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The significance of helium diffusion measurements in studying the removal of structural water in inorganic hydrated systems

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**THE SIGNIFICANCE OF HELIUM DIFFUSION MEASUREMENTS IN
STUDYING THE REMOVAL OF STRUCTURAL WATER
IN INORGANIC HYDRATED SYSTEMS**

ANALYZED

by

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THE SIGNIFICANCE OF HELIUM DIFFUSION MEASUREMENTS
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IN INORGANIC HYDRATED SYSTEMS

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ABSTRACT

Helium diffusion studies were made on six different inorganic hydrated systems: portland cement, magnesium oxysulfate, magnesium oxychloride, tricalcium silicate, gypsum and selected molecular sieves. The helium intake versus time curves obtained after structural water was removed incrementally, starting at 11% RH, provided data that enabled an assessment of the changing character of the solid phase. Changes in solid volume and solid density were monitored as water was removed from these systems. Factors influencing physico-chemical processes such as structural collapse due to removal of interlayer or compositional water are discussed with reference to the systems studied. This comparative study also provided a further elucidation of the factors that affect the relocation of the water molecule into the structure.

Des études de la diffusion de l'hélium ont été faites sur six différentes compositions inorganiques hydratées: le ciment Portland, l'oxysulfate de magnésium, l'oxychlorure de magnésium, le silicate tricalcium, le gypse et des tamis moléculaires choisis. La prise d'hélium contre les courbes de temps obtenues, après que l'eau structurale par accroissement ait été enlevée à partir d'une humidité relative de 11%, a produit des données qui permettent une évaluation des propriétés changeantes de la phase solide. Les changements de volume et de densité du solide ont été observés à mesure qu'on réduisait la teneur en eau de ces compositions. Les facteurs influençant les procédés physico-chimiques tel que l'effondrement structural à cause de l'enlèvement de l'eau à l'intercouche ou de l'eau composante, sont discutés en faisant référence aux compositions étudiées. Cette étude comparative permet de tirer au clair les facteurs qui influencent la relocalisation de l'eau moléculaire dans la composition.

Introduction

Helium diffusion studies on hydrated portland cement paste have demonstrated that changes to the solid phase of this system, which occur when water is removed, can be systematically followed (1). Helium intake versus time curves for samples having different moisture contents provided the basic data for an assessment of these changes. The data was presented in several ways: curves were plotted for total helium intake (when the flow rate approaches zero) versus weight change, solid density versus weight change, and solid volume versus weight change. Inferences regarding microstructural change were drawn from the shape of each curve. In the calculation of solid density, initial solid volume, measured within 15 s after helium was admitted to the sample, and total helium intake were taken into account. Alternatively, the change in solid density on removal of water from the system was calculated by using a value of 1.27 g/cc obtained from helium flow data for the density of the water removed. Comparison of the solid density versus weight change curve plotted for each method of density measurement provided a means of determining the extent to which helium was able to fill space vacated by water. Helium intake versus time curves for rewetted specimens of dried portland cement paste were analyzed similarly and conclusions drawn regarding microstructural changes (1).

The relationship between the weight change (ΔW) and the algebraic sum of the initial solid volume change (ΔV) and the total helium intake (ΔD) provided a means of estimating the density of the water removed as well as the extent to which helium entered the available microspace.

It was thought that presenting the helium flow data as described helped to elucidate the processes involved in the drying and wetting of hydrated portland cement and that this analysis would be applicable to studies of other hydrated systems. The purpose of this study was to assess the significance of the helium diffusion technique - as previously applied to the hydrated portland cement systems - and to examine factors influencing the physico-chemical processes operative in several different hydrated systems when structural water is removed. Six hydrated systems were studied.

Experimental

The preparation details of the six systems studied have been reported elsewhere (2-5). Samples for all systems were discs 3.2 cm in diameter, 1.3 mm thick. Four of the systems were paste hydrated and two systems were powders that were compacted. All systems were conditioned to 11% RH prior to drying. Drying was carried out in vacuo by pumping or combinations of pumping and heating.

