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Dimensional change and elastic behavior of layered silicates and Portland cement paste

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ABSTRACT

The role of water in hydrated Portland cement paste (hpc) is germane to understanding the nature of nanostructure – property relationships of the material. The irreversible dimensional changes of hpc and phase pure C–S–H that occur on wetting and drying are dissimilar to those observed for other silicate minerals of interest to cement science. This irreversibility in hpc is also observed for the modulus of elasticity parameter. Length change, mass change and modulus of elasticity isotherms (including drying–wetting cycles) were determined for specimens of hpc, Ca-montmorillonite and 1.4 nm tobermorite. Length change and modulus of elasticity versus mass loss curves were also obtained for phase pure C–S–H (C/S = 0.8, 1.0 and 1.5). All the isotherms exhibit significant irreversible behavior. Similarities and differences in the nature and character of the isotherms and the relevance of the C–S–H data are discussed. Inferences are made with respect to the nanostructural nature of hpc, its dimensional response in aqueous media and the correspondence in behavior of synthetic C–S–H and that formed in hpc. It is apparent that hpc has unique characteristics that are responsible for stability.

1. Introduction

The volume stability and performance of cement-based materials are known to be affected primarily by the response of the calcium silicate hydrates (C–S–H binders) in aggressive environments [1]. This may have an impact on the micro and nanostructural integrity of the binder in concrete and consequently on its durability. An improved understanding of the nature of C–S–H in hydrated cement products, the energetics of its interaction with water and the corresponding changes in engineering characteristics are essential for predicting and controlling the behavior of cement-based materials. This understanding may also lead to new technologies for enhanced service-life of concrete structures.

Models of C–S–H nanostructure, generally derived from an eclectic body of physico-chemical evidence, have been useful but not definitive in explaining durability phenomena [2]. The evolution of these models has provided an appreciation of the moisture sensitivity of cement hydrates. For example the layer models proposed by Feldman and Sereda [3], Taylor [4] and Jennings [5] can account for the large primary and secondary hysteresis associated with water isotherms (mass and length change). Feldman [6] clearly demonstrated that there is no unique value of fundamental engineering parameters over the entire humidity range and that sorbed water has structural properties. It is apparent that changes (up to 100%) in the elastic response of a material due to differences in the equilibrium state of water can affect the distribution of internal strain in a heterogeneous binder such as hardened cement paste.

Although water plays an important role in the stability and stiffness of some layered silicate systems, the intrinsic characteristics of these materials may also contribute to the overall volume change and elastic response at various humidity levels. It has been suggested that the intrinsic modulus of elasticity (i.e. the zero porosity value) of phase pure C–S–H is independent of its chemical composition [7]. In nanoindentation studies, it has been shown that decalcification of C–S–H reduces the modulus of elasticity [8,9]. The modulus values computed from the dynamic molecular modeling and free energy minimization methods for various layered silicate systems are significantly higher than those obtained from experimental techniques [10–12]. These measurements do not follow any specific trend regarding their dependence on the C/S ratio of the material.

A study was designed to investigate the role of water in the mechanical characterization of layered silicates and evaluate the irreversible nature of volume change in cement systems (undergoing several wetting–drying cycles). Model layer silicate systems – Ca-montmorillonite and 1.4 nm tobermorite – in addition to synthetic C–S–H preparations were utilized to establish similarities and differences in nanostructural performance. Differences in the

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effect of moisture on the engineering behavior of these systems are interpreted in nanostructural terms. The relevance of the results in terms of durability is discussed. Some insights on the validity of using synthetic C–S–H as a model for studying the behavior of hydrated Portland cement paste (hpc) are presented.

2. Structure and properties of layered C–S–H analogs

The understanding of the structure of C–S–H in hydrated Portland cement has evolved and advanced from the structure of 1.4 and 1.1 nm tobermorite [13–15]. An idealized structure for 1.1 nm tobermorite is presented in Fig. 1a. Later, Taylor suggested that the C–S–H in hydrated cement contains elements of structure derived from both 1.4 nm tobermorite and jennite [4]. He observed that a Ca/Si ratio similar to that occurring in cement paste could be derived from a mixture of the two structures. These naturally occurring minerals along with jennite have often been used as structural models for the C–S–H produced in the hydration of Portland cement [15]. Other hypotheses supported mainly by NMR investigations [16–18] for lime-rich tobermorites include: omission of "bridging" silica tetrahedra; structures based on $H_2SiO_4^{2-}$ groups; replacement of regions of dreierketten by hydroxyl ions which form part of the central CaO layers. There is, however, evidence that considerable amounts of orthosilicate and dimer silicate chains exist in C–S–H (gel) after lengthy periods of hydration. This suggests the possibility of a simplified structure (as proposed by Feldman) including silica in many states of polymerization together with hydroxyl groups and Ca^{2+} ions on the surfaces of the sheets [19].

There are structural similarities between Ca-montmorillonite and C–S–H (II), a semi-crystalline material, described by Taylor [4]. Fig. 1b shows an idealized representation of Ca-montmorillonite. In the tetrahedral sheet, Si might be replaced by trivalent Al. In the octahedral sheet, the replacement of trivalent aluminum by divalent Mg without complete filling of the third vacant octahedral position is possible. A deficit of positive charge results. This is compensated for by the adsorption on the layer surfaces of cations which are too large to be accommodated in the interior of the lattice. These ions can be easily exchanged in the presence of water.

The structure of C–S–H as described above (idealized in Fig. 1c) has not been fully resolved and relatively poor information has been obtained considering interactions with ionic species. The structure of smectites and their interactions with cations are well known [20]. The analogy between C–S–H and clays with reference to cation fixation and other physico-chemical properties of interest has been widely investigated [21]. There is however a paucity of data available on the mechanical properties of phase pure C–S–H and for example a layered clay system such as Ca-montmorillonite. For this reason and the primary objective of providing additional evidence for the layered nature of C–S–H that is formed in hpc, Ca-montmorillonite specimens were included in the study. The calcium form of montmorillonite was chosen as it is more similar structurally to C–S–H than the sodium form.

