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Solvent Replacement Studies of Hydrated Portland Cement Systems: The Role of Calcium Hydroxide

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A study to determine the role of $Ca(OH)_2$ in hydrated cement systems concerning the processes involved in the removal of water by solvent replacement methods was conducted. The length change characteristics of $Ca(OH)_2$ compacts containing varying amounts of water and immersed in large volumes of organic liquids (methanol, isopropanol, benzene, and acetone) were analyzed and compared with those of hydrated cement paste. Inferences regarding the relevance of the Bangham effect and possible chemical interaction with the solid as to the mechanisms responsible for length change were made. Dependencies of the latter on compaction pressure and solvent species are discussed. The implications of the results with respect to microstructural investigations of cement paste are suggested. ADVANCED CEMENT BASED MATERIALS 1998, 8, 56–65. *© 1998 Elsevier Science Ltd.*

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The solvent replacement technique (in effect a counterdiffusion process) has been used by several researchers as a precursor treatment to characterize the microstructure of hydrated cement systems [1,2]. Arguments for its use are based on the assumption that the original microstructure of cement paste is less affected (and possibly "preserved") if drying takes place by removal of water with a solvent. The technique has been used to condition specimens prior to mercury intrusion experiments to determine pore-size distribution curves and for studies of the effect of drying shrinkage on pore structure [3,4].

A basic requirement in the application of the solvent replacement technique was that any interaction between the solid and organic solvent should not produce an artifact detectable with the microstructural method to be used. Preliminary pore structure investigations of CH compacts by the authors using mercury porosimetry have not revealed any significant pore structure changes. This work will be reported elsewhere.

It has also been of some concern to researchers that interactions with the solvent would influence determinations of degree of hydration and other physical characteristics of the hydrated cement system. A number of investigators have studied the solvent replacement process [5–12]. Taylor and Turner [5] have confirmed that methanol, acetone, and some other organic liquids are strongly sorbed by tricalcium silicate paste. Compounds identified after immersion in acetone included mesityl oxide, phorone, and isophorone.

Day [6] concluded that methanol or some reaction product could not be removed from cement paste by normal drying procedures and that it reacted with calcium hydroxide to form a "carbonate-like" material. Similar observations were made by Beaudoin [7], who determined that the surface area of calcium hydroxide samples nearly tripled after 24 hours immersed in methanol. Dollimore et al. [8] and Parrot [9] reported that no special features were detected by differential thermal analysis of cement pastes with organic liquids and specifically methanol. Thomas [10] concluded that methanol exchange was suitable for the preparation of samples for pore structure determinations. The techniques he used included thermogravimetric analysis, x-ray diffraction, infra-red spectroscopy, and mercury intrusion porosimetry. Thomas reported that no alterations were observed in the thermogravimetric data obtained for solvent-treated $Ca(OH)_2$ samples.

The strong interaction of methanol and isopropanol with the hydrated cement paste was reported by Mikhail and Selim [11]. In their study, the authors observed that the adsorption-desorption loops were not totally reversible. Part of the irreversibility was

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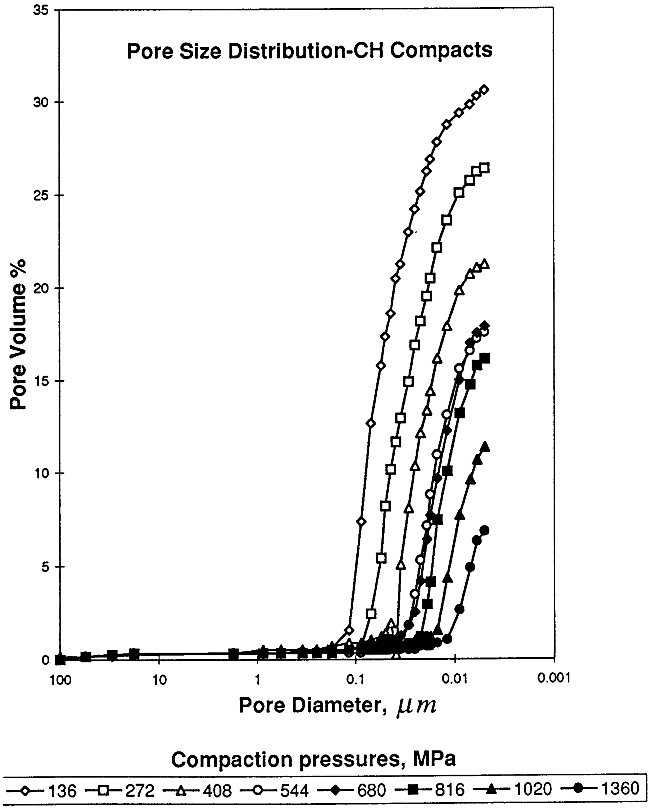

FIGURE 1. Pore size distribution curves of $Ca(OH)_2$ specimens compacted at different pressures.

associated to the sorption of the solvent molecules on the surface. The mechanisms of ethanol exchange have also been studied recently by Hand ^{13}C-NMR spectroscopy [12]. Results indicated extensive exchange between water and ethanol. No signs of chemical interaction between the solvent and the solid were detected.

