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Decalcification shrinkage of cement paste

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Abstract

Decalcification of cement paste in concrete is associated with several modes of chemical degradation including leaching, carbonation and sulfate attack. The primary aim of the current study was to investigate the effects of decalcification under saturated conditions on the dimensional stability of cement paste. Thin (0.8 mm) specimens of tricalcium silicate (C_3S) paste, white portland cement (WPC) paste, and WPC paste blended with 30% silica fume (WPC/30% SF) were decalcified by leaching in concentrated solutions of ammonium nitrate, a method that efficiently removes calcium from the solid while largely preserving silicate and other ions. All pastes were found to shrink significantly and irreversibly as a result of decalcification, particularly when the Ca/Si ratio of the C-S-H gel was reduced below ~ 1.2. Since this composition coincides with the onset of structural changes in C-S-H such as an increase in silicate polymerization and a local densification into sheet-like morphologies, it is proposed that the observed shrinkage, here called decalcification shrinkage, is due initially to these structural changes in C-S-H at Ca/Si ~ 1.2 and eventually to the decomposition of C-S-H into silica gel. In agreement with this reasoning, the blended cement paste exhibited greater decalcification shrinkage than the pure cement pastes due to its lower initial Ca/Si ratio for C-S-H gel. The similarities in the mechanisms of decalcification shrinkage are also discussed.

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1. Introduction

Decalcification, or loss of calcium through chemical reaction, is an important and widespread degradation mechanism of cementitious materials. For cement paste in concrete, decalcification occurs by various means including leaching by soft or acidic waters [1–6], carbonation [7,8], and sulfate-attack [9–11]. Calcium hydroxide (CH) and calcium silicate hydrate (C–S–H) gel, the most important calcium-bearing hydrated phases in cement paste, are both susceptible to decalcification. Dissolution of CH generally occurs more readily, while decalcification of C–S–H occurs when CH is inaccessible or locally depleted [12].

The dissolution of CH from cement paste produces several well-known deleterious effects, the most obvious of which are

an increase in porosity and subsequent loss in strength [6,13,14]. Ionic diffusivities can also increase by an order of magnitude if the degree of leaching is sufficient to create a percolated porous structure [15]. A reduction in the pH of the pore solution will also result from CH dissolution, thereby allowing for the decalcification of C–S–H gel and increasing the susceptibility of steel reinforcement to corrosion.

Decalcification of C–S–H induces pronounced changes in the nanostructure of C–S–H. For example, the degree of silicate polymerization in C–S–H increases with leaching [16–18] due to the removal of interlayer Ca ions (i.e., Ca at interlayer sites balancing silicate anions) below Ca/Si ~1.2 [16,17,19]. Small-angle neutron scattering (SANS) measurements showed [20] a near doubling of the specific surface area when C₃S or cement paste was decalcified from the original Ca/Si ratio of 3 down to Ca/Si=1.1. Fractal analysis of the SANS data from saturated paste [20] indicated a transition in the morphology of C–S–H from a volume fractal structure based on 4–5 nm particles at Ca/Si near 1.7 to a sheet-like structure for Ca/Si <~ 1.1. Direct observation of dried cement paste with TEM [21–23] shows the C–S–H morphology

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changing from fibers to foils (or sheets) on going from high to low Ca/Si ratios. Changes in the content of hydroxyl groups in C-S-H (i.e., Ca-OH and Si-OH) are also induced by decalcification [19,24].

Due to the nanometer-scale internal pore structure of C-S-H and the heterogeneous nature of cement paste, it is experimentally difficult to separate the individual effects of different phases on the properties of cement paste. Nevertheless, Constantinides and Ulm [25] found that the elastic modulus of cement paste measured by nanoindentation decreases much more severely with decalcification of C-S-H than with dissolution of CH. Heukamp et al. [26] have further shown that C–S–H decalcified to a Ca/Si ratio of ~ 1 is a highly plastically deformable material that exhibits very little cohesion. As noted by Taylor and Gollop [12], weakening of C-S-H may be the primary mechanism of failure in certain cases of sulfate attack, particularly those involving blended cements with low CH contents, in which the extent of decalcification can be appreciable. Loss of cohesion and strength, presumably caused by decalcification of C-S-H, has been cited [27,28] as the principle mode of failure for external sulfate attack in the field.

