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Solvent exchange in partially saturated and saturated microporous systems
Length change anomalies

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Abstract

The results of a study to determine the volume stability of partially saturated and saturated microporous systems subjected to the solvent exchange process are reported. Length change measurements of several microporous systems (hydrated Portland cement, calcium silicate hydrate (C-S-H), calcium hydroxide (CH), vycor glass and molecular sieves) were monitored during immersion in excess amounts of methanol, isopropanol, and dimethyl sulfoxide (DMSO). Single and double exchanges were performed to assess the effects of the initial exchange on the reversibility of the length changes observed. Inferences were drawn from the length change results regarding the operative mechanisms responsible for volume change during the solvent replacement process. © 2000 Elsevier Science Inc. All rights reserved.

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1. Introduction

The results of studies of solvent exchange with the water in hydrated Portland cement paste have been widely reported [1–4]. The majority of these reports have focused on aspects of the counter-diffusion process that relate to mass change due to exchange of water with the solvent. Several researchers have used the solvent replacement technique to characterize the microstructure of hydrated cement systems. It is often assumed that any interactions between the hydrated cement solids and the organic solvent do not produce artifacts detectable with the technique utilized for microstructural investigation.

Some investigators have concluded that methanol, acetone, and other organic liquids interact with the surfaces of hydrated cement compounds [5–7]. Irreversible adsorption–desorption loops characteristic of adsorption isotherms for hydrated cement paste (hcp) where methanol and isopropanol are the adsorbates support this view [8]. Previous work by the authors with calcium hydroxide (CH) compacts has demonstrated that it is not only the silicate phases in Portland cement paste that influence the solvent exchange process [9]. Expansion of the compacts at various water contents following immersion in methanol and shrinkage behavior upon immersion in isopropanol were similar to the length change response for Portland cement paste under similar conditions.

Other authors [10,11] have reported that they found no evidence to support the above conclusion and suggested that methanol exchange was suitable for the preparation of samples for pore structure determinations. No signs of chemical interaction between ethanol and cement paste solids were detected by ^{13}C-NMR spectroscopy [12].

The volume instability of porous solids including cement systems in aqueous and non-aqueous media is complex and relevant to both microstructural and durability investigations. Microporous systems other than hcp have often been used to model and understand the behavior of the latter [13]. It would appear that this strategy could be useful in furthering understanding of the presence or absence of solvent interactions in cement paste systems.

The objective of this study was to establish more clearly the mechanisms responsible for the observed volume changes (some considered anomalous) in partially saturated

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and saturated microporous systems including Portland cement paste, calcium silicate hydrate (C-S-H), CH, porous vycor glass and molecular sieves. Emphasis was given to reporting more extensively the length change and volume stability observations as opposed to mass change data due to the large number of results and the greater facility for meaningful interpretation of phenomena.

1.1. Volume instability and length change

Microporous solids that chemically interact with pore fluids can expand significantly [14]. The attendant modification of the surface energy is apparently sufficient to cause significant distress. Several deterioration processes can be explained on this basis. Other traditional sources of expansion (e.g., crystal growth or osmotic pressure) are considered to be generated within the pore system and are not a result of chemical interaction with the solid matrix itself.

The physical adsorption of vapors on solid surfaces results in a decrease in surface-free energy and subsequent expansion. The free energy change is the product of surface area and the change in surface tension of the solid. Length change is directly proportional to changes in solid surface tension and is often referred to as the Bangham effect [15,16].

Length change in microporous systems can also occur due to intercalation of layered structures and meniscus effects due to adsorption–desorption in capillary pore systems [17].

Another type of length change mechanism that has been suggested is ‘molecular bridging’ in sub-nanometer sized spacings originally postulated for sorption on activated carbon [18]. Adsorption of methanol on activated carbon, for example, results in an initial expansion at very low vapor pressures followed by contraction and then significant expansion at partial pressure greater than 0.10. These effects are ascribed to co-operative van der Waal’s forces between neighboring adsorbate molecules and bridging single adsorbate molecules of neighboring sites, the sites bridged being either on the same solid surface or on opposite sides or faces of small pores. The decrease in entropy associated with bridging is equivalent to introducing a strain in the molecule, the strain being directed along the line joining the sites bridged. The surface forces of high-energy sites act on parts of polyatomic adsorbate molecules rather than on the molecules as a whole and are highly selective. Low energy sites tend to act on the molecules as a whole. Methanol was described as showing little or no bridging until the adsorbate density was sufficient for bridging to develop through co-operative interactions of the OH groups (hydrogen bonding). Tension in molecular sieves accompanied by contraction is produced by the process of water molecules leaving the necks of the pores and being replaced by solvent molecules.

A more comprehensive treatment of dimensional changes of porous solids is provided elsewhere [19].

2. Experimental

2.1. Materials

2.1.1. Portland cement paste

The specimens were made with normal type 10 Portland cement (w/c=0.50 and 1.00) and hydrated for 30 years. These were used for all the experiments. Specimens were sliced in the form of discs, 1-mm thick × 31.75 mm in diameter. The Portland cement had the following composition in percent: SiO_2 (20.72); Al_2O_3 (5.87); Fe_2O_3 (3.07); CaO (62.66); MgO (3.46); SO_3 (2.18); and free lime (0.24). The Bogue compound composition was as follows: C_3S (46.5); C_2S (24.6); C_3A (10.4); and C_4AF (9.3).

2.1.2. C-S-H

The C-S-H preparations were prepared and supplied by Lafarge Coppée Recherche. Details of the C-S-H synthesis are provided elsewhere [20]. The C/S ratio varied from 0.68 to 1.49. The C-S-H powders were compacted in the form of discs (at 340 MPa) 1-mm thick × 31.75 mm in diameter.

2.1.3. CH

Reagent grade CH was used. Specimens were prepared by compacting the powders (1.36 to 1360 MPa) in the form of discs 1 mm thick × 31.75 mm in diameter. Compacts were vacuum dried at 60°C for 24 h to provide the dry condition. Pre-treatment beyond the dry state was achieved by exposure of the compact to various humidities in equilibrium with saturated salt solutions. Additional details are provided elsewhere [9].

2.1.4. Vycor glass

Porous 96% silica glass was obtained from Corning glass in the form of 1 mm thick sheets. The glass had a nitrogen surface area of 175 m^2/g.

