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Length Change of C-S-H of Variable Composition Immersed in Aqueous Solutions

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Abstract

The dimensional stability of C-S-H (with varying C/S ratios) in saturated-lime water, distilled water and a methylene (MB) solution was investigated in this study. Two distinct regions of C/S ratio exhibited maxima in length change versus C/S ratio curves generated from results in all three test solutions. Differences in behavior in all three solutions were minimal. It would appear that the C-S-H nanostructures that quickly form in MB solution are comparatively stable in aqueous media. Possible mechanisms for the length change behavior are discussed.

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Methylene Blue

Introduction

Sustainability initiatives in the cement-based materials industry have received considerable attention [1]. These include the development of new materials to extend the service-life in aggressive environments [2]. The calcium silicate hydrate phases (C-S-H) play a major role in determining the performance of concrete and its sustainability [3]. Recent work has focused on the modification of C-S-H with the ultimate goal of improving its performance both chemically and physically [4,5]. This has led to international efforts in the development of organic/inorganic nanostructures [6-7].

Volume stability of phase pure C-S-H and its dependence on C/S ratio has not been previously reported. The results of a study designed to determine the volume stability of C-S-H in lime-saturated water, distilled water and a MB solution are presented. Comments on the operational length change mechanisms are given.

A MB solution was included in the study for the following reasons. MB dye adsorbs irreversibly on C-S-H surfaces and promotes increased polymerization of the silicate chains in the C-S-H nanostructure [8,9].

Brief arguments are presented to explain why it might be expected to see an effect of MB adsorption on length change at the concentration cited. The rationale is as follows. In general it is not unusual for significant length change to occur in silicate systems (e.g. cement paste) at low concentrations of adsorbate (e.g. water). For example, the length change isotherm for cement paste ($w/c=0.50$) illustrates this point [10]. The isotherm is very steep at low values of partial pressure. A weight change of 1.27% or 7×10^{-4} mol/g of cement paste (fractions of a monolayer) at a partial pressure of 0.27% results in a length change of 0.08%. This is a relatively large dimensional change (about 30% and 15% of the total length change in the specimen at 12%RH and 96%RH, respectively). MB dye adsorbs irreversibly on C-S-H surfaces at low concentrations indicating that it is very tightly held to the surface. An increase in the Q^2/Q^1 ratio of C-S-H ($C/S=1.5$) in the ^{29}Si MAS NMR spectra (Figure 1) can be explained by the strong adsorption of MB molecules at defect sites (i.e. locations of missing bridging tetrahedra). A schematic of the

modified C-S-H nanostructure is provided (Figure 2) [8, 9]. These nanostructural modifications occur at relatively low concentrations of MB i.e. fractions of a monolayer or very low mole ratios of MB to C-S-H. Preferred adsorption of MB at defect sites is well known in clay science where MB loadings are expressed in $\mu\text{mole/g}$ range [11]. The MB molecules mimic the missing bridging tetrahedra in C-S-H resulting in an increase in the number of Q^2 sites. The number of defect sites is dependent on C/S ratio. There are fewer sites at low C/S ratios as the length of the silicate chains increases significantly. For example, the Q^2/Q^1 ratio (C/S=0.80) is not greatly affected by the MB treatment. It was expected, then, that surface energy changes specific to MB adsorption sites might result in a relevant contribution to dimensional change despite the low concentration. It is difficult to quantitatively separate the individual contributions to length change of several mechanisms (some of which might be contractive) that may be acting simultaneously.

The extent to which C-S-H modification with organic phases such as MB can enhance engineering behavior has yet to be determined although early indications are that parameters such as modulus of elasticity can be enhanced [12,13]. Questions regarding the contribution of C-S-H based organic/inorganic nanostructures to sustainability in general and volume stability in particular remain.

Experimental

C-S-H Preparation

C-S-H samples with C/S ratios of 0.60,0.80,1.00,1.20,1.40,1.50,1.60,1.65,1.70, 1.75 and 1.80 were prepared. Stoichiometric amounts of CaO and amorphous silica mixed with a water/solids ratio of about 10 were used for samples with C/S ratio varying from 0.60 to 1.60. The preparations with C/S ratios 1.65 to 1.80 were prepared with stoichiometric amounts of CaO and amorphous silica corresponding to initial C/S ratios of 1.7 to 2.0. These samples contained significant amounts of free lime and the C/S ratios were corrected accordingly. The CaO was produced using precipitated calcium carbonate heated at 900°C for 24h. The CaO was purged with nitrogen gas and stored in a desiccator until required. The amorphous silica (Cab-O-Sil) was