The six systems investigated were as follows:

- (1) Magnesium oxysulfate paste. Two sets of samples were prepared having solution/solid = 0.72 and 1.07 using a $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution having specific gravity = 1.18. A third set of samples was prepared with solution/solid = 0.72 using $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution having specific gravity = 1.33. All samples were cured at 50% RH for 2 weeks and subsequently cured at 11% RH for 3 months.
- (2) C_3S paste. Two sets of paste samples were prepared having water/cement = 0.5 and 0.8. The paste was hydrated in the wet state for 2.5 years.
- (3) Portland cement paste. Samples were prepared at four water/cement ratios of 0.4, 0.6, 0.8, and 1.0. The samples were hydrated in water for 2.5 years.

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- (4) CaSO₄·2H₂O. Samples were prepared by compacting reagent grade gypsum at 680 MPa.
- (5) Magnesium oxychloride paste. Samples were prepared at MgCl₂·6H₂O/MgO solution/solid ratios of 0.86. Samples were cured at 50% RH for 10 months.
- (6) Molecular sieves. Samples were prepared from molecular sieves supplied by Linde Co., USA. Two sets of samples were prepared for each of the 3Å, 5Å and 10Å molecular sieves.

Helium Comparison Pycnometry and Helium Flow Data

The apparatus and procedure for helium flow measurements are described in detail in previous papers (1-3). The technique uses the gas laws and the assumption of ideal gas behaviour to calculate the solid volume of a sample. Small spaces or "pores" into which helium does not instantaneously flow are, in the first instance, regarded as part of the solid. The total helium intake (when helium flow rate approaches zero - usually about 48 h) is used in density calculations.

General Procedure

Helium intake as a function of time and density were measured at different moisture contents beginning with the 11% RH condition. Water was removed incrementally by evacuation alone and later by evacuation 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 pycnometer.

ResultsHelium Intake versus Time Curves

Typical helium intake curves for portland cement paste are presented in Fig. 1(a). Helium intake increases as water is removed (curves 1 and 2). As more water is removed, the initial flow rate is less but total intake is increased (curve 3). Further removal of water results in a decreased flow rate as well as decreased total intake (curves 4 and 5). Helium intake versus time curves for molecular sieve samples are presented in Fig. 1(b). All samples were heated for a minimum of 20 h. Total intake increased with sieve size and the rate of flow was significant after 144 h for the 5Å and 10Å samples.

All systems studied had exponential type flow curves; however, the initial flow rate and total intake, as well as the number and sequence of flow behaviours, varied with material and moisture content. The helium intake versus time curves for the other systems studied are not presented.

Total Helium Intake versus Weight Change

Helium intake after 48 h versus weight change is plotted in Fig. 2 for oxysulfate, C₃S and hydrated portland cement pastes. Increased total intake was observed for C₃S and hydrated portland cement pastes as water was removed; after reaching a maximum, the total intake decreased until all water was removed.

Two maxima were observed when the total helium intake versus weight change data was plotted for oxysulfate paste; these maxima occurred after water was removed by heating in vacuo at approximately 100 and 150°C. Largest total intake was observed when oxysulfate paste was heated to 200°C.

Fig. 1(a)
Helium intake versus time for hydrated
portland cement paste

Fig. 1(b)
Helium intake versus time for
molecular sieves

Total helium intake versus weight change plots for both magnesium oxysulfate and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ systems exhibited two or more maxima; the results are not presented. Interpretation of total helium intake versus weight change plots will be discussed later.

Density Measurements

Solid density versus weight change curves for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, C_3S , magnesium oxysulfate and oxysulfate pastes are presented in Fig. 3. Solid density values were determined by two methods: (a) from weight and solid volume measurements, the latter corrected for the amount of helium that had diffused into the system; (b) by accounting for volume changes, using a value for the density of the water removed.