Exposure of Ca-montmorillonite to humidity results in the penetration of water molecules between the unit layers. The basal spacing expands to definite values in the range of 1.25–2.00 nm depending on the type of cation. Nominally, two to three layers of water molecules may be intercalated. It is known that montmorillonite experiences substantial interlayer swelling [22]. The exact volume change mechanism has not been resolved. It may involve hydration energetics or certain geometric arrangements of the water molecules in the water layers. Further understanding of similarities and differences of the layered silicates in this study should contribute to the long-term objective of correlating volume change and durability with the structure of C–S–H in Portland cement products.

3. Experimental

3.1. Materials

Portland cement (type I) was used for preparing the paste. The chemical composition (in %) is as follows: SiO_2 (21.6); Al_2O_3 (5.2); Fe_2O_3 (0.3); CaO (66.8); MgO (0.9); SO_3 (2.9); Na_2O (0.03); K_2O (0.12). The 1.4 nm tobermorite was synthesized following the method described by Hara et al. [23] using lime and amorphous silica (at C/S = 1.0) suspensions at 60 °C subsequent to an initial treatment at 140 °C. No other phases were detected by X-ray diffraction. Surface area was about 45 m^2/g. Ca-montmorillonite samples were obtained from a commercial supplier. There were no impurities detected by X-ray diffraction. The material was ground and passed through a 100 mesh sieve. The BET nitrogen surface area was determined to be 14.6 m^2/g. C–S–H having C/S ratios of 0.8, 1.0 and 1.5 was synthesized from the reaction between amorphous silica and calcium oxide in aqueous solution at room temperature according to the procedure described elsewhere [24]. This range of C/S ratio fits in the category of C–S–H (I) proposed by Taylor [25]. All materials were kept in sealed N_2 purged bottles until used.

3.2. Specimen fabrication

A description of the different types of samples is presented in Table 1. The dimensional change and modulus of elasticity measurements for cement paste were made on paste prepared at water/cement ratio = 0.25. The paste was hydrated for several years in lime-saturated solution prior to fabrication of the test specimens. Specially designed, 'T'-shaped specimens 25.4 mm long were cut from paste cylinders. They had a cross-section, 7.00 mm deep with a flange width of 12.70 mm and flange and web thicknesses of 1.27 mm. Specimens for the 1.4 nm tobermorite and Ca-montmorillonite modulus of elasticity measurements were made from pow-

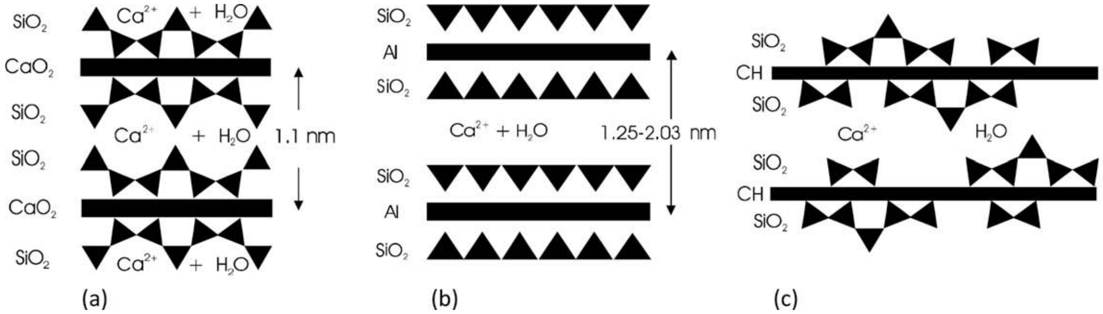

Fig. 1. Schematic representation of the structures of: (a) 1.1 nm tobermorite; (b) Ca-montmorillonite and (c) C–S–H in hydrated Portland cement.

Table 1
Specimen types for sorption and modulus of elasticity measurements.

System	Sorption (mass and length change)	Modulus of elasticity
Cement paste	Hydrated solid (1 mm thick slices)	• T-shaped specimens (1 mm thick)-static compression • Circular discs (1 mm thick)-static flexural loading • Prisms (1 mm thick) – dynamic loading
1.4 nm Tobermorite	Compacted powder (1 mm thick)	Circular discs (1 mm thick)-static flexural loading
Ca-montmorillonite	Compacted powder (1 mm thick)	Circular discs (1 mm thick)-static flexural loading
C–S–H-calcium silicate hydrate	Compacted powder (1 mm thick)	Prisms (1 mm thick) dynamic mechanical loading

ders compacted in the form of circular discs, 31.75 mm in diameter × 1 mm thick. Porosity values for the paste, 1.4 nm tobermorite and Ca-montmorillonite are 14%, 11% and 51% respectively. Comparisons of the measured quantities (mass and length change) for the systems studied will necessarily be qualitative and not quantitative due to the porosity differences. The C–S–H powders were compacted to form rectangular prisms (nominally $1 \times 12 \times 60$ mm). The porosity of all the C–S–H compacts was controlled at the 30% level. It has been suggested that the bonds forming between the powder particles in a compacted sample of hydrated cement are essentially similar to those in the original cement paste [26,27]. A key piece of evidence for the similarity of bonds formed in hpc and compacts of powdered hpc is provided by the coincidence of the mechanical property-porosity curves for these materials [28]. It would appear then that the bonds formed on compaction of these powders are similar to those formed during paste hydration. In addition, length change isotherms for compacted and paste hydrated systems (at equivalent porosity) are similar [29]. The compacts of clay minerals and phase pure C–S–H powders are therefore considered as valid structural models for studying their mechanical properties. The thickness of the compacted specimens was about 1 mm in order to decrease the equilibrium time during the humidity conditioning of the samples.

