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**FLOW OF HELIUM INTO THE MICROSPACES
OF MAGNESIUM OXYSULFATE
CEMENT PASTE**

ANALYZED

by
J. J. Beaudoin and R. F. Feldman

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THE FLOW OF HELIUM INTO THE MICROSPACES
OF MAGNESIUM OXYSULFATE CEMENT PASTE

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ABSTRACT

Helium flow measurements were made on samples of magnesium oxysulfate cement paste initially conditioned at 11% R.H. and dried in stages by combinations of pumping and heating. Physical changes in the microstructure of the cement paste due to chemical decomposition and water removal were monitored. It was concluded that helium can penetrate the microspaces of magnesium oxysulfate cement paste which form during removal of structural water. It appears that helium also enters discrete pores (unfilled with water) that become accessible when the cement paste is heated to 200°C. Mercury (at 407 MPa) can intrude into those microspaces not initially accessible to helium. Collapse of structure occurs when water is removed from this system. An estimate of the density of the water removed up to 15% weight change was 1.21 ± 0.07 g/cc.

Des mesures du flux d'hélium ont été pratiquées sur des échantillons de pâte de ciment d'oxysulfate de magnésium conditionnés initialement à 11% HR et séchés par étapes en opérations d'ensemble de pompage et de chauffage. Des changements physiques dans la microstructure de la pâte de ciment causés par la décomposition chimique et l'enlèvement de l'eau ont été observés. Il a été conclu que l'hélium peut pénétrer dans les vides microscopiques de la pâte de ciment d'oxysulfate de magnésium qui se produisent en enlevant l'eau structurale. Il apparaît que l'hélium entre aussi dans les petits pores (vides d'eau) qui deviennent accessibles lorsque la pâte de ciment est chauffée à 200°C. Le mercure (à 407 MPa) peut s'introduire dans ces vides microscopiques qui ne sont pas au départ accessibles à l'hélium. L'effondrement des structures se produit lorsque l'eau est retirée de ce système. Une évaluation de la densité de l'eau enlevée jusqu'à 15% du changement de poids était 1.21 ± 0.07 g/cc.

Introduction

Sorel was the first to recognize the potential use of magnesium oxysulfate cement as a binder (1). This cement has good fire resistance and insulation properties and is less sensitive to high temperatures than oxychloride. It is used particularly in prefabricated structural units that require processing at elevated temperatures. Recent proposals have discussed the use of this cement for nuclear applications as it is a more efficient neutron captor than portland cement. Magnesium oxysulfate is obtained by the reaction of an aqueous solution of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) with magnesium oxide.

Depending on the conditions of formation, four types of oxysulfate complexes are known to form (2,3). These are: $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (or $\cdot 2\text{H}_2\text{O}$), $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$; however, only $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ appears to be stable below about 35°C (3).

It has been shown that porosity is an important property in strength determinations of oxysulfate cement (4); however, there appears to be no published information elucidating the nature of the pore spaces in this system and how they are affected by the instability of the solid phase during drying. Recently, a new technique, employing the diffusion of helium gas, has been shown to be a useful tool in studying changes during drying in the solid phase of hydrated portland cement (5). This technique provides the means of observing changes in solid volume due to drying as well as the capability of measuring quantitatively the creation of space due to the decomposition of complex hydrates, i.e., space resulting from the removal of hydrate water.

Helium diffusion methods have detected collapse of structure on removal of structural water in hydrated portland cement paste as well as aging phenomena; this structural water had an important role in the mechanical behaviour of the solid material. These methods provided new information that was valuable in the evolution of a model for hydrated portland cement paste. It was thought that the helium diffusion technique could also be used to elucidate the pore structure of magnesium oxysulfate paste; this study is a report of the results obtained from the application of this technique to the oxysulfate system.

Experimental

Materials

(a) Magnesium Oxide. The MgO powder was supplied by Basic Chemicals, Cleveland, Ohio. It had the following characteristics: N_2 surface area, $20\text{m}^2/\text{g}$; active CaO 1.5%; ignition loss 4%; fraction passing through 200 mesh, 98%. The material satisfied the requirements of ASTM C-275-61.

(b) Magnesium Sulfate Solution. Aqueous solutions were prepared by mixing $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, as supplied by Anachemia, in a dry form with distilled water. A partially saturated solution having specific gravity 1.18 and a saturated solution with specific gravity 1.303 were prepared.