Although the volume stability of concrete is an important property linked to various performance criteria, the dimensional changes of cement paste during decalcification have not been extensively studied. It might reasonably be anticipated that some change in volume would be induced by the decalcification of C-S-H due to the fairly significant changes in structure noted above. However, the few studies that have investigated this problem have produced conflicting results. Litvan [29] reported a net linear expansion of cement paste bars $(28 \times 6 \text{ mm})$ leached in 1.0 N HCl or ethylene glycol. Similar but slightly greater expansions observed for porous silica glass leached in 0.2 N NaOH led Litvan to propose that expansion may be a general phenomenon linked to the dissolution of porous solids. In a later study, Feldman and Ramachandran [30] reached nearly the opposite conclusion: on leaching thin (0.64 mm) discs of cement paste in distilled water, they observed an initial expansion, followed by a net shrinkage. The expansion was attributed to relaxation of the paste associated with the dissolution of CH, while the contraction was attributed to removal of Ca from the interlayer spaces and from the Ca-O sheet of C-S-H.

Given the conflicting evidence in the literature, the present study was motivated to examine the dimensional changes of cement paste during pure decalcification. Specimens, which were intentionally thin (0.80 mm) to minimize compositional gradients, included neat C_3S and WPC pastes, as well as a WPC paste blended with 30% silica fume (WPC/30% SF).

2. Experimental

2.1. Specimen preparation

Experiments were conducted on pastes made from C_3S (described in Ref. [17]), a type I white portland cement (WPC), and a WPC blended with 30 wt.% silica fume (Construction

Technology Laboratories). The bulk composition of the WPC was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be: 68.8% CaO, 24.8% SiO₂, 2.4% Al₂O₃, 0.4% Fe₂O₃, 0.7 % MgO, 0.3 % Na₂O, and 0.7 % K₂O; based on this analysis, a Bogue calculation yields 74% C₃S, 14% β -C₂S, 6% C₃A, and 1% C₄AF. Pastes were prepared with deionized water using a water:solids ratio of 0.5. After casting in cylindrical polystyrene vials measuring 25 mm in diameter and 50 mm in height, samples were demolded after 1 d and cured in saturated CaO solution at 22±1 °C. The C_3S paste was cured for ~8 months (nearly to complete reaction [17]) and the neat and blended WPC pastes were cured for ~19 months. XRD showed small amounts of unreacted β -C₂S in the neat and blended WPC pastes. As suggested by the negligible Q^4 intensity shown by ²⁹Si NMR, the silica fume in the blended paste was completely consumed by pozzolanic reaction with CH and C-S-H; XRD showed only minor amounts of CH. Immediately prior to leaching (Section 2.2) pastes were cut into 0.8-mm thick discs using a waterlubricated diamond saw.

2.2. Leaching in NH_4NO_3 solution and in water

Decalcification was conducted in 6 M solutions of NH₄NO₃ [6,14,31], which offers several key advantages over leaching in water. The leaching rate is accelerated by approximately 2 orders of magnitude, and, in addition, the leaching reaction in 6 M NH_4NO_3 is nearly a pure decalcification; that is, there is little loss of Si, even at Ca/Si ratios as low as 0.3 [31]. The preservation of Si in the leached solid prevents complete dissolution of solid C-S-H gel, thus preventing the sample erosion [31] that occurs during a flowing-water leaching process (e.g. [4]). Decalcification in NH₄NO₃ solution therefore allows direct measurements of the strains arising from structural changes induced by decalcification. For comparison, similar specimens were also leached by exposure to a continuous flow of deionized water for up to 15 days. This was done in an enclosed 2 l plastic container equipped with an inlet for deionized water and an outlet for the displaced liquid.