3.3. Sorption measurements

Mass and length change isotherms were obtained using a high-vacuum apparatus. Samples were mounted in individual tubes on quartz spirals of the McBain-Bakr type that gave values of mass change to a sensitivity of 3.0×10^{-5} g. Length change was measured in separate cells with samples mounted on modified Tuckerman optical extensometers. The sensitivity of these devices is 1×10^{-6} mm/mm. The dry state of the cement paste was achieved using vacuum degassing at 85 °C for 3 h. This method produced the same result for the non-evaporable water as the conventional ‘d-drying’ procedure [6]. The ‘result’ refers to the ‘dry’ state or ‘outgassing’ treatment in an adsorption experiment. This was a contentious issue in cement science as debate centered on the influence of drying methods on the nature of the isotherm. Results (i.e. isotherm data, mass or length change) were often reported for specimens that were ‘d-dried’ (i.e. dried to the vapor pressure of dry-ice at −78 °C). An equivalent and more expedient drying procedure was found to be degassing at 85 °C for 3 h. The isotherms were qualitatively and quantitatively similar for either method of drying.

3.4. Modulus of elasticity measurements

The modulus of elasticity isotherm curves for cement paste were determined in compression. The ‘T’-shaped specimens were mounted on a miniature fixed frame linking the specimens to the load cell and to the modified Tuckerman optical extensometers used for the length change measurements. Details of the loading system are provided elsewhere [30]. The modulus values for the 1.4 nm tobermorite and Ca-montmorillonite were determined using a loading device designed for the disc specimens, [28,31]. Load–deflection curves (in flexural mode) of the compacted samples were used for the calculations.

The modulus values for the C–S–H compacts were determined using a dynamic mechanical analysis apparatus (Rheometrics RSA II) in the three-point bending mode. A maximum oscillating strain of 0.02% at the frequency of 0.1 Hz was applied on the samples. The response of the sample was recorded and analyzed by the RSI orchestrator computer software to obtain the values of storage modulus (E'). DMA analysis was conducted on C–S–H specimens at various drying increments starting from 11% RH. A combination of vacuum and heat at temperatures up to 110 °C (mostly below 50 °C) was used to remove the water from C–S–H.

The different methods of sample preparation for the mechanical property measurements (i.e. modulus of elasticity determinations) were made to correspond to the requirements of the various apparatus used. This was done primarily for convenience. Calibrations were performed on all apparatus with reference specimens, e.g. aluminum (having known modulus values). The value of the modulus of elasticity (a material property) is independent of the measurement method. Drying (in cement science) is important in order to distinguish the role of water in determining parameters of interest. An 11% RH datum is often used as a starting point as this is the monolayer position, i.e. the surface is covered with a monolayer of water. The influence of interlayer water is also obtained as it is removed on drying from 11% RH. Since hysteresis occurs over the complete humidity range, experiments where drying occurs from 100% RH are also important. This would necessarily entail some effects of the stress on the solid phase due to capillary action in the primary hysteresis region of an isotherm.

4. Results and discussion

The mass, length and modulus of elasticity isotherms for cement paste, 1.4 nm tobermorite and Ca-montmorillonite are described and compared. Length change versus mass loss curves for the C–S–H preparations are presented. Modulus of elasticity versus mass loss (from the 11% RH condition) curves are used to describe similarities in behavior between hpc and synthetic C–S–H. It is emphasized here that there are significant differences as well as similarities for all of the isotherm data and related curves for all systems. Differences will be noted in the following discussion of each set of curves. The large primary and secondary hysteresis present in the curves is, however, of primary interest here. The large primary and secondary hysteresis observed in mass, length change and modulus of elasticity isotherms of the systems studied have particular significance for hpc as the secondary hysteresis implies that processes other than reversible adsorption are taking place in the lower partial pressure region. This is central to the long-standing debate concerning the silicate structure of hpc, i.e. does it behave as a layered material or as a colloidal gel [32]?

4.1. Mass change isotherms

The mass change isotherms for cement paste, 1.4 nm tobermorite and Ca-montmorillonite are depicted in Fig. 2a–c. All isotherms exhibit large primary and secondary hysteresis and the existence of scanning loops. The isotherm for Ca-montmorillonite (Fig. 2c) was obtained up to an RH value of 69% as the sample did not retain structural integrity beyond this point. The issue of reversibility with respect to the swelling of Ca-montmorillonite merits additional comment. It is noted that the X-ray basal spacing data versus relative humidity (adsorption/desorption) after Senich et. al. show complete secondary hysteresis down to very low humidities ($\ll$7%) [33]. Further evidence that the hysteresis observed for our specimens is real is the existence of 'scanning loops' extending into the lower humidity regions. If the system were truly reversible there would be no 'scanning loops'. The authors also have confidence that the vacuum adsorption system functioned well and that the measurements were taken with extreme care. Comments related to the equilibrium sorption measurements of cement paste are also germane. In this system, equilibrium times ranging from a few days to months for each data point are required, especially below 11% RH. The issue of drying (hard drying versus soft drying etc.) for this system has also been debated at length as it related to the ability of water to re-enter the structure. It was later shown to be a non-issue [34–37]. It may however be an issue for Ca-montmorillonite. Equilibrium times for these specimens were similar and varied from several days to weeks. First drying of Ca-montmorillonite involved vacuum only (several days) in order to avoid possible irreversible collapse of structure effects. One explanation for reversible adsorption would be that the layered structure would not open up making intercalation negligible. This would be surprising and contrary to observations of a significant increase in X-ray basal spacing on wetting Ca-montmorillonite [33,38]. There is, however, not universal agreement on this issue as some numerical simulations would indicate [39].These simulations, however, were focused on stability of Ca-montmorillonite at high temperatures and pressures.

It is known that water in clays is not organized in well defined layers due to the presence of interlayer calcium ions. It is also the case for C–S–H in hpc. Nevertheless the ability of Ca-montmorillonite to facilitate intercalation of more than one layer of water molecules (e.g. using the change in X-ray basal spacing to represent a nominal capacity for water content) is a general qualitative descriptor of the expansive potential of the system. It is only an average quantity and does not imply molecular order.

