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C-S-H (I)- A Nanostructural Model for the Removal of Water from Hydrated Cement Paste?

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Abstract

Helium gas is used as a nanostructural probe to investigate structural changes to C-S-H (I) due to the removal of interlayer water. Changes to the 002 basal-spacing are correlated with helium inflow characteristics. Similarities with helium inflow experiments conducted on hydrated Portland cement and C_3S pastes are discussed. Conclusions are drawn with respect to the viability of considering C-S-H (I) as a physical model for the drying of Portland cement and C_3S pastes.

Introduction

The amorphous nature of the C-S-H product formed from the hydration of ordinary Portland cement has been a source of difficulty in ascertaining significant details of its nanostructure. Nanocrystalline regions have recently been identified in cement paste and the d -spacing of these regions observed for the first time using TEM methods [1]. The cement science literature contains substantial debate concerning relevant nanostructural

descriptors varying from 'gel-like' to 'layer-like' materials. The former include the structural models of Powers and Brunauer [2,3] and the latter the models of Feldman, Daimon, Taylor, Richardson and Jennings [4-8]. Much of the evidence for either type of model has been obtained through indirect experimental methods.

Feldman and Beaudoin have utilized helium gas as a nanostructural probe to assess the structural response to moisture loss of Portland and C_3S pastes [9-11]. Essentially the effects of incremental water removal from the hydrate structure on volume change are systematically and quantitatively followed utilizing helium-inflow measurements to estimate the volumes of the nanospaces vacated by water. The results obtained using the helium-inflow technique to study the Portland cement paste system correlate well with the behavior of a layered material despite its x-ray amorphous character.

Synthetic C-S-H (I) has been studied extensively [12,13]. It has a definite x-ray pattern with the three strongest peaks at 1.250; 0.304; 0.280 nm [14]. The 002 basal-spacing at 1.250 nm is sensitive to changes in relative humidity and moisture content [15-17].

Experiments were designed to utilize the helium-inflow technique to probe the volume change sensitivity of the C-S-H (I) nanostructure to moisture change on drying. The objective of this work was to examine additional evidence for the layered nature of C-S-H in hydrated Portland cement and C_3S pastes. The validity of using C-S-H (I) as a nanostructural model for Portland cement paste was also assessed.

Experimental

Materials:

C-S-H (I) with a C/S ratio of 1.20 was prepared using stoichiometric amounts of CaO and amorphous silica mixed at water-solids ratio of about 11.8. The CaO was produced using precipitated CaCO_3 heated at 900°C for 24h. The CaO was purged with nitrogen gas and stored in a desiccator until required. The amorphous silica (Cabosil) was heated at 110°C to thoroughly dry the material. The reactants for producing C-S-H (I) were placed in a high density polyethylene (HDPE) bottle that was continuously rotated (16 rpm) for a period of 1 year. The reaction temperature was 23°C . The material was then filtered to remove excess water and freeze-dried under vacuum for 4 days. The resulting product was placed into an HDPE bottle, purged with nitrogen gas and stored until further use. A sample of the C-S-H (I) was put aside for immediate characterization using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) methods.

Characterization of C-S-H (I):

TGA :

The C-S-H (I) sample (35 mg) was placed in a TAQ 600 TGA and heated at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1050°C . The analysis was conducted in a nitrogen

environment. The thermogravimetric curve (mass loss versus temperature) was qualitatively and quantitatively similar to that reported for C-S-H gel [6]. The mass loss in the region 400-600°C was very small for the latter. An even smaller loss was observed for the C-S-H (I) used in this study suggesting that the residual amount of Ca(OH)_2 is small or negligible. Constitutional water likely contributes to the small mass loss in this region.

X-ray Diffraction:

The x-ray diffraction measurements were performed with a Scintag XDS 2000 diffractometer using CuK_α radiation. Characterization of the C-S-H (I) was carried out in the range $5^\circ < 2\theta < 60^\circ$ using a continuous scan rate of $2^\circ/\text{min}$. A background correction was performed on the XRD pattern. The X-ray pattern indicated the presence of the primary peaks previously reported for C-S-H (I) [14]. Scans in the range $5^\circ < 2\theta < 15^\circ$ were used to follow changes in the 002 basal-spacing. A step size of 0.03° at 5 sec. intervals was used. C-S-H powder samples were covered by Mylar film in order to prevent any humidity change during the XRD analysis. The change in the 002 basal-spacing was determined by monitoring the change in the position of the reference peak (for the 11% RH condition) at $2\theta = 29.1^\circ$.

C-S-H (I) Compacts:

The C-S-H (I) powders were pressed at 172 MPa to make compacts (nominally 3.20 cm in diameter x 1 mm thick). Care was taken not to expose the compacts to CO_2 during the process. The compacts (about 15-20g) were used for the helium inflow experiments. The C-S-H (I) powder from which the compacts were made was conditioned for two weeks at

11% RH. The compacts then were conditioned an additional week at 11% RH prior to the helium-inflow experiments. The helium pycnometer apparatus and a microbalance were placed in a glove box under a positive pressure of nitrogen gas.

