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Detection of nanostructural anomalies in hydrated cement systems

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Abstract

Monitoring the flow of helium gas into the structure of hydrated cement systems has proven to be a useful method for following nanostructural changes in the C-S-H phase of hydrated cement systems. The method is sensitive to changes that occur on removal of structural water from the layered silicates. The helium inflow method was applied, in this study, to normally hydrated low-water-cement ratio (w/c) Portland cement pastes (w/c < 0.35) and to low w/c autoclaved cement systems containing fly ash and elemental sulfur. Nanostructural differences for the low w/c preparations were observed consistent with published structural models of layered C-S-H. Arguments for the existence of ‘trapped’ space between aggregates of C-S-H layers are advanced. Evidence for the preservation of C-S-H structures (similar to those formed during normal hydration) for the autoclaved systems containing fly

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ash and sulfur is presented. The evidence is compatible with the existence of ‘trapped’ space within layered agglomerates and the collapse of C-S-H structure on removal of water, typical of normally hydrated pastes.

Keywords: Cement systems; Nanostructure; Anomalies; Helium inflow

1. Introduction

The use of helium as a nanostructural probe in layered silicate systems has provided useful information about the character and response of these materials to the removal of structural water. It has been demonstrated that helium (a non-adsorbing gas) can penetrate the interlayer regions of C-S-H present in hydrated cement systems [1-3]. Quantitative information can be obtained for the following: drying and re-wetting effects, effects of applied stress, collapse of structure due to water removal, density of the solid, adsorbate and intercalate.

Models for the layered nature of C-S-H in hydrated Portland cement have been advanced by several authors e.g. Taylor, Feldman and Daimon [4-6]. The Feldman model has been particularly useful in explaining the role of structural water on mechanical behavior of cement-based materials [7]. This model is also compatible with the observed volume change behavior detected by the helium inflow method.

It was felt that the application of the helium inflow method could provide insight into the differences in nanostructural features specific to the following cement systems:

(a) low-water-cement ratio preparations: Powers and Brownyard indicated that there is a w/c (about 0.35) below which the amount of evaporable water can not exceed about 4 monolayers due to the limited amount of space that is present [8]. It was thought that additional information could be provided by the helium inflow experiments.

(b) autoclaved cement systems containing fly ash and elemental sulfur: The preservation of structure during the autoclaving process has been observed for cement systems containing pozzolans and small amounts of elemental sulfur [4,9].

Results of helium inflow experiments and their nanostructural implications are reported for the cement systems described above.

2. Experimental

2.1 Methods

The helium inflow method uses the gas laws and the assumption of an ideal gas to estimate the solid volume of a specimen. Helium is an inert gas commonly used for dead-space measurements in adsorption isotherm determinations as no interaction is expected with the surface of a material. The helium comparison pycnometer used for the experiments is described in detail elsewhere [1]. The

instantaneous solid volume measurement along with a known apparent volume allows for the calculation of the porosity of the material. Following the initial measurement the helium gas begins to diffuse into the interlayer regions of the cement hydrate specimens. The inflow can be monitored and the results plotted in the form of a helium inflow/unit mass versus time curve. The access of the test material to helium and the characteristics of these curves are dependent on the nature of the cement system and its equilibrium state with respect to water vapor. The method involves the step-wise removal of structural water from the cement system initially conditioned to the 11% RH condition. Water is removed by a combination of vacuum and/or heat treatment for various periods. The character of the inflow curve and quantities derived from the data are used to describe the nature of the nanostructural change.

2.2 Materials

Three series of cement pastes were prepared for the experiments:

Series 1. Portland cement paste ($w/c = 0.25$) was cast into cylindrical moulds (2.50 cm in diameter x 15 cm long). The material was demoulded after 1 day and hydrated in saturated lime water for about 1 year. The paste cylinders were cut into one mm thick slices and conditioned at 11% RH for several weeks prior to the helium inflow experiments.

Series 2. Portland cement pastes ($w/c=0.28$) were prepared from binary mixtures of cement and fly ash. Fly ash (class F) was used in amounts of 30 and 50 % by mass of solids. The pastes were hydrated for 24 hours at 25°C and 100% RH. They were then autoclaved for 3 hours at 2 MPa. One mm thick slices were conditioned at 11% RH as described for Series 1.