Fig. 2
Total helium intake versus weight
loss for selected hydrated systems

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Fig. 3
Changes in density due to removal of structural water from selected hydrated systems

CaSO₄·2H₂O. There is good agreement between the two methods up to approximately 15% weight loss, and the density increases from an initial value of 2.32 g/cc to 2.68 g/cc. From 15 to 19% weight loss there is a decrease in density to 2.62 g/cc as measured by method (a)

followed by a rapid increase in density to 2.75 g/cc as an additional small amount of water is removed (19.0 to 19.8% weight loss). The decrease in density up to 19% weight loss is accompanied by a decrease in the amount of helium intake, and the subsequent increase in density up to 19.8% weight loss is accompanied by a large increase in helium intake. The density as calculated by method (b) continues to increase over the whole weight loss range; the value of density measured by method (a) approaches the value calculated by method (b) at 19.8% weight loss.

C₃S paste. Density values obtained by both methods are similar up to about 5% weight loss and increase from 2.30 g/cc to 2.39 g/cc. As more water is removed from the system, the density measured by method (a) decreases to 2.32 g/cc at 7% weight loss. This decrease in density is also accompanied by a decrease in helium intake. The density calculated in method (b) continues to increase to 2.43 g/cc at 7% weight loss.

Magnesium oxysulfate paste. Density values measured by method (a) are larger than those calculated by method (b) at weight change intervals of 3 to 5% and 7.5 to 9.6%. In each interval the density value (method (a)) reaches a maximum and then decreases to the value obtained by method (b). Further removal of water to 10% weight change results in a large increase in density (method (a)). Increases and decreases in density are accompanied by increases and decreases in helium intake.

Magnesium oxychloride paste. Density values determined by both methods are similar up to 8% weight loss. Between 8 to 10% and 10 to 11.5% weight loss, density values (method (a)) rise to a maximum and then decrease.

From 11.5 to 14% weight loss, the density values increase to a maximum value of 2.20 g/cc. Increases in density values are accompanied by increases in helium intake.

Total Space Vacated by Water versus Degree of Drying

An estimate of the space vacated by water on drying samples was provided by calculation of the parameter $\Delta V - \Delta D$. In Fig. 4, $\Delta V - \Delta D$ was plotted against weight change for all systems studied. The curves for all systems were initially linear. The inverse slope of the line provided an estimate of the density of water removed for each system; the water density values are recorded in Table I.

TABLE I
Water Densities Determined from Slope of $\Delta V - \Delta D$ versus ΔW Plot

Density of Water (g/cc)	Material
1.21	Magnesium oxysulfate paste
1.26	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
1.27	C_3S paste
1.27	Portland cement paste
1.47	Magnesium oxychloride paste

Fig. 4
Parameter $\Delta V - \Delta D$ versus weight
loss for selected hydrated systems

Curves 1, 6 and 7 in Fig. 4 (data plotted for magnesium oxysulfate pastes) subsequently had a change in slope; the slope for curves 6 and 7 increased significantly for small changes in sample weight. The slope for curve 1 increased significantly over a greater range of weight change.

Curves 2 and 3 for C_3S and portland cement pastes had a significant decrease in slope after 6 and 7% weight loss, respectively. The slope of curves 4 and 5 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and magnesium oxychloride pastes) remained constant to approximately 15% weight change. The interpretation of these curves will be discussed later. At greater weight changes (15 to 19.8%) the slope of the $\Delta V - \Delta D$ versus weight change curve for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ decreased significantly. At 19.8% weight change, $\Delta V - \Delta D$ changed very

rapidly over a small weight change interval as the slope became very steep. These results for the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system will be discussed later.

