

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 < 0.38) and to low w/c autoclaved cement systems containing fly ash and elemental sulfur. Unusually, high amounts and rates of inflow were observed for these pastes. It was postulated that inflow occurred into both interlayer and other spaces in the latter. The inflow into the other or ‘trapped’ space was unexpected and considered anomalous in absence of a widely accepted explanation. The structural differences which were observed at the nanoscale for the low w/c preparations were consistent with behavioral aspects for published structural models of layered C–S–H. These include the models of Richardson and Jennings and concepts involving the existence of two types of 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 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 from interlayer space, typical of normally hydrated pastes.

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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., Tennis and Jennings, Richardson, Taylor, Feldman

and Daimon [4–8]. The Feldman model has been particularly useful in explaining the role of structural water on mechanical behavior of cement-based materials [9]. 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 0.38) below which the evaporable water cannot exceed a thickness of about 4 monolayers. This is due to the limited amount of space that is available for the adsorbate (water) to condense [10]. 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

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the autoclaving process has been observed for cement systems containing pozzolans and small amounts of elemental sulfur [6,11]. Elemental sulfur was added in an attempt to avoid the formation of high density crystallites during the autoclaving process. It was also thought to be a possible and simpler way of avoiding silica addition to achieve reasonable strength in autoclaved products. It was successful to a degree as evidenced by standard engineering measures e.g., compressive strength. No resolution of the sulfur interaction mechanism was attained.

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 volumetric apparatus used for 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 solid volume measurement (used for traditional porosity calculations) the helium gas begins to diffuse into the interlayer regions of the cement hydrate specimens and spaces that are not accessible to helium at the start of the experiment. The inflow can be monitored and the results plotted in the form of a helium-inflow/unit mass versus time curve. The inflow of 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 11% RH for several weeks. Water is removed by a combination of vacuum and/or heat treatment (using a heating mantle at temperatures varying from 40 °C to 100 °C) 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 \times 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 in a vacuum desiccator at 11% RH for several weeks prior to the helium-inflow experiments. The desiccator itself was placed in a glove box under a positive pressure of nitrogen gas to minimize any effect of carbonation. Carbonation was negligible as determined by TGA measurements.

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 h at 25 °C and 100% RH. They were then autoclaved for 3 h at 2 MPa (216 °C). One mm thick slices were conditioned at 11% RH as described for Series 1.

Series 3. Portland cement pastes ($w/c = 0.35$) were cast 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 h at 25 °C and autoclaved for 3 h at 2 MPa (216 °C). Samples were conditioned at 11% RH in a manner similar to that for Series 2.

No visual signs of microcracking were apparent during sample preparation and incremental drying. Microcracking (whether due to drying or autogenous shrinkage), however, is not an issue in a helium-inflow experiment as these spaces are filled instantaneously by helium gas. Therefore, time-dependent diffusion would not be influenced by their presence.

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3. Results and discussion

3.1. Low-water–cement ratio pastes

The limiting water–cement ratio concept described by Powers and Brownyard indicates that nanostructural differences exist when the water–cement ratio is lower than about 0.38 [10]. The limited space for the deposition of hydrates would appear to affect both the maximum degree of hydration and the extent of percolation in the pore structure. This view is supported by comparison of porosity values as measured by helium pycnometry and mercury intrusion porosimetry [12]. The values determined by mercury porosimetry diverge from equality and are generally less than those determined by helium pycnometry (based on instantaneous solid volume measurements) for low porosity pastes (i.e., $w/c < 0.38$). It would appear that mercury cannot enter (even at pressures exceeding 400 MPa) some spaces accessible to the instantaneous penetration of helium. Therefore, the time-dependent helium-inflow, which is measured after the instantaneous flow of helium, is therefore an estimation of the volume of spaces inaccessible to mercury.