2.1.5. Molecular sieves

The molecular sieves used are aluminosilicate based (potassium cations). The 0.3 nm material was supplied by W.R. Grace, USA. The 0.4 and 0.5 nm material was supplied by Union Carbide USA. Mixtures of 75% sieve material and 25% calcium carbonate were compacted at 340 MPa in the form of discs, 1 mm thick × 31.75 mm in diameter. Calcium carbonate diluents were used to reduce the very large expansion on wetting and to facilitate compaction.

2.2. Length change measurements

For length change measurements, samples were mounted on modified Tuckerman optical extensometers and placed in large vacuum dessicators (containing the solvents) equipped with optically flat lids. The specimens were placed on supports and immersed in 2 l of solvent giving a volumetric ratio of solid to solvent of 0.003%. Given the large volumetric ratio of solvent to solid, frequent renewal of the solvent was not required. The length changes could be determined with a sensitivity of 1 × 10^{-6} mm/mm. Duplicate specimens were used for each test condition. Differences between readings at 24 h varied from 1.2% to 3.4% of the lower value. Careful precautions to minimize carbonation were taken in all phases of the experiments including the use of glove boxes flushed with nitrogen where appropriate.

2.3. Solvents

Reagent grade solvents (methanol, isopropanol, and dimethyl sulfoxide (DMSO)) were used. The solvent exchange experiments (of the test systems) with DMSO are believed to be the first reported for this solvent. This solvent has been used in studies of layered silicates such as natural montmorillonite [21]. Physi- and chemisorbed DMSO complexes can form in their interlamellar spacings. Co-ordination of DMSO molecules with exchangeable cations can occur through their oxygen atoms. DMSO can also bond via its oxygen atom to clay hydroxyl surfaces. For these reasons, DMSO was considered for the present studies.

2.4. Thermal analysis

Thermogravimetric analysis (TGA) was performed on the paste specimens equilibrated at various relative humidities (RHs) using a Dupont Thermal Analyzer. The apparatus was placed in a glove box maintained at the test humidity. Specimens were transferred from dessicators within the glove box. Differential TGA curves were produced through the application of appropriate computer software.

3. Results and discussion

The length change results will be presented separately for the following systems: hcp, C-S-H, portlandite, vycor glass and the molecular sieves. Mass changes vs. time curves are not presented here due to the large amount of data. It is noted, however, that the ratio of the amount of solvent diffused at time, *t*, to the amount when the mass change approaches a constant value (vs. square root time) generally indicates that methanol diffuses much more rapidly than the other solvents into all systems. Methanol, in general, has a significantly greater exchange rate than all the solvents studied [3,9].

3.1. Hcp

3.1.1. Adsorption from the D-dry state

The cement paste samples (w/c = 0.50) that had been D-dried (drying to the vapor pressure of dry ice at −78°C) and subsequently immersed in solvents (methanol, isopropanol, DMSO) all exhibited an immediate (within the first 2 min after immersion) expansion followed by a slight contraction (except for the specimens immersed in DMSO) over the next few hours and eventual slow expansion, Fig. 1. In each case, the slight contractions were observed for each of the duplicate samples. Initial expansions are due primarily to the free energy change due to surface adsorption effects, some intercalation into the C-S-H structure (with particular reference to methanol) and chemical interaction with the solid hydrated phases [22,23]. The slow expansion (after 4 h) may be due to intercalation effects. The observation that DMSO does not have the same effect may be an indication that intercalation is less pronounced with this solvent.

Chemical interaction of solvents with solids usually produces significant immediate expansions [17]. These have been attributed to surface-free energy changes, osmotic

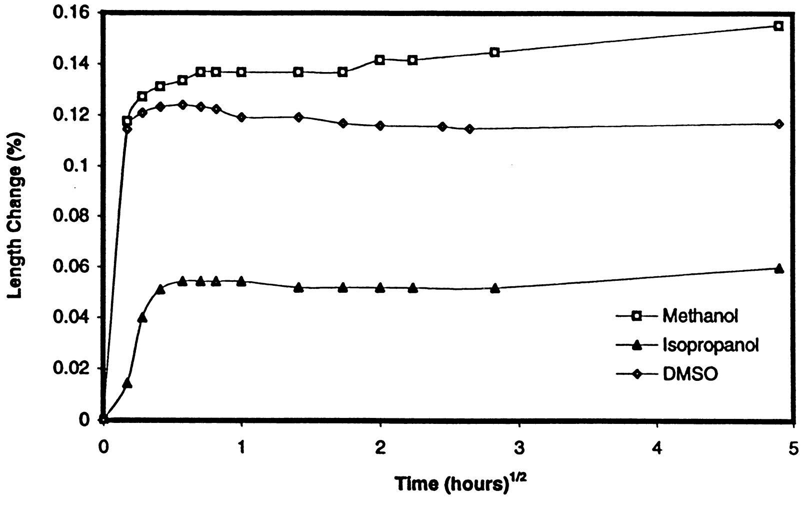

Fig. 1. Length change of cement paste (w/c = 0.5) D-dried and immersed in solvent.

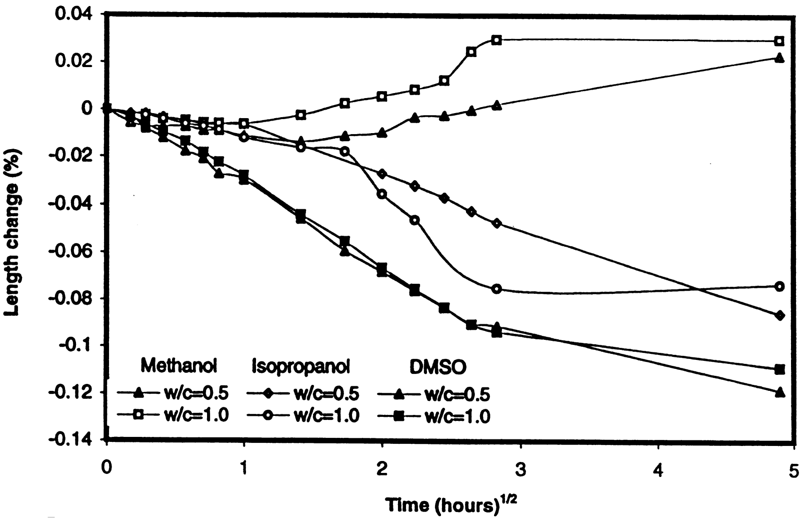

Fig. 2. Length change of saturated cement paste (w/c = 0.5 and 1.0) immersed in solvent.

pressure, disjoining pressure and strain energy considerations due to pre-treatment conditions.