In view of the differences of opinion cited concerning the effects of solvent replacement on hydrated cement solids and the paucity of data pertaining to calcium hydroxide itself, a study was conducted to provide more information concerning possible interactions of calcium hydroxide with a wide range of organic solvents. Length change of calcium hydroxide compacts pre-conditioned to various water contents was monitored following immersion in various liquids in a strategy designed to separate out Bangham length change effects from those due to chemical interactions with solid surfaces. Weight change versus time measurements were carried out to support interpretation of the length change data.

TABLE 1. Ranges of water content for pre-conditioned CH compacts

Solvent	Water Content (mass %)
Water	0; 0.5; 0.7; 1.9–2.5; 5.2–9.6
Isopropanol	0; 0.5; 0.7; 1.4–1.5; 1.9–2.5; 4.8–6.9
Methanol	0; 0.5–0.7; 1.4–1.5; 1.9–2.5; 5.0–6.8
Benzene	0; 0.5–0.7; 1.4–1.5; 1.9–2.5; 5.1–10.5
Acetone	0; 0.5–0.7; 0.7–1.0; 1.4–1.5; 1.9–2.5; 4.8–6.9

The objective of the work reported was to establish more clearly the role of Portlandite or calcium hydroxide (a mineral that can occupy up to 26% by volume of cement paste) in the solvent replacement process as applied to hydrated cement systems. This is the first article in a series on solvent replacement in microporous materials.

Theory

Volume Instability of Porous Solids

It was demonstrated [13] by experiments with porous silica glass and hydrated cement paste immersed in aggressive solutions (e.g., 0.2N aqueous NaOH, 1N aqueous HCl) that microporous solids under chemical attack expand significantly (up to 0.3%). 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. It is apparent that sorption of inert ions or dissolution of a constituent of a nonhomogeneous matrix or a portion of the entire solid can result in expansion that is sufficiently large to induce cracking [14]. Such modification of the surface energy is apparently sufficient to cause significant distress. Several deterioration processes can be explained on this basis.

Length Change Due to Adsorption

The adsorption of vapors on solid surfaces results in a decrease in surface free energy and subsequent expansion [15]. This can be expressed by the equation:

$$\Delta F = -RT \int_0^p n \frac{dp}{P}$$

where ΔF represents the change in free energy of pure adsorbent from its initial state under its own vapor pressure to its combining state provided that the integral represents a path of thermodynamic reversibility. The term *n* represents the number of moles of adsorbate on a fixed mass of adsorbent.

The free energy change can be written as:

$$\Delta F = \sigma \Delta \gamma$$

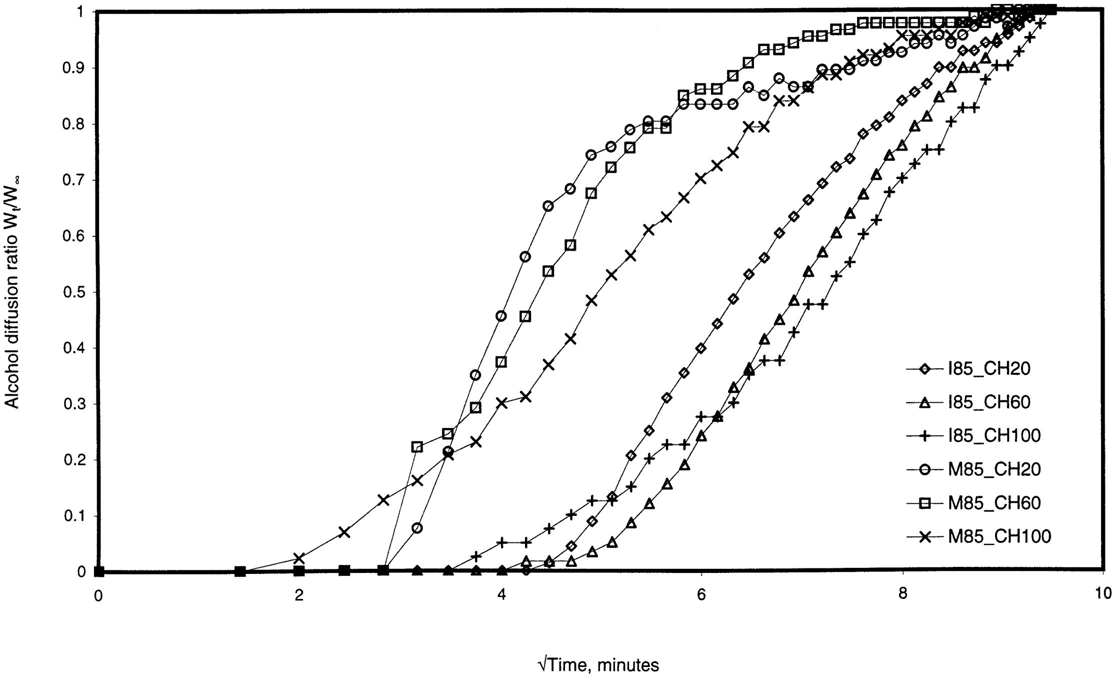

FIGURE 2. Ratio of the quantity of isopropanol and methanol exchanged in CH compacts at time *t* to that when the amount reaches a constant value versus square root time. CH samples were pre-conditioned at 85% RH. Compacts prepared at 20, 60, and 100 MPa are designated CH20, CH60, and CH100, respectively.

where σ is the surface area and $\Delta\gamma$ is the change in surface tension of the solid.