For smectite in general (montmorillonite) bonding between successive layers is by van der Waals forces and by cations that are present between the layers to balance charge deficiencies in the structure. These bonds are weak and easily broken by cleavage or adsorption of water or other polar liquids. The sheets are consequently separated to complete exfoliation. The character of all the isotherms is qualitatively similar, e.g. they all exhibit primary and secondary hysteresis. This suggests that the irreversible effects of intercalation of the adsorbate are manifested in a similar way in the three systems. It is apparent that there is no unique equilibrium position at low humidities (e.g. 11% RH) for each layered system. The appearance of a clear 'knee' in the graph at about 11% RH is attributed to the completion of the formation of a surface 'monolayer' and the beginning of the 'multilayer' adsorption process. The 'knee' has also been observed by other investigators [40]. It can be inferred from this that the susceptibility of C–S–H-based binders (and indeed other layer silicates) to deleterious processes is dependent on wetting–drying history, i.e. the position on the water isotherm is relevant to durability concerns. This has been observed previously [41]. The relatively larger hysteresis, seen in Fig. 2a, for the cement paste sample may suggest that it is more difficult for water molecules to re-enter interlayer regions of the C–S–H compared to Ca-montmorillonite and 1.4 nm tobermorite.

4.2. Length change isotherms

The isotherms are plotted in Fig. 3a–c. They all exhibit similar characteristics of irreversibility evident in the mass change versus humidity curves. It serves to preface the discussion of these isotherms with a few comments that provide some relevant context. A primary objective of this work was to obtain additional evidence that the nanostructure of the C–S–H phase in hpc behaves as a layered silicate and not as a colloidal gel. This point has been debated for more than 50 years without complete resolution although the evolution of structural models favors the former [3]. Primary evidence for 'layered-silicate' behavior in hpc has been based on the irreversible nature of mass and length change isotherms and elastic deformation-humidity measurements [29,42]. The isotherms exhibited massive primary and secondary hysteresis indicating that HPC was not a thermodynamically 'reversible' adsorption system. It was possible to separate the 'irreversible' and 'reversible'

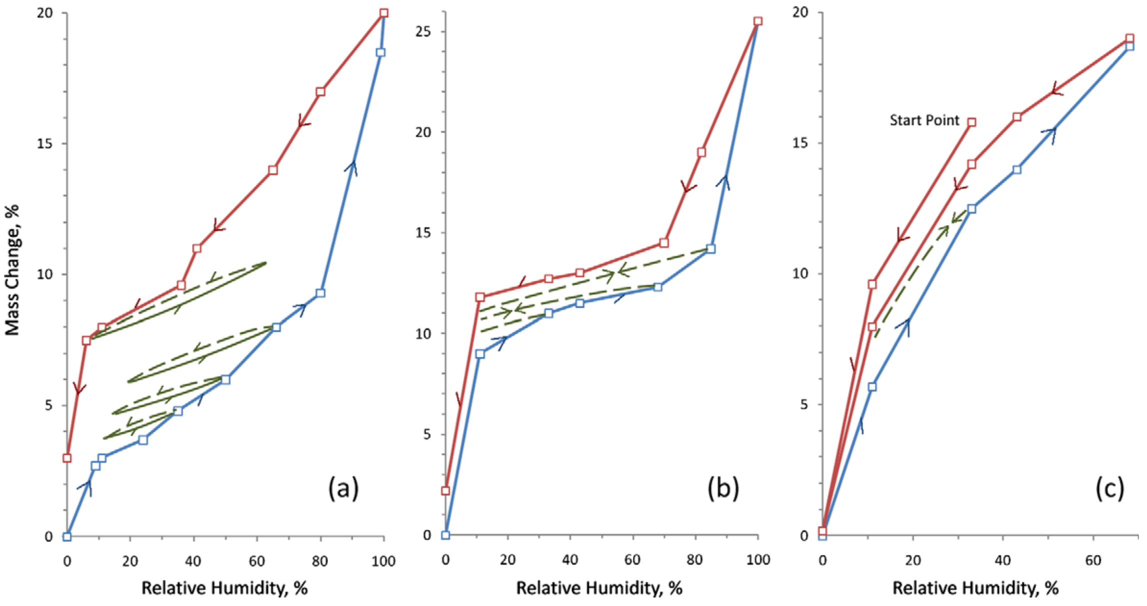

Fig. 2. Mass change isotherms (water adsorbate) at 25 °C of: (a) cement paste, w/c = 0.25; (b) 1.4 nm tobermorite and (c) Ca-montmorillonite.

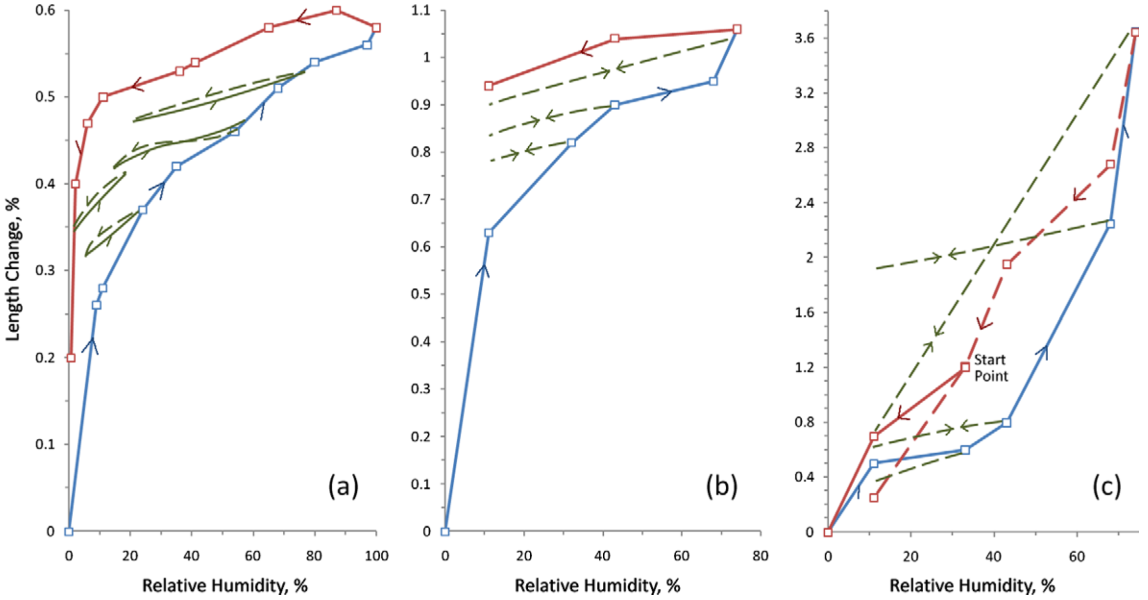

Fig. 3. Length change isotherms (water adsorbate) at 25 °C of: (a) cement paste, w/c = 0.25; (b) 1.4 nm tobermorite and (c) Ca-montmorillonite (first and second drying curves are shown by solid and dashed lines, respectively. The scanning loops are shown by dashed lines and reciprocal arrows.).

