

A comparative study of the volume stability of C–S–H (I) and Portland cement paste in aqueous salt solutions

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Received: 2 May 2006 / Accepted: 28 November 2006 / Published online: 1 May 2007
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Abstract Ordinary Portland cement (OPC) paste specimens and compacted C–S–H (I) powders were immersed in distilled water and aqueous salt solutions of varying concentration to study their volume change behavior. Immersion resulted in ionic interaction leading to various degrees of expansion, leaching, softening and dissolution of the test samples. In all cases relatively rapid expansion occurred. The expansion of C–S–H (I) in aggressive media was found to be large and fast in MgCl_2 , MgSO_4 , LiOH , LiNO_3 and calcium (magnesium) acetate (CaMgAc) solutions. LiCl , CaCl_2 and NaCl were moderately aggressive towards C–S–H (I) depending on the solution concentration. Trends in the length change behavior of OPC paste are similar to that of synthesized C–S–H (I). Similarities were observed between the length change behavior of compacted C–S–H (I) and the swelling of smectite clays in contact with these osmotic media. The similarities are compatible with explanations of expansion provided by both the osmotic and the electrical double layer (EDL) theories. The relationship between the expansive behavior of C–S–H and both Na and Ca Montmorillonite in contact with aqueous salt solutions is discussed extensively in the context of its significance in cement science.

Introduction

The volume stability of hydrated Portland cement and concrete is central to durability issues concerning exposure to aggressive media [1]. Disruptive expansion often occurs in concert with deleterious reactions between hydrated cement phases and ions in the pore solution present as a result of various transport processes [2]. The mechanisms of expansion due to reactions with specific ions, e.g., sulfate and chloride, have been extensively discussed in the literature [3–7]. Degradation theories have generally focused on mechanisms occurring at the micrometer scale. In most cases expansions are attributed to pressures originating from the formation of quasi-crystalline or crystalline phases e.g., ettringite, brucite and gypsum. This study focuses directly on the behavior of C–S–H (I) in aggressive solutions. Previous studies on volume stability have emphasized the behavior of Portland cement (OPC) or C_3S hydrates [8]. Limited volume change information is available for C–S–H specimens exposed to salt solutions.

The exact nature of C–S–H formed in hardened cement paste is affected by many factors, including the composition of cement, the water–cement ratio (w/c), the curing temperature, the degree of hydration and the presence of chemical and mineral admixtures. The crystalline nature of the C–S–H phases was recently shown by Roßler et al. [9]. The result is that there is a significant variation in its composition, nanostructure and morphology [10]. It follows that a study of the volume change behavior of synthetic C–S–H (C–S–H (I) with awas chosen as a model system for the calcium silicate hydrate typically identified in cement products) could provide useful insights on concrete durability. The C–S–H was prepared in powdered form necessitating the use of specimens prepared by powder compaction techniques. The validity and use of

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compact specimens has been discussed in several publications concerned with engineering performance, surface chemical phenomena and durability assessment [11].

C–S–H (I)

Synthetic C–S–H phases with $0.7 < C/S < 1.7$ have been referred to as C–S–H (I) [12]. Calcium silicate hydrate phases (C–S–H), $x\text{CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$, constitute the major hydration products and the primary binding phases in Portland cement products [10, 13]. C–S–H phases in the latter are poorly crystalline. Their structure is often referred to that of tobermorite and jennite and their mixtures [10, 14].

C–S–H products present similarities to the clay minerals in crystal structure assembly. They are comprised of composite sheets made up of distorted calcium hydroxide sheets flanked on both sides by parallel rows of wollastonite type chains. The remaining calcium atoms are positioned in interlayer regions. A pH dependent surface charge is the result of silanol sites associated with the bridging silica tetrahedra or end chain tetrahedra [10, 13, 15, 16]. The C–S–H in cement binders, like clay, exhibits variation in water content, in degree of crystallinity and C/S ratio [1].

The C–S–H in Portland cement paste contains Al that substitutes for some of the silicon. It is argued that this will increase the acidity of Si–O and Si–OH bonds and hence the strength of alkali binding [17]. Al-substituted C–S–H referred to as C–A–S–H binds significantly more alkali than unsubstituted C–S–H. For example (for $C/S = 1.5$) C–A–S–H incorporates about two times the amount of Na ions in the solid as does C–S–H i.e., 0.35–0.17 mM/g at a Na solution concentration of 0.27 mM/mL [18]. The amount of Na incorporated in the solid increases significantly at lower C/S ratios. The alkali adsorption capacity of C–S–H (I) is an important factor that will be taken into account in explanations of volume instability.

Swelling clay-C–S–H analogs for expansive behavior

It is an objective of this study to assess the validity of using swelling clay behavior to understand volume stability issues in cement-based materials. Clay particles are formed from aluminosilicates arranged as parallel octahedral and tetrahedral layers. These layers carry a negative surface charge density, which arises from isomorphous substitutions in the tetrahedral or octahedral layers. Smectite clays such as montmorillonite are expandable clays in the sense that they have exchangeable cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+}) and water molecules situated between the layers. These ions neutralize the surface charge density on the wall and make

the solid electrically neutral [19–21]. When the solid is immersed in an aqueous solution an electrical double layer (EDL) is developed and an electrostatic interaction between the double layers appears [19, 20, 22, 23]. An increment in the basal separation of the parallel layers is observed and a swelling pressure can be measured [20, 24]. The experimental data of Lubertkin et al. [24] suggests that not only specific adsorption but also the finite size of the electrolyte ion, its valency, electronegativity and hydration energy play an important role in the description of the swelling of montmorillonite [19, 20, 21, 25]. Swelling leads to dispersion of the clay particles, especially those in parallel arrangement, until they reach equilibrium separation under a given pressure. The increase in basal spacing depends on the cations located in the interlayer region. If the interlayer cations are monovalent (i.e., Na^+ , Li^+), the interlayer repulsion is stronger and the degree of layer separation larger [21–23].