The time-dependent inflow of helium into the low-water–cement ratio pastes (Series 1, $w/c = 0.25$) is illustrated in Fig. 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 maxi-

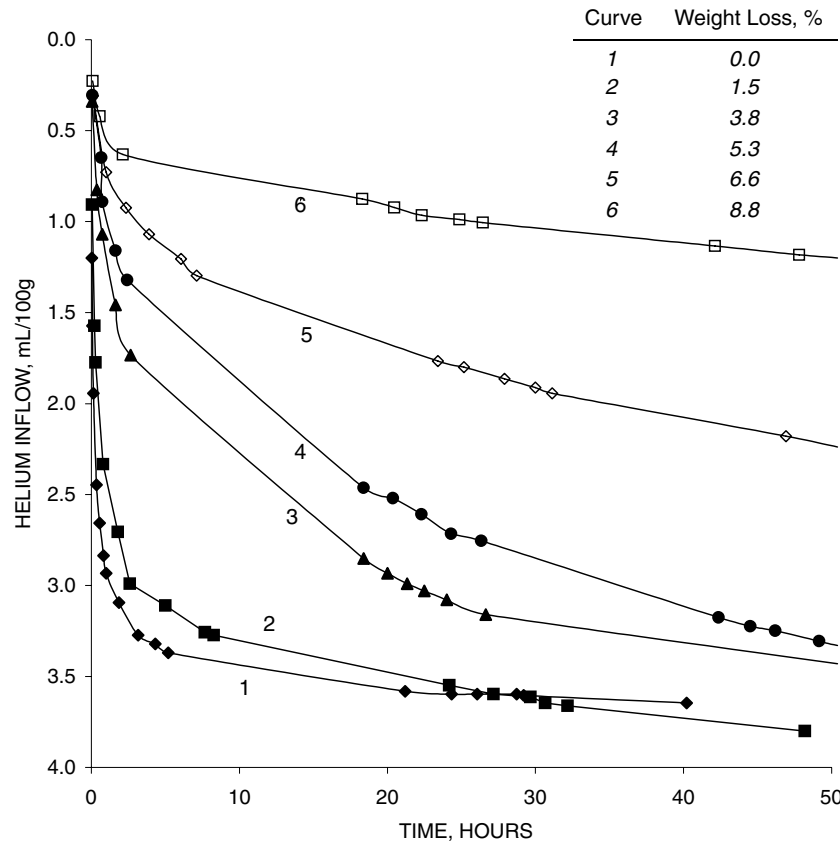


Fig. 1. Helium inflow versus time curves for a $w/c = 0.25$ cement paste at different water contents.

imum as water is removed and then decreasing as the structure collapses [1]. Helium inflow at 40 h versus weight loss is plotted in Fig. 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 about 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

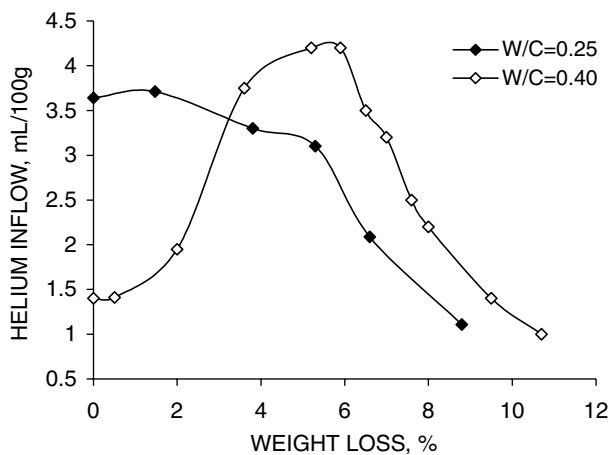


Fig. 2. Helium inflow at 40 h plotted as a function of weight loss for cement pastes prepared at $w/c = 0.25$ and 0.40.

rapidly filled through the time-dependent diffusion of helium. This is analogous to the flow of helium into molecular sieve structures and ‘holes’ formed by the removal of water from dehydrated gypsum crystals [13]. This is also compatible with the mercury porosimetry results referred to earlier [12]. The influence of structural collapse becomes more predominate as water is removed from interlayer regions even at low weight losses. The interlayer positions are nearly full at the 11% RH condition. The ‘trapped’ space does not appear to be present in the pastes with $w/c = 0.40$ or greater.