The weight loss of NH_4NO_3 - and water-leached specimens was monitored during leaching. These values were correlated with bulk Ca/Si ratios of the solid using empirical relationships between Ca/Si ratio and weight loss. The bulk Ca/Si ratios of solids were measured directly by ICP-AES after solubilization of the solids through fusion with LiBO₂ at 1000 °C [32].

2.3. Measurements of radial shrinkage during decalcification

The radial shrinkage of 0.8-mm thick discs was measured during decalcification in NH_4NO_3 solution. At intervals of generally 3–5 min, a sample was removed from a NH_4NO_3 solution, quickly measured for weight loss and radial shrinkage (as described below), and then promptly returned to the stirred NH_4NO_3 solution. Longer intervals of up to 15 min were sometimes used near the end of an experiment to minimize handling of the fragile leached specimen. Care was also taken to measure samples in the saturated state in order to isolate the shrinkage strains caused by decalcification and to minimize those caused by drying. For the specimens leached in flowing water, longer intervals, generally 1 day in length, were allotted between measurements due to the slower leaching kinetics.

The diameters of the specimens were measured with a digital caliper accurate to 0.01 mm. Greater precision was obtained when mounting the caliper on a fixed, flat surface. For each measurement, 3 marked diameters, separated by approximately 120° , were recorded; the average of these readings is reported. A satisfactory level of precision was achieved by this method as indicated by the relatively smooth variations with time and degree of leaching.

3. Results

3.1. Correlations between weight loss and Ca/Si ratio

Fig. 1 shows the weight loss as a function of bulk Ca/Si ratio for neat and blended WPC pastes leached in NH_4NO_3 solution; the weight loss values relate to decalcified samples saturated with 6 M NH_4NO_3 . Since weight loss and dimensional changes were both measured during decalcification, the relationships in Fig. 1 allow the dimensional changes to be related directly to the compositional changes of the solid. Similar results for C₃S paste leached in NH_4NO_3 have been reported elsewhere [31].

As with C₃S paste, the weight loss of WPC paste during decalcification in 6 M NH₄NO₃ follows two linear curves. Quantitative X-ray (QXRD) studies on C₃S paste [31] show that the change in slope coincides with the complete dissolution of CH from the paste. Assuming analogous behavior for the WPC paste, the initial linear region (slope=-0.149) is attributed to the simultaneous dissolution of CH and the initial decalcification of C–S–H; the second region (slope=-0.067) is attributed solely to the decalcification of C–S–H. This interpretation is consistent with the CH-free blended cement paste, which only showed the single curve associated with the



Fig. 1. Relationship between weight loss and Ca/Si ratio for neat WPC paste (\Box) and blended WPC/30% SF paste (\blacksquare) decalcified in NH₄NO₃ solution. Weight loss values relate to samples saturated with 6 M NH₄NO₃.



Fig. 2. Relationship between weight loss and Ca/Si ratio for neat WPC paste leached in NH_4NO_3 solution (\Box) and in water (Δ). Weight loss values relate to samples saturated with water.

decalcification of C–S–H. Fig. 1 also illustrates the greater extent of decalcification of C–S–H gel in the blended paste at a given weight loss.

Fig. 2 compares the weight loss-Ca/Si ratio relationships for neat WPC paste discs leached in flowing deionized water and in 6 M NH₄NO₃ solution. (To compare the two series, the weight loss values for the NH₄NO₃-leached samples are reported after rinsing in water.) Results show that, to achieve the same bulk Ca/ Si ratio, the water-leached specimens must undergo a greater weight loss than the NH₄NO₃-leached specimens. As leaching in NH₄NO₃ solution results in a nearly pure decalcification of the solid [31], the additional loss in weight required for the waterleached specimens indicates that other elements, principally Si, are dissolved from the solid. As suggested by the visibly thinned edges of the water-leached specimens, this loss of Si is also likely facilitated by the physically erosive action of flowing water. The NH₄NO₃-leached specimens, in contrast, showed no visible signs of erosion.