A further objective of the present study is to determine to what extent the expansion phenomena observed in the case of C–S–H (a calcium-rich material) exposed to aqueous salt solutions could affect the durability of concrete structures. Calcium rich hydrated silicates are known to have significantly different swelling potential than sodium rich silicates. Ca-montmorillonite, for example, does not swell to the same extent as Na-montmorillonite [26, 27]. Illite crystals, unlike montmorillonite, do not swell appreciably [28]. Hence, swelling in illitic material due to the uptake of water results from the separation of crystals themselves i.e., intercrystalline swelling [29]. It was observed that compressed cores of Ca-illite swelled to a much lesser extent in dilute solutions than Na-illite. The limited intercrystalline swelling of Ca-illite (similar to that of calcium montmorillonite) was attributed to the existence of a potential minimum between the plate-shaped illite crystals at regions of overlap within the assemblage of clay particles [29]. It therefore appears reasonable to seek a correlation between the volume change and durability characteristics of Ca-clay to C–S–H since the latter, as previously described, contains sheets of distorted calcium hydroxide flanked on both sides by parallel rows of wollastonite-type chains having between them the remaining or interlayer calcium atoms and water molecules. The presence, activity or mobility and location of calcium should be considered when interpreting the expansive behavior of C–S–H. Two types of calcium are generally considered: non-labile: (Ca linked to silica chains) and labile (Ca linked to Si–OH (silanol) groups). These groups may be located on the ends of the silica chains or on the surface of the solid [13].

In this paper an analogy between the length change behavior of hydrated calcium silicate (C–S–H (I)) and clay (based on the similarity of their structural assembly) while

in contact with dilute and concentrated aqueous salt solutions is presented. The applicability of the electrical double layer (EDL) theory including ion-ion interaction effects is assessed. The effect of ionic size and the nature of the cation and anion of the electrolytes on the length change of the C–S–H (I) as well as the mechanism of ion–ion interaction and specific adsorption at the surface will be discussed. The aggressive and expansive behavior of C–A–S–H (in Portland cement paste) and synthetic C–S–H (I) in aqueous salt solutions was monitored. Specifically the length change induced by exposure to MgCl_2 , MgSO_4 , LiOH , LiCl , NaCl , LiNO_3 and CaMgAc salt solutions was determined.

Experimental

Materials

C–S–H (I) synthesis

C–S–H (I) was synthesized by mixing CaO and reactive SiO_2 powders (in stoichiometric proportions required to yield C–S–H having C/S ratio $\cong 1.6$) in 250 g of de-aerated distilled water under nitrogen to avoid exposure to atmospheric CO_2 . The preparation of CaO consisted of heating reagent grade CaCO_3 at 900 °C for 3 h followed by cooling in a nitrogen atmosphere. Commercially available amorphous silica (Cabosil) was heated at 110 °C for 3 h prior to mixing intimately with the previously prepared CaO in a 500 mL high-density polypropylene bottle. The de-mineralized de-carbonated water was added to the bottle and the system was flushed with nitrogen before sealing and agitating on a rotating roller for a period of 14–70 days. A ‘reference’ C–S–H (I) product was filtered in a nitrogen atmosphere and dried under vacuum at 25 °C for 12 h for the majority of the experiments. Other preparations were vacuum dried at elevated temperatures i.e., 47–50 °C; 60–65 °C; 70–75 °C for 12 h. Extreme care was taken during the drying procedure to ensure the reproducibility of results and stability of the material. The issue of reproducibility in terms of volume stability will be discussed further in the results section of the paper.

C–S–H (I) characterization

The C–S–H was characterized using several spectroscopic techniques:

Powder X-ray diffraction (XRD). XRD measurements were performed with a Philips PW3710 diffractometer using $\text{CuK}\alpha$ radiation. The powder patterns were recorded at 45 kV and 40 mA, using step scanning with a step size of $0.02^\circ 2\theta$ at a scan rate of $0.5^\circ 2\theta/\text{min}$ in the intervals

$1.41^\circ < 2\theta < 35^\circ$, $1.41^\circ < 2\theta < 15^\circ$ or $1.41^\circ < 2\theta < 4^\circ$ when a more detailed pattern was needed. A background subtraction correction was performed on all XRD patterns. The XRD pattern indicated the presence of the primary peaks previously reported for C–S–H (I), [14]. These were (in order of intensity) at ‘d’ values of 1.25, 0.304, 0.280 nm. A low angle peak at $d = 1.82$ nm was also observed. A small residual amount of calcium hydroxide was detected. XRD spectra were also obtained for C–S–H (I) specimens immersed in various solutions including the MgCl_2 and MgSO_4 solutions.