Series 3. Portland cement pastes ($w/c=0.35$) in a manner similar to that for Series 1. The pastes were prepared with additions of 0, 2 and 10% elemental sulfur powder. The pastes were hydrated for 24 hours at 25°C and autoclaved for 3 hours at 2 MPa. Samples were conditioned at 11%RH in a manner similar to that for Series 2.

3. Results and Discussion

3.1 Low-water-cement ratio pastes

The limiting water-cement ratio concept described by Powers and Brownnyard clearly indicated that nanostructural differences exist when the water-cement ratio is lower than about 0.35 [8]. The limited space for deposition of hydrates would appear to affect both the maximum degree of hydration and the pore structure. This view is supported by comparison of porosity values as measured by helium pycnometry and mercury intrusion porosimetry [10]. The values determined by mercury porosimetry diverge from equality and are generally less than those determined by helium pycnometry for low porosity pastes (i.e. $w/c < 0.35$). It would

appear that mercury can not enter space accessible to the instantaneous penetration of helium.

The time-dependent inflow of helium into the low water-cement ratio pastes (Series 1, $w/c=0.25$) is illustrated in Figure 1. The initial inflow curve for the 11% RH starting condition gives the maximum flow. This is followed by reduced inflow as both adsorbed and interlayer water is removed and the C-S-H structure collapses. The inflow behavior for pastes with $w/c>0.35$ is, however, minimal at the 11% RH condition proceeding to a maximum as water is removed and then decreasing as the structure collapses [1]. Helium inflow at 40 hours versus weight loss is plotted in figure 2 for pastes prepared at $w/c=0.25$ and 0.40. The plots illustrate the differences for pastes prepared at water-cement ratios above and below a limiting value of 0.35. The maximum flow that occurs at zero weight loss for the $w/c=0.25$ paste suggests that empty ‘trapped’ space between aggregates of C-S-H sheets exists and is rapidly filled through the diffusion of helium. This is compatible with the mercury porosimetry results referred to earlier [10]. The influence of structural collapse becomes more predominate as water is removed from interlayer regions. The interlayer positions are essentially full at the 11% RH condition. The ‘trapped’ space does not appear to be present in the $w/c=0.40$ paste. Total helium inflow versus w/c ratio (11% RH condition) is plotted in Figure 3. The effect of ‘trapped’ space is evident for the low w/c ratio preparation as the inflow is significantly increased. The modest increase in inflow as w/c ratio is increased from 0.40 to 1.00 may reflect differences in the C-S-H with w/c ratio such as density, C/S ratio and degree of polymerization [11].

3.2 Autoclaved low water-cement ratio cement-pozzolan pastes

The chemistry of autoclaved cement and cement-silica pastes is well documented [4]. The C-S-H that forms in absence of an added pozzolan (e.g. reactive silica) is generally in the form of dense crystalline phases i.e. α -C₂SH, xonotlite. The presence of reactive silica promotes formation of a low Ca/Si ratio C-S-H. A bulk Ca/Si ratio of about 1.0 crystallizes to give 1.1 nm. tobermorite. Optimum mixtures of dense and less dense phases in combination with low porosity are important for the development of high strength products [12]

The helium inflow-time curves for the autoclaved cement-fly ash systems containing 30 and 50 % ash (Series 2, water/solids = 0.28) show similar behavior to the normally cured w/c=0.25 paste, (see curves for 30% fly ash content, Figure 4). Maximum inflow occurs at the 11% RH starting condition followed by a step-wise decrease in inflow as water is removed. The maximum is significantly larger for the pastes containing 50% fly ash (curves not shown) as opposed to 30% fly ash (3.2 compared to 2.2 mL/100g). The w/c paste (normally cured) had a maximum of 3.5 mL/100g. The collapse of structure in the fly ash pastes is modest as indicated by the relatively small change in helium inflow at 40 hours, (Figure 5, fly ash= 30%). It is apparent that these C-S-H nanostructures also contain 'trapped' space.