Preparation of Specimens

Series I - Cement paste samples were prepared at $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}/\text{MgO}$ solution-solid ratios of 0.72 and 1.07 using the partially saturated $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution. Specimens having a solution-solid ratio of 0.72 were cast in cube molds and cured at 50% R.H. for 2 weeks. Discs 3.2 cm in diameter, 1.3 mm thick, were cut from 3.2 cm cores obtained from the cube samples. The discs were stored at 11% R.H. for periods up to 3 months. Specimens having a soln/solid ratio of 1.07 were cast in 3.2 cm diameter tubes that were rotated during the hydration process to prevent segregation. After demolding, the samples were sliced into discs 1.3 mm thick and then conditioned at 11% R.H. Series I samples had surface areas as determined by N_2 adsorption of $15.7\text{ m}^2/\text{g}$ (soln/solid = 0.72) and $20.4\text{ m}^2/\text{g}$ (soln/solid = 1.07).

Series II - Cement paste samples were prepared at a soln/solid ratio of 0.72 using, in contrast to Series I, the saturated $\text{Mg} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ solution. Series II samples had a surface area as determined by N_2 adsorption of $5.2 \text{ m}^2/\text{g}$. Disc samples were prepared as described previously for Series I samples. The discs were conditioned at 11% R.H. as with Series I, except that they were placed at 32% R.H. for approximately 3 days prior to the helium diffusion experiments. As Series I and Series II samples represent two distinctly different preparations, results are not directly comparable; however, it was felt that placing Series II samples at 32% R.H. prior to drying would generate some preliminary information regarding volume change characteristics resulting from re-wetting this system.

Procedures

Helium Comparison Pycnometry and Helium Flow

The apparatus and procedure for helium flow measurements are described in detail in previous papers (5,6,7). At the end of 60 h of helium flow, the density of the material is measured. 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", which cause a delayed flow of helium into the sample, are, in the first instance, regarded as part of the solid.

General Procedure

The helium flow and density were measured at different moisture contents, starting from the 11% R.H. condition for Series I samples and 32% R.H. condition for Series II samples. Moisture was then 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. Helium was allowed to flow into the sample for 60 h at 2 atm. After the flow was terminated, the pressure was reduced to 1 atm and recompressed to 2 atm for solid volume determinations.

Mercury Porosimetry

Pore size distributions for Series I samples were determined using an Aminco porosimeter (407 MPa). The samples were conditioned at 11% R.H. prior to testing.

Differential Thermal Analysis

Differential thermograms were obtained using the 990 Dupont thermal analysis system. Twenty mg of the material were used for each run. The rate of heating was $20^\circ\text{C}/\text{min}$ ($T = 150 \text{ s/in.}$) and the sensitivity was $\Delta T = 5 \text{ mcal/s/in.}$

Results

Helium Flow as a Function of Time

Helium inflow versus time curves for Series I samples (soln/solid ratio = 0.72) are presented in Fig. 1 (weight loss up to 9.93%). The results for the soln/solid ratio = 1.07 are qualitatively similar and are not presented. The curves in Fig. 1 are of three types and are numbered for reference in the text. The curve for the sample at 11% R.H. and the subsequent 3 curves up to a weight loss of 2.6% show a very rapid helium flow for approximately the first hour. After approximately 10 h, the flow rate is negligible and one can assume that helium is no longer flowing into the sample. This is the first type of curve designated Type I. At 3% weight loss, there is even more rapid flow during the first hour, the flow continues throughout subsequent hours and equilibrium is not attained even after 60 h. This type of curve is designated Type II. Curves numbered 5, 6, 8, 9, 10, 12, 13, 14, 16, 17 and 18 fall into this category. Curve 7 at 4.0% weight loss cuts across the first six

curves after 4 h with appreciable flow continuing even after 60 h. This curve is designated Type III as are curves 11, 15, 19, 20, 21, 22, 23, 24, 25 and 26.

Some specific features of the helium flow versus time curves are of interest. At 4.39% weight loss, Type II flow occurs; however, the total flow during the first hour is much larger than any of the preceding Type II curves. At 4.53% weight loss, the total flow is again greatly reduced but the flow curve remains Type II. At 4.87% weight loss, Type III flow occurs and equilibrium is not achieved even after 60 h. The next three curves up to weight loss 5.57% are Type II and the flow (curve 14) is further reduced. The next curve at 5.96% weight loss (Type III) has greatly reduced flow (just slightly greater than the flow for the first two curves) but the curve cuts across the first two curves after 27 h and unlike Type I, there remains low but discernible flow after 60 h. There is also a decrease in flow rate with respect to Type I curves in the first hour. The four curves starting at weight loss 8.05% are Type III and equilibrium is not reached after 60 h. At weight loss = 9.52%, the flow is again greatly reduced and is Type III. The final two curves, at 9.83 and 9.93% weight loss, respectively, show the largest flow rate at any time and are also Type III. The flow curves for Series I, soln/solid = 1.07, are qualitatively similar to those for soln/solid = 0.72 and are not presented.