Fourier Transform Infrared (FTIR). The spectra were obtained using a Bomem Michelson MB 100 FTIR spectrometer. Thirty to 50 averaged scans at 4 cm^{-1} resolution were taken. The samples were prepared using the KBr pellet method. The FTIR spectra indicated the presence of bands at $3,640 \text{ cm}^{-1}$ (OH stretching vibrations of CaOH_2), $3,450 \text{ cm}^{-1}$ (OH stretching vibrations of C–S–H), $1,700$ – $1,500 \text{ cm}^{-1}$ (bending of OH groups in the C–S–H), $1,200$ – 800 cm^{-1} (stretching vibrations of SiO_4), 500 – 400 cm^{-1} (bending vibrations of SiO_4).

Thermogravimetric Analysis (TGA). A Polymer Labs STA 1500H instrument (TGA/DTA) with a nitrogen flow rate of 25 cc/min and a heating rate of 20 °C/min (30–1,000 °C) was used. The thermogravimetric curve (mass loss versus temperature) was qualitatively and quantitatively similar to that reported by Taylor for C–S–H gel [14]. The mass loss in the region, 400–600 °C, was very small for Taylor’s specimen. An even smaller loss was observed for the C–S–H (I) used in this study suggesting that the residual amount of Ca(OH)_2 is small or negligible. Constitutional water likely contributes to the small mass loss in this region.

BET Surface area. A Quantachrome surface area analyzer was used for the measurements. The nitrogen surface area of the C–S–H prepared was $54 \text{ m}^2/\text{g}$.

Aqueous salt solutions. Sets of aqueous salt solutions with different concentrations (1, 5, 5, 10, 15, 60, 180 g/L and saturated) were prepared. The salts used were: NaCl , CaCl_2 , LiCl , LiOH , LiNO_3 , MgCl_2 , MgSO_4 , and CaMgAc (calcium magnesium acetate).

Preparation of solid specimens—compacted powders and paste prisms

C–S–H (I) compacts in the form of circular discs ($31.7 \text{ mm} \times 1.2 \text{ mm}$ discs) were prepared by compaction of powders (at 170 MPa) previously dried for 12 h at 25 °C under vacuum. Drying was also carried out at elevated temperatures of 47–50 °C, 60–65 °C, 70–75 °C. Prisms ($10.0 \times 31.6 \times 1.2 \text{ mm}$) were cut with a sharp knife from the disc samples for length change measurements. The Portland cement paste was cast in cylindrical molds

(31.7 mm in diameter \times 250 mm long). They were made with a w/c ratio = 0.50 and hydrated for 30 years. The pastes were jacketed with rubber membranes containing a few drops of lime-saturated water. This allowed the specimens to be maintained at 100% RH without leaching of calcium hydroxide. The cement used was a normal ASTM type 10 Portland cement. Disc specimens (1.2 mm thick) were cut from the cylinders using an Isomet low speed saw. Prisms were cut in a manner similar to that for the compacted specimens.

Length change measurements

Length change measurements of the disc specimens were obtained with an accuracy of 1 microstrain using modified Tuckerman extensometers [8]. A brief description follows. The sample rests on a holder and is held in the assembly by a light spring. The device consists of a knife-edge contact at one end and a tilting mirrored lozenge at the other end. The whole extensometer is supported by a stand and constructed of invar to minimize any thermal effects. Readings are taken with an optical collimator. It is noted that the sample is free to move and is unrestrained. The force exerted on the sample is not significant. The knife-edge contacts the specimen in a direction perpendicular to the length change measurement. Creep effects should be negligible in this direction. Calibrations of the extensometers with reference samples (e.g., metals) reproduce standard values of thermal expansion [8]. The specimens were placed in vacuum desiccators containing 1 L of the test aqueous salt solutions of varying concentrations. The solutions were stirred with magnetic stirrers for 20 s every 20 min. Distilled water was used as a reference medium. The specimens were completely immersed and length change was measured continuously. Measurements were made on two replicate specimens for each test solution. The technique has been successfully used in several other studies [30, 31].

The pH of the solutions was measured with a calibrated Orion pH meter model 920A.

Results and discussion

Expansion was observed in all the experiments reported in this study utilizing hydrated Portland cement paste, and compacted powders of synthetic C–S–H (I) (C/S ratio = 1.6). Typical expansion results of the materials studied at specified times of immersion in distilled water and the various aqueous salt solutions are presented in Figs. 1–9. No contraction or shrinkage was observed in any experiment. Length change measurements on two replicates were made for each salt concentration investigated

and average values were plotted against time of immersion in the salt solution. A separate test of reproducibility was performed for C–S–H samples in a few solutions e.g., C–S–H (I) in distilled water. The data were closely clustered over the time period reported. An additional two replicates of the same experiment were run if it was considered necessary to validate the data.

OPC pastes in NaCl and LiCl solutions

The OPC paste exhibits concentration dependent expansion when exposed to the NaCl solutions (Fig. 1). The expansion is greater in dilute NaCl solutions. The OPC paste contains alkali substituted C–A–S–H, CH and relatively minor amounts of other compounds. Both C–S–H (or C–A–S–H) and CH contribute to expansion of the pastes immersed in aqueous salt solutions. There appear to be at least three competing effects contributing to volume change:

1. Structural collapse (shrinkage) due to prolonged leaching of CH from C–S–H.
2. Structural collapse resulting from osmotic forces i.e., mass transfer of water from the C–S–H to the surrounding salt solution.
3. Expansion due to intercalation effects including cationic hydration forces and the dissolution of both structural and bulk CH.