The forces due to changes in the state of stress of the solid place the latter in a state of compressive stress.

The Bangham equation relates the length change $\Delta L/L$ to $\Delta\gamma$ by the simple expression:

$$\Delta L/L = K\Delta\gamma.$$

Adsorption on CH Compacts

The Bangham equation has been shown to be applicable to compacted CH systems (compaction pressure, 133 MPa) in the adsorption region of the water isotherm up to a partial pressure of 0.40 [16]. The corresponding length change was about 0.12%. Dissolution of CH at points of contact, diffusion from these points, and recrystallization at other sites in the porous solid likely occur at relative pressures greater than 0.40. Length change up to 10.0% has been measured at saturation. Length change at pressures below 0.40 is due essentially to physical adsorption, indicating that insufficient water molecules are present for a very extensive diffusional process to take place in a short period of time.

The shrinkage process of CH compacts on desorption was attributed to the activation of van der Waals forces causing the crystallites to move together into the holes made by the diffusion process. Menisci forces were considered to have a role at higher vapor pressures. The possibility of adsorbed water becoming trapped in these spaces has been proposed as a reason for the large secondary hysteresis observed.

Experimental

Reagent grade $Ca(OH)_2$ of the following composition was used to make the compacts for these experiments: $Ca(OH)_2$ 97.7; $CaCO_3$ 0.58; SiO_2 0.38; Al_2O_3 0.05; Fe_2O_3 0.05; MgO 0.49; $CaSO_4$ 0.15; and sulfur 0.035 mass %. The procedure for making the compacts and the samples has been described previously [17]. Compacts were formed (at pressures of 136, 272, 408, 544, 680, 816, 1020, and 1360 MPa) in a mold 31.3 mm in diameter.

The pore size distribution curves for the CH compacts are presented in Figure 1. Pore size ranges vary from 0.20 to 0.007 μm and 0.20 to 0.007 μm for compacts prepared at 136 and 1360 MPa, respectively. Total porosity ranges from about 31% to 7.5%. The mercury intrusion measurements were carried out with a Quantachrome Autoscan-33 instrument (Quantachrome Corp., Syosset, N.Y. 11791) at pressures up to 212 MPa.

For length change measurements, samples were mounted on modified Tuckerman optical extensometers and placed in cells or vacuum dessicators equipped with optically flat lids. The length changes could be determined with a sensitivity of 1×10^{-6} mm/mm. Duplicate specimens were used for each test

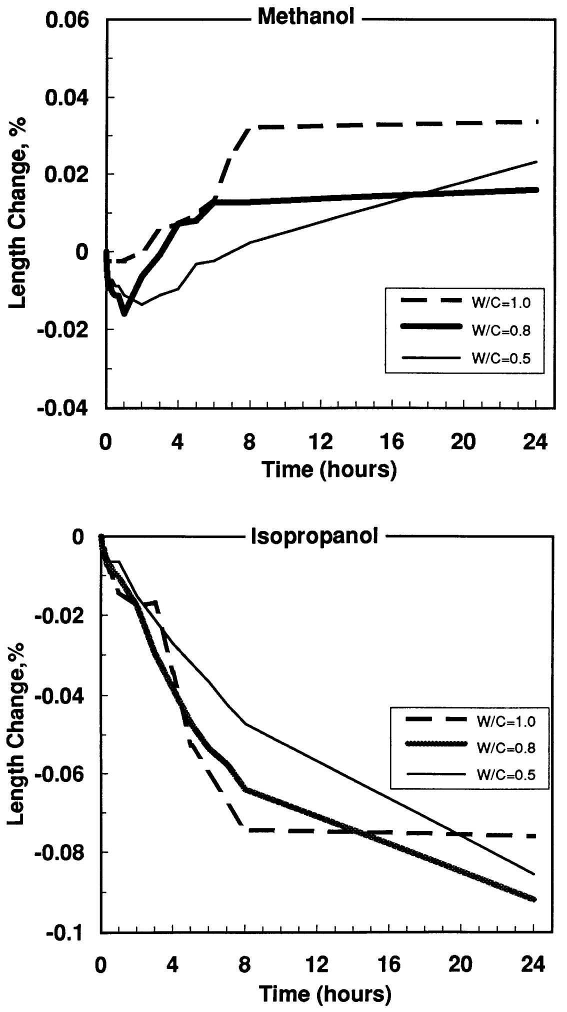

FIGURE 3. Length change of Portland cement paste (immersed in methanol and isopropanol) hydrated 30 years.

