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Discussion

Reply to the discussion by J.J. Beaudoin and R. Alizeadab of the paper “Refinements to colloid model of C–S–H in cement: CM-II” by H.M. Jennings

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The comments of Beaudoin and Alizeadab on my paper [1] are both appreciated and important. They address one of the core points of the updated version of the colloid model of C–S–H (referred to as CM-II), and indeed one of the more important and still unresolved points of discussion in cement science over the last 40 years. The principal area of disagreement is in the interpretation of complex data (primarily density data obtained from *He* inflow measurements published in the 1970s by Feldman and coworkers), which bears directly on efforts to build quantitative relationships between the nanostructure and properties of C–S–H, and, more generally, of portland cement based materials. For the purpose of this reply, I will refer to the extensive modeling efforts of Feldman and colleagues, including Beaudoin, as the *Canada* model.

CM-II is an attempt to refine a model [2, and other refs included in my original paper] that reconciles a large body of diverse data. Occam's razor is applied by developing a model that quantitatively explains as much data as possible in the simplest way possible. The approach is that C–S–H is granular in nature, and that its properties are best described as an assemblage of tiny particles (characteristic dimension of 4 nm) called globules in my model, and referred to as bricks elsewhere (perhaps not a bad term). This granular approach has shown promise as a foundation for employing granular and poro mechanics to model bulk properties [e.g.3,4]. It also provides a basis for modeling the irreversible or viscous deformation behavior of C–S–H [5], using the mechanism of rearranging the packing of particles. This mechanism is largely in contrast to mechanisms of layer slip, despite the fact that the C–S–H particles have a layered structure, and that permanent restructuring of the interlayer spaces may contribute.

If C–S–H is fundamentally granular (a term that is essentially interchangeable with colloidal) then packing of nanosized particles implies nanosize pores between the particles, called small gel pores (SGP) in CM-II, the number of which depends on the packing arrangement of the particles. According to the colloid model these pores control many properties. On the other hand the *Canada* model minimizes the abundance and importance of these tiny pores (a point of concern in the comment). One of the core issues is the value assigned to the specific surface area, which depends on the method used for measurement (already discussed extensively [2]).

Another issue, discussed in the comment, is the density of C–S–H. Feldman and colleagues [e.g. 6] published the results from a landmark series of experiments that measured *He* penetration into samples of C–S–H, results that were used to develop the *Canada* model. These measurements provide important information about the density C–S–H under different drying conditions, but there are disagreements about how to interpret this data. Initial penetration of *He* is rapid, followed by long period of slow penetration. These two regimes were characterized by reporting values after standard penetration times of 50 min and 40 h. According to the *Canada* model, the short-term penetration provides information about the “true” density of C–S–H. It is contended that *He* does not penetrate any of the internal spaces at 50 min and that when measurements are made at 11% relative humidity *He* stays outside the monolayer. The long term data measure C–S–H with all internal (including interlayer) space penetrated, that is, all space vacated by water. On the other hand, CM-II interprets the data at 40 h penetration as representing the “true” density of C–S–H, meaning that *He* does not enter any of the interior spaces in a globule, interlayer or intraglobular pores (IGP), even after 40 h. In this interpretation, the slow rate of penetration between 50 min and 40 h is the penetration of the small gel pores (SGP) trapped between the solid particles. A well defined pore system is incorporated into C–S–H and the density depends on how much of the very finest pores are included, and whether or not they are filled with water. At the most fundamental level even a globule contains some porosity. In a sense true density does not exist. Most of Beaudoin and Alizadeh's comments are aimed at this difference.

While there are several issues about how the interlayer spaces may or may not close and reopen as water leaves and reenters, or about whether the kinetics of *He* inflow is best described by diffusion into interlayer space and/or into the smallest pores, the major questions implied by the comment are: What is interlayer space and what is nanoporosity? These questions are not explicitly addressed in the literature. A good distinction can be made from a modeling perspective. Water in each of these spaces has a unique relationship to density.

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Thus if f_H is volume fraction of water in either the interlayer space or on the outside surface (both of which expand the volume of solid) the density of the particle is

$$\rho_{C-S-H+H} = \rho_{C-S-H} - (f_H(\rho_{C-S-H} - \rho_H))$$

where $\rho_{C-S-H+H}$ is the density of C–S–H including any water on the surface or in the interlayer space and ρ_{C-S-H} is the density of C–S–H without surface or interlayer water (dried) but including any (if it exists) internal pore (empty), and ρ_H is the density of water. Noting that the term in parenthesis is always positive, no matter what reasonable density is assumed for water, water is less dense than C–S–H, the addition of water into either of these sites always decreases the overall density of the particle. As water is removed the associated volume is removed and not included in the overall density.

On the other hand, if water is added to an internal pore the density of the particle is

$$\rho_{C-S-H+H} = \rho_{C-S-H} + f_H\rho_H$$

Density always increases as internal pores are filled with water, since the mass increases with no increase in volume. Thus, a pore, no matter how small or whatever its shape, can be assigned a volume and free surface with specific thermodynamic characteristics. Various possible densities for C–S–H are described in CM-II.

Using the above definition (simple equations), it is easy to see that in order for the density measured by *He* inflow to first increase and then decrease as water is removed (after prior equilibration to 11% RH), as is observed, water must first leave the surface and/or the interlayer space (density increase) and then leave the internal porosity (density decreases). There must be an internal porosity that is not penetrated (observed by Feldman at all *He* inflow times). Thus, at 40 h, while there is flexibility about whether the internal pores (IGP) are a result of imperfect alignment of layers as they collapse (probable) or whether they are distinct pores before collapse, there is only one explanation for density lowering as water leaves, and vice versa. These pores are the IGP in CM-II. They are analyzed with respect to the 40 h *He* inflow experiments, with results included in Table 2 of ref [2], which employs the assumption that *He* never penetrates the IGP or the interlayer space. This assumption allows the *He* density to be reconciled with other values of measured density, notably the exact value determined using neutron and X-ray scattering measurements [7], with the conclusion that the density of C–S–H without the monolayer is about 2.6 g/cc, and therefore in CM-II with a monolayer of water is about 2.5 g/cc.