The leaching and dissolution of CH is dependent on the solubility of the CH in the NaCl solutions [30]. The solubilities of CH in distilled water and NaCl solutions of 20, 60 and 180 g/L are 0.0212, 0.0288, 0.0293 and 0.0193 mol/L, respectively.

The effective swelling behavior of the OPC paste immersed in NaCl solution is analogous to the swelling of Na^+ -smectites. A reduction of interlamellar spacing with

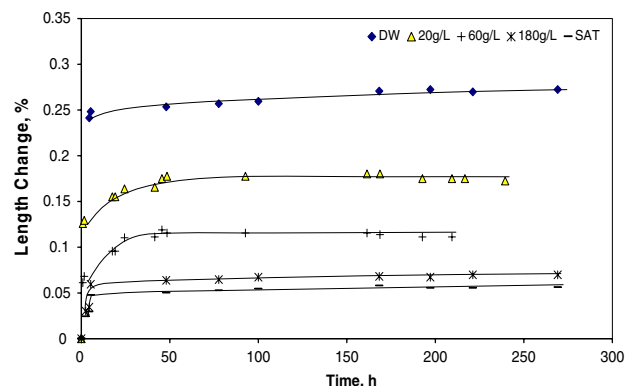


Fig. 1 Length change of Portland cement (OPC) paste (w/c = 0.5, hydrated 30 years) immersed in distilled water and NaCl solutions of varying concentration

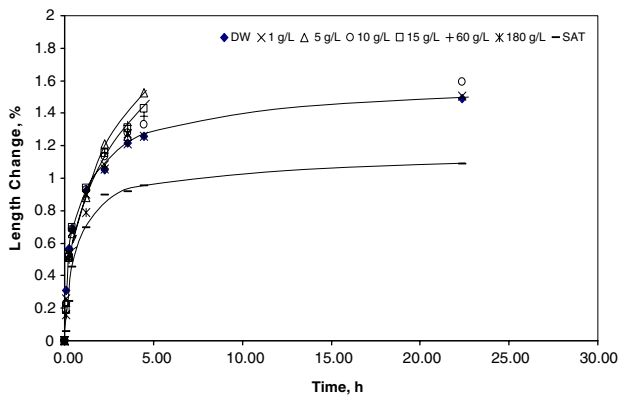


Fig. 2 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in distilled water and NaCl solutions of varying concentration

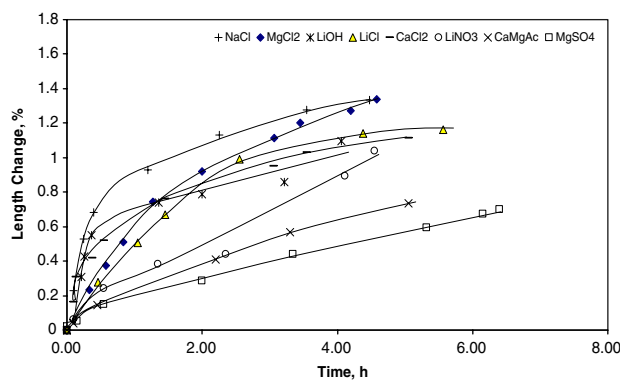


Fig. 5 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in 10 g/L of different salt solutions

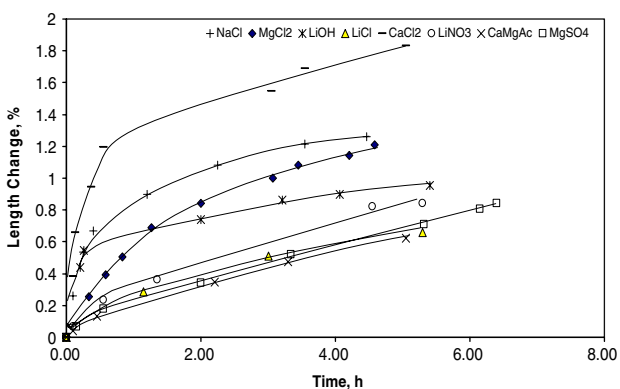


Fig. 3 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in 1 g/L of different salt solutions

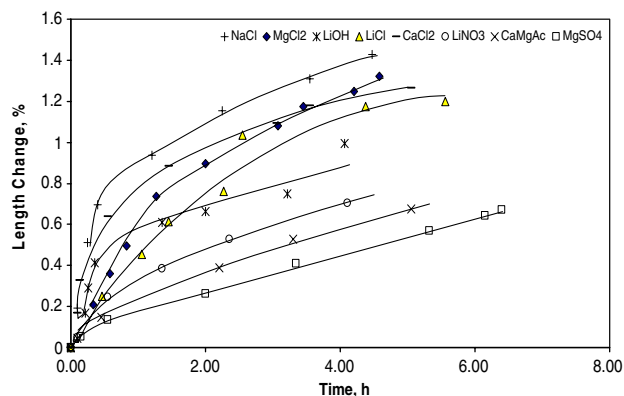


Fig. 6 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in 15 g/L of different salt solutions