3.2. Homogeneity of the leached specimens

Since compositional gradients are inevitably produced by leaching processes, the Ca/Si ratios reported here are strictly mean, bulk values of the solid. Nevertheless, we attempted to minimize compositional gradients by using thin, 0.8-mm thick discs. An adequate level of homogeneity for this study was confirmed [17] by SEM-EDX spot analyses traversing a cross-section of a decalcified specimen (bulk Ca/Si=0.83), which showed that nearly 75% of the volume of the solid possessed compositions within 5% of the bulk value.

In interpreting the bulk Ca/Si ratios of the decalcified WPC paste measured in this study, it should be noted that a small fraction of the total Ca is segregated into phases other than C–S–H, most notably sulfoaluminate compounds such as ettringite. This phase was detected in well-leached WPC pastes with bulk Ca/Si ratios less than 1, which suggests a relative

insolubility in 6 M NH₄NO₃ solution (as also found by Carde et al. [6]). Taking into account the low Al₂O₃ content of the WPC, the bulk Ca/Si ratio of the WPC paste is no more than 0.2 units higher than the Ca/Si ratio of C–S–H gel in the decalcified WPC paste. Therefore, it is still meaningful to compare the bulk Ca/Si ratio of the decalcified WPC with the bulk Ca/Si ratio of the decalcified WPC with the bulk Ca/Si ratio of the decalcified (and aluminate-free) C₃S paste (the latter being essentially that of C–S–H gel).

3.3. Shrinkage during decalcification in NH₄NO₃ solution

Fig. 3 shows the radial shrinkage strains of a C_3S paste disc during decalcification in NH₄NO₃ solution; expansions were not observed at any time during the measurement. Strains are plotted versus the bulk Ca/Si ratio of the specimen, using the empirical relationships between composition and weight loss noted above. Three stages are observed. After initial contact with NH₄NO₃ solution, there is an initial, gradual shrinkage of the disc. Once the bulk Ca/Si ratio decreases to 2, there is a near plateau in shrinkage, which persists until a Ca/Si ratio of ~ 1.2. With continued decalcification of C–S–H below Ca/Si ~ 1.2, there is an appreciable increase in shrinkage to radial strains approaching 0.8%. For comparative purposes, these values exceed the drying shrinkage strains produced in parallel samples exposed to a relative humidity of 47% [31].

Also shown in Fig. 3 are the mean silicate chain lengths previously measured by ²⁹Si NMR [17] on a parallel series of leached C_3S pastes. An important observation in this study is that the increase in mean silicate chain length during decalcification correlates closely with the increase in bulk shrinkage. This correlation is particularly evident at compositions near Ca/Si=1.2, when both polymerization and shrinkage increase rapidly with continued decalcification of C–S–H.

Fig. 4 shows the radial shrinkage strains of the neat and blended WPC pastes during decalcification in NH_4NO_3 solution. Although the initial strains for the neat WPC paste are slightly greater than those of the C_3S paste shown in Fig. 3,



Fig. 3. Changes in radial shrinkage (\bigcirc) and mean silicate chain length (- \bullet -) [17] during decalcification of a C₃S paste in NH₄NO₃ solution.



Fig. 4. Radial shrinkage of neat WPC paste (□) and blended WPC/30% SF paste (■) during decalcification in NH₄NO₃ solution.

the general trends are similar: an initial period of gradual shrinkage, followed by a plateau, and then by a marked increase in shrinkage below a Ca/Si ratio of ~ 1.2 .

Fig. 4 also shows the markedly different results for the blended WPC/30% SF paste. Upon exposure to NH₄NO₃ solution, the CH-free blended paste with a Ca/Si=1.35, bypassed the initial period of gradual shrinkage and instead began to immediately shrink at an appreciable rate. This result constitutes additional evidence that the shrinkage that occurs during leaching is closely associated with the decalcification of C-S-H below a Ca/Si ratio of ~ 1.2.