FIG. 1

Helium inflow versus time for oxysulfate cement paste Series I, soln/solid = 0.72 (see Table I for weight change data).

The flow curves for Series II samples are presented in Fig. 2, and although there are qualitative similarities to those curves for Series I samples, Type I curves were not observed. Crossover of curves throughout the test sequence was minimal for Series II samples.

The character of the helium flow versus time curve was observed to be influenced by dissociation of hydrates and water removal as a result of temperature increases and pumping. The sequence of these operations is given in Table I with the weight changes for each of the curves of Fig. 1.

Effect of Weight Loss and Temperature on the Volume of Helium Flow

To illustrate how the helium flow varies with moisture content, the volume that flowed into the sample at 48 h was plotted as a function of moisture removed from the 11% R.H. condition for Series I samples and from the 32% R.H. condition for Series II samples. The plots for soln/solid = 0.72 are shown in Fig. 3. The numerical subscripts for the plot points correspond to the curves numbered in Figs. 1 and 2 and Table I. For Series I samples, there is an increase in flow from 1.60 cc/100 g at 11% R.H. up to 4.9 cc/100 g at approximately 4% weight loss, where

	$\Delta\omega$	
1	-	there is a small
2	0.86	decrease in flow
3	1.25	followed by a large
4	2.08	increase to 6.1 cc/
5	4.07	100 g at 4.39%
6	4.11	weight loss. The
7	4.56	next six points up
8	5.15	to weight loss of
9	5.76	5.96% indicate a
10	6.12	reduction in flow
11	6.55	to approximately 2.5
12	7.05	cc/100 g; the addi-
13	7.69	tional weight loss
14	8.10	is achieved by pum-
15	8.53	ping and heating
16	8.99	from 50°C to 100°C.
17	9.36	Further heating to
18	9.64	150°C results in a
19	10.03	large increase in
20	10.54	flow to 5.80 cc/
21	10.84	100 g at 8.05%
22	11.09	weight loss. It is
23	11.24	noteworthy that DTA
24	11.59	results (Fig. 4)
25	11.88	show two low-
26	12.14	temperature endo-
27	12.36	thermic peaks at
		approximately 100°C
		and 150°C correspon-
		ding to the loss of
		four and three mole-
		cules of water,
		respectively, from
		3 Mg(OH) ₂ ·MgSO ₄ ·8H ₂ O
		(3).

FIG. 2

Helium inflow versus time for
oxysulfate cement paste
Series II, soln/solid = 0.72

Additional pumping and heating to 200°C resulted in a large decrease in flow to 2.6 cc/100 g at a weight loss of 9.51%. Further heating at 200°C resulted in extremely large increases in flow, the latter being greater than 8.5 cc/100 g at a weight loss of 9.93%. Results for Series I, soln/solid = 1.07, are qualitatively similar and are not presented.

For Series II samples, the helium flow versus weight loss curve is plotted with values obtained by removal of water from the sample in equilibrium with 32% R.H., which includes the removal of adsorbed water in excess of a monolayer as well as structural water. It is noted that the changes in helium flow with weight loss observed for the curve for Series II samples follow a similar pattern to those observed for Series I samples, but the magnitude of flow is much less for Series II samples up to 9% weight loss. This may not be readily apparent as the peaks for Series II samples are slightly displaced along the weight change axis; drying from 32% R.H. may partially explain this. It is not expected that the removal of the extra sorbed water due to 32% R.H. conditioning would result in similar behaviour for both Series I and Series II samples because they are two distinctly different preparations; Series II was prepared with a saturated salt solution and Series I was made with partially saturated salt solution.

FIG. 3

Helium inflow at 48 h versus weight loss for oxysulfate cement paste

There are several fluctuations of increasing and decreasing flow for Series II samples as for Series I samples but differences between maxima and minima are less. Heating to 200°C, however, yields an 11.59% weight loss and results in an extremely large increase in flow (similar to that observed with Series I samples).