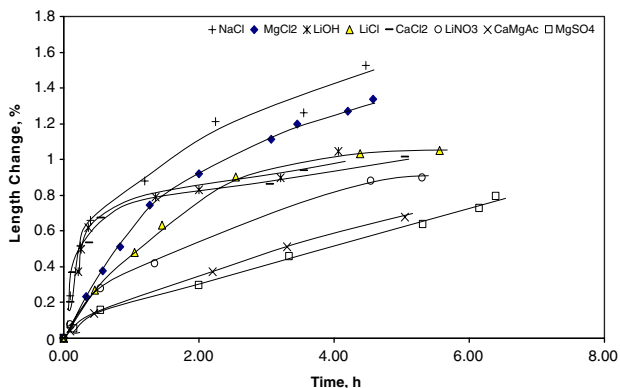


Fig. 4 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in 5 g/L of different salt solutions

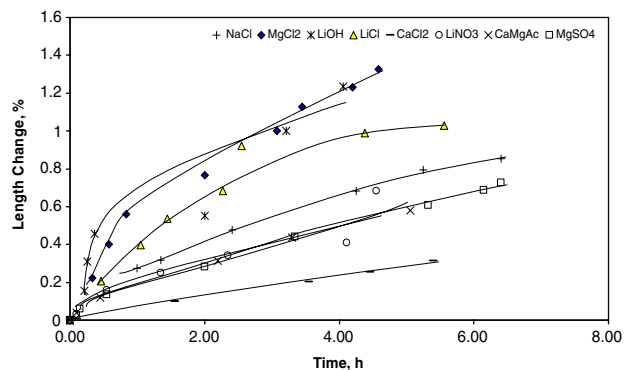


Fig. 7 Length change of compacted C-S-H (I) powder (C/S = 1.6) immersed in 60 g/L of different salt solutions

increasing NaCl concentration occurs for the latter [25]. The magnitude of the swelling at lower concentration is also inversely related to the layer charge. Smectites with high tetrahedral charge have limited expansion in concentrated sodium chloride solutions. The length change of

OPC pastes (a net swelling is observed) also decreases with concentration of the NaCl solution. It appears that a significant component of the swelling attributed to the behavior of Na-rich C-A-S-H in OPC paste may be osmotic in nature. The total effective swelling is the

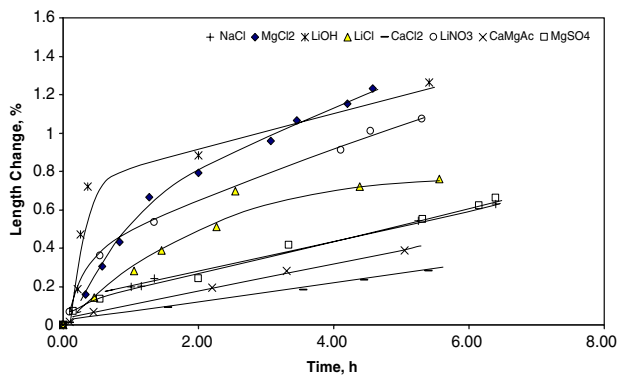


Fig. 8 Length change of compacted C–S–H (I) powder ($C/S = 1.6$) immersed in 180 g/L of different salt solutions

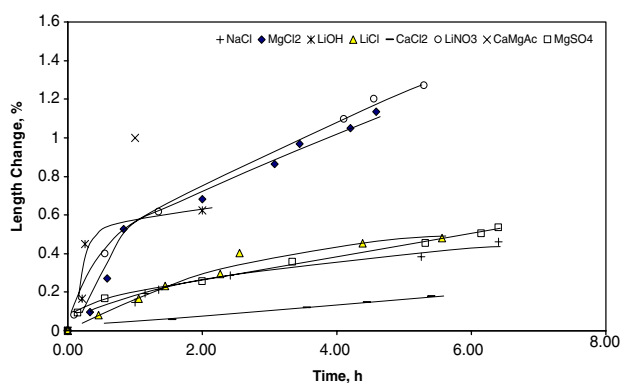


Fig. 9 Length change of compacted C–S–H (I) powder ($C/S = 1.6$) immersed in different saturated salt solutions

resultant volume change of both the C–A–S–H and CH phases. Other possible effects including EDL phenomena will be discussed later in the context of Ca^{++} rich layered silicates.

Volume stability of C–S–H (I) ($C/S = 1.6$)

The results of the length change measurements of C–S–H (I) immersed in the various salt solutions are reported in this section (Figs. 2–9). The parallel behavior of C–S–H (I) to OPC paste although less pronounced is noted i.e., the significant expansion levels observed in NaCl solutions (Fig. 2). Expansive processes can involve the leaching of CH and softening and dissolution of C–S–H due to the action of aggressive media. The results for immersion in salt solutions with concentrations of 1, 5, 10 and 15 g/L are presented in Figs. 3–6, respectively. Sodium chloride solutions have the most significant effect on expansion at concentrations up to 15 g/L. At higher concentrations (60 g/L to saturation) C–S–H is most expansive in $MgCl_2$

and LiOH salt solutions. $MgCl_2$ solutions promote significant expansions at all concentrations. All three-lithium salt solutions promote large expansions at high concentrations. $CaCl_2$ solutions generally have a minimal effect on expansion except at very low concentration levels. The substantial expansion of C–S–H (I) in $CaCl_2$ and NaCl (at low concentration levels) relative to that of LiCl may be due to their respective hydration energy differences. Expansion of C–S–H (I) in LiCl solutions exceeds that in NaCl and $CaCl_2$ solutions at concentrations of 60 g/L or greater (Figs. 7–9).