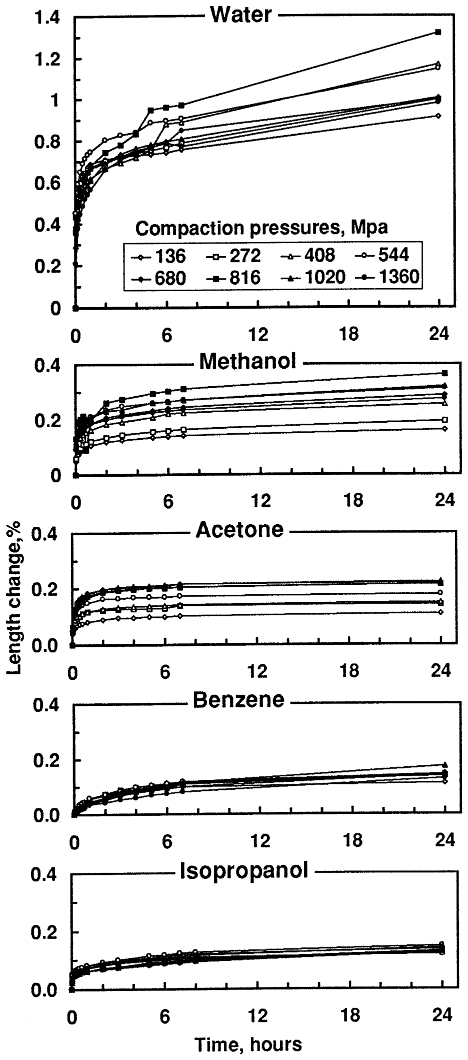

FIGURE 4. Length change of CH compacts pre-conditioned to 0% RH and immersed in various solvents.

condition. Careful precautions to minimize carbonation were taken in all phases of the experiments including the use of glove boxes flushed with nitrogen where appropriate. This was considered extremely important, as appreciable carbonation can significantly affect length changes and microstructure. The carbon dioxide contents were determined by decomposition with sulfuric acid, absorption of the evolved gas in barium hydroxide, and titrating with standard hydrochloric acid. CO_2 contents were on average about 0.8%.

Compacts were vacuum dried at 60°C for 24 hours to provide the dry condition. Pre-treatment beyond the dry state was achieved by exposure of the compacts (for periods varying from a few days to several weeks) to various humidities in equilibrium with saturated salt solutions. The humidity was varied from 11% relative humidity to 85% relative humidity. The range of water contents for the CH compacts is summarized in Table 1. Compacts for each compaction pressure level within each water content range were immersed in excess solvent for up to 25 hours. Length changes were continuously monitored.

Weight change versus time measurements were made for the CH compacts prepared at 20, 60, and 100 MPa. The compacts were pre-conditioned at humidities ranging from 11% to 85% as described previously. The microbalance mechanism, samples, and solution containers were placed in a glove box purged periodically with N_2 gas. The balance was interfaced with a personal computer for recording of weight changes resulting from the solvent exchange process.

Length change measurements of water-saturated cement paste samples immersed in excess methanol and isopropanol were also obtained. The cement pastes were hydrated 30 years and prepared at water/cement ratios of 0.5, 0.8, and 1.0. Samples were cut in the shape of disks, 31 mm in diameter × 1 mm thick. The

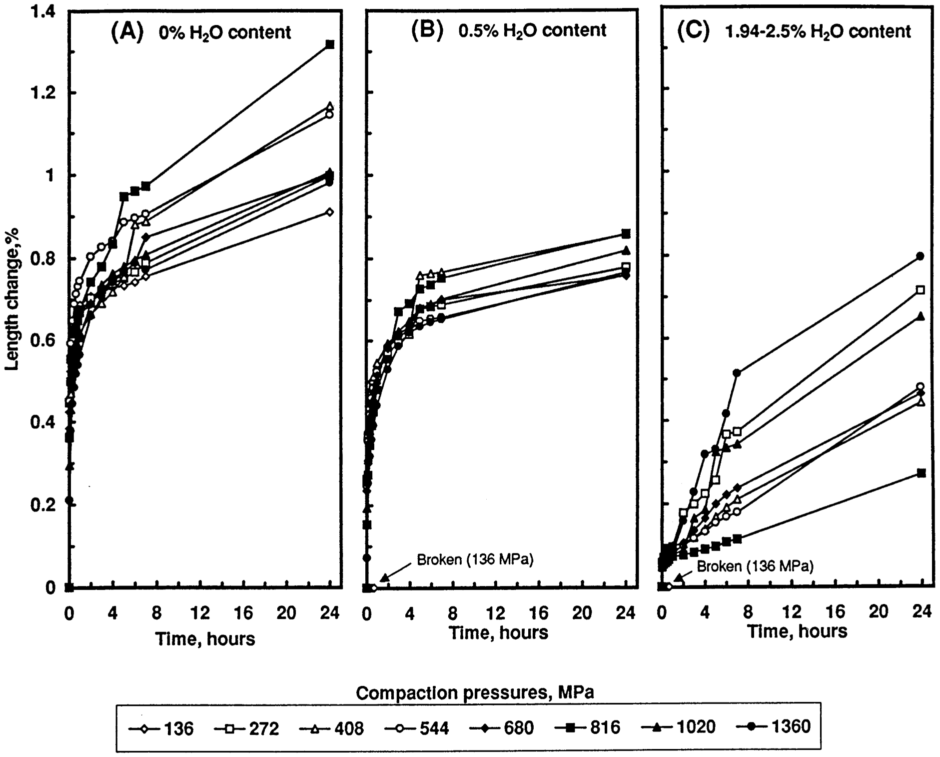

FIGURE 5. Length change of $Ca(OH)_2$ compacts of varying water content immersed in water.

composition of the Portland cement used was reported elsewhere [2].

