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DIMENSIONAL CHANGE AND ELASTIC BEHAVIOR OF HARDENED PORTLAND CEMENT PASTE, Ca-MONTMORILLONITE AND 1.4 nm TOBERMORITE: A COMPARATIVE STUDY

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ABSTRACT

The role of water in hardened Portland cement paste (hpc) is germane to an understanding of the nature of nanostructure – property relationships. The irreversible dimensional changes of hpc that occur on wetting and drying are dissimilar to those observed for other silicate minerals of interest to cement science. This irreversibility is also observed for the modulus of elasticity parameter. Length change, mass change and modulus of elasticity isotherms (including 1st and 2nd drying-wetting cycles) were determined for specimens of hpc, montmorillonite and 1.4 nm tobermorite. All exhibit significant irreversible behavior. Similarities and differences in the nature and character of the three types of isotherms are discussed. Inferences are made with respect to the nanostructural nature of hpc and its dimensional response in aqueous media. It is apparent that hpc has unique characteristics that are responsible for stability.

INTRODUCTION

The volume stability and performance of cement-based materials are known to be affected by the response of the C-S-H in aggressive environments, Beaudoin et al. (1). This may have an impact on the micro and nanostructural integrity of the binder in concrete and 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 may 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, Taylor (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 (3) and Taylor (4) can account for the large primary and secondary hysteresis associated with water isotherms (mass and length change). Feldman (5) 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.

A study was designed to further investigate the irreversible nature of volume change in cement systems (undergoing several drying-wetting cycles). Two other model layer silicate systems – montmorillonite and 1.4 nm tobermorite – were utilized to establish similarities and differences in nanostructural performance. Differences in the 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.

STRUCTURE AND PROPERTIES OF LAYERED C-S-H ANALOGS

The understanding of the structure of C-S-H in hydrated Portland cement has evolved from the structure of 1.4 and 1.1 nm tobermorite, Brunauer (6). An idealized structure for 1.1 nm tobermorite is presented in Figure 1(a). 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. Other hypotheses for lime-rich tobermorites include: omission of “bridging” silica tetrahedra; structures based on $\text{H}_2\text{SiO}_4^{2-}$ group; replacement of regions of dreierketten by hydroxyl ions which form part of the central CaO_2 layers. However evidence that in C-S-H (gel), after lengthy periods of hydration, considerable amounts of orthosilicate and dimer silicate chains exist, 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, Beaudoin (7).

There are structural similarities between the structure of Ca-montmorillonite and the more crystalline C-S-H (II) described by Taylor (4). Figure 1(b) is an idealized representation of Ca-montmorillonite. In the tetrahedral sheet, Si is sometimes replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent aluminum by divalent Mg without complete filling of the third vacant octahedral position. A deficit of positive charge results. This is compensated 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. Contact with water results in penetration of water molecules between the unit layers. The basal spacing expands to values in the range of 1.25 – 2.00 nm depending on the type of cation.

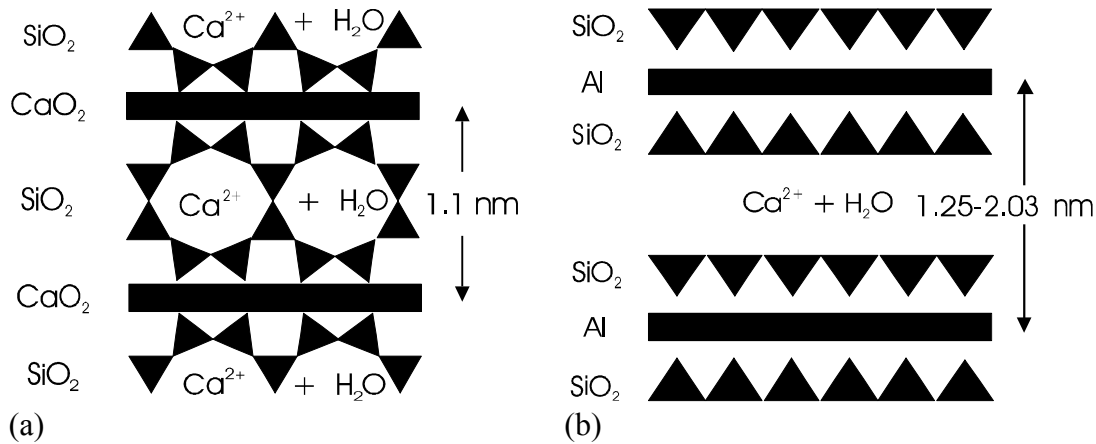


Figure 1 Diagrams depicting the idealized structures of (a) 1.1 nm Tobermorite and (b) Ca-Montmorillonite

Four layers of water molecules may be intercalated. It is known that montmorillonite clays experience substantial interlayer swelling, Grim (8). 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. The argument for inclusion of Ca-montmorillonite in this study is that further understanding of similarities and differences of the title systems should contribute to the long-term objective of correlating volume change and durability with the structure of C-S-H in Portland cement products.

