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Discussion

Discussion of the paper "A model for the microstructure of calcium silicate hydrate in cement pastes" by H. M. Jennings[☆]

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In his paper, H.M. Jennings presents a new model of the structure at the nanometer scale of the C–S–H phase formed in the hydration of Portland cement. The model is intended to explain the known experimental findings, including the existing discrepancies in the specific surface area values as determined by different methods.

The model assumes the setup of the paste out of nearly spherical, equiaxed "basic units" with a radius r of approximately 1.2 nm, which are "flocculated" to larger units, ultimately yielding a solid body at the macroscopic scale. Even though the existence of such rather uniform basic building blocks of this size has not been directly proven, this assumption does not contradict known experimental facts, and their occurrence in cement pastes is conceivable.

A fundamental postulate of Jennings' model is the assumption of the existence of two distinct types of the C–S–H phase, which are built from the same basic building blocks, yet differ in their degree of packing. It is also assumed that nitrogen can penetrate and measure the specific surface area of only the low-density type of the C–S–H phase (LD C–S–H) formed preferentially at shorter hydration times, but is unable to do so in the high-density type (HD C–S–H) that is produced preferentially in the later stages of hydration. A logical consequence of such assumption is that the specific surface area of the cement paste undergoing hydration must increase in the later stages of hydration with a gradually decreasing rate or must stay unchanged if the HD form of C–S–H becomes the only one formed. It cannot, however, decrease as the hydration progresses.

Measurements performed on both cement and C_3S pastes revealed, however, that the specific surface area, as measured by nitrogen adsorption, declines with progressing hydration, after reaching a maximum shortly after mixing. Obviously, this observation is inconsistent with Jennings' hypothesis. We believe that such decline of the measured specific surface area may be explained by assuming the formation of only a single type of C–S–H, which, initially, is only loosely packed, but becomes gradually more compactly arranged, and thus less permeable for nitrogen, as the hydration progresses. Under these conditions, nitrogen will be able to penetrate the whole pore space and register the whole surface area of the material initially, but will gradually loose this capacity as the packing within the C–S–H phase will increase. Such model, in our view, reflects the actual situation more closely than one that postulates the existence of two separate, distinctly different phases, which remain unchanged once they were formed.

In line with our hypothesis is also the observation that, above a certain degree of hydration, the "final uptake," i.e. the amount of nitrogen taken up by a cement paste at a relative partial pressure $p/p_s = 1.00$, remains below that needed to fill — in condensed form — the existing pore space (emptied by d-drying). In addition, the fraction of the pore space not accessible to nitrogen increases, as the hydration progresses.

The limited capacity of nitrogen to penetrate the pore space at higher degrees of hydration is due to the low temperature at which the measurement is being done. The transport of the molecules of the adsorbate through very narrow entrances existing in the C–S–H phase, whose abundance increases with progressing hydration, can, namely, take place only by "activated diffusion", whose kinetics, unlike that of normal vapor diffusion, is highly temperature dependent. One can estimate that it would take months or even years until an equilibrium state would be attained and the whole pore space would be filled with nitrogen, in N_2-adsorption measurements performed at 77 K as usually done. This, in practice, is obviously impossible to realize. In line with this interpretation is also the observed increase of the found BET_{N_2}

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value and the amount of N_2 taken up, if the temperature in the experiment is increased from 77 K (liquid N_2) to 90 K (liquid O_2).

It is also postulated in Jennings' paper that a monolayer of water molecules becomes adsorbed on the surface of the C–S–H globules at a relative humidity of 11%. Such assumption is an obvious oversimplification, as, in truth, monolayers, multilayers and regions not covered by the sorbate molecules coexist side by side on the surface of the solid in an adsorption at subcritical temperatures. But even if one would consider — hypothetically — an exclusively monomolecular adsorption, the amount of water, which becomes adsorbed at a partial water vapor pressure of $p/p_s=0.11$ would not be sufficient to produce a densely packed monolayer of water molecules on the surface of the sorbent.

For the composition of the C–S–H phase in water-saturated pastes Jennings suggests a stoichiometric composition of $C_{1.7}SH_4$, which assumes 4 mol of water bound within 1 mol of C–S–H. As in cement pastes, different fractions of water are bound differently strong, the definition of the term "bound water" is necessarily an arbitrary one and is open to discussion. In our laboratory, we defined the "bound water" as that fraction of "total water," which is unable to migrate within the existing pore space, as it is also spatially bound within the solid phase. We determined this water as that fraction of total water that did not become exchanged if a water-saturated paste was percolated with D_2O-enriched water. From it and the free $Ca(OH)_2$ content, we established the stoichiometric composition of the C–S–H phase in fully hydrated C_3S pastes as being $C_{1.70}SH_{1.88}$ (average value for five pastes with w/s between 0.45 and 1.00). This stoichiometry is to be compared with that of $C._{1.70}SH_{1.69}$ found in the same pastes if d-dried and that of $C_{1.70}SH_{2.26}$ found in pastes in which the free water had been removed by extraction with acetone.

We believe that Jennings' paper represents a valuable step towards the understanding of the structure of the C–S–H phase and will stimulate discussion and experimental work on this interesting subject.