Contractions following expansions during dissolution experiments are known to occur (e.g., porous silica glass in $NaNO_3$ solution) and are attributed to the adsorption of reaction products on the undissolved solid. The slight contractions observed (for each of the duplicate cement paste specimens) may have a similar origin as surface interactions with methanol, for example, are known to occur.

3.1.2. Solvent exchange of water-saturated hcp

The paste samples (w/c = 0.50 and 1.00) underwent an initial contraction during the first hour in all the test solvents, Fig. 2. The methanol-exchanged samples began to expand after 2.25 h and continued expanding to the end of the test at 24 h. The samples exchanged with isopropanol and DMSO contracted continuously over the 24-h period.

The changes in free energy of the adsorbent due to exchange of solvents (water for methanol, isopropanol or DMSO) can result in contraction if the surface-free energy increases. The expansion observed during methanol exchange could be the result of intercalation into the layered C-S-H structure, surface interaction between the solvent and the C-S-H and adsorption effects on the portlandite surfaces [3,9].

3.1.3. Double exchange of solvents

The irreversible effects of solvent exchange on the solid phases in cement paste can be assessed through a double exchange process. Solvent exchange experiments were carried out where the starting condition was either the D-dried state and subsequent saturation with solvent or the water-saturated state and subsequent saturation with solvent. Specimens prepared with these pre-treatments as the

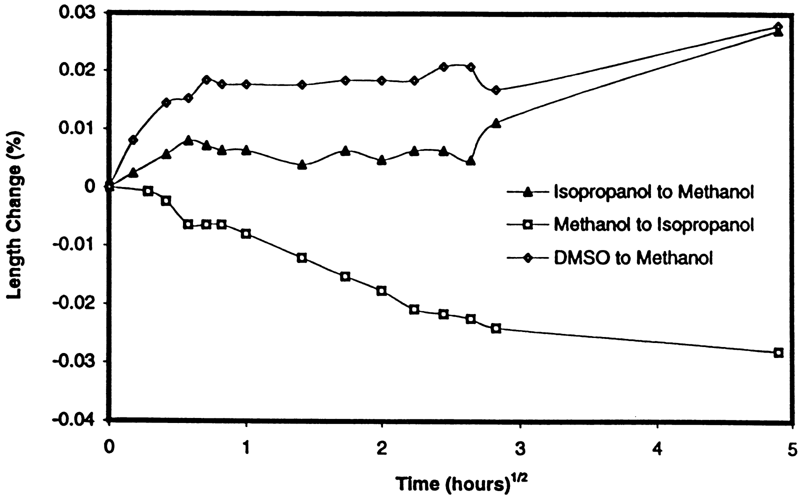

Fig. 3. Length change of cement paste (w/c = 0.5) D-dried, saturated in solvent, and immersed in an alternate solvent.

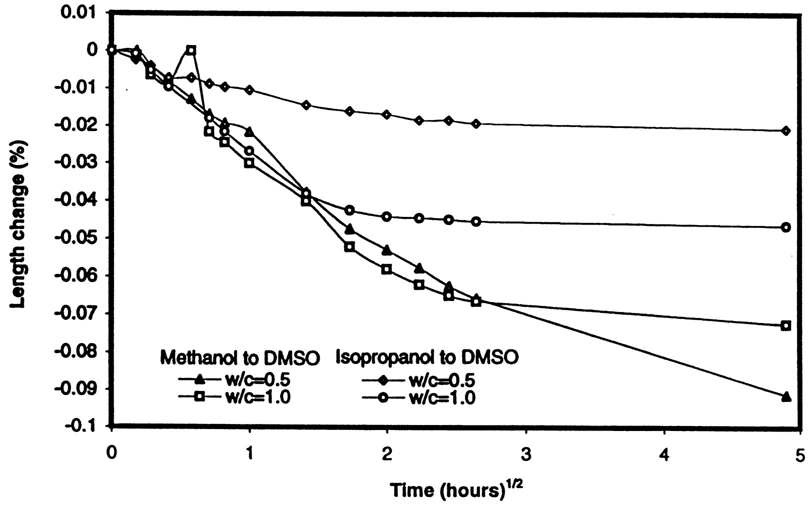

Fig. 4. Length change of cement paste (w/c = 0.5 and 1.0) conditioned at 100% RH, exchanged with methanol or isopropanol and re-exchanged with DMSO.

starting condition were subjected to a second exchange (see length change data, Figs. 3, 4). Table 1 provides the data representing the net length change after the second solvent exchange process. The length of the sample at the starting condition is taken as the reference length. The net length change is referred to this length. Data for the initial reference starting conditions, i.e., D-dry and 100% RH are also included in the table.

The double exchange for initial saturated samples (methanol to DMSO) would indicate that a first exchange with methanol has an irreversible effect on length change (the net length change of the sample being −0.050% compared to −0.110%). However, the double exchange (isopropanol to DMSO) would appear to have a reversible effect on length change, the net length change being similar to that observed for a direct exchange with DMSO. When the starting condition is the D-dry state saturation with isopropanol or DMSO prior to exchange with methanol appears to have an irreversible effect for the former and a reversible one for the latter saturant. Saturation of specimens with methanol prior to exchange with isopropanol also has irreversible effects on sample length.

It is apparent that the starting condition (D-dry or water saturated), selection of solvent, and sequence of exchange have an effect on the stability of the solid. Solvent exchange of water-saturated samples would appear to best be carried out using isopropanol. D-dry samples would appear to be least affected by saturation with DMSO compared to methanol or isopropanol.

3.1.4. Equilibrium drying — single and double exchange

Cement paste specimens were equilibrated at various positions along the desorption branch of the water isotherm (85% to 11% RH). The strains that were observed during the first equilibrium drying are presented in Table 2. The paste specimens were then immersed in the test solvents and length change was monitored.

Length change results (normalized to zero strain after equilibrium has been established) for both the w/c = 0.5 and 1.0 paste specimens were obtained. For the w/c = 1.0 paste (Fig. 5), the length change at 48 h generally increases with equilibrium humidity for all the test solvents. The length change–time curves are clustered into two groups. The first comprises those for specimens pre-

Table 1
Single and double exchange length-change data for D-dried or water-saturated cement paste

Length change ($\Delta l/l$, %) at 24 h[a]				
Starting condition	Methanol (M)	Isopropanol (I)	DMSO (D)	Net length change
D-dry	+(0.12–0.15)	+(0.05–0.08)	+(0.12–0.14)	–
100% RH	+(0.025–0.030)	−(0.08–0.09)	−(0.11–0.12)	–
100% RH → M			−0.08	−(0.050–0.055)
100% RH → I			−(0.02–0.045)	−(0.10–0.135)
D-dry → M		−(0.028–0.030)		+(0.090–0.132)
D-dry → I	+(0.020–0.027)			+(0.070–0.107)
D-dry → DMSO	+(0.028–0.030)			+(0.148–0.170)

[a] Zero length change is referenced as the D-dry or 100% RH condition.