The initial rate of length change was significant in $MgCl_2$, LiOH and $LiNO_3$ solutions at concentrations >60 g/L. The aggressive action of the solutions was sometimes noticeable by the extent of the alteration of the surface of the C–S–H (I) specimens at the end of the measurements suggesting that in cases where reaction products are deposited on C–S–H (I) surfaces interlayer swelling of the C–S–H (I) itself is not necessarily the dominant mechanism of deterioration. XRD results indicated the presence of only minor amounts of brucite or gypsum in $MgCl_2$ and $MgSO_4$ solutions. No reaction products resulting from immersion in all other solutions were detected. It is noted that while expansions of OPC are appreciable (i.e., up to 0.25%) they are small in comparison to those observed for C–S–H (I) (>1.0%). The C–S–H phase in OPC is a highly disordered poorly crystalline material with much shorter silicate chain lengths than C–S–H (I), which has a well-defined basal spacing. This coupled with the presence of other surrounding phases in OPC that can provide restraint (not to mention the dilution effect) are likely causes of differences in the magnitude of expansion between OPC and C–S–H (I). Recent work by two of the authors has demonstrated similarities in the structural collapse mechanism due to the removal of water from both OPC pastes and C–S–H (I) [32]. The collapse of structure as detected by the use of helium gas as a nanostructural probe was similar in character and corresponded in the case of C–S–H (I) with significant changes in the basal-spacing-weight loss function. Severe deterioration of concrete in general would not be expected from the swelling of C–S–H alone. The relative magnitude of the swelling of C–S–H (I) in various salt solutions is however an indicator of the degree of severity of the different solutions themselves. In the case of magnesium chloride solutions where both decalcification of the C–S–H (I) and precipitation of reaction products are involved the large length change values are a warning sign that these solutions are overly aggressive.

Expansion of C–S–H (I) is also low in CaMgAc and $MgSO_4$ solutions at all concentrations despite the presence of minor amounts of gypsum in the latter solution. The parallels of C–S–H (I) expansion with metal cation exchanged smectites are noted. Volume increases for all systems are in the following order: $Na^+ > Li^+ > Ca^{2+}$.

Expansion of C–S–H (I) in CaCl_2 , MgSO_4 and CaMgAc solutions

Expansion of C–S–H (I) in concentrated CaCl_2 , MgSO_4 and CaMgAc solutions (Figs. 7–9) is less than in NaCl and Li salt solutions. This may be due to the fact that high-charge exchange cations strongly attract the dipoles of water molecules around them creating a phenomenon called ‘‘dielectric saturation’’ [20]. Small, high-charge exchange cations are associated with a large number of water molecules, which make up the so-called hydration sphere. For example, the hydration sphere of Na^+ , a fairly low charge cation, consists of about four water molecules while that of the smaller Mg^{2+} ion comprises about 16 water molecules [20]. Consequently, as is the case for smectite, it is assumed that the calculated dielectric constant of Ca^{2+} –C–S–H will be smaller than for the Na^+ –C–S–H and this may explain in part why the electrostatic (attractive) component of the total energy is larger in the Ca^{2+} –C–S–H or generally in the M^{2+} –C–S–H system. The result is the limited expansion observed at higher salt concentrations in the CaCl_2 , MgSO_4 and CaMgAc solutions. Other factors may also contribute to the limited expansion. Expansion due to leaching and dissolution of CH from the C–S–H may be counterbalanced by the formation of reaction products (e.g., brucite and gypsum) that occupy space within the C–S–H surfaces, the latter being a contractive process [3, 30, 33]. This mechanism is in contradistinction to the acknowledged expansion resulting from the formation of brucite and gypsum in open pore space. It refers to a surface energy effect occurring in microspaces or holes in the solid filled by precipitated products. The difference in the length change results between the MgCl_2 and MgSO_4 solutions may be due to the compensating effect of some of the reaction products filling the microspace in C–S–H surfaces.

In general C–S–H (I) immersed in salt solutions at lower salt concentrations exhibits expansive behavior similar to that occurring in distilled water. The dependence of C–S–H expansion on the initial drying condition is shown in Fig. 10. It is apparent that extreme care must be taken to ensure reproducibility of the data and correct assessment of the stability of the C–S–H (I) structure. The expansion during water uptake is clearly dependent on the temperature of the vacuum drying process. There appears to be two drying temperature zones influencing length change behavior (i.e., above and below 50 °C). Above 50 °C length change is significantly reduced.

The solution salt concentration clearly affects the expansion of C–S–H (I). It may be possible to establish a threshold expansion for different solutions i.e. a critical salt concentration above which the C–S–H (I) layers do not

