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Discussion

Reply to the discussion of the paper by Ivan Odler "A model for the microstructure of calcium silicate hydrate in cement paste"☆

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The comments of Ivan Odler address some key issues of the proposed model for C-S-H [1]. First, the central point of Odler's concerns requires some elaboration on a particular detail of the model.

The question is whether the variation in surface area measured by nitrogen is due to variable quantities of low-density C-S-H (LD C-S-H), which forms preferentially during early hydration, or whether it results from changes to "normal" C-S-H (as traditionally understood) that more or less collapses. Odler favors the latter explanation and he notes that only this mechanism can explain a decreasing surface area with age. However, the decreasing surface area with time is inconsistent with several other published works [2–5] that show an increase in the nitrogen surface area with time. However, other variables that influence surface area can be explained by either model, and, if this is so, then the simpler model would indeed be preferred. However, the situation is more complicated than this.

Putting aside for the moment the details of specific trends in surface area, one must justify the more complex proposition of two densities. More open porosity would certainly lead to higher surface areas as measured by nitrogen. This simple scenario was explored intensively in the early stages of the development of my proposed model but without a consistent quantitative result. A schematic form of such a model is shown in Fig. 1, where two structures with different size of entering pores, or openness, are shown. This model predicts not only that a collapsed or more compact structure leads to lower surface area as measured with nitrogen, but also that the BET surface area is inversely proportional to the size of the sorbate molecule. Although this latter relationship is observed in a qualitative way [6,7], no quantitative relationships could be found.

Once I imposed the condition that a viable model must accurately predict gel pore volumes as well as surface areas, I could not find a simple model. Progress was made when the volume of porosity was examined with the following question in mind. If water measures the total porosity, then how much gel pore volume does nitrogen miss? The result, which is counterintuitive, is shown in a new form in Fig. 2. Here the porosity measured by water is taken as the total porosity and the difference between it and the porosity measured by nitrogen is defined as the inaccessible porosity and is plotted against surface area. C_3S and PC exhibit almost identical straight lines and C_2S pastes exhibit a different line but a similar trend. All of the data indicate that higher surface areas cannot be correlated with more open porosity, but rather with material that contains more porosity inaccessible to nitrogen. This is the opposite of what would be expected from the simple schematic of Fig. 1, namely that higher surface area as measured with nitrogen must also indicate higher pore volumes because nitrogen penetrates further into the structures. Put another way, higher nitrogen surface areas should miss less pore volume compared to measurements using water, but Fig. 2 shows that higher surface areas are associated with greater missed (or inaccessible) pore volume. This observation is central to the proposed model [1].

At first there was no physical explanation for such an observation [10] (a detail of some annoyance), but recently the idea of HD and LD C-S-H has been invoked [1,11]. Higher surface areas are measured when LD C-S-H is more abundant because low-density units are packed less tightly together than higher density units. This is the basis for my new model for the microstructure of C-S-H, which successfully rationalizes the density and surface area of C-S-H [1] and the volume of gel porosity. Furthermore, it rationalizes surface areas as measured by other techniques including small-angle neutron scattering and NMR relaxation. I cannot think of any other scenario that allows nitrogen to

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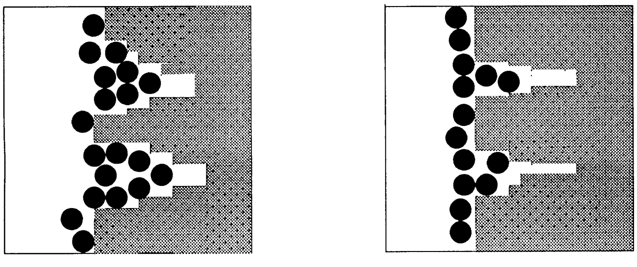

a.) b.)

Fig. 1. A highly schematic representation of pores with (a) large pore opening and (b) smaller pore opening, representing less and more collapse of C-S-H, respectively.

see more surface area while simultaneously missing more gel pore volume.

The above argument is important enough that further analysis of Fig. 2 is presented here. The slope of the line in Fig. 2 represents the increase of missed porosity per measured surface area. From this slope, the volume of inaccessible porosity per volume of LD C-S-H can be computed.

The following assumes that all the surface area comes from LD C-S-H. The slope is the volume of inaccessible porosity per surface area [Eq. (1)]:

$$\frac{\Delta V_{\mathrm{p}}}{\Delta S} = \frac{V_{\mathrm{p}}/g}{S/g} = \frac{V_{\mathrm{p}}}{S} \tag{1}$$

where V_{p} is the missed pore volume, S is the measured surface area and g is a gram of paste. Note that the lines pass almost precisely through the origin.

The ratio of surface area S to volume of LD C-S-H is the specific surface area S/g times density [Eq. (2)]:

$$\frac{S}{V_{\mathrm{LD}}} = \frac{S \cdot \rho}{g} \tag{2}$$

where ρ is the density of LD C-S-H. The volume of LD C-S-H is defined in Fig. 3 of the paper [1]. The inaccessible pores are within this unit.

