



## Discussion

A discussion of the paper “The BET-specific surface area of hydrated Portland cement and related materials” by Ivan Odler<sup>☆</sup>Hamlin M. Jennings<sup>a,b,\*</sup>, Jeffrey J. Thomas<sup>a</sup><sup>a</sup>Department of Civil and Environmental Engineering, Northwestern University, Evanston, IL 60208, USA<sup>b</sup>Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

Received 24 November 2003

In the paper referred to in the title of this comment [1], Ivan Odler provides a comprehensive and useful review of pertinent data and interpretations of BET gas sorption measurements of cement paste. The focus of that paper is the well-known differences in the surface area and pore volume obtained using water vapor ( $BET_{H_2O}$ ) or nitrogen ( $BET_{N_2}$ ) as the sorbate gas. We agree with many of his findings and interpretations, including the general conclusion that  $BET_{N_2}$  values do not represent the total specific surface area of C–S–H. We also find his assertion that the lower  $BET_{N_2}$  surface areas arise, at least partially, from a low rate of thermally activated diffusion through the smallest pore entrances at the low temperature (77 K) used during measurement to be intriguing and likely correct.

A number of papers published from our own research [2–6] have also reported and analyzed  $BET_{H_2O}$  and  $BET_{N_2}$  data for cement paste and have reached similar conclusions. We assert that because nitrogen does not access the entire C–S–H pore system and because the  $BET_{N_2}$  values vary significantly with many curing parameters, such as w/c, admixtures, and hydration temperature,  $BET_{N_2}$  actually provides much more information about the differences in the microstructure than do the nearly constant (and more “correct”)  $BET_{H_2O}$  values that are simply proportional to the degree of hydration.

One of us has proposed a quantitative “colloid” model for the structure of C–S–H gel in cement paste [5] that explains a large amount of data, including the different values of specific surface area measured by different techniques. The colloid model postulates two types of C–S–H, low density (LD) and high density (HD), which are formed by different

packing arrangements of the same basic approximately 2-nm-sized units of C–S–H. Fig. 1 shows a diagram of the LD C–S–H structure. The small circles are the basic units. These cluster into globules, which are illustrated as circular groupings of seven basic units in the 2D representation of Fig. 1. The globules then cluster more loosely and randomly into the characteristic structure of LD C–S–H. The different packing density of C–S–H at different length scales results in a fractal microstructure, which has been clearly observed using small-angle scattering (e.g., Ref. [7]). The HD C–S–H structure is structurally similar to LD C–S–H, but the globules are more tightly packed. These structures take time to form, a process that continues well after the C–S–H basic building units form. The final structure is influenced by many variables including temperature, type and extent of drying, and even the application of load [6].

A key feature of the colloid model is that the LD C–S–H structure has a significant amount of internal porosity accessible to nitrogen and thus a high  $BET_{N_2}$  specific surface area, while the HD C–S–H does not. According to the model, nitrogen can penetrate the larger pores between the LD C–S–H structures but does not penetrate the intraglobule pores inside the LD C–S–H structure although it is small enough to do so. (See below and Odler’s paper for a reasonable explanation). Few pores of the larger size exist in the HD C–S–H structure, so little surface area is measured by nitrogen. Water, on the other hand, can enter most of the intraglobule porosity in both the LD and HD C–S–H, explaining the significantly higher  $BET_{H_2O}$  surface areas.

From this discussion, it is clear that an increase in the ability of nitrogen to diffuse into small pores would allow nitrogen to measure more porosity (and surface area) within the LD C–S–H structure and perhaps also some surface area within the HD C–S–H. Thus, the colloid model is in agreement with, and would in fact predict, that an increase in the activated diffusion rate of nitrogen (via an increase in measurement temperature) would increase the measured  $BET_{N_2}$  surface area, as suggested by Odler. We must

<sup>☆</sup> *Cem. Concr. Res.* 33 (2003) 2049–2056.

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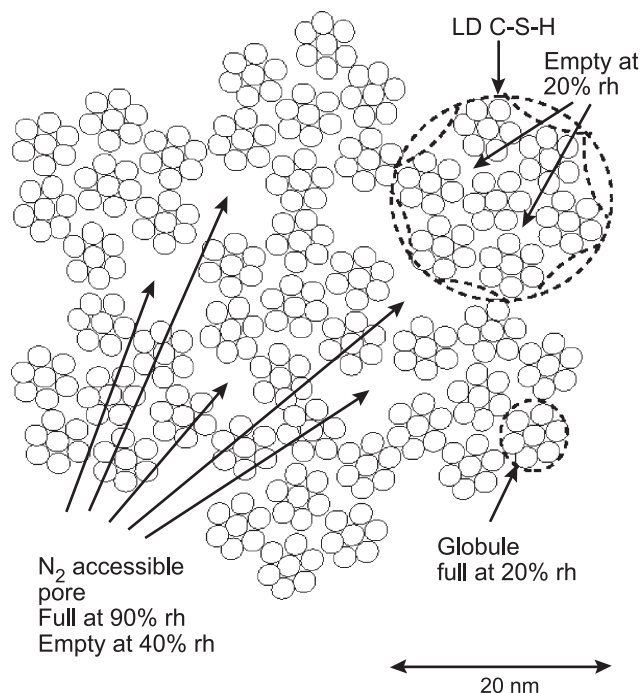


Fig. 1. Two-dimensional schematic of the colloid structure of C–S–H, after Ref. [5]. The captions identify the size of unit that is full of water at a particular relative humidity.

therefore disagree with his following statement, made on p. 2055 [1]:

The assumption that lower BET values are due to the presence of a C–S–H phase, which nitrogen cannot penetrate in addition to one readily accessible to  $N_2$ , is contradicted by the finding of temperature dependence of the  $BET_{N_2}$  value; it cannot be assumed that the mutual ratio of these two forms of C–S–H in the hardened material will shift merely by altering the temperature at which  $N_2$  adsorption takes place.

This is an important issue because it goes to the core of the colloid model and is one of the main ways it can be misinterpreted. The above statement presumes that *all* of the surface area in the LD C–S–H is measured by nitrogen, and *none* of the surface area in the HD C–S–H can ever be measured by nitrogen. If this were the case, then indeed the only way for the measured  $BET_{N_2}$  surface area to vary would be for the relative proportions of LD C–S–H and HD C–S–H to change, and this would obviously not occur simply because the measurement temperature was changed. However, as noted in the foregoing discussion, the LD C–S–H contains a significant proportion of porosity that is not normally accessed by nitrogen, although it is large enough to accept a nitrogen molecule. We agree with Odler that the exclusion of nitrogen from these pores is likely for kinetic reasons, that is, equilibrium is not reached during a  $BET_{N_2}$  measurement.

## References

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