heated at 110°C to dry the material thoroughly. The reactants for producing C-S-H were placed in high density polyethylene (HDPE) bottles that were continuously rotated for periods up to one year. The reaction temperature was 23°C. The material was then filtered to remove excess water and dried under vacuum for 4 days. The resulting products were placed in HDPE bottles, purged with nitrogen gas and stored until further use. Samples of the various C-S-H preparations were put aside for immediate characterization using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) methods. The TGA results were quantitatively and qualitatively similar to that reported for C-S-H gel [14]. The X-ray patterns indicated the presence of the primary peaks previously reported for C-S-H [3]. Additional details have been provided by the authors elsewhere [8, 9].

Test Solutions

Test solutions were prepared for the length change measurements of the C-S-H samples: saturated-lime water, distilled water and a MB solution. Lime-saturated water solutions were prepared by dissolving reagent grade $\text{Ca}(\text{OH})_2$ in deionized water. The MB solutions were prepared with a relatively low MB concentration of 15mg/L typical of concentrations used in clay adsorption experiments where loadings of MB are expressed in units of $\mu\text{mole/g}$ [11]. Approximately 0.3 mg per g of C-S-H is adsorbed [9]. This relatively low loading is not surprising, as unlike clays, C-S-H does not contain several layers of interlayer water. MB adsorption is very rapid and equilibrium is attained in a few minutes. The length change results therefore simulate the behavior of C-S-H-MB nanostructures.

Compacts

The C-S-H powders were formed into solid bodies by compaction at 140MPa. Circular discs (32mm in diameter x 1mm thick) were prepared. A small variation in the porosity of the compacts with C/S ratio occurs. This was not considered significant. The use of compacts of hydrated Portland cement and C_3S powders in studies of engineering behavior is now well established [15-19].

Length Change Measurements

Prisms (5 x 25 x 1mm) were cut from the compacted disc samples and mounted on modified Tuckerman extensometers (accurate to 1 microstrain). These were placed in the test solutions (so that the specimens were completely immersed) and length change measurements were taken continuously. Details of the test set-up have been reported previously [15].

Results and Discussion

The dimensional stability of microporous cement-based solids is a possible performance indicator when these materials are exposed to aggressive environments. There is a paucity of information available on the length change of phase pure C-S-H in liquid media [20]. The length change results of a suite of C-S-H preparations ($C/S = 0.60$ to 1.75) are presented in Figures 3(a), 3(b) and 3(c). Length change data for all the C-S-H samples is plotted as a function of time up to 24h. The samples in Figure 3(a), (b), (c) were exposed to saturated-lime solution, distilled water and MB solution respectively. The data up to 672h follows the same trend and is not shown. The length change versus time curves of all the C-S-H samples immersed in the three liquids follow a typical power law and are dependent on C/S ratio. This dependence is illustrated by the C/S ratio plots of total length change at 24h and 672h as shown in Figure 4. The curves exhibit two distinct regions- one at C/S ratios of 0.60 to 1.2 , the other at C/S ratios > 1.20 . Two maxima occur- one at C/S ratio $= 0.80$ and the other at C/S ratio $= 1.50$ - 1.60 . The 24h data for the samples immersed in each of the three solutions is generally similar (qualitatively and quantitatively) with a few exceptions e.g. at $C/S = 1.50$ where the length change in lime-saturated water and MB solution is significantly higher than in distilled water. The trends for the data at 672h are similar to the 24h data- the magnitude of the length change is, of course, larger. It can be concluded that the primary expansion has occurred within the first few hours.

The mechanisms responsible for the length change of cement and cement mineral hydrates has been widely discussed [21]. Those applicable to layered silicate systems such as C-S-H include surface adsorption, intercalation and dissolution of solids e.g. Ca(OH)_2 . In Portland cement and C_3S pastes surface adsorption (specifically the Bangham effect) has been shown to account for

considerably less expansion than intercalation i.e. about 20% of the total [22]. Intercalation of water has a more pronounced effect. Dissolution of solids e.g. $\text{Ca}(\text{OH})_2$ has also been shown to be an expansive process[23]. It is proposed that the length change results (Figure 4) can be explained by accounting for the relative influence of the C-S-H nanostructure on two complimentary expansive mechanisms i.e. swelling due to intercalation of water molecules and expansion due to solid dissolution. Evidence of the dissolution of $\text{Ca}(\text{OH})_2$ in C-S-H immersed in MB solutions is provided by the pH versus C/S ratio curve (Figure 5). The pH of the MB solution increases with C/S ratio. For all C/S ratios, the pH rapidly increases and plateaus. Decalcification of C-S-H in distilled water has been previously reported [24].