Results and Discussion

The weight change versus time measurements of the CH compacts were obtained to facilitate interpretation of the length change information. The results are too numerous to all be presented. Selected results for methanol and isopropanol exchange are given, as these have received greater attention in the literature. The CH samples pre-conditioned from 11% to 85% RH were all partially saturated. Therefore, the weight change-time curves all had the following general characteristics. The weight increased to a maximum within the first few minutes and then steadily decreased to a constant value after 2 hours. The initial increase in weight is due to the rapid ingress of solvent into empty pore space. The process of counterdiffusion is considered to begin at the time the maximum increase in weight is reached. Calculations to determine the relative amount of solvent taken up by diffusion utilize the time at maximum weight increase as the starting point or zero.

Figure 2 is a plot of the ratio w_t/w_∞ (the amount of sovlent diffused at time *t* or w_t to the amount when the weight change reaches a constant value w_∞) versus the square root of time for CH compacts pre-conditioned at 85% RH and immersed in isopropanol (I85) and methanol (M85). Compacts designated CH20, CH60, and CH100 were prepared at 20, 60, and 100 MPa. The curves have similar shape to that of carbon spectra of ethanol in the cement paste pore system [12]. It is apparent that methanol diffuses much more rapidly than isopropanol into the pacts during the exchange process. The rate of exchange is dependent on compaction pressure and is is in the following order for both solvents: CH20 > CH60 > CH100. Maximum rates of exchange for methanol were determined to 0.192, 0.180, and 0.090 g/h and for isopropanol, 0.072, 0.042, and 0.018 g/h. Methanol, in general, has a significantly greater exchange rate than all the solvents studied.

The length change results for the saturated hydrated cement paste specimens are shown in Figure 3. These are intended to support inferences on the role of CH in cement paste drawn from the length change data of the CH compacts. In methanol, all the pastes exhibit a small contraction in the first few hours followed by expansion. Expansion is greatest at 24 hours for the water/cement ratio of 1.0 preparation. In isopropanol there is a contraction over the first 24 hours (0.08% to about 0.09%) for all pastes.

The length change results for the compacted CH systems prepared at the dry condition and immersed in various solvents are presented in Figure 4, with a common Y-axis scale for clarity. The length change results for the compacted CH systems pre-conditioned

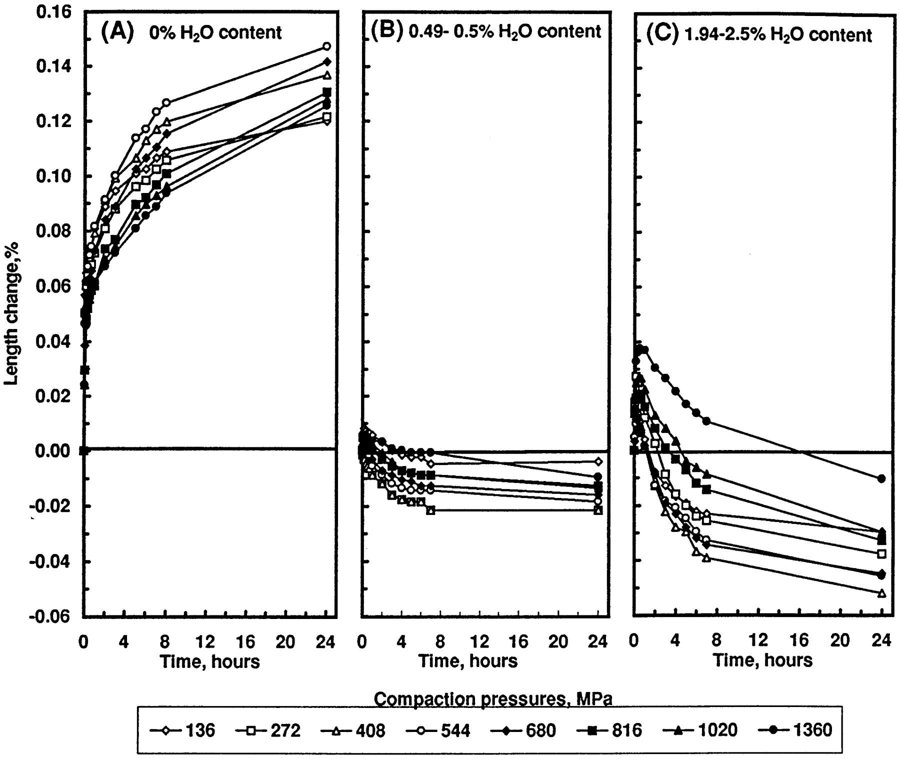

FIGURE 6. Length change of $Ca(OH)_2$ compacts of varying water content immersed in isopropanol.

at various moisture contents are presented for each adsorbate separately in Figures 5 to 9.

Dry CH Compacts

All compacts pre-conditioned at 0% RH expanded when immersed in any of the test solvents (Figure 4). Total expansion was generally in the following order: water > methanol > acetone > benzene > isopropanol. Compacts prepared at the lowest pressure (136 MPa) expanded the least in all solvents. Compacts prepared at the highest pressure (1360 MPa) did not give maximum expansion. The mechanisms of expansion are discussed in detail in the following sections for each solvent.

Water

The CH compacts prepared at pressures ranging from 136 to 1360 MPa were pre-conditioned at water contents ranging from 0% to 9.6%. Expansion subsequent to immersion increased with time at all levels of moisture content and compaction pressure (Figure 5). There was no clear dependence of total expansion on compaction pressure.