It has also been shown that two types of C–S–H exist in Portland cement. These are labeled as inner product (Ip) and outer product (Op). Richardson describes in detail the composition and characteristics of these products, explaining that the Ip has a compact, fine scale and homogenous morphology with pores smaller than 10 nm [5]. Constantinides and Ulm have characterized the Ip as a high density–high stiffness product as differentiated from Op which is associated with lower stiffness and density [14]. Tennis and Jennings have taken into account two different types of C–S–H, each with a specific density, for improved modeling of the pore structure [14]. Variations in water–cement ratio can result in varying proportions of Ip and Op. Layering ‘efficiency’ during the formation of C–S–H would be different for the two types of C–S–H.

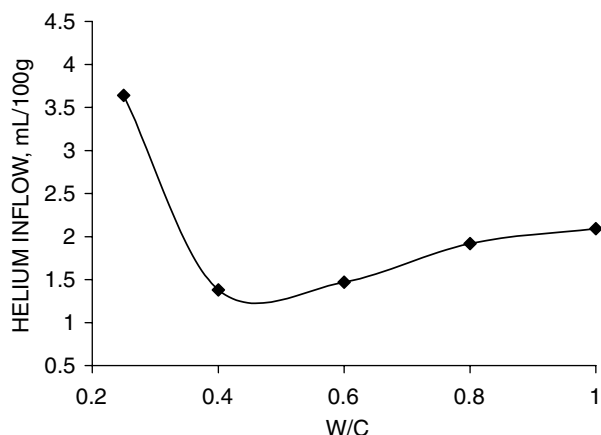


Fig. 3. Helium-inflow at 40 h plotted as a function of water-cement ratio. All specimens were equilibrated at the 11% RH condition.

It is likely that the I_p with the finer pores and greater uniformity would be influenced by helium diffusion to a greater extent. It is apparent that the pore system is less percolated at low-water-cement ratios and the space for the deposition of C–S–H is more confined. This should contribute to the likelihood of an imperfect agglomeration of C–S–H layers during their formation (kinks in the layered structure) resulting in ‘trapped’ spaces. Daimon has referred to these spaces as intercrystallite pores in his model for cement paste, which depicts a poor alignment of the C–S–H layers [8]. A poorer alignment is likely to occur in

confined space such as is present at a low-water-cement ratio.

Further research work is currently being conducted by the authors in order to investigate the effect of various Ca/Si ratios on the helium-inflow characteristics of synthetic C–S–H (I), a layered calcium silicate material.

Total helium inflow at 40 h versus w/c ratio (11% RH condition) is plotted in Fig. 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 [4,5,14,15].

3.2. Autoclaved low-water-cement ratio cement–pozzolan pastes

The chemistry of autoclaved cement and cement–silica pastes is well documented [6]. 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., $\alpha\text{C}_2\text{SH}$, xonotlite. The presence of reactive silica promotes formation of a lower 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 (analogous to the presence of two types of C–S–H in normally hydrated paste) in combination with low porosity are important for the development of high strength products [16].

