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Discussion

A discussion on, “The use of nitrogen adsorption to assess the microstructure of cement paste” by M.C.G. Juenger and H.M. Jennings[☆]

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Useful data on the nitrogen surface area measurement of hardened Portland cement paste is presented in this paper. A few additional points that may further clarify some issues are offered.

The large hysteresis exhibited by the sorption isotherm (water as adsorbate) over the entire range of partial pressure indicates that irreversible processes other than adsorption are taking place. Separation of the isotherm into reversible and irreversible components as carried out by Feldman led to the construction of a reversible isotherm and an estimation of the nitrogen BET surface area having a similar value to that of the recalculated water surface area (i.e. 30–40 m^2/g) [1]. The original water surface area (assuming such a calculation is valid) based on a total (unseparated) water isotherm would approach a value in the range 140–200 m^2/g.

A comment about the relevance of small angle X-ray scattering (SAXS) is germane. It has been reported by Winslow and Diamond that the SAXS surface area of saturated Portland cement paste varies from about 682 to 708 m^2/g [2]. This high value is similar to that determined for montmorillonite, a layered silicate, and indicates that the technique measures surface area internal to the layers themselves. D-drying of cement paste reduced the values of surface area to 214–240 m^2/g and oven drying at 105 °C to values of 132–180 m^2/g. These values are similar to those of surface areas determined using water as the adsorbate and led to the contentious conclusion by Brunauer et al. [3] that ‘water’ isotherms provided the correct vehicle for BET surface area calculation. Differences between nitrogen and water surface areas were attributed to an exclusion principle involving inhibition of the access of the nitrogen molecule to all surface sites. This argument was negated by the observation (based on SAXS) that vacuum resaturation results in recovery of all the lost surface [2]. The structure could reopen (i.e. the intercalation process was functional) and accommodate structural water reinforcing the view that water as an adsorbate was not admissible for surface area calculations. More importantly, it strengthened the view that nitrogen and water had similar accessibility to the external C-S-H surfaces. Calculations by Feldman based on the quantity (SAXS area – nitrogen area) gave reasonable values of interlayer separation and capacity for water [4].

It is clear from the work of the authors and several others cited by them that the nitrogen surface area value obtained for cement paste is path dependent with respect to its previous drying–wetting history. The maximum surface area loss appears to occur after an initial exposure of between 40% and 60% RH. Litvan and Myers [5] have proposed that this is a combined result of aging and a transport process involving the making and breaking of interparticle bonds. A ‘true’ test of the equivalence of the ‘reversible’ water and nitrogen surface areas would be a confirmation that similar preconditioning histories prior to outgassing quantitatively affect the character of the sorption isotherm and in particular the scanning loops. An equivalence between the ‘reversible’ water areas and the nitrogen area would indicate that in spite of changes to the C-S-H (i.e. the adsorbent), nitrogen is accessing either all of the newly created or the remainder of the original surface that is available for interaction. There can of course be differences in the character of the isotherm even though the total water contained at saturation is similar.

It is also important to note that the differences in the D-drying procedure and the oven drying at 105 °C described in the paper are strongly dependent on the length of the drying period. First, the D-drying procedure does not reach equilibrium in 14 days. Detectable mass losses can occur even after several months of drying. Second, oven drying for 2–3 h as opposed to 24 h results in nitrogen surface area

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values that are similar to those obtained by D-drying. This is not surprising as both methods of drying (i.e. D-drying and 3 h of oven drying) produce similar sorption isotherms (both mass and length change). It would appear that short duration oven drying might be a critical element of any standardized surface area measurement procedure.

Further, it is apparent (as the authors emphasize) that variations in sample preparation affect the measurable nitrogen surface area. The C-S-H phase is clearly not stable with respect to moisture movement. In effect, we have a structurally transient adsorbent with an inherently different sorption potential. That is likely a primary reason for the pretreatment path dependence of the surface area determination. It is suggested that the nitrogen adsorbate is measuring the correct surface area in each case. The term 'subset' of the C-S-H surface is confusing as it implies that an alternate surface subset that is not accessible to nitrogen exists.

The discussion on methanol exchange is moot. The authors cite three independent studies indicating a chemical reaction between paste constituents and the solvent. If this is the case, any similarities between D-drying and drying procedures involving methanol exchange on surface area determination would be fortuitous.

The authors are to be commended for their comprehensive attempt at reevaluating and interpreting the significance of the nitrogen surface area measurement of hydrating cement paste. There remains, however, several unanswered questions.

References

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