Table 2
Length change ($\Delta l/l$, %) on first drying of cement paste to various equilibrium RHs

	w/c	
RH, %	0.50	1.00
85	0.06	0.08
75	0.14	0.14
57	0.25	0.22
42	0.28	0.31
32	0.31	0.32
11	0.39	0.34

conditioned to humidities ranging from 11–42% RH. It is apparent that the specimens in this group contain predominately interlayer water. Fig. 6 indicates that at 42% RH, only the peak at 110°C is present in the differential TGA spectra obtained under controlled humidity conditions. Above this humidity, there are two low temperature peaks, the lowest temperature peak being attributed to adsorbed and bulk pore water [24]. The second group represents specimens equilibrated at humidities, 57–85% RH. The results for the w/c = 0.50 paste (not shown) can be grouped in a similar manner.

For the methanol exchange experiments, group two specimens expanded significantly in the first few minutes and continued to expand over the test period. The expansion was greater than 0.20% at the 85% RH condition. It is suggested that partial drying of the layered silicates (at higher humidities, e.g., 85% RH) facilitates the intercalation process and resultant expansion due to penetration of methanol. This would appear to be the predominant mechanism of expansion for this condition and solvent. The first group of specimens either slowly expand over the entire test period (42% RH) or slightly contract (up to about 4 h) and then slowly expand.

The isopropanol exchange experiments were characteristically different from those for methanol exchange. Specimens in both groups expanded during the first 15 min and then contracted. Expansion reached 0.12% for specimens conditioned at 75% and 85% RH. Some intercalation into the C-S-H structure may be possible at high humidities as spaces at layer entrances may be more readily accessible. Contractions for group one specimens were as high as 0.10%.

Group one specimens exchanged with DMSO continuously contract and a value of 0.12% was reached on the specimen conditioned to 32%. Group two specimens behaved similarly to those exchanged with isopropanol.

The 100% RH condition (curve not shown in Fig. 5) yields results that are similar in character and magnitude to those for specimens conditioned at 11% and 32% RH. Minimum drying to 85% RH however, appears to open up the C-S-H structure (facilitating intercalation) prior to collapse with further drying.

Any significant intercalation of the solvent into the C-S-H structure is unlikely at low humidities. Contraction is possibly due to changes in surface-free energy resulting from the solvent exchange.

Double exchange experiments were conducted on specimens preconditioned to 11%, 32%, and 85% RH. The results are summarized in Table 3. The data for net length change (with respect to the original starting condition at 11%, 32%, or 85% RH) clearly indicate that a first exchange (on specimens pre-conditioned to equilibrium at 11%, 32% or 85% RH) with any of the test solvents has irreversible length change effects on samples that have been partially dried. This is an important consideration when preparing samples for tests that involve the use of mercury porosimetry [2,8].

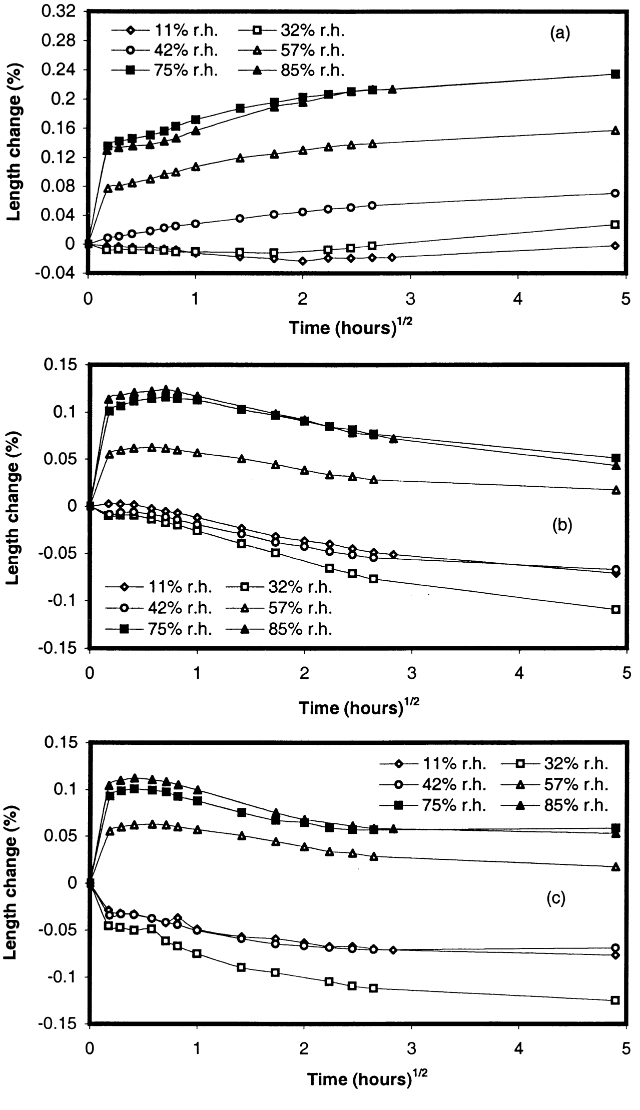

Fig. 5. Length change of cement paste (w/c = 1.0) conditioned at different humidities and immersed in (a) methanol, (b) isopropanol, and (c) dimethylsulfoxide.