components of the mass and length change using very detailed ‘scanning’ loops obtained during construction of the isotherms. The primary hysteresis region of the isotherm occurs in the relative humidity (RH) range (45% < RH < 100%) where compressive stresses on the solid due to formation of menisci in large capillary pores influence deformation. At RH values below 45% (the adsorption region of the isotherm) the meniscus ruptures and no longer contributes to deformational stress. The ‘reversible’ isotherm data (in the adsorption region) can be used to calculate thermodynamic quantities (free energy changes) that with the Bangham equation [43] can provide an estimate of the elastic modulus of the solid. The estimate compares well with that obtained from direct measurement [6]. An important point is that the ‘irreversible’ length change isotherm accounts for about 80% of the total length change. This cannot be attributed to surface adsorption phenomena which is essentially ‘reversible’. The ‘irreversible’ length change has been interpreted as due to the exit and entry of interlayer water on wetting and drying. The increase of the static modulus of elasticity of hpc on wetting (up to 100%) and decrease on drying (large primary and secondary hysteresis) underscores the structural role of interlayer water and compliments the mass and length change data. The focus of the present study therefore concentrated on the ‘irreversible’ nature of the isotherms and data that reinforced arguments in support of the primary objective, i.e. evidence for the layered nature of hpc.

The similarity of the isotherms refers to the existence of primary and secondary hysteresis and is qualitative. The nature of the length change curves and in particular the ‘scanning loops’ exhibit similarities for the three systems. The curve for Ca-montmorillonite has some distinct differences from the other two curves. Total expansion is more than three times greater. The slopes of the scanning loops on desorption from the higher humidities are much steeper. Expansion at intermediate humidities (e.g. from 40% to 60% RH) is also significantly greater. It is, however, not necessarily surprising that the length change processes appear to be mechanistically similar. This is an integral part of the argument in this work that the C–S–H formed in hpc behaves as a layered material. The authors have presented evidence based on XRD and helium diffusion methods to further support this view [44]. The systems other than cement paste were selected for study and comparison because they are well-studied layered materials. Tobermorite-based models for the C–S–H of cement paste have been previously postulated due to structural similarities [21]. The absence of uniqueness at 11% RH refers to the fact that the position on the isotherm at a given humidity (e.g. 11% RH) is path dependent (i.e. it is dependent on which scanning loop is taken). One can have a very different value of mass or length change at, e.g. 11% RH if adsorption/desorption follows a different scanning curve. The absence of uniqueness at any given humidity suggests that volume stability is sorption path dependent. This would be expected in a classical layered silicate where exit and entry of water molecules do not take place at the same partial pressure of water vapor. It is also observed that significant changes happen in the length of the specimens at humidity levels below 11%, where minimal mass changes occur. It is suggested that the changes at these low humidity levels are primarily associated with the interlayer water. The relatively larger length change for Ca-montmorillonite is likely due to the higher interlayer capacity to accommodate at least two layers of water molecules whereas in C–S–H ideally only a monolayer of water can exist [45]. The length change of the 1.4 nm tobermorite sample exhibits higher values compared to that for cement paste. Both materials have about a monoloyer of water in the interlayer regions. Differences in the length change of 1.4 nm tobermorite and cement paste (C–S–H) are attributed to differences in the solid phase nanostructure: interlayer ionic interactions (Ca^{2+}, OH^{-}); degree of silicate polymerization; number of missing bridging silica tetrahedra; dimer/polymer ratio; nature of stratified CH layers in the structure; nature of the ionic substitutions in the structure [46]. They could account for differences in the restraint of any potential swelling. The length change isotherms were obtained over several months due to long equilibrium times, particularly at low humidities. There were six length change cells-two for each system. Repeatability was within 1% for the duplicate samples. Confidence in the results was also enhanced by the large number of data points on each isotherm. No apparent outliers were observed.

It should also be noted that the scanning loops themselves in the cement paste samples show some irreversibility whereas these parts of the curves have a single path for 1.4 nm tobermorite and Ca-motmorillonite, probably due to the structural characteristics of these samples. Differences in expansive behavior of the studied systems relate to the role of interlayer water and the interaction of the latter with the solid. Calculations of hydraulic radius (hpc system) for C–S–H [45] yield values of about 0.15 nm indicating that only one layer of water can be present between the silicate sheets. The length change values of the hpc and 1.4 nm tobermorite specimens at 100% RH were 0.58% and 1.05% respectively. The length change of Ca-montmorillonite (often labelled a 'limited-swelling' clay) was about 3.6% at 65% RH. Measurements could not be made beyond this point. The X-ray basal spacing of Ca-montmorillonite from two well known sources [33] increases from about 0.95 to 1.47 nm on wetting and has been shown to be irreversible in the adsorption region of the isotherm. It was reported that for these samples two layers of water resided in the interlayer. The cations were all hydrated. These factors would suggest that the swelling forces developed on wetting Ca-montmorillonite (in spite of its 'limited' swelling in comparison to Na-montmorillonite) far exceed those in hpc and 1.4 nm tobermorite. This is supported by the modulus of elasticity data. The Ca-montmorillonite specimens lost stiffness (decrease in modulus of elasticity) on wetting in contrast to the hpc and 1.4 nm tobermorite specimens suggesting that the extra layer of water in the interlayer space was at least partially responsible for its different behavior.