Since decalcified cement paste can be recalcified by exposure to a saturated CaO solution [17], it was important to determine whether the shrinkage strains induced by decalcification could be reversed. Several discs of decalcified C_3S and WPC pastes were placed in an excess volume of saturated CH solution. After several months, the specimens



Fig. 5. Radial shrinkage for neat WPC paste leached in water (\bigtriangleup) and in $\rm NH_4NO_3$ solution (\Box).

showed a gain in weight (and an associated depolymerization of the silicate chains [17]) but no appreciable expansion, indicating that the shrinkage induced by decalcification is largely irreversible.

3.4. Shrinkage during leaching in flowing water

Fig. 5 compares the shrinkage strains of neat WPC pastes leached in flowing deionized water and in NH₄NO₃ solution, plotted as a function of the bulk Ca/Si ratio of the solid. The shrinkage strains of the NH₄NO₃-leached specimen are consistently lower than those of the water-leached specimen at the same bulk Ca/Si ratio. The higher strains in the latter can be largely attributed to the physical erosion of the specimen that occurs during a flowing water experiment (Section 3.1). However, the cause of the increase in shrinkage of the waterleached specimen at Ca/Si \sim 1.2 is ambiguous: the shrinkage could be due to intrinsic structural changes in C–S–H, the enhanced erosion of the solid (caused by increased Si-solubility in water), or both. This complication is avoided when specimens are leached in NH₄NO₃ solution.

4. Discussion

4.1. Mechanism of decalcification shrinkage

Careful leaching experiments have demonstrated that thin specimens of cement paste undergo macroscopic shrinkage during decalcification. In contrast to other studies, transient [29] or net expansive [30] strains were not observed. Because erosion was minimized by leaching in concentrated NH₄NO₃ solution rather than in water, the observed contractions during decalcification can be attributed to structural changes within the paste. Figs. 3 and 4 suggest that the relevant structural changes occur in the C–S–H gel phase, since the shrinkage only becomes appreciable when the Ca/Si ratio of C–S–H is decreased below ~ 1.2. Three mechanisms are proposed below to account for this shrinkage, here called *decalcification shrinkage*.

Previous studies on parallel samples of C_SS paste [17] have shown that a Ca/Si ratio of 1.2 marks the initial point when interlayer Ca ions (i.e., Ca at interlayer sites balancing silicate anions) are removed from C–S–H gel during decalcification. The removal of interlayer Ca ions in C–S–H creates an excess negative charge, which is most readily balanced through protonation and subsequent formation of Si–OH groups. Neighboring Si–OH groups may then condense according to Eq. (1),

$$\equiv Si - OH + HO - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H_2O, \tag{1}$$

thus lengthening the mean chain length. It is proposed that at least some of these siloxane bonds (i.e., \equiv Si-O-Si \equiv) form bridges between neighboring surfaces or regions, thus pulling them closer together and shrinking the sample. By this process, the polymerization of the silicate chains in C-S-H is the direct cause of the shrinkage, which would agree very well with the coinciding onset of polymerization and shrinkage at Ca/Si ~ 1.2 (Fig. 3). This mechanism is analogous to syneresis in inorganic

gels [33,34], which is the spontaneous contraction of a saturated inorganic gel induced by condensation of labile hydroxyl groups. An important distinction between the two processes is that inorganic gels such as silica gels can polymerize freely in three dimensions to form a cross-linked structure, whereas C– S–H is restricted to polymerize in linear chains (i.e., dreierketten). This geometric restriction implies that the silicate chains on two adjacent surfaces must be sufficiently aligned before forming a siloxane bridge. As discussed below, the enhanced mobility of C–S–H at low Ca/Si ratios facilitates this alignment. A further distinction between syneresis and decalcificationinduced shrinkage of C–S–H is that the former occurs spontaneously, whereas the latter requires an aggressive (decalcifying) environment.