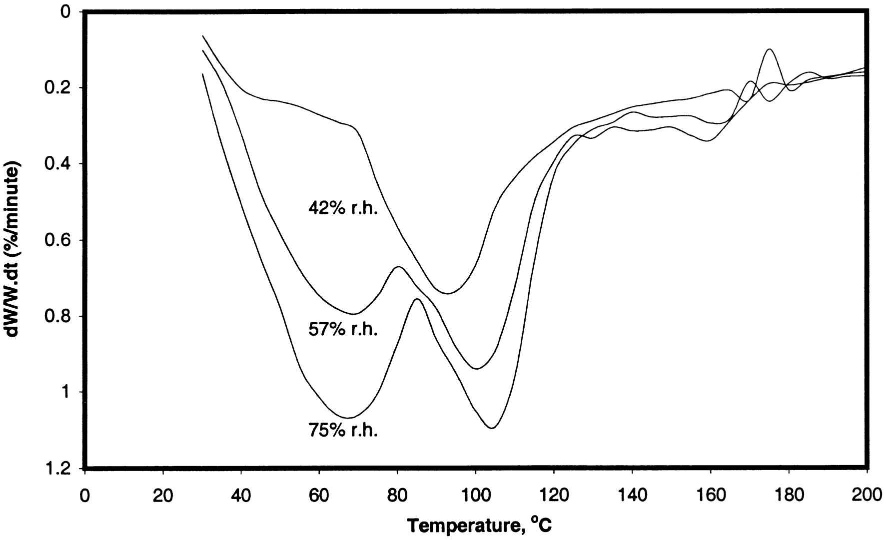

Fig. 6. Differential TGA curves for cement paste (w/c = 1.0) conditioned at 42%, 57%, and 75% RH.

Preparation of cement paste specimens for mercury intrusion involves drying to completely remove the water. The drying process perturbs the system resulting in a coarser pore structure. The argument for replacing the water with a solvent is that removal of a liquid with a lower surface tension results in a lower applied stress on the solid matrix. The resulting pore structure is less disturbed. It would appear that replacement of water with methanol is highly expansive indicating the possibility of intercalation effects and chemical interaction with the solid phase [5]. Replacement of water with other solids is not a net expansive process. Isopropanol appears to have the minimum net effect on dimensional stability [3,9]. It appears to be an appropriate solvent for specimen preparation. Vacuum drying for 24 h to remove the isopropanol is recommended prior to porosimetry measurements.

Table 3
Single and double exchange length-change data for cement paste conditioned to various equilibrium humidities

Length change ($\Delta l/l$, %) at 24 h				
Starting condition	Methanol (M)	Isopropanol (I)	DMSO (D)	Net length change
11% RH	0.000	−0.060	−0.080	–
11%→M		−0.030		−0.030
11%→I	+0.030			−0.030
11%→DMSO	+0.030			−0.050
32% RH	+0.020	−0.100	−0.120	–
32%→M		−0.070		−0.050
32%→I	+0.035			−0.060
32%→DMSO	+0.035			−0.090
85% RH	+0.240	+0.050	+0.060	–
85%→M		−0.080		+0.160
85%→I	+0.090			+0.140
85%→DMSO	+0.090			+0.150

3.2. C-S-H

3.2.1. D-dry condition

Length change–time curves for D-dried C-S-H (C/S = 0.68, 0.87) immersed in the test solvents and lime-saturated water are presented in Fig. 7. Large expansions (0.09% to 0.14%) were observed during the first hour of wetting with methanol and water. Expansion for the C/S = 0.68 preparation exceeded the expansion for the C/S = 0.87 preparation. It is suggested that intercalation of water and methanol is a primary cause of expansion. A secondary cause could be chemical interaction between the solvent and the C-S-H. Small expansions in the first few minutes were observed during the isopropanol exchange experiments followed by continuous contractions. Contractions were greater for the C/S = 0.68 specimens reaching −0.15% at 24 h. Continuous small contractions or expansions were also observed for the DMSO exchange. Contractions during either isopropanol or DMSO exchange could be due to adsorption of reaction products (assuming chemical interaction between the solvent and C-S-H) on unreacted C-S-H [4].

3.2.2. Water-saturated condition

The length change–time curves for water-saturated C-S-H (C/S = 0.68, 0.87, 1.26 and 1.49) immersed in the test solvents are characteristically different from those for the D-dried C-S-H specimens, Fig. 8. In methanol, the specimens either slightly contract or expand during the first 4 h. Length change at 24 h is −0.01%, 0.02%, 0.06% and 0.04%, respectively for the four C-S-H preparations. In isopropanol, large contractions occur at 24 h (−0.24%, −0.13%, and −0.17%) for C/S = 0.68, 0.87, and 1.49, respectively. For the C/S = 1.26 preparation, there is an expansion of 0.05%. Intercalation may occur to a larger

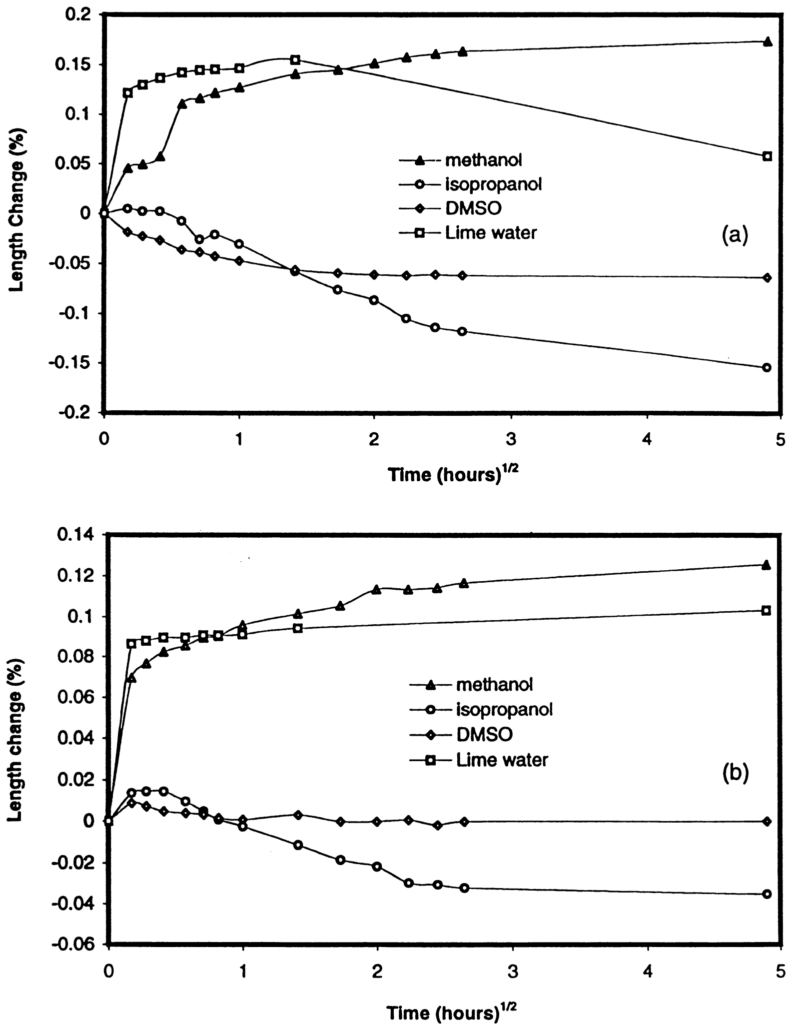

Fig. 7. Length change of D-dried C-S-H (a) C/S = 0.68 and (b) C/S = 0.87 immersed in solvent.

extent for this particular C/S ratio. The large contractions may be due to both changes in surface-free energy of the C-S-H on exchange with water and possible deposition of reaction products if any chemical interaction has taken place.