EXPERIMENTAL

Materials

Normal Portland cement was used. 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. (9) using lime and amorphous silica (at $\text{Ca/Si} = 1.00$) 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 $45.0 \text{ m}^2/\text{g}$.

Ca-montmorillonite samples were obtained from a commercial supplier. The surface area was determined to be $14.6 \text{ m}^2/\text{g}$. The material was ground and passed through a 100 mesh sieve.

Specimen Fabrication

The modulus of elasticity measurements for cement paste were made with paste prepared at water-cement ratio = 0.25. The paste was hydrated for several years 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 powders compacted in the form of discs, 31.75 mm in diameter x 1.00 mm thick. Porosity values for the paste, 1.4 nm tobermorite and Ca-montmorillonite are 4, 11 and 51% respectively.

Sorption Measurements

Mass and length change isotherms were performed in 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^{-8} kg. 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. It was established prior that vacuum degassing at 85% for 3 h (cement paste) produced the same result for the non-evaporable water as the conventional 'd-drying' procedure, Feldman (5).

Modulus of Elasticity Measurements

The modulus of elasticity values 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, Tamtsia and Beaudoin (10).

The modulus values for the 1.4 nm tobermorite and Ca-montmorillonite were determined using a loading device designed for the disc specimens, Sereda et.al. (11). Load-deflection curves (flexural mode) were used for the calculations.

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.

Mass Change Isotherms

The isotherms are depicted in Figure 2(a) – 2(c). All isotherms exhibit large primary and secondary hysteresis and the existence of scanning loops. The isotherm for Ca-montmorillonite was obtained up to an RH value of 69% as the sample did not retain structural integrity beyond this point. The character of all the isotherms is similar suggesting 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 layer system. 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 drying-wetting history.