Accompanying the polymerization-induced decalcification shrinkage described above, the loss of interparticle cohesion in C-S-H and the subsequent propensity of C-S-H to structurally reorganize at low Ca/Si ratios is also believed to contribute to the marked shrinkage below Ca/Si ~ 1.2 . This loss of interparticle cohesion at low Ca/Si, which has been observed in triaxial mechanical tests on decalcified cement pastes [26], can be understood from computer simulations [35,36] and AFM studies [37] that show that the interlayer Ca ions are responsible for creating attractive interparticle forces. These attractive forces are formed through short-range innersphere complexes (i.e., ionic-covalent bonds between interlayer Ca and Si-O⁻) as well as through long-range ionic correlation forces (i.e., attractive van der Waals forces created by instantaneous polarizations of Ca ionic clouds). Here it is hypothesized that the loss of cohesion resulting from the removal of interlayer Ca provides C-S-H with a sufficient mobility to structurally reorganize. These reorganizations can range from slight rotations of particles (so as to permit bridging by siloxane bonds as described above) to more substantial changes such as the progressive layering of sheet-like C-S-H at low Ca/Si ratio. This latter transformation, which accounts for the marked Q^{-2} SANS scattering [20] (i.e., the hallmark of a sheet morphology), would be expected to cause a local densification of C-S-H, and thus a driving force for shrinkage. The progressive layering of C-S-H would also account for the continuous decrease in specific surface area below Ca/Si ~ 1.2 [20]. The tendency to form layered (but not necessarily crystalline) regions represents a morphological progression toward the equilibrium crystal structures of layered calcium silicate minerals such as tobermorite.

At extensive levels of decalcification when C–S–H begins to decompose (theoretically below Ca/Si=0.66), shrinkage can also result from the decomposition of the Ca–O sheets and the subsequent precipitation and polymerization of silica gel. This mechanism has been proposed during the carbonation of cement paste [38] as well as of 1.1-nm tobermorite [39]. The silica gel decomposition product is more susceptible than C– S–H to polymerization-induced shrinkage (i.e., syneresis), since, as noted above, it can freely polymerize in three dimensions rather than being restricted to two. This thus accounts for the significantly larger volumetric contractions for silica gels during syneresis, reaching up to 10-12% [40], compared to the $\sim\!1\%$ volumetric contractions illustrated here for C–S–H during decalcification.

Although the shrinkage below Ca/Si \sim 1.2 has been stressed above, an equally important finding is the comparatively low shrinkage strains observed during decalcification above Ca/Si \sim 1.2, when CH and Ca–OH groups in C–S–H are removed [17]. The rather insignificant role of CH and Ca–OH in C–S– H agrees with the polymerization-induced shrinkage mechanism discussed above, since neither species induces a change imbalance (and thus a polymerization) in C-S-H upon removal. The role of CH and Ca-OH on the propensity of C-S-H to structurally reorganize is less clear; however, it may be speculated that the intimate association of CH and C-S-H at the nanometer level could physically block major structural reorganizations in C-S-H until the CH has been completely, or at least substantially, removed. This requirement is consistent with the QXRD data on a series of decalcified C₃S pastes, which show that the last traces of CH are removed at a bulk Ca/Si ratio of ~ 1.4 [31].

4.2. Cracking due to differential decalcification shrinkage

Whether caused by leaching, carbonation (see Section 4.4), sulfate attack, or other chemical processes, decalcification proceeds via the propagation of a reactive front that moves inward from the sample surface. Since this process is governed by diffusion, decalcification inevitably produces a gradient in Ca/Si ratio such that the driving force for decalcification shrinkage is greatest at the exposed surface. Decalcification-induced shrinkage would thus be expected to generate differential stresses, placing the surface in tension. If the tensile stress is sufficient to induce fracture, shallow cracks (i.e., crazing) may form at the specimen surface, as is commonly observed during the drying of gels [41].

Faucon et al. [4] leached 15-mm thick portland cement paste specimens by an electrochemical method and subsequently observed relatively large and evenly spaced cracks, aligned perpendicular to the surface. Microanalysis showed that the cracks originated in the zone with the steepest gradient in Ca/Si ratio. The cracks were attributed [4] to the precipitation of silica gel or to a hypothetical structural transformation of C-S-H associated with the decrease in Ca/Si ratio. Given the results of the present study, is likely that these cracks can be more precisely attributed to the differential stress induced by high decalcification-induced shrinkage in the severely decalcified surface region. It should be noted that no appreciable surface cracking was observed in the NH₄NO₃-leached samples of the present study. This is likely due to the thinner specimens used (0.8 mm compared to 15 mm), which resulted in considerably smaller gradients in Ca/Si ratio [31] and thus smaller differentials in stress.