Total Space Vacated by Water Versus Degree of Drying

In the helium pycnometric technique, one measures a "solid volume" of the sample by using the instantaneous value obtained by compressing the gas to 2 atm in the sample cylinder. No helium flow is taken into account. One may then plot a curve of change in "solid volume" (ΔV) with weight loss as shown in Fig. 5. (This weight loss is due to the water removed in incremental drying from the starting condition - 11% R.H. for Series I and 32% R.H. for Series II.)

FIG. 4

Differential thermogram for magnesium oxysulfate cement

In Fig. 3, "total inflow" at 48 h has been plotted against weight loss. The term "total inflow" refers to the time-dependent helium flow into the micro-spaces. Removal of moisture results in a negative change in "solid volume" and a change in helium flow (ΔD). The algebraic sum of these two, $\Delta V - \Delta D$, can be regarded as the space vacated by water, if it is assumed that little helium entered the small spaces vacated by water during compression and measurement of density, and if the flow curves indicate equilibrium has been obtained. It is also assumed that the helium does not interact with the surface or other body forces and is at 2 atm within all the small spaces that water has vacated; this follows from the other assumptions.

In Fig. 6, $\Delta V - \Delta D$ is plotted against weight loss

TABLE I
Weight Change due to Removal of Water
from Magnesium Oxysulfate Cement Paste

Curve No. (Fig. 1)	Series I, Soln/Solid = 0.72 Weight Change, %	Treatment
1		
2	1.54	1 h pumping
3	2.17	1 h pumping
4	2.61	1 h pumping
5	3.02	1 h @ 50°C
6	3.80	1 h @ 50°C
7	4.00	1 h pumping
8	4.22	1 h pumping
9	4.39	1 h pumping
10	4.53	1 h pumping
11	4.87	1 h @ 50°C
12	5.13	2 h @ 50°C
13	5.32	1 h @ 75°C
14	5.57	1 h @ 75°C
15	5.96	1 h pumping @ 100°C
16	6.51	1 h pumping @ 100°C
17	6.73	1 h pumping @ 100°C
18	7.74	1 h pumping @ 150°C
19	8.05	1 h pumping @ 150°C
20	9.31	2 h pumping @ 175°C
21	9.35	1 h pumping @ 175°C
22	9.49	1 h pumping @ 175°C
23	9.52	1 h pumping @ 200°C
24	9.51	1 h pumping @ 200°C
25	9.83	1 h pumping @ 200°C
26	9.93	1 h pumping @ 200°C

(ΔW) for Series I samples (soln/solid = 0.72, 1.07) and Series II samples (soln/solid = 0.72). For Series I pastes, the parameter, $\Delta V - \Delta D$, appears linear up to about 15% weight loss. The plot points for soln/solid = 0.72, with numerical subscripts 7, 9 and 19-26, have values of $\Delta V - \Delta D$ which fall below the line described by most of the data and actually form a separate line having a very steep slope. The plot points for soln/solid = 1.07 having numerical subscripts 15-21 at weight losses larger than 15% also fall below the line and lie along yet another line having a very steep slope. The reason for this will be discussed later.

For Series II pastes there is a linear relationship between $\Delta V - \Delta D$ and weight change (ΔW) up to a weight loss of approximately 8.5% where there is a change in slope. The relationship between $\Delta V - \Delta D$ and weight change at higher values of weight loss is also

linear but has a steeper slope similar to that observed for Series I samples. The $\Delta V - \Delta D$ lines for Series II samples are displaced to the right of the line for Series I samples.

A linear regression analysis was applied to the $\Delta V - \Delta D$ versus ΔW data for Series I and II samples with the exclusion of the plot points with subscripts mentioned previously. The straight line for Series I samples is

$$\Delta V - \Delta D = -1.401 (\pm 0.261) - 0.827 (\pm 0.049) \Delta W, \quad \{0 < \Delta W < 15\} \quad (1)$$

The 90% confidence limits for intercept and slope are given in brackets. If all the assumptions are correct and helium filled all the space that the water vacated, the inverse of the slope gives the density of the water removed. This value comes to 1.209 ± 0.07 for Series I samples as described by Eq. (1), and appears to support the assumptions; results of density for some adsorbates up to 30% above their bulk values are recorded in the literature (8).

FIG. 5

Change in solid volume versus weight loss for oxysulfate cement paste

However, the line for Series I, soln/solid = 0.72, drawn through plot points 18-26 and the line for soln/solid = 1.07 through plot points 16-21 appear not to result from the formation of space created by removal of water because the steep slope of these lines results in a density for water which is far too low.