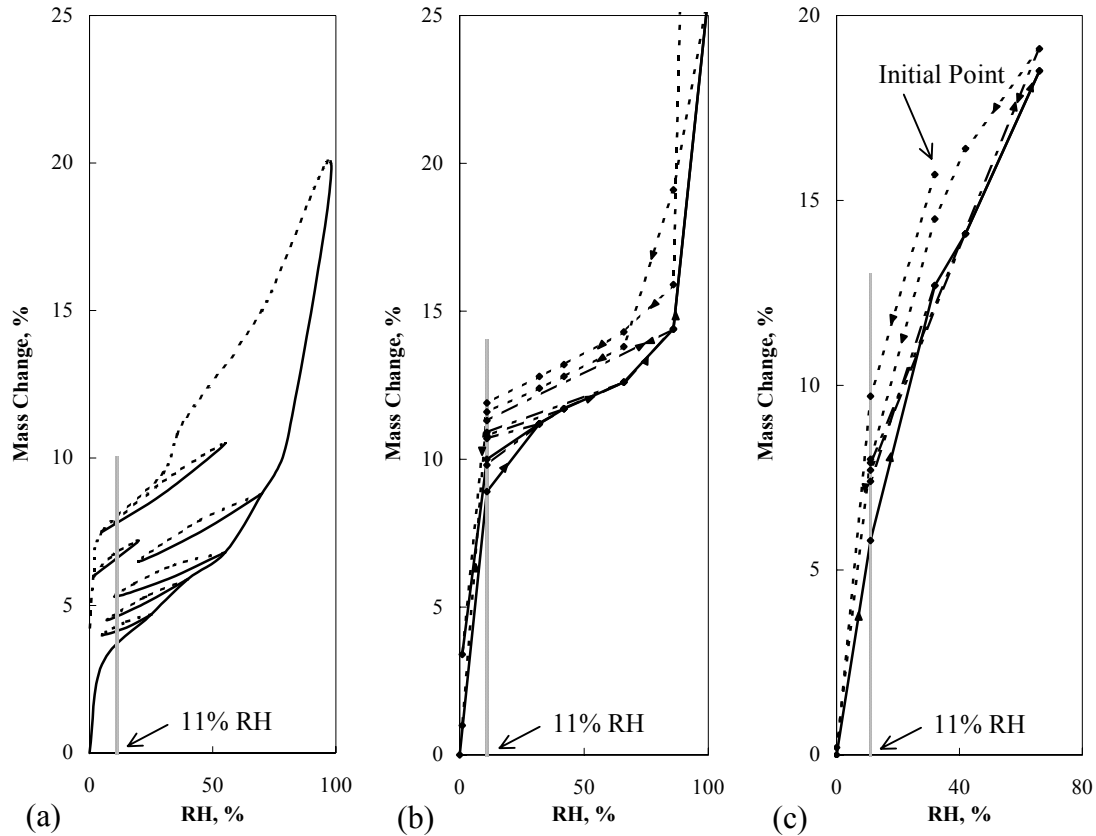


Figure 2 Mass Change Isotherms (water adsorbate) at 25°C of (a) Cement Paste, w/c = 0.25; (b) 1.4 nm Tobermorite and (c) Ca-Montmorillonite

Length Change Isotherms

The isotherms are plotted in Figure 3(a) – 3(c). They all exhibit similar characteristics of irreversibility evident in the mass change versus humidity curves. The nature of the length change curves and in particular the scanning loops are strikingly similar for the three systems. The volume change processes due to uptake of water would appear to be mechanistically similar. The absence of uniqueness at any given humidity suggests that volume stability is sorption path dependent.

Modulus of Elasticity Isotherms

The isotherms are plotted in Figure 4(a) – 4(c). The role of water in the nanostructure of the three systems is more clearly understood on 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 on that basis.

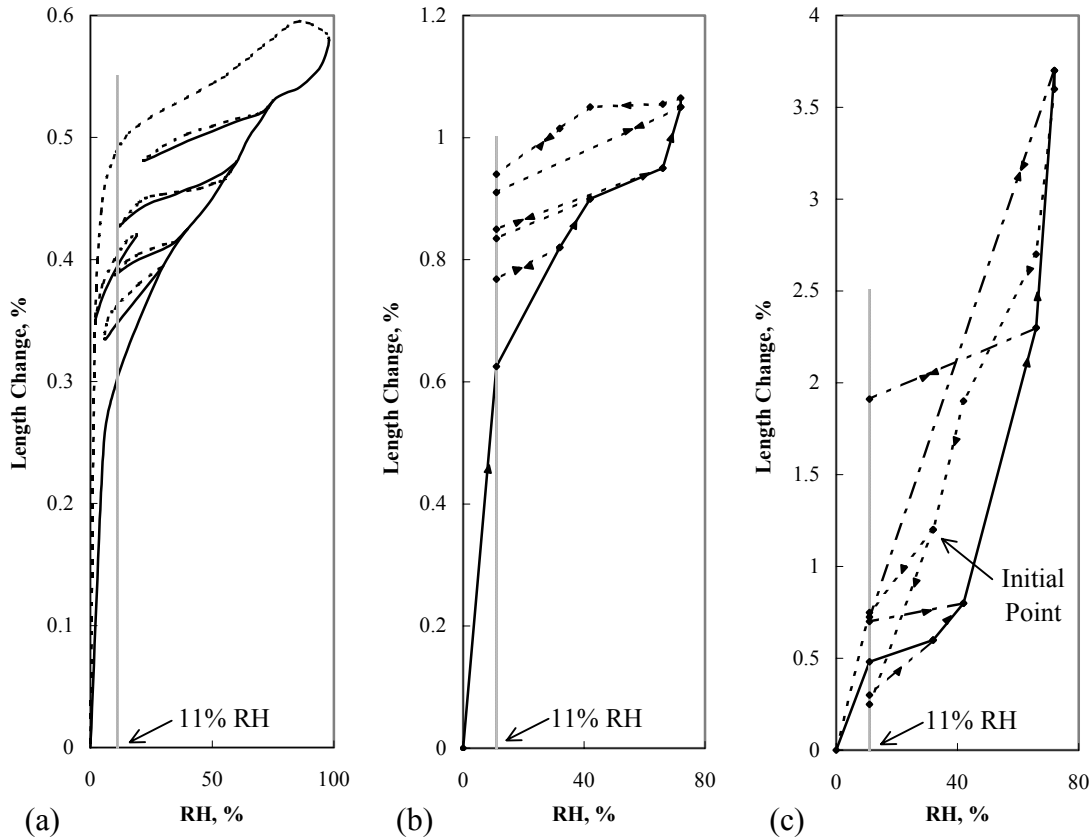


Figure 3 Length Change Isotherms (water adsorbate) at 25°C of (a) Cement Paste, w/c = 0.25; (b) 1.4 nm Tobermorite and (c) Ca-Montmorillonite

- (i) **Portland cement paste:** The large hysteresis observed on first drying and rewetting has been previously observed by Sereda et.al. (Figure 4(a)) (11). The only difference was the mode of the applied stress i.e. flexural as opposed to compressive 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 similar to first drying. However second rewetting 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 humidities. Second drying delays the re-intercalation of water (possibly due to a higher degree of structural collapse).
- (ii) **1.4 nm tobermorite:** The dependence of the modulus of elasticity on relative humidity (Figure 4(b)) has similar features to that for Portland cement paste. Intercalation of water into the structure has a stiffening effect that is maintained 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 a mixture of tobermorite and jennite. 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 indicate that the intercalate in hydrated Portland cement occupies one molecular layer, Feldman (12). The intercalate in 1.4 nm tobermorite also occupies about one molecular layer. The energetics favors a modification of the structural properties of the solid.