3.3. CH

Compacted specimens of CH prepared at 136–1360 MPa and various equilibrium water contents continuously expand when immersed in methanol (see Fig. 9 and Ref. [9]). Expansions at 24 h were up to 0.36%, 0.18%, and 0.8% for CH specimens containing 0%, 1.4–1.5%, and 4.8–6.9% water, respectively. The large expansions were attributed to changes in surface-free energy and possible chemical interaction of the solvent with CH.

CH samples immersed in isopropanol initially expanded and either continued to expand or contracted depending on the equilibrium water content. At 24 h, the dry specimens expanded up to 0.14%. Contractions up to 0.02% and 0.05% occurred for specimens containing 0.49–0.50% and 1.94–2.50% water. Surface-free energy changes and chemical interaction effects can account for the observed expansions and contractions.

It is important to note that it is not only the C-S-H phase in hydrated cement systems that is affected by the solvent exchange process. Parallel behavior (i.e., observations of expansions or contractions specific to methanol and isopropanol exchange) was observed for the hydrated Portland cement, C-S-H and CH specimens.

3.4. Vycor glass

Water-saturated vycor glass samples were immersed in the test solvents (Fig. 10). The specimens expanded during the first 15 min and then contracted. Expansion was less and contraction more when the exchange took place in isopropanol. The contraction at 24 h was −0.05%. The general behavior was similar to that of partially saturated cement paste (11–85% RH) immersed in isopropanol. Volume stability studies of vycor glass in sodium hydroxide have led to the suggestion that dissolution of glass leads to

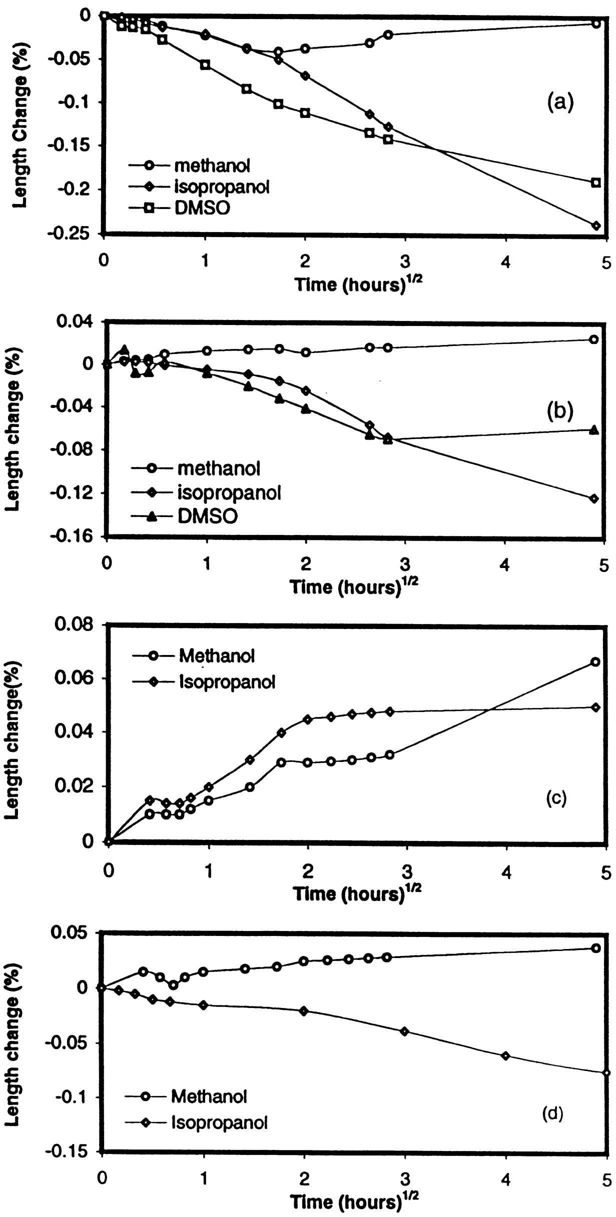

Fig. 8. Length change of C-S-H (a) C/S = 0.68, (b) C/S = 0.87, (c) C/S = 1.26 and (d) C/S = 1.49 conditioned at 100% RH then immersed in solvent.

expansion and that surface reaction and chemisorption lead to contraction. In the present experiments, the surface energy of the glass may change as a result of (a) elimination of surface irregularities; (b) changed composition of the surface as water molecules are replaced by solvent molecules; and (c) adsorption of the reaction products on the interior surfaces of the solid.

Length change–time curves for double exchange experiments are also given in Fig. 10. A summary of the length change data for the single and double exchange of the test solvents with water-saturated vycor glass is given in Table 4.

Examination of the data indicates that a first exchange with methanol or isopropanol produces highly irreversible effects with respect to the volume stability of water-saturated vycor glass. A first exchange with DMSO leads only to a small irreversible effect.

3.5. Molecular sieves

The 0.3, 0.4, and 0.5 nm molecular sieves were saturated with water and immersed in the test solution. The 0.3 nm sieve material expanded in methanol (0.15%) at 24 h and contracted the same amount in DMSO (Fig. 11). Isopropanol had very little effect on length change. The 0.4 nm sieve material immersed in methanol expanded slightly in the first few minutes and then contracted, reaching a value of about 0.14% at 24 h. Isopropanol and DMSO exchange resulted in continuous contractions reaching values of 0.37% and 0.39%, respectively. The 0.5 nm material expanded rapidly in methanol reaching 0.22% at 24 h. Isopropanol exchange