3.3 Autoclaved cement pastes containing additions of elemental sulfur

It has been shown that small additions of elemental sulfur can ‘preserve’ the nanostructure of the normally hydrated systems when C-S-H formation occurs under autoclave conditions [9]. The helium inflow-time curves for autoclaved cement-pastes (Series 3, w/c=0.35) are consistent with the results presented for the autoclaved cement-fly ash pastes. The total amount of helium inflow (at the 11% RH condition) at 40 hours for the autoclaved paste containing no sulfur additive is relatively small (about 0.8 mL/100g). A small amount of structural collapse occurs on removal of water. The total amount of helium inflow is 0.6 mL/100g at a weight loss approaching 2%. A low amount of helium inflow would be expected as the hydration products are dense crystallites of α -C₂SH and xonotlite. The ‘preservation’ of structure referred to above is evident upon examination of the helium inflow-time curves for the pastes containing 2% sulfur (Figure 6). The curves exhibit an increase in total inflow as structural water is removed reaching a maximum at 2.4% weight loss followed by a decrease in the total inflow (Figure 7). This behavior is similar to that for normally hydrated cement paste (w/c=0.40) as illustrated in Figure 2. Similar helium inflow characteristics were observed for the autoclaved paste containing 10% elemental sulfur. The maximum in total inflow was, however, observed at a higher weight loss, i.e. 6% (Figure 7). It is apparent that it is more difficult to flow into the C-S-H structure for the pastes containing 10% sulfur compared to those containing 2% sulfur. The C-S-H sheets may contain more interlayer water delaying collapse upon water removal.

4. Conclusions

- Characteristic helium inflow-time curves are markedly different for low- water-cement ratio cement pastes ($w/c < 0.35$). Significantly increased inflow at the 11%RH condition suggests the existence of ‘trapped’ space between aggregates of C-S-H layers.
- Collapse of structure is detected by the helium inflow method for cement pastes after removal of an optimum amount of interlayer water. Prior to reaching this optimum the filling of ‘trapped’ space with helium dominates the inflow behavior for low-water-cement ratio preparations (i.e. $w/c < 0.35$). Flow of helium into interlayer space is the predominate flow mechanism for pastes with $w/c > 0.35$.
- Detection of collapse of structure as determined by helium inflow versus weight loss curves for autoclaved pastes containing fly ash and prepared at low-water-cement ratio is minimal. The total amount of helium inflow for the initial condition at 11%RH is much greater than for normally hydrated ordinary Portland cement systems prepared at $w/c > 0.35$. This supports the view that some ‘trapped’ space between C-S-H aggregates exists.
- The preservation of nanostructure typical of normally hydrated cement paste can be achieved for autoclaved cement paste containing small additions of elemental sulfur. Helium inflow-weight loss curves are typical of those obtained for normally hydrated cement paste. Autoclaved pastes without sulfur addition

exhibit a low initial inflow and no maximum in the helium inflow versus weight loss curves. This suggests that most of the flow is into ‘trapped’ spaces between aggregations of C-S-H crystallites.

- The flow of helium gas into cement hydrates can be used to detect nanostructural changes due to the removal of water from normally cured or autoclaved cement systems.

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Figure captions

Figure 1. Helium inflow versus time curves for a $w/c=0.25$ cement paste at different water contents.

Figure 2. Helium inflow at 40 hours plotted as a function of weight loss for cement pastes prepared at $w/c=0.25$ and 0.40 .

Figure 3. Helium inflow at 40 hours plotted as a function of water-cement ratio. All specimens were equilibrated at the 11%RH condition.

Figure 4. Helium inflow versus time curves for a $w/c=0.28$ cement-fly ash autoclaved paste at different water contents. Fly ash content =30% of total solids.

Figure 5. Helium inflow at 40 hours plotted as a function of weight loss for an autoclaved cement fly ash paste ($w/c=0.28$, fly ash content = 30% of total solids).

Figure 6. Helium inflow versus time curves at different water contents for autoclaved cement paste with a 2% elemental sulfur addition. ($w/c=0.35$).

Figure 7. Helium inflow at 40 hours plotted as a function of weight loss for autoclaved cement pastes containing 0,2,10% additions of elemental sulfur, ($w/c=0.35$).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.