Helium Comparison Pycnometry and Helium-inflow Experiments:

The apparatus and procedure for helium-inflow measurements are described in detail in previous papers [9,10]. The technique enables calculation of solid volume using the gas laws and the ideal gas assumption. Small pores or interlayer spaces which cause a delayed flow of helium into the sample are, in the first instance, regarded as part of the solid. The space vacated by interlayer water can then be estimated from considerations of solid volume change and the total volume of helium gas resulting from this delayed flow. The helium-inflow versus time curves, starting from the 11%RH condition, were obtained at each step following the incremental removal of water. Helium was allowed to flow into the sample for 40 h at 0.20 MPa. The water was removed by vacuum alone and finally a combination of vacuum and heating at increasing temperatures for different periods of time. This was done in a separate vacuum vessel and the sample was then transferred to the helium pycnometer. The heating temperature for most runs did not exceed 50°C.

Results and Discussion

Portland Cement and C₃S Pastes:

Typical helium-inflow versus time curves for Portland cement paste, $w/c=0.40$, are shown in Figure 1, [9]. The starting condition is 11% RH. This condition corresponds to the presence of about one monolayer of adsorbed water. A 'knee' occurs on the adsorption isotherm at this point. The inflow increases as water is removed incrementally and then begins to decrease at a weight loss of about 5.0%. The total inflow at 40h versus weight loss is plotted in Figure 2. The curve exhibits a corresponding maximum at 5.0% weight loss. The changing inflow behaviour is attributed to the removal of interlayer water. The inflow increase to a maximum is the result of increased interlayer space becoming accessible to helium without significant structural reorientation of the layers themselves. The C-S-H nanostructure begins to collapse after a weight loss exceeding 5%. Further collapse occurs as the weight loss increases and the helium-inflow decreases. The helium inflow curves for hydrated C_3S (water/solid=0.50) are qualitatively and quantitatively similar having a maximum inflow at about 5% weight loss [10]. The above results can not be explained by fixed-wall pore models (e.g. porous vycor glass). The pores (mean pore size=3 nm) in this system are completely and instantaneously filled. No time dependent diffusion occurs.

C-S-H (I):

Helium-inflow versus time curves for the C-S-H (I) compacts ($C/S=1.20$) are presented in Figure 3. The correspondence between the helium-inflow curves and weight loss is remarkably similar to that observed for cement paste. This is further illustrated in Figure 4 as the helium inflow at 40 h increases to a maximum at 5% weight loss and then

decreases. Changes in the 002 basal-spacing of C-S-H (I) as a function of weight loss were also determined. The 002 basal-spacing versus weight loss curve (determined from the 11%RH condition) is also plotted in Figure 4. The curve is divided into 3 regions. A gradual decrease in the 002 basal-spacing occurs in the first region i.e. 1.175 to 1.120 nm. A much more rapid decrease in basal-spacing (1.120 to 1.015 nm) occurs in the weight loss region between 4.5-6.5%. This is followed by a further gradual decrease to about 0.970 nm at 11.5% weight loss. The changes in the 002 basal-spacing with weight loss parallel the changes in helium-inflow. The beginning of the linear portion of region 2 corresponds to the maximum in the helium-inflow versus weight change curves and the onset of nanostructural collapse. X-ray patterns of C-S-H (I) corresponding to basal-spacing shifts at points A, B, and C in each region of the curve in Figure 4 are shown in Figure 5. The peak at point B is much broader and less intense than the peaks for points A and C. This indicates that the C-S-H (I) nanostructure is more disordered at this weight loss consistent with a structural collapse process. Additional weight loss (point C) appears to result in a realignment of the C-S-H (I) sheets. It is apparent that the correspondence of the structural collapse and helium-inflow characteristics for C-S-H (I) and the similarities in behavior between C-S-H (I) and hydrated Portland cement and C_3S pastes reinforce the arguments that the C-S-H present in the pastes is layer-like. C-S-H (I) would appear to be a strong candidate as a nanostructural model for the drying behavior of hydrated cement paste. The physical response to the removal of water from all these systems is mechanistically similar.

Conclusions

1. The diffusion of helium gas into the nanospaces of C-S-H (I) vacated during the incremental removal of water is sensitive to the nanostructural changes that occur during this process.
2. The changes in the 002 basal-spacing with the removal of water from C-S-H (I) correlate well with the total helium-inflow. Large changes in basal-spacing and the onset of collapse of the layered structure correspond to weight losses exceeding the water content at which the maximum helium- inflow occurs.
3. The diffusion of helium into the nanospaces of hydrated Portland cement and C_3S pastes (due to the incremental removal of water) follows a similar pattern to that of C-S-H (I).
4. C-S-H (I) would appear to be a viable physical model for the C-S-H present in Portland cement and C_3S paste.

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Figure 1. Helium-inflow into (0.4 water-cement ratio) cement paste at different water contents, as a function of time.

Figure 2. Helium-inflow at 40 hr, plotted as a function of weight loss for (0.4 water-cement ratio) cement paste.

Figure 3. Helium inflow versus time curves for C-S-H (I) – C/S=1.20.

Figure 4. Total helium inflow (40hr) and 002 basal-spacing as a function of weight loss for C-S-H (I) – C/S=1.20.

Figure 5. X-ray diffraction patterns for C-S-H (I), C/S=1.20 showing changes in 002 basal –spacing corresponding to the points A, B and C (with different water contents) indicated in figure 4.