Expansion is attributed to the Bangham effect (at least up to a weight change of 0.70%) and solution/precipitation at points of contact involving diffusion and recrystallization to other sites. A dual mechanism is consistent with the observations of Feldman [15] and Litvan [13,14]. The Bangham effect is likely operative at least up to a weight change of 0.70% and can account for length change up to 0.10%. This was demonstrated by Ramachandran and Feldman [16] for CH compacts. They obtained a linear Bangham relation for length change on adsorption in accordance with eq 3. Larger total expansion at higher pressures is likely due to greater strain energy release on dissolution in spite of the lower surface area available to the adsorbate. The possible existence of holes in the structure at higher water content may account for reduced expansion due to the countereffect of van der Waals forces or bridging of molecules across microspaces. There would also be a dilution effect as the amount of bulk water (per unit mass of solid) would be greater in compacts prepared at high pressure for the same percentage of adsorbate.

Isopropanol

The expansion of the CH compacts vacuum dried prior to exposure to isopropanol increases with time up to about 0.15% (Figure 6A). The lowest expansion generally occurs at lowest pressures, i.e., 136 and 272 MPa. Most of the expansion is probably due to the Bangham effect, as a value of about 0.12% would be expected. Calcium hydroxide is insoluble in isopropanol and a dissolution/precipitation mechanism for length change is not considered likely.

The length change behavior for CH compacts pre-conditioned to various water contents prior to immer-

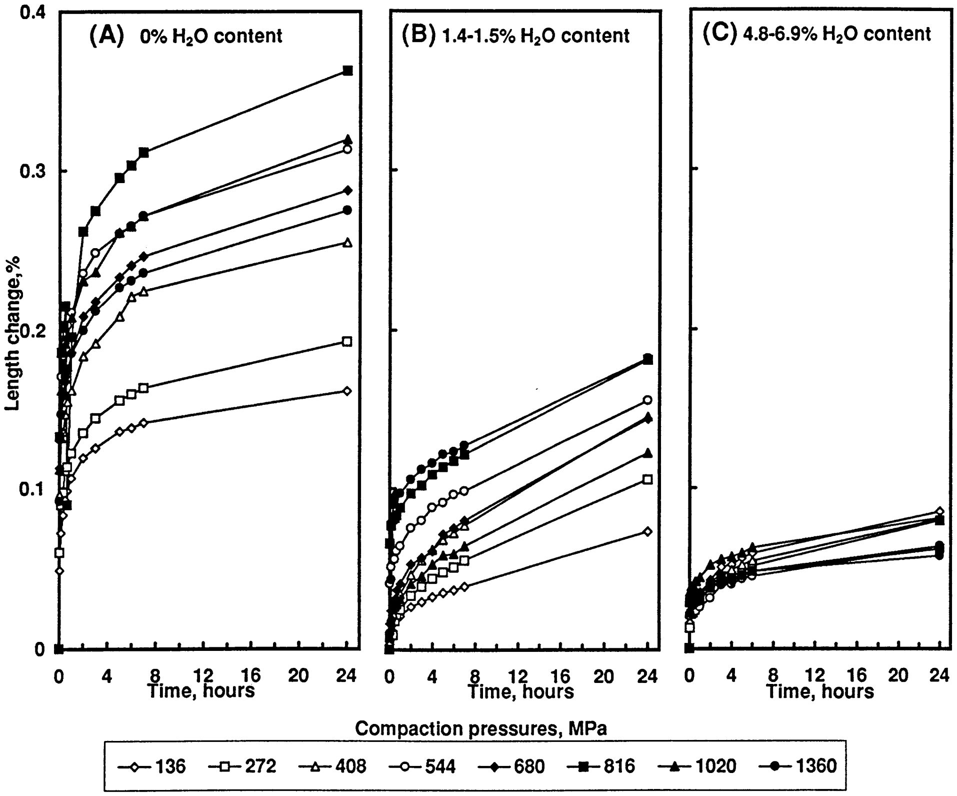

FIGURE 7. Length change of $Ca(OH)_2$ compacts of varying water content immersed in methanol.

sion in isopropanol is markedly different (Figures 6B and 6C). In general, ther is an immediate expansion (up to 0.04%) followed by a rapid progressive contraction. The immediate expansion may be due to some surface interaction between isopropanol and CH, as water at the solid surfaces is replaced with the solvent. This cannot be explained by the Bangham efect, for an immediate net shrinkage would be expected as the surface free energy balance (Bangham effect) would favor a reduced length change for the reduced molar surface coverage when water is replaced by isopropanol. The progressive contraction (beyond the first few minutes of immersion) can be explained as a shrinkage resulting from a bulk removal of water by isopropanol where the rate of removal exceeds the rate of replacement. These observations are consistent with the results of Litvan [14] for cement paste immersed in ethylene glycol and those of Hughes [18] for paste samples immersed in isopropanol and ethanol. This is also observed in hydrated cement paste where water is removed from the interlayer regions/micropores and not replaced by solvent [2]. The cement paste system undergoes continuous contraction on exposure to isopropanol solvent consistent with the results of Feldman [2]. No intial expansion, however, was observed. Any initial expansion of CH contained in the paste may be compensated by a net shrinkage of the paste.