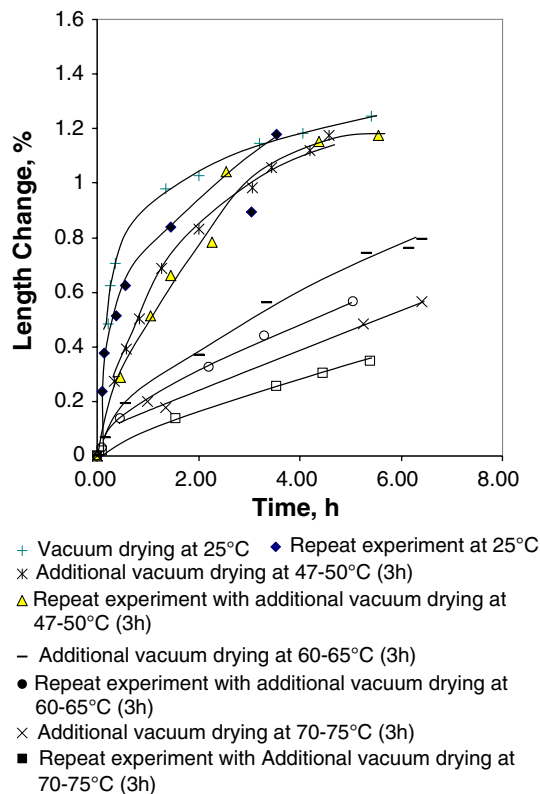


Fig. 10 Length change of compacted C–S–H (I) powder (C/S = 1.6) dried at different temperatures and immersed in distilled water

significantly expand similar to the critical coagulation concentration (CCC) concept developed in soil science [20, 34].

Expansion of C–S–H (I) in salt solutions containing monovalent and divalent ions

The fact that greater expansion of C–S–H (I) in the LiCl solution (in comparison to NaCl and CaCl_2 solutions) occurs at high solution concentrations may be due to a salt concentration effect related to the small size of the Li cation and its high hydration energy. It was also observed that LiNO_3 and LiOH solutions promote greater expansion of C–S–H (I) than LiCl . The behavior of C–S–H (I) exposed to monovalent and divalent ions in salt solutions containing various concentrations of Ca^{2+} , Na^+ , Mg^{2+} , Li^+ ... is similar to the one observed with smectite clays. In the case of Mg^{2+} , a saturated MgCl_2 solution has a very aggressive effect on the silicate hydrate resulting in the weakening or softening of the C–S–H (I). This is also the case for OPC pastes. High values of length change in MgCl_2 solutions may be the result of the superposition of expansion due to dissolution–leaching of CH and swelling due to intercalation effects. Lower expansion values, in saturated CaMgAc solutions are associated with a softening of the surface.

Electric double layer theory

The application of electric double layer theory (EDL) [19–21] wherein lithium, sodium, magnesium and calcium cations may induce or inhibit expansion merits consideration. C–S–H (I) is assumed to act as a colloid composed of negatively charged particles [35]. According to the EDL theory the valence and radius of hydrated cations in the colloid are important factors in determining expansion in clays e.g., montmorillonite. The theory predicts that clay suspensions containing higher concentrations of cations with larger valences will exhibit less expansion. That is, higher proportions of trivalent (e.g., Al^{3+}) and bivalent (e.g., Ca^{2+} , Mg^{2+} ...) cations relative to monovalent cations (e.g., Na^+ , K^+ and Li^+) should induce less expansion. It has been suggested that the presence of bivalent and trivalent cations in salt solutions lowers the surface charge density of the colloid compared to systems where monovalent cations are present. Hydrophilic colloids, e.g., C–S–H (I), owing to their affinity for water are unaffected by small amounts of added electrolyte which can cause hydrophobic sols to coagulate but are often precipitated (salted out) when the electrolyte concentration is high [30]. The ions of the added electrolyte dehydrate the hydrophilic colloid by competing for its water of hydration. The salting out efficacy of an electrolyte, therefore, depends on the tendencies of its ions to become hydrated. The “salting-out” power of the cations and anions can be arranged in the following order: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ [30].

The length change measurements of C–S–H (I) immersed in salt solutions of varying concentration are in accord with EDL theory and the above statements. The data in this study showed expansion increasing with cation charge in the order: $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Li}^+ < \text{Na}^+$ (at low solution concentrations). The anionic effect was in the following order: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ (at high solution concentrations) [30].

As stated previously, the radius of the hydrated lithium ion is larger than those for sodium or potassium. Therefore EDL theory predicts that lithium will produce greater expansion compared to that for other monovalent cations. In this study this effect was observed only at salt concentrations above 60 g/L where expansion in LiOH and LiCl solutions exceeds that in NaCl solutions (Figs. 7–9). Expansion or swelling of C–S–H (I) in NaCl solutions increased when salt concentration decreased suggesting the existence of a critical coagulation concentration (CCC).

A comparison of the expansion of C–S–H (I) in LiCl, LiOH and LiNO_3 solutions illustrates the effect of both concentration and different anions on swelling behavior. The LiCl solutions induce greater expansion at lower salt

concentrations (1–60 g/L) while immersion in LiNO_3 solution results in expansion that exceeds those in LiCl solutions only at higher salt concentrations (180 g/L-saturated).

Leaching and dissolution–precipitation effects

The LiOH solutions are very aggressive resulting in softening of the C–S–H (I) surface and relatively large expansions. This may be due to a leaching effect resulting in an increase in the alkalinity of the pore solution of the C–S–H (I).

It appears that expansion in LiCl solutions is inhibited at higher concentrations. The strong interaction of MgCl_2 solution with the C–S–H (I) surface compared to that of MgSO_4 solution can be observed from the steep slope at the beginning of the length change curves (Figs. 3–9). The activity of the anions agrees well with previous discussion. The comparison between MgCl_2 and CaCl_2 solutions (same anion) shows the aggressive action of the former at any concentration. Expansion in CaCl_2 solution exceeds that in MgSO_4 solution at dilute concentrations only.