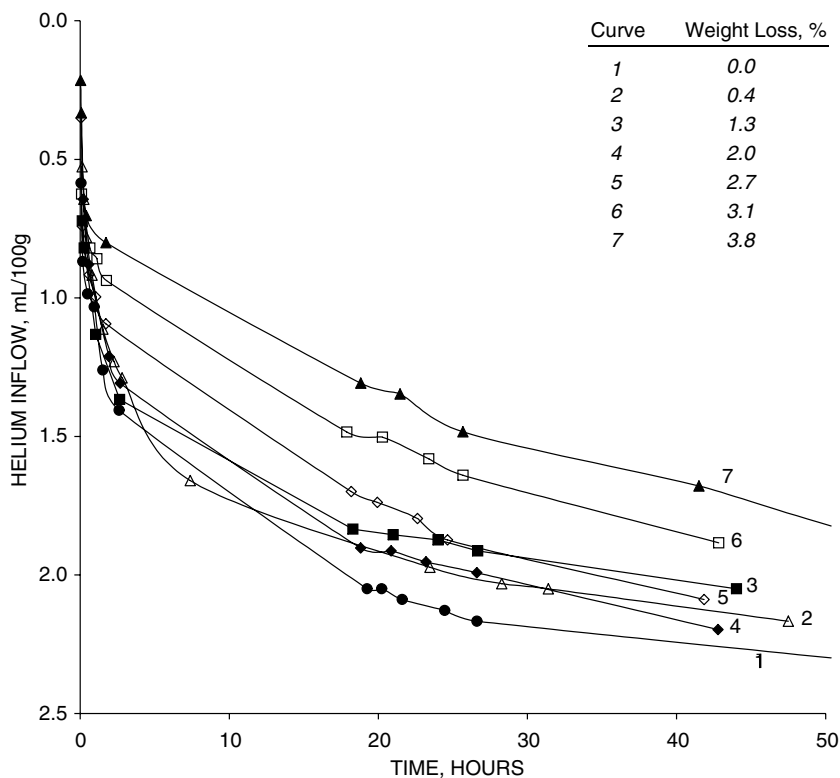


Fig. 4. Helium inflow versus time curves for a w/c = 0.28 cement–fly ash autoclaved paste at different water contents. Fly ash content = 30% of total solids.

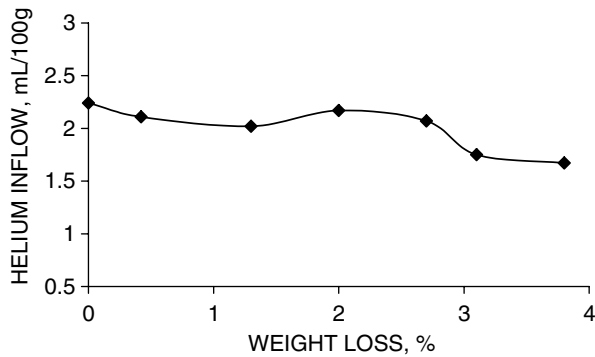


Fig. 5. Helium inflow at 40 h plotted as a function of weight loss for an autoclaved cement fly ash paste ($w/c = 0.28$, fly ash content = 30% of total solids).

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, Fig. 4). The maximum inflow, however, is relatively high, typical of pastes containing fly ash. This occurs at the 11% RH starting condition, and is then followed by modest decrease (up to 3.8% weight loss) as water is removed. This distinguishes these pastes from the normally hydrated OPC pastes. The inflow cannot be accounted for by diffusion into the interlayer regions alone as most of this space would be filled by interlayer water. 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/100 g). The $w/c = 0.4$ paste (normally cured) had a maximum inflow of 3.5 mL/100 g. The collapse of structure in the fly ash pastes is modest as indicated by the relatively small change in helium inflow at 40 h, (Fig. 5, fly ash = 30%). This suggests that the volume stability of these pastes is markedly different. It is apparent that these C–S–H nanostructures also contain ‘trapped’ space as indicated by relatively large inflow at 11% RH. It is noted that the influence of the C/S ratio of the C–S–H on helium inflow has yet to be determined as mentioned in Section 3.1.

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 [11]. 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 h for the autoclaved paste containing no sulfur additive is relatively small (about 0.8 mL/100 g). A small amount of structural collapse occurs on removal of water. The total amount of helium inflow is 0.6 mL/100 g at a weight loss approaching 2%. A low amount of helium inflow would be expected as the hydration products are dense crystallites of $\alpha\text{C}_2\text{SH}$ and