The initial expansion is greater for the systems compacted at high pressure irrespective of the water content due to the pretreatment. For high pressure compacts there is significantly less surface water to be replaced by solvent; however, the strain energy release may exceed that of CH compacts prepared at low pressure.

Methanol

The CH compacts undergo expansion (at all water contents and compaction pressures) during solvent replacement with methanol (Figure 7). Unlike the case for isopropanol, there is no contraction observed with time. It is noted that water-saturated paste specimens expand on solvent exchange with methanol up to about 0.035%, whereas isopropanol solvent replaces pastes shrink by up to 0.08%. The expansion isotherm for a methanol adsorbate/cement paste adsorbent system indicates length change due to adsorption of degassed cement paste systems can alone account for expansions of up to 0.10% at saturation [15].

The total expansion of the CH compacted systems in the dry state ranges from 0.12% to 0.36% (Figure 7A). It is suggested that this is due to a combination of the Bangham effect and some type of chemical interaction. Several authors have presented evidence that some form of chemical interaction occurs between methanol and the constituents of hydrated cement systems.

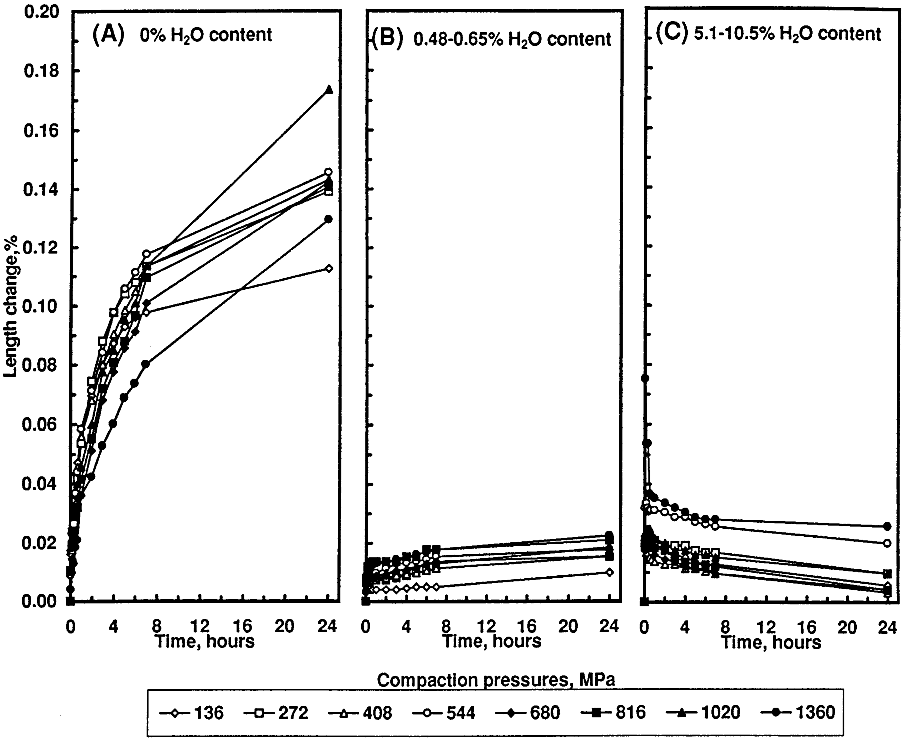

FIGURE 8. Length change of Ca(OH)$_2$ compacts of varying water content immersed in benzene.

The compacted CH systems pre-conditioned at various water contents all exhibit reduced expansion (i.e., about 50% of that in the dry state) (Figures 7B and 7C). It would appear that the expansive nature of the chemical interaction (as proposed by Litvan) dominates any tendency for contraction due to solvent replacement action or changes in surface free energy due to replacement of water with solvent molecules at the solid surface.

Low pressure compacts exhibit the least expansion in the dry state and up to a water content of about 1.52%. At higher water contents the high pressure compacts have the least expansion. It is possible that the solvation effects at high water contents are more pronounced in compacts prepared at low pressures accelerating and increasing interaction with methanol. Strain energy release due to chemical interaction with methanol may be the dominant mechanism at lower water contents. This can account for higher expansion at higher compaction pressures.

Benzene

The behavior of the CH compacts immersed in benzene (a solvent only slightly soluble in water) exhibited some similarities and some differences to that observed in isopropanol. The general character of the length change curves was either continuous expansion or immediate expansion followed by progressive contraction (Figure 8). The compacts that were vacuum dried expanded up to 0.12% when immersed in benzene. The length change is attributed primarily to the Bangham effect and is consistent with observations for the other solvents.

Compacts at a water content of about 0.50% also expanded continuously, unlike those immersed in methanol. The expansion was relatively small, ranging from 0.008% to 0.02%. The expansion suggests there may be some chemical interaction between benzene and the CH surface. The surface interaction would appear to continue at higher water contents as manifested by the immediate expansion in all cases. The contraction at higher water contents is possibly due to an increase in the rate of solvent replacement becoming a dominant influence. Unlike compacts immersed in isopropanol, the net length change is always positive.