Discussion

This study has provided necessary data for an assessment of the significance of the helium diffusion technique to monitor microstructural changes resulting from the removal of water from several different hydrated cement systems. The data has been presented in several ways:

- (1) Helium intake versus time curves - Changes in quantity and rate of flow as water was removed in increments from these systems provided a means of detecting changes that occur to the solid phase during drying. The systematic increase in total intake to a maximum value followed by a decrease in the amount of total intake for the C_3S system has been attributed to structural collapse due to removal of interlayer water (3). Similar observations for the magnesium oxysulfate system have been attributed to structural collapse resulting from the thermal decomposition of oxysulfate complexes at approximately 100 and 150°C. The curves for the molecular sieves indicate that the rate and amount of flow are controlled by the size of entrances to available microspace. Processes that alter the dimensions of these entrances, such as structural collapse, probably result in changing the character of the helium intake versus time curve. Processes that result in the opening of diffusion paths to previously discrete or trapped empty space can result in large increases in rate and amount of helium intake with very little weight change. This type of flow behaviour appears to occur for the magnesium oxysulfate system. When $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was heated in vacuo at 200°C, there was a transformation from soluble to insoluble anhydrite. This transformation process was accompanied by a large increase in flow rate and amount of helium intake. The structure apparently opens up and helium becomes accessible to previously trapped space. This will be discussed in detail elsewhere.

- (2) Total helium intake versus weight change curves - For systems studied, it was observed that helium intake increases to a maximum value and then decreases as more water is removed from the system. This decrease in intake as more water is removed is attributed to structural collapse. The structural collapse as discussed above may be due to the removal of interlayer water (portland cement and C_3S paste systems) or to thermal decomposition of complex hydrates (magnesium oxysulfate and oxychloride systems).

Fig. 5
Schematic of parameter $\Delta V - \Delta D$ versus weight loss

- (3) Density versus weight change curves - Densities of the solid phase were determined by taking into account the space into which helium had diffused. Where densities determined from weight and volume measurements were larger than those densities calculated by assuming a value for the density of the water removed, it was apparent that helium entered empty spaces that were present initially but had been inaccessible. These may have been trapped or discrete spaces to which diffusion paths opened up as a result of internal cracking due to heating or the drying process.
- (4) ΔV - ΔD versus weight change curves - A schematic of ΔV - ΔD versus weight change is plotted in Fig. 5. Curve 0-4 is a straight line. The inverse slope of this line gives a value for the density of water removed from the system studied. With the exception of the magnesium oxychloride cement system, the values obtained in this study were realistic and similar to values for adsorbed water in other systems (6). It is probable that helium entered all the space made accessible by the removal of water. Further drying of C_3S , portland cement and $CaSO_4 \cdot 2H_2O$ pastes resulted in smaller changes of ΔV - ΔD with change in weight such as indicated by the segment of the curve (4-5). Helium cannot enter all space vacated by water; this is interpreted as a result of structural collapse. Large increases in ΔV - ΔD with small weight changes (segments 4-6 and 1-3) are probably due to discrete empty pores or trapped space becoming accessible to helium; this phenomena was observed for magnesium oxysulfate and oxychloride systems. Curve 0-1-2 has an inverse slope which gives an unrealistically high value for the density of water removed. It is apparent that helium is not entering all the space vacated by water.

The following is a summary of the possible mechanisms that are operative during exposure of inorganic hydrated systems to helium after water has been removed incrementally from these systems:

- (1) Space vacated by bulk, adsorbed or interlayer water is completely filled with helium.
- (2) Space formed by decomposition of hydrates is filled with helium.
- (3) New, unfilled (with water) spaces are opened and filled with helium.
- (4) Previously water-filled space is incompletely filled with helium.
- (5) Combinations of these mechanisms.

Conclusions

The helium-flow technique is a useful tool in cements research because it permits evaluation of the following:

- (a) changes in solid volume and density of cementitious systems resulting from removal of structural water because of (i) drying and (ii) decomposition due to heating;
- (b) density of structural water removed on drying;
- (c) factors influencing physico-chemical processes such as structural collapse due to removal of interlayer or compositional water, or other types of decomposition;
- (d) factors which affect the relocation of water molecules into the structure, such as reentry of interlayer water or rehydration on wetting.

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