Discussion

A discussion of the paper "Refinements to colloidal model of C–S–H in cement: CM-II" by Hamlin M. Jennings ☆

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The writers of this discussion commend the author for a very insightful contribution toward modelling C–S–H in cement systems. The recognition that the author gives to pertinent details of micro-structural changes that influence engineering behavior of C–S–H are appreciated. Many of the arguments supporting the CM-II are compelling. Many, however, are not and invite further debate.

Validation for the CM-II utilizes extensive results of helium inflow experiments published by Feldman. In this context additional comment on the helium flow method citing relevant results not mentioned in the paper is necessary. This will be useful in clarifying differences in interpretation. A number of salient points are given as follows:

- Helium flows instantaneously into the micropore space of Vycor glass. This material has a mean pore size of about 3 nm and contains some pore space having least dimension < 1 nm. The density of the glass based on calculations using the instantaneous solid volume agrees with reference values. This supports arguments claiming that time dependent helium flow penetrates the interlayer space bounded by about a 1.1 nm separation distance between silicate sheets through a diffusion controlled mechanism.
- Helium inflow-weight change curves for cement paste, starting from the 11% RH condition, go through a maximum indicating structural collapse occurs at about 5% weight loss. This behavior is similar for phase pure C–S–H and is accompanied by a decrease in the basal spacing [1]. The decrease is pronounced at the maximum indicating that the origin of the collapse detected by helium flow is associated primarily with the removal of interlayer water.
- Helium inflow experiments can be used to follow volume changes associated with the incremental removal of water from non-cement pastes e.g. $CaSO_4 \cdot 2H_2O$ [2]. The density of $CaSO_4 \cdot 2H_2O$ as a function of weight change can be determined from solid volume measurements corrected for helium intake. The helium flows into space vacated by crystal water in a manner analogous to that describing the removal of interlayer water in C–S–H. The density values are in agreement with independent calculations where the change in volume is estimated assuming the density of water to be 1.26 g/cm³.

- Helium intake curves for some systems exhibit a 'spike' (i.e. a rapid increase in flow with a small weight change) when water molecules blocking empty nanospace are removed. This occurs during the dehydration of gypsum at large weight change values and during the removal of water from magnesium oxychloride cement pastes [3]. This characteristic also appears in plots of total helium inflow versus weight change. Differences in slope of the total volume (including the helium inflow component) versus weight change curves for the removal of structural water from sepiolite correspond exactly to known structural processes such as dehydroxylation [4]. This has been confirmed by X-ray diffraction results. This is further evidence supporting the view that helium inflow is associated primarily with interlayer water removal in C–S–H.
- Helium intake (time dependent) can detect trapped space analogous to the small gel pores (SGP) in the CM-II. The character of the helium inflow-time curve is however very different for this situation. The initial flow is extremely rapid and equilibrium can take several days/weeks. This is typically the case for very low water/cement ratio pastes and pastes containing supplementary cementing material. The helium flow in normal cement pastes is essentially complete after 40 h. No 'spikes' in the total inflow versus weight change curves occur for these pastes indicating that the trapped spaces are minimal or inaccessible. This behavior will be relevant in discussing the concept of IGP space proposed by the author.

Values of the density of water of about 1.2 g/cm³ are not the result of an unlikely assumption but are determined using actual volume change measurements. The volume occupied by water that is removed is the sum of the solid volume change and the volume determined by the helium intake. The density estimates for the dehydration of gypsum are relevant in this context as the hemihydrate value is known with reasonable precision. This value can be predicted simply from weight loss and utilization of a water density of 1.26 g/cm³ as mentioned previously. The implication is that helium is flowing into

space vacated by water molecules for which we know the exact location in the structure.

The globules in the schematic shown in Fig. 1 depict the location of interlayer water and the IGP space. The implication (at least pictorially) is that there is more than one layer of water molecules within the interlayer. This is unlikely as calculations of hydraulic radius based on helium inflow measurements indicate that only one layer is possible [5]. This is a major factor distinguishing C–S–H from clays. The elastic modulus for montmorillonite (which can accommodate several layers of water in the interlayer) decreases with humidity until it falls apart. The opposite is true for C–S–H. This comment will be discussed further shortly.

It is difficult to see how water in the IGP (CM-II) could vacate or enter this space before the exit or entry of interlayer water. The latter would be removed or enter from layer ends and likely precede any entry or exit of IGP water. Access to the IGP space (if it exists) would be detected by an abrupt change in the rate of helium inflow. This does not occur for normal pastes. The SGP space is detectable as stated above and is a feature of previous models after Feldman and Daimon. It is true that on rewetting the bulk of the re-entry of water occurs at humidities greater than 11%RH. However re-entry below 11%RH is not zero [6].The sum of the solid volume change and helium intake is small but positive. The process is slow as re-entry is occurring at layer ends. This is important as it is a rate controlling factor and has a bearing on interpretation of behavior in terms of CM-II.

It is stated in section 3.1.2.1 that the mean value of the modulus of elasticity does not appear to change with drying. It has been shown, however, that under equilibrium conditions the modulus decreases on drying (much of this occurring below 11%RH due to the removal of interlayer water) and increases on wetting. The magnitude of the increase can exceed 100%. Changes of this magnitude are unlikely to be accounted for by re-orientation (e.g. particle overlapping) within a globular floc. The stiffening effect is more plausibly explained through a structural role for interlayer water i.e. interlayer water is intimately associated with the solid. This leads to the conclusion that this water should be included as part of the solid volume in any density calculation for C–S–H — a feature not recognized by the CM-II model.

It is instructive to consider the author's interpretation of helium inflow experiments upon first drying from 11%RH (section 3.1.2). Again volume reduction is attributed to more effective packing in the globules. A more likely explanation attributes volume change to short range basal spacing reduction due to translation of the silicate sheets on drying. This is supported by the helium flow results for phase pure C–S–H which mimic those for Portland cement paste even though the latter is more or less X-ray amorphous. It is agreed that the SGP, when present, are empty and can fill over time. It is felt however that the SGP are not present in any significant amounts in all pastes as previously discussed. The character of the helium flow curves can indicate their presence or absence. The time dependent helium inflow is primarily due to diffusion of helium atoms into interlayer regions. The writers agree that the arrangement of globule surface can change the amount of interlayer space. As stated prior it is our view that water does not enter the IGP (if this space exists in any significant amount). The character of the total helium inflow-weight loss curves would change due to any IGP space. Further the entry of helium into interlayer space is not directly linked to an expansive process. However if new interlayer space is created water can enter.

It is clear from our perspective that a correct interpretation of the helium inflow results is paramount if the C–S–H density values predicted by CM-II are to be considered meaningful.

Finally, a comment on the applicability of the disjoining pressure concept in explaining volume change on adsorption appears warranted. It is our view that it is not necessary to invoke this concept. A correct application of the Bangham equations is adequate providing the isotherm in Fig. 3 is separated into reversible and irreversible components using the scanning curves. The theory assumes a reversible adsorption–desorption process occurs in the Bangham region of the isotherm. The predictions of modulus of the solid are consistent with those determined by Helmuth [7]. Helmuth's isotherms are similar to those of Feldman that are presented in Fig. 3.

The discussion is concluded by invoking the Occam's razor principle which is deemed applicable in this case.

References

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