The effect of compaction pressure is described as follows. There is generally less expansion at high pressures for CH compacts that were vacuum dried. There is less surface for the realization of the Bangham effect. In the presence of 0.50% water, the high pressure compacts expand the most. This suggests that there is a larger release of strain energy due to CH solid/benzene interaction at higher pressures.

The initial expansions of the compacts observed at the highest water contents (5.1% to 10.5%) are followed by progressive contractions. The initial expansions and the subsequent contractions are greater at higher pressures. The greater contraction may be due to generation of van der Waals forces resulting from surface pertur-

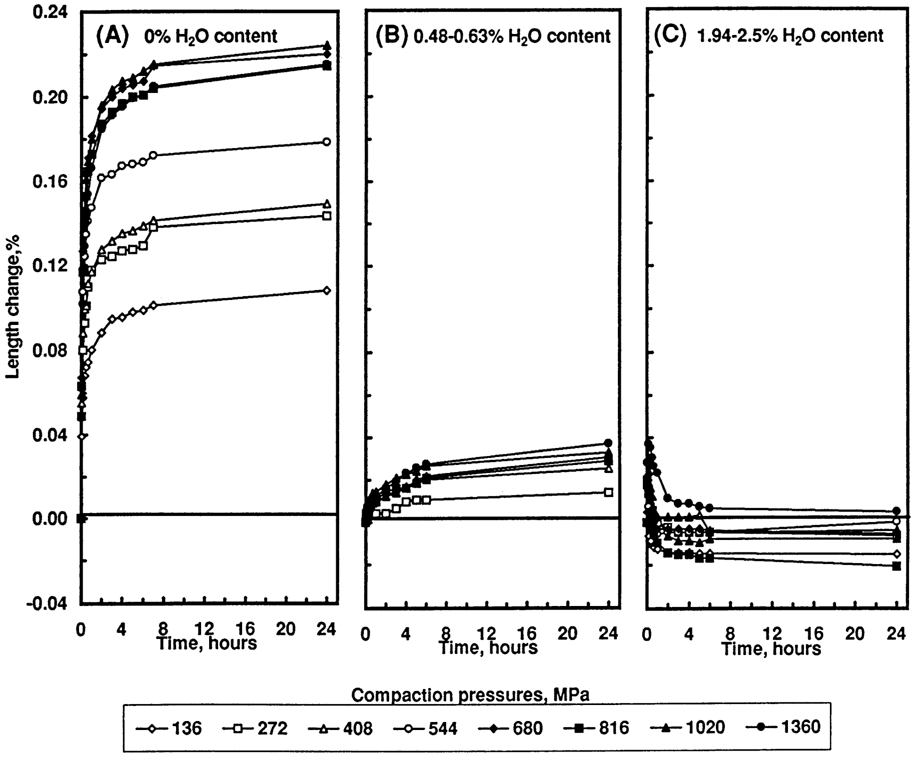

FIGURE 9. Length change of $Ca(OH)_2$ compacts of varying water content immersed in acetone.

bation effects on the rapid removal of a smaller amount of adsorbate from a larger number of fine pores.

Acetone

Acetone is highly soluble in water and reported to interact with the constituents of cement paste [5]. Expansion of CH compacts prepared in the dry state and immersed in acetone ranges from 0.08% to 0.20% (Figure 9A). It is likely due to a combination of the Bangham effect and chemical interaction with the surface. It is noted that there was a color change exhibited by the compacts (light to medium brown). The high pressure compacts expanded the most, suggesting the interaction effects were sufficient to produce a larger strain energy release.

A significantly reduced expansion (by a factor of 10) occurred at all pressures when the water content of the samples was about 0.50% (Figure 9B). This suggests that chemical interaction at the surface remains the dominant mechanism for expansion.

At higher water contents (Figure 9C), there is an initial immediate expansion followed by a progressive contraction similar to that observed for isopropanol and benzene exchange. The explanation of the length change behavior is also similar. The compaction pressure effects also have similarities to those observed for the isopropanol experiments.

Conclusions

1. The expansive character of the length change response of calcium hydroxide compacts when immersed in water, isopropanol, methanol, benzene, and acetone suggests that the length change is primarily due to both the Bangham effect and chemical interaction with the solid surfaces.
2. Expansion of calcium hydroxide compacts preconditioned to water contents in excess of that required for the full potential of Bangham expansion to be realized indicated that some form of chemical interaction mechanism between the adsorbate and the solid was likely operative.
3. Shrinkage (observed in certain cases), following the immediate expansion of CH compacts preconditioned to various water contents, was similar to that observed during isopropanol replacement of water in cement paste, suggesting that the length change on removal of water may be related to surface energy changes not always specific to the C-S-H phase alone.
4. Expansion of calcium hydroxide compacts (at all moisture contents) following immersion in methanol is similar to the length change response for cement paste immersed in methanol. This would appear to corroborate published evidence that

methanol interacts with cement paste including the calcium hydroxide phase.

5. The similar pattern of length change behavior of calcium hydroxide compacts immersed in solvents with low affinity for water (benzene) and high affinity (acetone) suggests that the length change mechanisms are similar.
6. The general transition of the length change dependence on compaction pressure (for CH compacts) from a direct to an inverse relationship during solvent replacement as a result of the pre-conditioning with water as an adsorbate suggests that the solvation processes activated by water are sufficient to further activate the release of strain energy during the solvent replacement process.

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