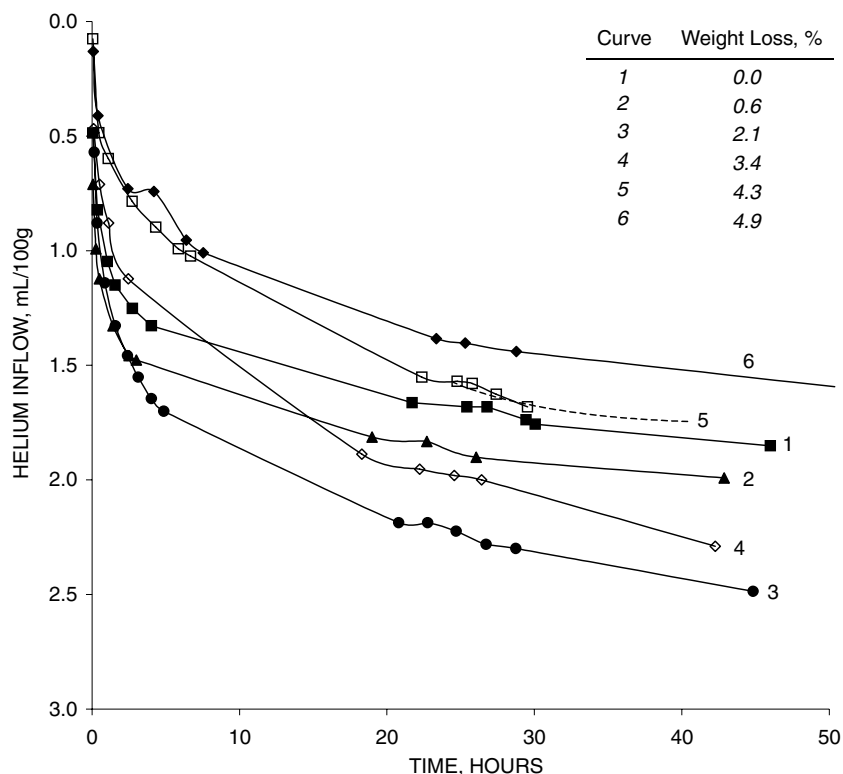


Fig. 6. Helium inflow versus time curves at different water contents for autoclaved cement paste with a 2% elemental sulfur addition ($w/c = 0.35$).

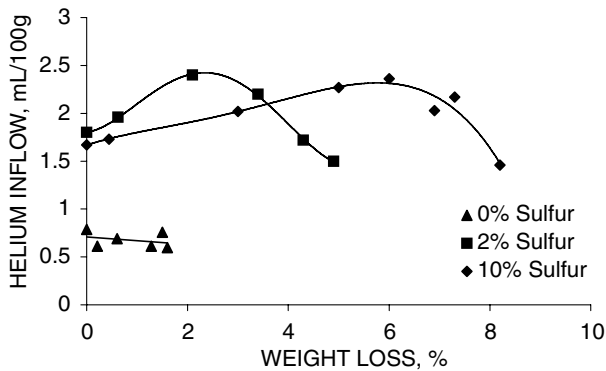


Fig. 7. Helium inflow at 40 h plotted as a function of weight loss for autoclaved cement pastes containing 0%, 2%, 10% additions of elemental sulfur, ($w/c = 0.35$).

xonotlite. Also, large pores, which are formed as a result of autoclaving, are filled instantaneously in the first part of the helium diffusion experiment. The ‘preservation’ of structure referred to above is evident upon examination of the helium inflow–time curves for the pastes containing 2% sulfur (Fig. 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 (Fig. 7). This behavior is similar to that for normally hydrated cement paste ($w/c = 0.40$) as illustrated in Fig. 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% (Fig. 7). It is apparent that it is more difficult for helium gas 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 ($w/c < 0.38$). Significantly increased inflow at the 11% RH condition suggests the existence of ‘trapped’ space between aggregates of C–S–H layers.
- The concept of ‘trapped space’ is compatible with the models for C–S–H attributed to Tennis and Jennings and Richardson wherein the presence of low and high density C–S–H is described. It is likely the high density C–S–H is influenced by helium inflow to a greater extent.
- 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., $w/c < 0.38$). Flow of helium into

interlayer space is the predominate flow mechanism for pastes with $w/c > 0.38$.

- 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 $w/c > 0.38$. 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.
- Further research is required in order to improve understanding of the nature of the anomalies detected by the helium-inflow technique in the current work.

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