Thus the volume fraction of nitrogen-inaccessible porosity in LD C-S-H is [Eq. (3)]:

$$\frac{V_{\mathrm{p}}}{V_{\mathrm{LD}}} = \frac{\Delta V_{\mathrm{p}}}{\Delta S} \cdot \frac{S\rho}{g} \tag{3}$$

where V_{LD} is the volume of LD C-S-H shown in Fig. 3 of the paper [1]. Using $\Delta V_{\mathrm{p}}/\Delta S = 8.86 \times 10^{-10}$ $\mathrm{m}^3/\mathrm{m}^2$, $S = 2.5 \times 10^5$ m^2/kg and $\rho = 1440$ kg/m^3, the increased volume fraction of missed porosity per volume of LD C-H-S is 0.32. This compares to the model value, computed using the ratio of densities of the basic unit and LD C-S-H, for fraction of porosity in LD C-S-H of 0.41 or 0.49, depending on the density of the basic building block. This model value must be considered an upper bound because it assumes that higher surface areas, in mature samples, are associated with an increase of LD C-S-H while HD C-S-H remains constant. This is only partly true, as there is probably less HD C-S-H in samples with high surface area. The lower bound is the difference of inaccessible porosity between HD and LD C-S-H that is about 0.12.

The agreement is good given that the data presented here is from a completely different type of experiment than that on which the model is based. In some ways, this is a remarkable statement of the self-consistent nature of the

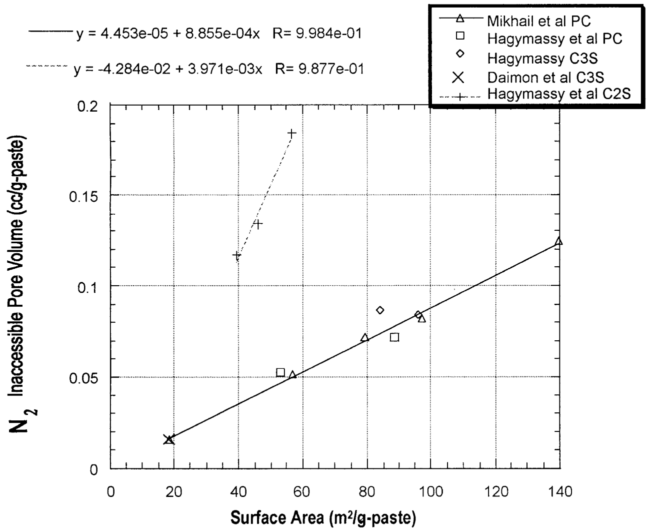

Fig. 2. The inaccessible pore volume is the difference between pore volumes measured by water and nitrogen. Data taken from Mikhail et al. [7] for PC △, Hagymassy et al. [8] for PC □, Hagymassy et al. [8] for C_3S ◇. Daimon et al. [9] for C_3S ×(this point is on top of △ at $S \cong 20$ m^2/g) and Hagymassy et al. [8] for C_2S+. This represents all of the published data known to the author except on point from Ref. [7] for W/C=0.57 that was very far from the points shown here. Also, the volume for pores measured by Daimon et al. [9] is reversed from that published because nitrogen must measure a smaller volume of porosity than water.

model. Thus, independent measurements support the basic need for the two densities. On the other hand, a model based on the idea of collapsing C-S-H has so far not lead to a quantitative prediction of pore volume, surface area and density of C-S-H.

The general question raised by Odler is, however, more complex than can be addressed by the simple analysis provided here. Variation in surface area measured by adsorption techniques is also related to drying. Different drying conditions certainly collapse the structure differently and the magnitude of the difference depends both on the rigidity of C-S-H and the harshness and rate of drying. The surface areas predicted by the new model are for standard D-dried samples typical of preparation for the research cited. The model does not address the issue of drying or, based on Fig. 2, the C-S-H produced from hydration of C_2S. I can envision certain drying procedures that will cause more collapse at later ages than at earlier ages. Some drying procedures are unique [12,13] and the results could be different from the trends cited above. Models that incorporate different drying are yet to be developed.

Two other points are relevant to the issue of two types of C-S-H. Different microstructures seen by both TEM and SEM support the possibility of their validity as described in my paper [1]. Also, the sharp transition in kinetics from rates controlled by chemical reactions to rates controlled by diffusion suggests the sudden start of the formation of denser product.

The other points noted by Odler are addressed as follows. Both HD and LD contain pores that nitrogen does not penetrate. That this pore space increases with hydration is, therefore, not surprising. What is surprising is that surface area and this pore space increase together in samples of similar age (i.e., more or less fully reacted). Also, the reason nitrogen does not penetrate some pores may well be related to thermally activated processes, a possibility we are investigating. In any case, the validity of the model does not depend on knowing why nitrogen does not enter certain pores in both the LD and HD structure. Finally, the idea that, at 11% RH, on average a monolayer is adsorbed, comprised of both bare spots and areas of multilayer adsorption, is correct, and this is the basis of the BET analysis. As for the composition of C-S-H, water in the finest pores is certainly bound with various energies and the composition depends on how much water is included. Comment cannot be made on the reported compositions until results are published.

In summary, there are many experiments to do and refinements yet to be made to the model, but I believe that the assumptions of two densities of C-S-H, or maybe more correctly, packing efficiencies of C-S-H, although more complex than a collapsing C-S-H, is necessary to explain a range of experimental observations.

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