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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-

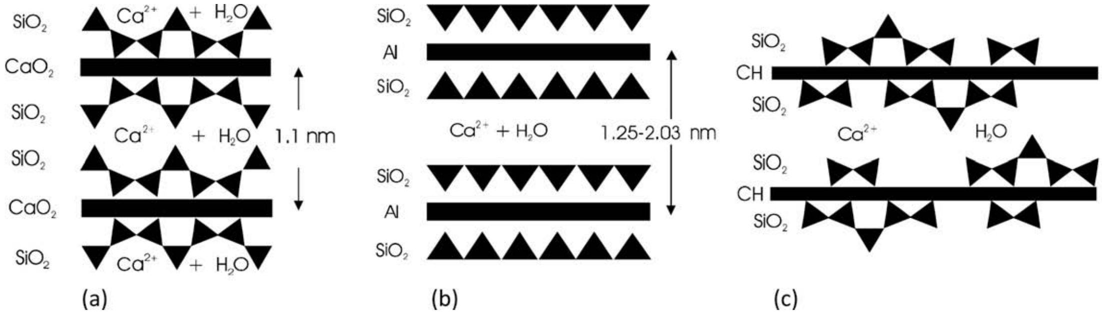

Fig. 1. Schematic representation of the structures of: (a) 1.1 nm tobermorite; (b) Ca-montmorillonite and (c) C–S–H in hydrated Portland cement.