The two lines for Series II samples are as follows:

$$\Delta V - \Delta D = -0.156 (\pm 0.487) - 0.432 (\pm 0.084) \Delta W, \quad \{0 < \Delta W < 8.5\} \quad (2)$$

and

$$\Delta V - \Delta D = 11.436 (\pm 1.72) - 1.75 (\pm 0.159) \Delta W, \quad \{8.5 < \Delta W < 12.5\} \quad (3)$$

The inverse slope of the line given by Eq. (2) is 2.310, which is too high to be accounted for by the removal of water from the microspaces alone. The inverse slope of the line given by Eq. (3) is 0.571, which is too low to be accounted for by the removal of water from the microspaces alone.

The curves for ΔV versus ΔW as presented in Fig. 5 indicate a change in ΔV with respect to ΔW , which is much larger for Series I than for Series II samples.

Density by Helium Comparison Pycnometer

Density calculations were made with the helium flow volume included as pore volume, and the results were plotted versus weight loss (Fig. 7). The density versus weight loss curve is similar in shape to the helium flow versus weight loss curve (Fig. 3). In general, the density (Series I samples) increases from about 2.09 g/cc to 2.23 g/cc at 4% weight loss and after a decrease to 2.16 g/cc at 4.25% weight loss increases to 2.29 at 4.4% weight loss. There follows a general decrease to approximately 2.16 g/cc at 5.1% weight loss and subsequently a general increase to 2.39 g/cc at 8.05% weight loss. The density decreases to 2.26 g/cc at 9.6% weight loss and increases to greater than 2.60 g/cc at approximately 10% weight loss. Density was also calculated on the basis of weight loss alone (assuming a water density of 1.20 g/cc) and plotted in Fig. 7.

In general, the solid densities of Series I samples determined from the helium flow results are similar to those calculated from weight loss alone. However, densities determined by helium periodically deviate from the calculated curve at several weight losses, i.e., densities by helium give higher values. This can be attributed to trapped (empty) space (due to irregular collapse of structure) becoming accessible to helium, or discrete empty spaces opening up and suddenly becoming accessible to helium. The densities by helium for Series II samples all lie below the calculated line (based on weight loss only). This can be attributed to the inability of helium to penetrate spaces on removal of water from this system.

FIG. 6

Parameter $\Delta V - \Delta D$ versus weight loss for oxy-sulfate cement paste

HELIUM FLOW, MAGNESIUM OXYSULFATE CEMENT

FIG. 7

Density calculated with helium flow included as "pore" volume versus weight loss

In general the densities for Series II samples are lower than Series I samples at the same weight loss. After small fluctuations to a low value of approximately 2.03 g/cc at 4.5% weight loss, there is a general increase up to 2.55 g/cc at 11.6% weight loss.

Mercury Porosimetry

Mercury porosimetry results (intrusion pressure 407 MPa) for Series I samples conditioned at 11% R.H. gave values for total porosity which exceeded those determined by helium pycnometry at 11% R.H. This was surprising because for most other systems, such as porous glass, the porosity measured by helium is equal to or greater than that measured by mercury.

It was thought that this discrepancy might be due to the penetration of mercury into those spaces which became accessible to helium only after heating to 200°C (see plot points 24-26 (Series I) Fig. 3). The contribution to total porosity that these spaces provide is calculated from flow curves ($\Delta(\Delta D)/V_T$) obtained at weight changes subsequent to heating to 200°C. Results are presented in Table II.

TABLE II

Comparison of Hg Porosity and the Porosity of Oxysulfate Cement

Soln/Solid	He Porosity, %	$\frac{\Delta(\Delta D)}{V_T}$ [Fig. 6], %	He + $\frac{\Delta(\Delta D)}{V_T}$ Porosity, %	Hg Porosity, %
0.72	7.13	9.22 (pts 24-26)	16.35	14.20
1.07	12.26	15.95 (pts 15-19)	28.21	32.10
		(pts 19-20)	>50.0	32.10

The data in Table II indicate that most of the space which mercury enters can be accounted for by the sum of the instantaneous helium porosity and the space which becomes accessible to helium after heating to 200°C. For Series I samples, it is apparent that continued heating at 200°C opens up spaces that become accessible to helium.

Discussion

It has been observed that helium enters the pores of porous Vycor glass instantaneously and that no time-dependent flow takes place. The pores contained in Vycor glass have an average pore radius of approximately 30Å and hence it is likely that helium, observed in the present experiments, flowed into space with openings having least dimension much less than 30Å.