The ^{29}Si NMR spectral studies show that the silicate chain length of C-S-H decreases with an increase in C/S ratio[25]. At C/S ratios > 1.0 missing bridging tetrahedra frequently occur and the chains consist predominately of dimers. The gaps or defects at sites between the dimers can act as access points for migration of water molecules into the layered structure in addition to the normal location for intercalation at the ends of the C-S-H layers. Length change of C-S-H immersed in the test solutions can therefore be considered the result of a combination of interlayer swelling and the dissolution of interlayer $\text{Ca}(\text{OH})_2$. The kinetics of either of these processes is influenced by the presence and frequency of the defects in the C-S-H nanostructure. At C/S ratio = 0.60 the length change is low as the C-S-H is comprised of long chains with relatively few defects. As entry of interlayer water occurs primarily at the layer ends the rate of dissolution of $\text{Ca}(\text{OH})_2$ is slower. Complete penetration of water molecules is inhibited due to irregularity in the stacking of the layers.

At the first maximum in Figure 4 (C/S ratio = 0.80) both the number of defects and intercalation amount increase moderately. At C/S ratio = 1.0-1.2 the significant decrease in chain length reduces the contribution of interlayer swelling and the dissolution process is marginally more effective. The second and largest maximum occurs at C/S=1.5-1.6. In this case conditions are optimum for the greatest effect of dissolution and interlayer swelling to occur as the number of defects and rate of interlayer penetration of water molecules are maximum. The C-S-H preparations at C/S ratio > 1.60 are not pure as they contain free lime. Well dispersed particles of $\text{Ca}(\text{OH})_2$ may restrain the length change accounting for the reduced values.

The length change results for the C-S-H samples immersed in saturated-lime solution are similar to those obtained in MB solution or distilled water. It has been reported that the length change of hydrated C_3S paste immersed in lime-saturated solution is similar in magnitude to the same paste immersed in distilled water [26]. It would appear then that the dissolution mechanism involving $Ca(OH)_2$ would not apply in this case. It is noted however that the silicate network in glass is susceptible to significant attack at high values of pH (>12) [27]. It is suggested that the expansion component of C-S-H in lime-saturated water may be due to some dissolution of the silicate network itself. The explanation for the length change-C/S ratio dependence would be similar as described above except for the nature of the solids under attack. It is also possible that some silicate dissolution occurs in MB solution at high pH.

Conclusions

1. The length change behavior of C-S-H immersed in saturated calcium hydroxide solutions, distilled water and in methylene blue (MB) solutions is qualitatively and quantitatively similar.
2. The length change of C-S-H immersed in saturated-lime solution, distilled water and a MB solution is dependent on C/S ratio.
3. There are two distinct regions of C/S ratio, [(0.60 to 1.2) and (1.2 to 1.75)], that affect the length change – C/S ratio dependence. Each region exhibits a maximum length change. This effect is related to differences in the C-S-H nanostructure.
4. It is suggested that the mechanisms responsible for the length change of the layered C-S-H phases are primarily interlayer swelling and dissolution of calcium hydroxide. The relative contribution of each of these mechanisms varies with C/S ratio and is a function of silicate chain length and the concomitant number of defect sites in the silicate nanostructure of the C-S-H.
5. A contribution to the length change of C-S-H resulting from the dissolution effect in the high pH saturated calcium hydroxide solution is attributed to a possible dissolution of the silicate network at critical points. This may also be a factor contributing to length change in the methylene blue solutions at high pH conditions and hence any cement-based products containing MB modified binders.

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Figure Captions

Figure 1. ^{29}Si MAS NMR spectra for C-S-H ($\text{C/S}=1.5$) treated in MB solution (15mg/L) : (a) reference sample (b) treated sample.

Figure 2. Schematic of C-S-H nanostructure showing possible sites for MB interaction.

Figure 3. Length change of C-S-H of varying C/S ratio immersed in (a) saturated-calcium hydroxide solution (b) distilled water (c) methylene blue (MB) solution (15mg/L)

Figure 4. Total length change at 24 and 672h versus C/S ratio following immersion of C-S-H in saturated calcium hydroxide solution, distilled water and methylene blue solution.

Figure 5. pH values of methylene blue (MB) solutions following immersion of C-S-H samples for 24h plotted as a function of C/S ratio. The original concentration of the MB solution is 15mg/L.

Figure 1

Figure 2

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 4

Figure 5