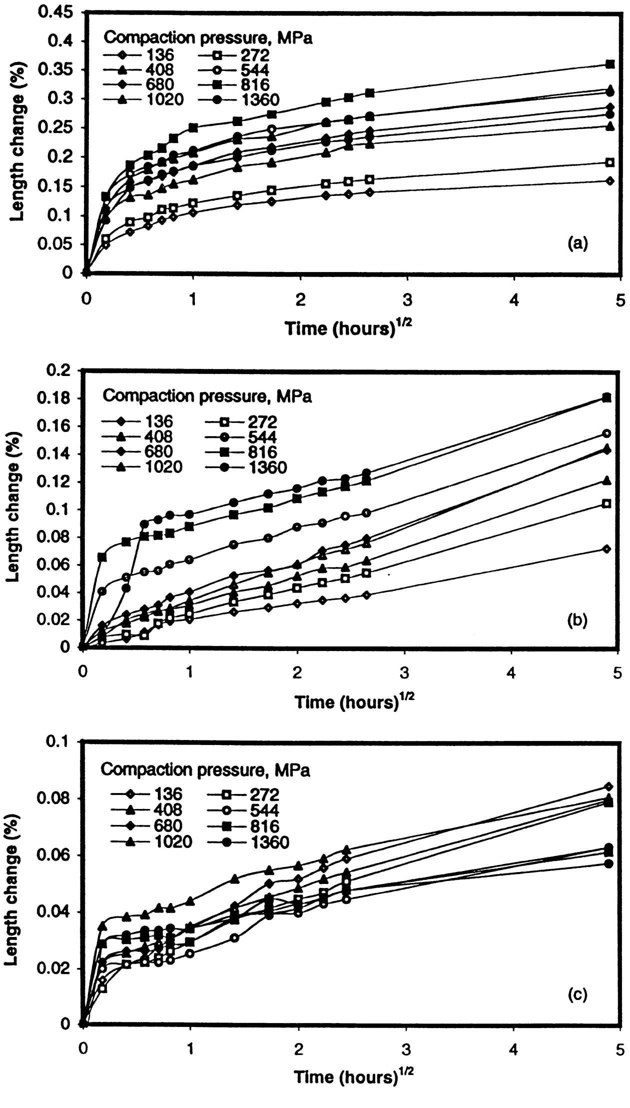

Fig. 9. Length change due to methanol exchange of $Ca(OH)_2$ compacts containing (a) 0%, (b) 1.4–1.5%, and (c) 4.8–6.9% water.

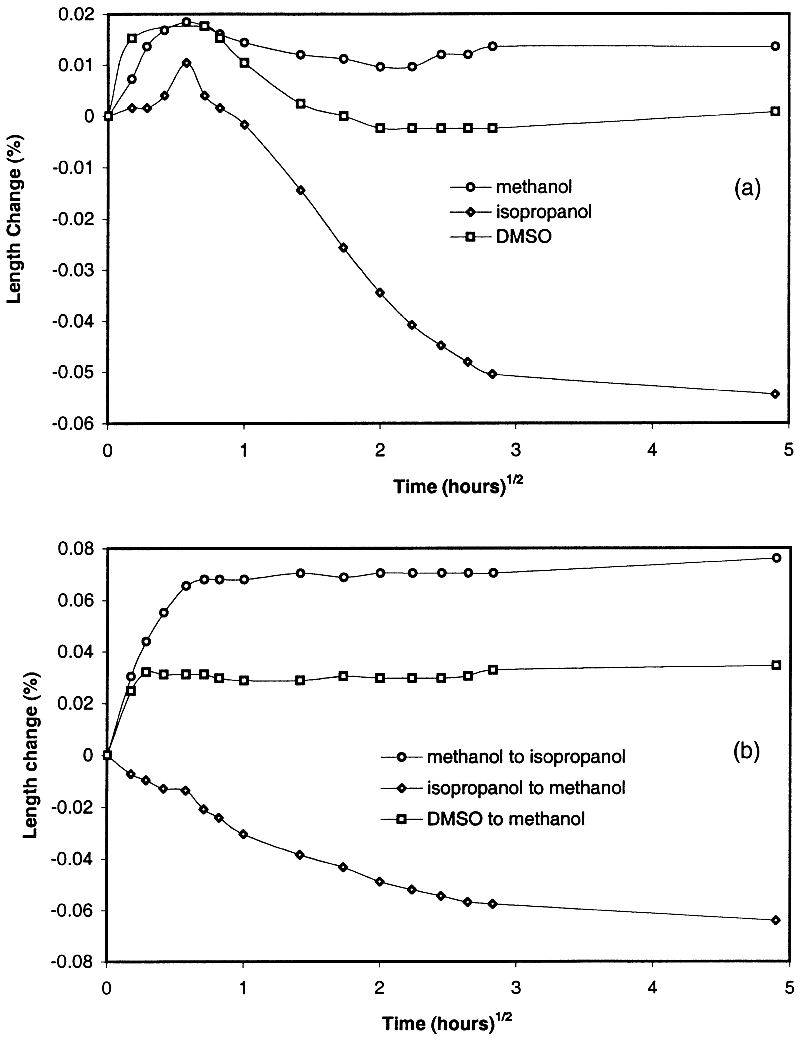

Fig. 10. Length change of vycor glass immersed in solvent (a) after conditioning to 100% RH and (b) after 14 days of initial immersion and reimmersion in another solvent.

resulted in contractions of the system reaching a value of 0.12% at 24 h. Exchange with DMSO resulted in an initial contraction to −0.07% at 1 h followed by a slow recovery to −0.055% at 24 h.

Comparison of the length change behavior of the molecular sieve systems with the hcp systems reveals similar behavior in most cases with some significant differences. Both systems experienced expansions with methanol exchange and contractions with isopropanol and DMSO exchanges. The slight expansion of the 0.3 nm molecular sieve resulting from isopropanol exchange and the continuous contractions (after the first few minutes) of the 0.4 nm sieves during methanol exchange are exceptions. The 0.5 nm molecular sieve has similar behavior to the cement paste in all test solvents. The expansion at 24 h after methanol exchange was considerably larger for the molecular sieve material than the corresponding value for cement paste (0.21% and 0.03%, respectively).

Table 4
Solvent exchange length-change data of water-saturated vycor glass

Length change ($\Delta l/l$, %) at 24 h				
Starting condition	Methanol (M)	Isopropanol (I)	DMSO (D)	Net length change
100% RH	+0.015	−0.055	0.000	
100% RH→M		+0.080		+0.095
100% RH→I	−0.065			−0.110
100% RH→DMSO	+0.030			+0.030

A summary of the length change data for single and double exchange of the water-saturated molecular sieves is given in Table 5.

Examination of the data in Table 5 would indicate that initial exchanges with any of the test solvents do not irreversibly affect the volume stability of the material, e.g., the exchange sequence 100% RH→I→M has a net length change of 0.165% compared to 0.150% for an initial exchange with methanol.