As referred to earlier, the helium molecule can give indications of what changes are occurring in a solid matrix during change in its chemical nature (e.g., decomposition) or during change in its physical nature (e.g., collapse of structure). The reason is that the helium molecule is very small and inert. If holes are created into which helium can enter, this will be indicated; if regions are formed from which helium is excluded, this should also be indicated. Values of density can be computed with some knowledge of what these values mean.

The following mechanisms are suggested to be operative during exposure of the magnesium oxysulphate to helium, and it is felt that they explain the changing character of the time-dependent helium flow and thus the changes to the solid as water is withdrawn:

- (1) Space containing bulk or adsorbed water empties completely and fills with helium.
- (2) Space formed by decomposition of magnesium oxysulfate complexes fills with helium.
- (3) New unfilled (with water) spaces open and fill with helium.
- (4) Previously water-filled space is incompletely filled with helium, possibly because of structural collapse (which may involve a change in dimension of pore entrances).

Mechanisms (1) and (2) seem to be applicable to the data described by the regression line for Series I samples having an inverse slope = 1.209. This value represents the density of the water removed and is in line with measurements made on expanding and non-expanding clays for water contents of less than one monolayer (9).

Mechanism (3) can account for large increases in flow and solid density with small changes in weight, e.g., large increases in flow (Fig. 1, curves 9, 19-26, soln/solid = 0.72) and density when the system is heated to 200°C. This can also account for unrealistically low values for density of water obtained from a plot of $\Delta V - \Delta D$ versus ΔW .

Mechanism (4) can account for unrealistically high values for water density obtained from a plot of $\Delta V - \Delta D$ versus ΔW . It is also possible that some previously accessible (to helium) microspace may simultaneously become inaccessible as diffusion paths may disappear with structural collapse. It is apparent that a microporous material, which contains microspace with entrances having least dimension sufficiently small so as to regulate the inflow of helium, will present difficulty in the measurement of its solid density. The inability of a fluid to enter the microspaces in this system would necessarily result in a value for solid density that is too low. The ability of helium to enter microspaces vacated by water enables determination of solid density that includes structural water remaining in the microspaces.

Increasing temperature probably affects the kinetics of structural collapse associated with decreased flow and removal of bulk, adsorbed and structural water. The two low-temperature DTA peaks reach a maximum at approximately 100°C and 150°C. However, the peaks are broad and there is gradual dehydration of the oxysulfate complexes and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ up to 300°C. The microspaces which are formed by the decomposition of these hydrates appear to be accessible to helium because the density value for water 1.209 g/cc obtained from the plot of $\Delta V - \Delta D$ versus ΔW is within limits that would be expected for this type of water. For Series I samples, increased flow to 4.5% weight loss followed by decreased flow to 6% weight loss results from pumping and heating in stages up to approximately 100°C.

The second cycle of increased and decreased flow up to a weight loss of 9.5% involves pumping and heating in stages from 100°C to 175°C. It seems likely that this cyclic behaviour is related to the gradual decomposition of the oxysulfate complexes.

Mercury intrusion experiments in this study give somewhat anomalous results; calculations, where one assumes a structurally stable matrix (to pressure) and the validity of the Kelvin equation, predict the filling of relatively large pores at 407 MPa ($>30\text{\AA}$ depending on the contact angle). It seems likely that the above assumptions do not hold for this system and that structural damage or alteration occurs to the matrix such that mercury penetrates into space that was not immediately accessible to helium. Internal isolated space may be opened up by differential pressure. In this case, calculations from the data based on conventional assumptions may not be valid but the results (total porosity) (Table II) support the above conclusion.

Conclusions

The helium-flow technique can follow physical changes in the microstructure of magnesium oxysulfate cement paste, which are due to chemical decomposition and water removal, and establish the physical nature of the structure formed.

1. There are discrete, unfilled (with water) microspaces that are not initially accessible to helium. Removal of moisture and application of increased temperature opens up diffusion paths to these microspaces allowing the inflow of helium.
2. The density of the water removed during drying from 11% R.H. was determined to be 1.209 ± 0.07 g/cc, which is in accord with results for adsorbed water reported in the literature.
3. When water is removed from this system (Series I), structural collapse occurs, i.e., as a result of solid volume changes due to drying, the microspace is reduced as solid surfaces come closer together.
4. Hg (at 407 MPa) can intrude into those microspaces not initially accessible to helium; this is probably the result of some structural damage or alteration to the system resulting from large differential pressures that open up internal, isolated microspace.

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