It is noted that Ca-montmorillonite exhibits distinct length-change behavior (Fig. 3) from the other studied systems. It is felt that the important similarity is the significant primary and secondary hysteresis that all systems exhibit.

4.3. Modulus of elasticity isotherms

The isotherms are plotted in Fig. 4a–c. The role of water in the nanostructure of the three systems is more clearly understood on the examination of the humidity effects on the elastic stiffness of these materials. The results are discussed for each system separately. It is noted that differences in the absolute values of the modulus of elasticity would be expected as the porosity values of the compacts are substantially different. Our focus is on the characteristics of the isotherms themselves and comparisons are made qualitatively on that basis. There are significant differences in the modulus of elasticity isotherms for the studied systems (Fig. 4a–c). The emphasis again was placed, rather, on the similarities, i.e. the nature of the hysteresis exhibited by all the studied systems. The differences exhibited by Ca-montmorillonite (i.e. decreasing modulus with increasing RH) are explainable in terms of the resultant effect of the interlayer water as described in the preceding section on length change. The differences in magnitude of modulus of elasticity values of all three systems clearly indicates that the composition of the solid phase has an effect on the mechanical performance. Mechanisms associated with aspects of the composition that affect performance are beyond the scope of this investigation. It is apparent that hpc behaves as a layered system but that within a family of layered systems the composition of the solid and the role of interlayer water can have varying effects on engineering performance.

4.3.1. Portland cement paste

A large hysteresis can be observed following the first and second drying and re-wetting cycles (Fig. 4a). Similar results have been previously reported by Sereda et al. [28,31]. They applied stress in flexure on circular discs as opposed to compression of the T-shape samples used in this work. Significant stiffening occurs on wetting at higher humidities. Loss of stiffening occurs on drying at lower humidities as incremental amounts of the remaining interlayer water are removed. Second drying is qualitatively similar to first drying as they both exhibit rapid decrease in the modulus of elasticity at humidity levels below 20% RH. However second re-wetting exhibits a significant reduction in stiffening up to about 50% RH after which the value of the modulus gradually returns to its original value at high humidity. Second drying delays the re-intercalation of water (possibly due to the effects of a higher degree of structural collapse).

4.3.2. 1.4 nm Tobermorite

The dependence of the modulus of elasticity on relative humidity (Fig. 4b) is very scattered but has similar features to that for Portland cement paste. Again the similarity refers only to what is considered as the most important feature of the Fig. 4b, i.e. the large hysteresis at RH < 20% for both cement paste and tobermorite suggesting that the irreversibly sorbed water is not only a factor in the hysteresis but it also has a 'structural' role. The modulus value

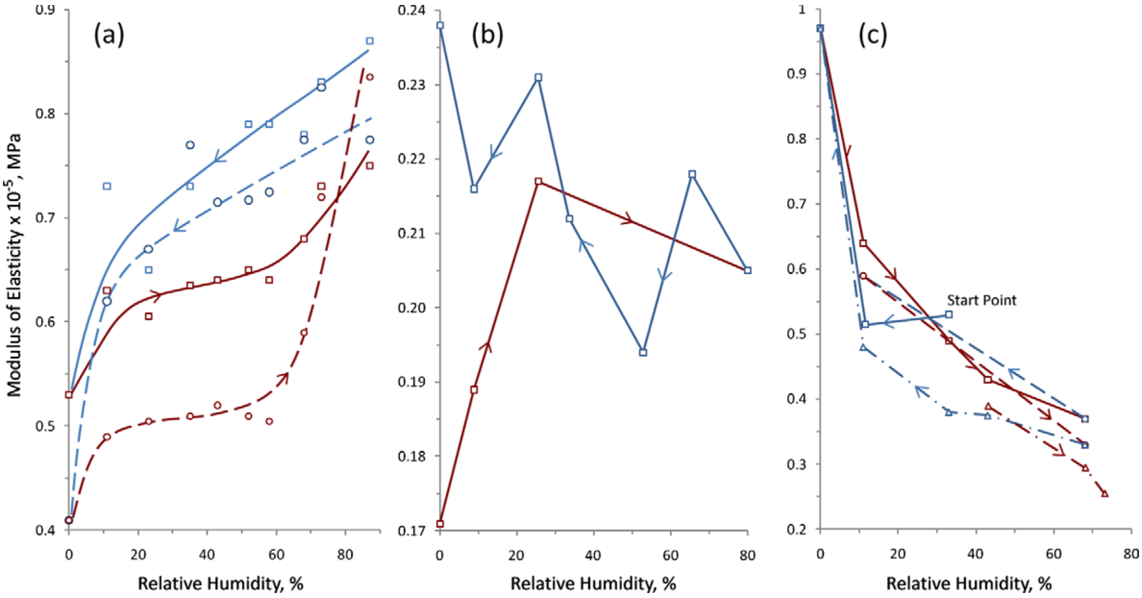

Fig. 4. Modulus of elasticity isotherms (water adsorbate) at 25 °C of: (a) cement paste, w/c = 0.25 (drying–wetting cycles are shown by solid lines (first cycle) and dashed lines (second cycle)); (b) 1.4 nm tobermorite and (c) Ca-montmorillonite (three cycles are presented in solid, dashed and dashed-point curves).

of tobermorite at the dry state is about 38% higher following wetting. Intercalation of water into the structure has a stiffening effect that is maintained or increased moderately on drying to low humidities. This observation would be compatible with Taylor's [4] description of the C–S–H phases in hydrated Portland cement as possibly being a mixture of tobermorite and jennite. The compatibility lies in the like-behavior of layered materials, i.e. 1.4 nm tobermorite and the C–S–H phases in hydrated Portland cement. The similar behavior is of course qualitative. Taylor's model based on this mixture is by definition a layered model. It also reinforces the view that C–S–H products in hydrated Portland cement systems behave as layered materials. The intercalate takes on structural characteristics. Estimates by Feldman indicate that the intercalate in hydrated Portland cement occupies one molecular layer [45]. The intercalate in 1.4 nm tobermorite also occupies about one molecular layer [47]. The mass of water molecules intercalated and de-intercalated favors a modification of the structural properties of the solid.