The *Canada* model interprets the rapid penetration of *He* during the first 50 min as defining the bounds of C–S–H without pores, and therefore a measure of its true density, which is, at 11% rh, about 2.3 g/cc, significantly less than the above values. CM-II interprets this lower value as including the SGP and the increase and decrease in density with removal of water has a similar interpretation as described above, but this time with SGP being penetrated as they empty, leading to an increase in density, followed by a decrease as the IGP are emptied. If this lower density does not include SGP, then I could not reconcile these values with densities measured by other techniques. All of the explanations of the *Canada* model for the slower entry of *He* after 50 min can be applied (with modification that diffusion into the tiniest pores is slow, particularly when inside a volume of C–S–H, and *He* does not enter into interlayer spaces). Following the same philosophy that guided the development of the original colloid model, the development of CM-II is aimed at explaining as much quantitative data as possible.

While the above arguments may explain why CM-II is self consistent, they do not explain why surface and interlayer water should leave before IGP as C–S–H is dried. In this regard, the reasons advanced in CM-II are qualitative, and further study is required. However, if the IGP are a result of imperfect alignment of layers, they may not be vacated until the layers have come together in a way that establishes the misalignment. In other words the IGP may effectively form as the interlayer water leaves, which means that the IGP water is the last to leave.

Finally the removal of water from IGP may induce stress in the globule, which on reentry of water is released, thus providing an energy explanation for water reentering the IGP first. There is a question as to why the tiny globules do not grow larger over time as do other soluble particles suspended in an aqueous phase. The relationship of surface energy to internal energy is not well understood. Further study may help establish relationships between structure and properties such as creep (depends on rate of water diffusion at the smallest scales) that can be used to design new materials.

With this overview a few specific comments are as follows:

- The density of water in C–S–H was determined by Feldman from experiments in which water was re-adsorbed after full drying. Since some of this water may enter the IGP (which does not change the volume of the solid) the apparent density of water can easily exceed 1 g/cc. While this does not preclude an increased density for surface water it does not demand it either, and values less than 1.2 g/cc are possible. This is an open question and whereas an increased water density will alter certain values reported for CM-II, the effect is small.
- If the 40 h *He* experiments penetrate all of the empty porosity and interlayer space I could not model the density changes with water removal and reentry, and in particular could not model the reduction in density with removal of water past the maximum density at 5 or 6% weight loss (from 11%). Feldman recognized this difficult to understand point [6] more than 30 years ago. The explanations that have been offered do not translate to quantitative models easily.
- After the first drying and rewetting cycle, the 50 min *He* experiments (on samples of higher w/c and all those that experienced the most extensive drying) exhibited reduced density during second drying at all water contents compared to first drying [6]. This was not the case for the 40 h experiments. In CM-II the density of the globule remains a constant function of water content while the rearrangement of globules during drying changes the SGP volume (perhaps by closing entrance), which controls the 50 min *He* density. I could not model the 50 min *He* densities with any other assumptions.
- Bangham forces dominate deformation of particles at RH's less than 11%. According to CM-II, the water is removed in stages: first, surface; second, interlayer (1 and 2 may be removed simultaneously without changing any aspect of CM-II); and third, IGP. The removal of interlayer water is associated with the greatest change in 002 spacing. At 5% weight loss (from 11% RH) much of the surface and interlayer water is removed while much of the IGP water remains, which could easily produce a highly distorted globule. These observations are consistent with results from C–S–H(I), recently suggested as a model material for C–S–H [8].
- While it is acknowledged that Daimon et al. [9] have extended the *Canada* model to include small pores in some pastes, these pores do not play a major role in modeling properties, as reinforced in the comment. The granular approach to properties places these pores between grains, SGP, in center stage when modeling properties.

Fig. 1. The interlayer space is full on the left and empty on the right. Irregularities that cannot collapse further contain water in the IGP space. When this water is removed the IGP porosity remains (no further collapse), and it is the first space where water reenters upon rewetting.

- With CM-II it is straightforward to compute the number of water molecules in the interlayer space. If for example the globule or brick has dimensions of 4 × 5 × 10 nm then the interlayer area (four layers thick, containing three interlayer spaces) is essentially identical to the surface area. The quantity of both of these, surface water (monolayer) and interlayer water, are 0.25 M, indicating that it is entirely reasonable for only one layer (with the same packing density as on the surface) to exist in the interlayer space under saturated conditions. Assuming a sharp distinction between IGP and interlayer space a clearer drawing of Fig. 1 might be possible.
- While the elastic modulus falls at RH's less than 11%, it does not change much at higher RH's either at the nanoscale or at the bulk scale, while drying at higher than 50% RH causes large changes in the 3–12 nm pre population. Explanation of this phenomena may well come from studying the material using a granular approach. The very large change in bulk paste seen in samples dried to less than 11% RH could well be the result of large change in the modulus of the globule. I have no problem with the idea that interlayer water contributes to properties of the globule, and that these properties change with the removal of this water, indeed I agree that this water is in some fashion load bearing. The saturated globule appears to have a modulus of about 62 GPa [10], but the modulus of the C–S–H depends on the packing density of the particles, and therefore on the volume of SGP. This could well change when a sample is dried to less than 11% RH.

Occam's razor is indeed an important principle, but any model must also explain as much reliable data as possible.

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