cem Concr Res 31 (2001) 883–892.* Corresponding author. Tel.: +1-847-491-4858; fax: +1-847-467-1078.
E-mail address: h-jennings@northwestern.edu (H.M. Jennings).

more light on the differences between water vapor and nitrogen adsorption would be to compare the hysteresis loops from adsorption and desorption isotherms for both gases using different drying and rewetting histories.

References

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