4.3.3. Ca-montmorillonite

The elastic response as a function of humidity is significantly different to that for hydrated Portland cement paste and 1.4 nm tobermorite (Fig. 4c). Sorption of moisture results in a significant decrease in stiffness. It is known that two or more layers of water molecules can reside in the interlayer space. This has a weakening effect on the solid as separation distances increase. Any structural effect of the intercalate is negated. It is also evident that hysteresis occurs over the entire humidity range. The energetics of intercalation and de-intercalation is a function of drying history and compatible with observations for the hydrated Portland cement paste upon re-wetting, i.e. a second drying causes additional decreases in stiffness. Stiffness in the dry state is recoverable. It is also evident that there is no unique equilibrium position, e.g. at 11% RH the modulus can vary by more than 50% depending on drying–wetting history. In general, the swelling and shrinkage properties of Ca-montmorillonite follow the same pattern as their plasticity properties – the more plastic is the mineral the more the potential to swell and shrink. This depends on factors such as mineralogy, initial water content, type of interlayer cations, humidity and pressure.

4.4. Dimensional change and elasticity of synthetic C–S–H

Length change versus mass change curves for C–S–H (C/S = 0.8, 1.0 and 1.5) and the corresponding curve for the irreversible component of cement paste [29] are plotted in Fig. 5a–d. It is noted that measurements of mass change of these systems generally require lengthy equilibrium times (often months) especially at low humidities (<11% RH). These times may be even longer for length change measurements. Asymptotic values of mass are often reached before those for length change. This may be due to slow ageing effects that affect dimensional stability. A separation of the length change isotherm for cement paste into 'reversible' and 'irreversible' components shows that the curves in Fig. 5 for pure C–S–H (Fig. 5a–c) are qualitatively and quantitatively similar to the 'irreversible' ones for cement paste (Fig. 5d), [29]. It is suggested therefore that this supports the view that C–S–H in paste behaves in a similar way to layered synthetic C–S–H which exhibits irreversible behavior. Sample preparation and equilibration for dynamic modulus of elasticity measurements below the 11% RH datum require extensive time periods. This work is being considered for future experiments.

Specimens were exposed to high humidity levels starting from the 32% RH condition and subsequently dried to 11% RH. Although the initial swelling during the wetting cycle is higher, the shrinkage for the low C/S ratio preparation is significantly less than that for the other C/S ratio specimens. This is in accord with previously reported observations that major structural differences occur in C–S–H materials when the C/S ratio is below 1.0 [24,48,49]. This may suggest that the volume stability of C–S–H increases when the silicate structure is more polymerized. The comparison of the final and initial mass of the specimens (at 11% and 32% RH, respectively)

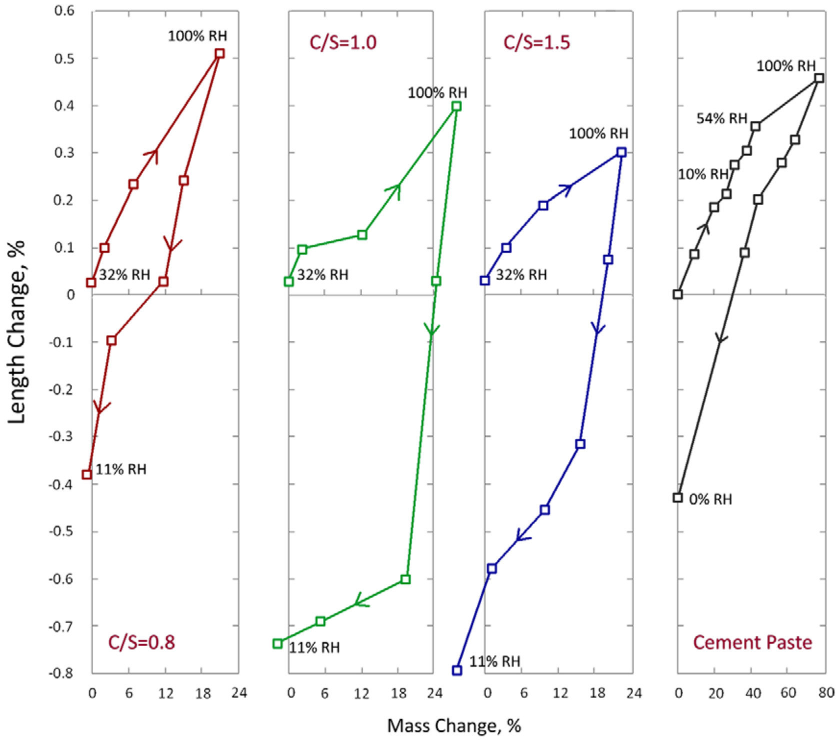

Fig. 5. Length change versus mass change curves for C–S–H preparations exposed to water vapor.

show that there is less mass loss in low C/S ratio C–S–H. This may indicate that the water that has entered the interlayer regions is more loosely held in lime-rich C–S–H preparations.

There are likely several reasons for the observed hysteretic behavior (Fig. 5) of the C–S–H samples. A few words about the nanostructure of C–S–H may be in order. The ^{29}Si MAS NMR results indicate that the length of the silicate chains and degree of silicate polymerization increase as C/S ratio decreases [16]. The C–S–H with C/S ratio = 0.8 has a significantly longer chain length and higher degree of polymerization. The number of defects or missing bridging tetrahedra in the silicate chain is significantly less at this low C/S ratio. The X-ray basal spacing of these specimens decreases with mass loss from the 11%RH condition. For C/S ratio > 1.0 there is a dramatic decrease from about 1.15 nm to about 0.95 nm at about 5% mass loss. The decrease with mass loss is more gradual at low values of C/S ratio. The basal spacing values are also higher at low C/S ratio (1.40 nm at 11% RH for C/S = 0.8). The nanostructural texture is therefore significantly different as C/S ratio varies and the response to mass loss changes. It is also not surprising to observe hysteresis in the curves as structural collapse (evidenced, for example by helium diffusion measurements as water is removed) occurs [44]. There is a possibility of bond formation as silicate sheets come into close proximity. The significant hysteresis in the length change curves of phase pure C–S–H (known layered silicates) reinforces the view that hysteresis observed for C–S–H in hpc reflects the layered nature of this material.