It was observed that expansion of C–S–H (I) in MgSO_4 and CaMgAc (a source of combined Ca and Mg cations) solutions is relatively small at all concentrations. As stated previously the precipitation of reaction products in the microspaces of dissolving C–S–H solids (including minor amounts of gypsum or brucite crystals) may oppose expansive tendencies including those of the precipitated brucite or gypsum crystallites. It is noteworthy to mention the severe leaching–dissolution effect of the CaMgAc salt solution on the C–S–H surface (i.e., significant softening) compared to other salt solutions. This particular salt is currently being considered as a replacement for NaCl in many Canadian cities for deicing.

Collapse of C–S–H (I) structure

The reaction of C–S–H (I) specimens immersed in distilled water and the resulting expansion observed in dilute solutions (≤ 15 g/L) could be attributed to the hygroscopic nature of C–S–H (I). The possible diffusion and hydration of interlayer calcium by water molecules due to intercalation into the interlayer regions suggests that an osmotic transport mechanism is operative. The diffusion is due to the difference in free energy of the water molecules in the salt solution and the interlayer region of the solid. In solutions with high salt concentrations (>60 g/L) the high-charge cations (as described above) order the dipoles of water molecules around them creating a phenomenon called “dielectric saturation” [20] with a subsequent collapse of the interlayer. It can be inferred from osmotic swelling or expansion of C–S–H (I)

also (observed for clays) that any influence on the C–S–H (I)-water system that lowers the free energy of water in the aqueous phase will reduce the expansion of the C–S–H (I) solid. As discussed previously a high salt concentration reduces the interlayer spacing. Nevertheless a statistical mechanical analysis of Ca^{2+} and Na^+ -smectite [36] has indicated that the Ca^{2+} ion in the interlayer interacts sufficiently with other interlayer Ca^{2+} ions (so-called “correlation forces”) resulting in the development of a net electrostatic attraction between layers. The Na^+ - Na^+ interactions are weaker so that “correlation forces” are too weak to counter the repulsive osmotic and hydration forces. By analogy, one can explain the expansion inhibition in saturated Ca-rich C–S–H (I) in CaCl_2 solution (with increasing concentration) by the increased diffusion of Ca^{2+} ions in the interlayer region and the resulting increase of electrostatic interaction between them leading to the partial collapse of the interlayer region. In view of the differences observed for C–S–H (I) expansion in the dilute CaCl_2 solution as opposed to the concentrated one, it can be inferred that the C–S–H expansion is not due to “intercrystalline” swelling but to interlayer expansion of the C–S–H. The molecular nature of water which is a dipolar solvent, ion hydration energy and concentration and the electrostatic forces resulting from intercalation processes are responsible for the expansion behavior of C–S–H (I) specimens submitted to the action of a salt solution. The effect of water, nature of the cations and anions (involved in transport processes), concentration of the salt solutions, combined with the hygroscopic nature of C–S–H (I) are important factors to consider for the development of meaningful models for service-life prediction of concrete structures.

Conclusions

1. Ordinary Portland cement (OPC) paste specimens and compacted C–S–H (I) powders all exhibit concentration dependent expansive behavior in aqueous sodium chloride and lithium chloride solutions.
2. A decrease in swelling of OPC pastes with concentration (in NaCl and LiCl solutions) suggests that a component of the volume change may be osmotic in nature.
3. The parallel length change behavior of synthetic C–S–H (I) ($C/S = 1.6$) (in salt solutions) particularly at high concentrations suggests that the C–A–S–H phase in OPC pastes plays a major role in the volume stability of cement-based products.
4. The expansion of OPC pastes immersed in various aqueous salt solutions is a resultant of volume change

contributions of both the C–S–H (I) (or C–A–S–H) and CH phases.

5. No evidence of a reaction product other than C–S–H and CH was found for OPC pastes immersed in NaCl and LiCl solutions. This implies that differences in expansive behavior are primarily due to the nature of the C–S–H, the amount of CH and the interaction of the cation with the solid products.
6. The role of alkali on the swelling behavior of C–S–H (I) or C–A–S–H in a Portland cement paste matrix is analogous to the behavior of swelling clays e.g., Na^+ -smectite.
7. The volume stability of C–S–H (I) in aqueous salt solutions is complex. Several mechanisms may be operative including osmotic effects, electrical double layer phenomena (including ion-ion interactions), intercalation effects, dissolution-precipitation (surface energy effects), leaching and softening processes.
8. Lower expansion of CH and swelling of C–S–H (I) in CaMgAc and CaCl_2 solutions due to intercalation effects may result from the formation of reaction products on C–S–H surfaces and concomitant softening. Electric double layer theory incorporating ion-ion interaction effects (as applied to clay systems) predicts limited swelling in the presence of Ca^{2+} ions. This is compatible with observed behavior in both C–S–H (I) and OPC pastes.
9. The leaching-dissolution effect (accompanied by softening) of the CaMgAc salt solution on the C–S–H (I) surface was the most severe suggesting that the use of this salt as a de-icing agent for concrete should be carefully examined.
10. The relatively good correlation between the expansive behavior of compacted C–S–H (I) specimens immersed in aqueous salt solutions of increasing osmotic gradient and EDL theories (accounting for ion-ion interaction) based on the behavior of other naturally occurring colloids would appear to merit consideration of C–S–H (I) compacts as structural models for durability studies of cement systems.

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