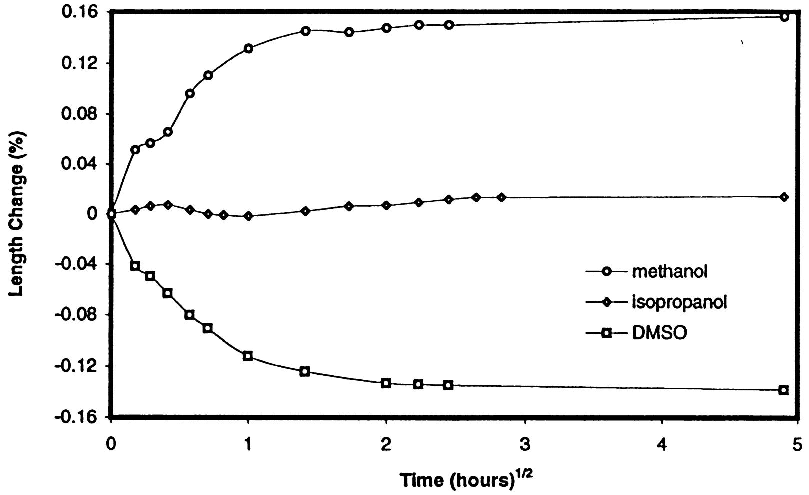

Fig. 11. Length change of compacts (75% 3A molecular sieve+25% $CaCO_3$) immersed in solvent.

The molecular sieves consist of a network of cage-like structures with entrances having dimensions indicated. Expansions and contractions occur on adsorption of water due to both surface energy changes and molecular bridging [18]. In a solvent exchange experiment, the solvent may be excluded from or enter the cage structure depending on the size of the solvent molecule or the cage opening. The solvent exchange data for the 0.3 nm system would suggest that the expansion occurring on immersion of the specimens in methanol might occur as a result of a "disjoining pressure" effect due to surface double layers at cage entrances. If the electric fields of two surfaces overlap, a repulsive force is created. It is unlikely that any of the solvents would penetrate into the cages with entrances smaller than the molecular diameter of the solvent.

Chemical interaction of the solvents with the molecular sieves is ruled out as the double exchange data (Table 5) indicate length change is not irreversibly affected by the solvent. Changes in surface energy (in addition to the disjoining pressure described above) can account for the length change behavior with isopropanol and DMSO. It is suggested that the balance between disjoining pressure and the surface energy changes results in a small expansion (0.01%) at 24 h for the isopropanol exchanged specimens. The change in surface-free energy change appears to be the predominant length change mechanism during exchange with DMSO.

Table 5
Solvent exchange length-change data of water-saturated molecular sieves

Length change ($\Delta l/l$, %) at 24 h

Sieve (nm)	Starting condition	Methanol (M)	Isopropanol (I)	DMSO (D)	Net length change
0.3	100% RH	+0.150	+0.010	−0.140	–
	100%→I	+0.155			+0.165
	100% RH→DMSO	+0.310			+0.170
0.4	100% RH	−0.140	−0.360	−0.390	–
	100% RH→M		−0.160		−0.300
	100% RH→I	+0.180			−0.180
	100% RH→DMSO	+0.280			−0.110

Contractions for the 0.4 nm molecular sieves at 24 h are very large being 0.14%, 0.36%, and 0.39% for exchange with methanol, isopropanol, and DMSO, respectively. It is suggested that in addition to surface energy changes, some penetration of the solvents into the cage structure may produce contractions due to molecular bridging.

The cause of expansion for the 0.5 nm sieve material exchanged with methanol is not clear. Large contractions resulting from exchange with isopropanol and DMSO can be explained by a combination of surface energy changes and molecular bridging.

4. Conclusions

(1) Length change of water-saturated hcp resulting from methanol exchange is different in character from that observed for methanol and DMSO exchange. Expansion as opposed to contraction (observed for other solvents) generally occurs. This is an indication that intercalation effects may be operative and supports expressed views that chemical interactions with the solid phase are possible in the presence of methanol. It is not recommended for use in pretreating specimens for mercury porosimetry tests.

(2) Double exchange (i.e., with two different solvents) experiments with water-saturated cement paste provide evidence that initial exchange with methanol has an irreversible effect on length change. An initial exchange with isopropanol has a reversible effect on length change.

(3) The starting condition of hcp (D-dry or water-saturated), selection of solvent, and sequence of exchange have an effect on the volume stability of the hcp solids. Minimum effects on volume stability suitable for specimen preparation for porosimetry tests are desirable. Exchange of saturated specimens with isopropanol followed by vacuum drying for 24 h is recommended.

(4) Length change of hcp due to the solvent replacement process is dependent on drying history. This implies that if solvents are used as microstructural probes or as part of pretreatment procedures for pore structure determination, the test results will be dependent on drying history. This applies to practical cases where cores from concrete structures are subject to examination.

(5) Partial drying of hcp to equilibrium pressures near saturation (prior to solvent exchange) results in significantly larger expansion than is obtained for the water-saturated condition. This observation for exchange with all test solvents suggests that at higher equilibrium pressures, length change may be due to intercalation processes.

(6) Solvent exchange of partially dried hcp with any of the test solvents has irreversible length change effects as indicated by the results of double exchange experiments.

(7) There are similarities in the length change behavior of water-saturated C-S-H and hcp exchanged with the test solvents. The expansive nature of the methanol exchange process on both systems is similar.

(8) Anomalous length change behavior (isopropanol exchange) occurs for C-S-H with C/S = 1.26. It is the only C-S-H preparation for which isopropanol exchange results in expansion (similar to the methanol exchange). It is possible that isopropanol intercalation effects are similar to those of methanol at this C/S ratio.

(9) Length change of CH due to solvent exchange is significant and similar in character to that of hcp. This is an indication that both C-S-H and CH contribute to the length change process.

(10) Length changes of water-saturated vycor glass (resulting from the solvent exchange) have some similarities and some differences to those of hcp. A first exchange with methanol or isopropanol produces highly irreversible effects with respect to volume stability. Second exchanges of isopropanol for methanol and vice-versa result in increases in expansion or contraction trends associated with the first exchange. This suggests that the first exchange interactions are similar for cement paste and vycor glass and involve surface energy effects. The glass surfaces are perturbed to a greater extent and length-change direction is not reversible on second exchange.

(11) Length changes of water-saturated molecular sieves (resulting from the solvent exchange) also have similarities and differences to those of hcp. It is significant that initial exchanges with any of the test solvents do not irreversibly affect the volume stability of the material. It is suggested that the mechanisms responsible for length change in these materials are physical in nature.

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