Curves of modulus of elasticity values (storage modulus, E') versus mass loss from the 11% RH condition are plotted in Fig. 6 for hpc (w/c = 0.40) and C–S–H. It is noted that the curve (Fig. 6) most similar to cement paste is the curve for the C–S–H (C/S = 1.5). This is not surprising as the C/S ratio for C–S–H in cement paste varies from about 1.5–1.7. The points of inflection, on close examination of the paste curve, are present in similar mass loss regions. It appears that the state and amount of water seems to be the dominant factor controlling the changes in the elasticity of C–S–H. There is an initial rapid decrease in E' up to about 2% mass loss due to the removal of adsorbed water and interlayer water. This is followed by an increase in the stiffness of material as more water is removed for C–S–H preparations at about 4% mass loss. The decrease in modulus of cement paste in this region (4–6% mass loss) is small and gradual (<1 GPa). The increase in the stiffness of phase pure C–S–H is possibly due to the cross-linking of silica tetrahedra that occurs on the drying of layered C–S–H systems [50,51]. The storage modulus then decreases as the remaining molecules of interlayer water are released and the C–S–H structure collapses. A much more subtle change in slope for cement paste occurs in this mass loss region. Cross-linking is more likely to occur for lower C/S ratio C–S–H preparations due to the greater number of Q^2 sites (NMR nomenclature). This is evident in the plots for C/S ratio = 0.8 and 1.0 in Fig. 6. The maxima are much more pronounced compared to the curve for C/S = 1.5. The C–S–H in cement paste is nearly amorphous and its structure is not well-ordered [23]. Differences in the magnitude of the modulus values observed for cement paste as compared to those of C–S–H are likely due to the fact that other phases in the paste contribute to the measurement. There includes a dilution factor for C–S–H as well as pore structure differences at the microstructure level.

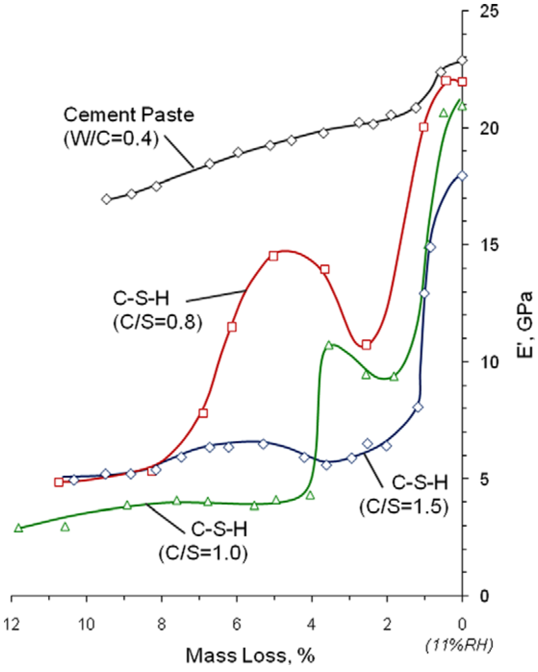

Fig. 6. Storage modulus of cement paste and C–S–H preparations containing different levels of moisture on the removal of water starting from 11% RH condition.

The authors are of the view that synthetic C–S–H's are indeed very good models for studying cement physical chemistry as indicated by their previous work demonstrating the correspondence of changes in helium inflow and basal spacing with mass loss of hpc [44]. Qualitatively the shape of the curve for the C–S–H with C/S ratio = 1.5 (Fig. 6) is similar to the cement paste response. The C–S–H present in cement paste has a C/S ratio varying from about 1.5–1.7 so this comparison is the most relevant. Non-silicate phases in cement paste (e.g. CH, aluminates) can contribute to stiffness. The phase angle results (tan δ) for cement paste mimic those of the C–S–H more precisely [52] These systems all exhibit two maxima in the mass loss curves and can be explained well using a layered silicate model. Therefore, it is felt that synthetic C–S–H behavior has in many cases similar behavior to the C–S–H formed in hydrating Portland cement.

4.5. Volume stability and engineering performance

Differences in the volume stability of cement paste and other layered silicates lie in the extent to which the intercalate imparts structural modification to the solid. These modifications will influence the energetics of processes associated with durability, e.g. dissolution, microcracking and mass transport. The dependence of the physico-mechanical characteristics of C–S–H and other layered silicate minerals on moisture content is non-linear and non-unique. This underlies the importance of drying–wetting history on the durability of concrete in aggressive environments.

5. Conclusions

1. There are striking similarities in the sorption behavior of Portland cement paste, 1.4 nm tobermorite, and Ca-montmorillonite. Mass, length and modulus of elasticity exhibit hysteresis over the entire humidity range for these systems.
2. The response of the modulus of elasticity property as a function of humidity is non-linear and non-unique. For example, the equilibrium values are dependent on drying–wetting history.
3. Structural stiffening of the layered systems (as a function of humidity) can occur. It is dependent on the number of layers of intercalate present in the material. Ca-montmorillonite however actually undergoes a decrease in stiffness on wetting due to multilayer intercalation and a weakening of the material.
4. Similarities in the irreversible nature of the energetics of intercalation and de-intercalation in layered silicates suggests that the C–S–H solids in hydrated Portland cement products are compatible with structural models described by Taylor and Feldman.

5. The changing nature of the C–S–H solids in concrete is likely to influence processes affecting durability. These include decalcification, microcracking and mass transport.
6. Changes in modulus of elasticity versus mass loss curves for synthetic C–S–H have analogous features to those observed for hydrated Portland cement paste.
7. Synthetic C–S–H can be considered as a possible model for the dimensional stability and elastic properties of hydrated Portland cement paste.

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