- (iii) **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 (Figure 4(c)). Sorption of moisture results in a significant decrease in stiffness. It is known that up to four 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 i.e. 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.

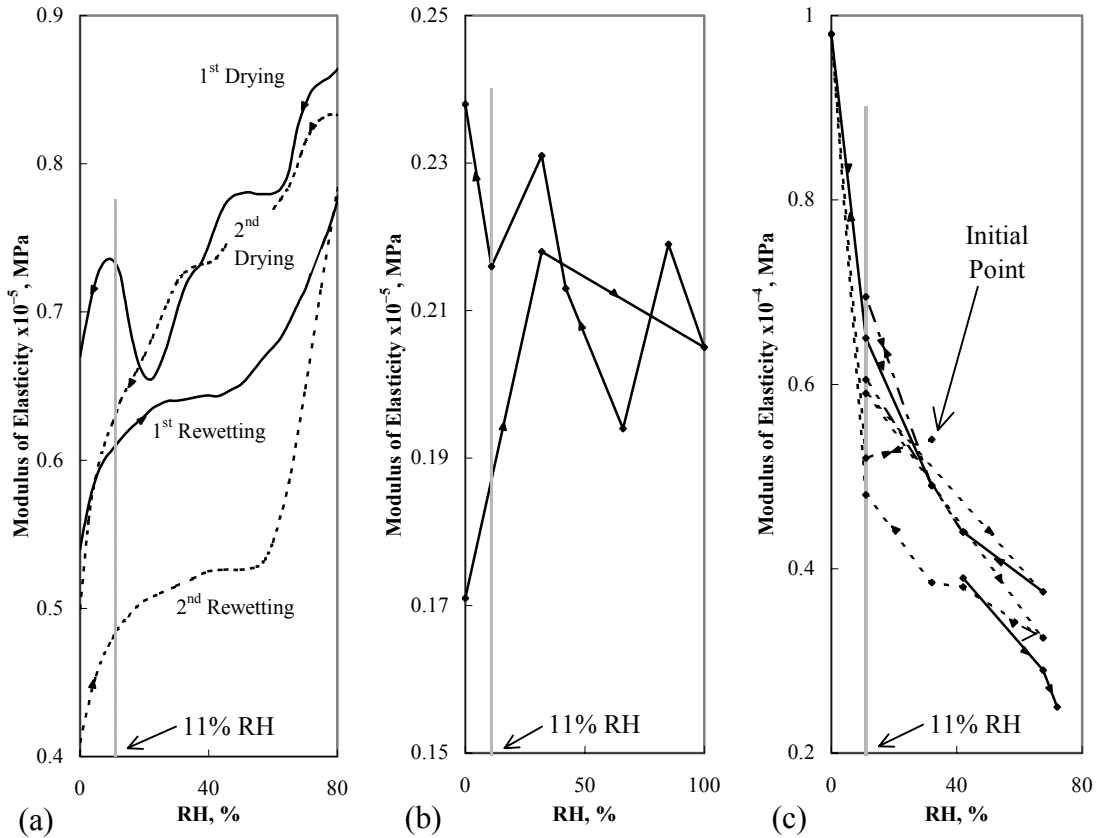


Figure 4 Modulus of Elasticity Isotherms (water adsorbate) at 25°C of (a) Cement Paste, w/c = 0.25; (b) 1.4 nm Tobermorite and (c) Ca-Montmorillonite

Volume Stability and Engineering Performance

It is apparent that volume stability and engineering performance are linked in similar ways for all three of the layer systems investigated. Differences 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 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.

A comparison of the sorption characteristics of the three systems studied suggests that the durability of concrete in aggressive environments can be influenced by the 'layered' nature of the C-S-H binder.

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 the three title systems suggest that the C-S-H solids in hydrated Portland cement products are compatible with structural models described by Feldman and Taylor.
5. The changing nature of the C-S-H solids in concrete is likely to influence processes affecting durability. These include dissolution, microcracking and mass transport.

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