4.3. Vulnerability of blended cement pastes with low bulk Ca/Si ratios

Unlike the neat C_3S or WPC pastes, which showed an initial stage of gradual shrinkage during decalcification, the

blended WPC/30% SF paste exhibited rapid decalcificationinduced shrinkage upon initial leaching (Fig. 4). The different behavior of the blended paste can be attributed to its low CH and Ca–OH content, as indicated by its initial (unleached) Ca/Si ratio of 1.35 [17]. At this composition, the primary species initially leached from the blended paste is the interlayer Ca ions in the C–S–H gel. As discussed in Section 4.1, removal of this species causes significant shrinkage of the C–S–H.

These results demonstrate, for the first time, the intrinsic chemical vulnerability of blended cement pastes to decalcification shrinkage. However, caution should be exercised in extrapolating these results to the general long-term field performance of blended cement based materials, because the rate of decalcification shrinkage in a given environment will also be closely related to the permeability of the paste. While inadequately-cured or poorly formulated blended cement paste would indeed be particularly prone to shrinkage, the general tendency for concrete made with blended cement to have a low permeability would counteract the tendency to shrinkage more for a given amount of decalcification.

4.4. Relation between decalcification shrinkage and carbonation shrinkage

Decalcification and subsequent polymerization of C-S-H can occur by processes other than leaching: carbonation is perhaps the most well-documented example [8,39,42–44]. The similarities in these structural changes in C-S-H at the nanometer scale immediately suggest a possible correlation between carbonation shrinkage and the decalcification shrinkage described in this study. After reviewing the evidence in the literature (presented below) it is proposed that carbonation shrinkage, when induced by the carbonation of C-S-H, is simply a manifestation of the general phenomenon of decalcification shrinkage.

Carbon dioxide dissolves in the pore solution of cement paste, producing CO_3^{2-} ions that react with Ca^{2+} ions, supplied by CH and C-S-H, to form CaCO₃. Although this process has long been known to cause carbonation shrinkage, particularly at intermediate relative humidities [45,46], the mechanism is still somewhat unsettled. In an early interpretation, Powers [47] hypothesized that, under partially saturated conditions, shrinkage was due to the temporary increase in compressibility of cement paste resulting from the dissolution of CH from regions under compressive stress (created by capillary tension in the liquid); the decalcification of C-S-H was not believed significant. While Powers's interpretation may account for the carbonation shrinkage of pure CH compacts [38,48], or for the individual contribution of CH to the carbonation shrinkage of cement paste, his hypothesis cannot account for the greater carbonation shrinkage of cement paste compared to CH compacts [38], or for the greater carbonation shrinkage of bottle hydrated cement with decreasing CH content [38]. The evidence in the literature clearly suggests that the carbonation of C-S-H substantially contributes to the carbonation shrinkage of cement paste.

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More recent studies show that carbonation of C-S-H and CH occurs simultaneously [7,8,42], and, in fact, if cement paste is exposed to high concentrations of CO₂, C-S-H will eventually provide more Ca than CH due to the formation of an impermeable layer of $CaCO_3$ on the latter [7,8]. Groves et al. [7] have speculated that decalcification of C-S-H, particularly of the higher density (inner product) C-S-H, is largely responsible for carbonation shrinkage. Later ²⁹Si NMR work [8] showed that the mean silicate chain length in C-S-Hprogressively increases with the extent of carbonation and (accompanying) decalcification. For Ca/Si ratios of C-S-H gel in a C₃S paste of 1.7 (control), 1.3 (carbonated 1 h in pure CO_2 at 72.6% RH), and $1.0-1.25^2$ (carbonated 2 months in air), the mean silicate chain lengths were 3.1, 3.6, and 4.5, respectively. None of these samples contained silica gel. These data follow the general trend of increasing mean chain length with decreasing Ca/Si ratio [16,17,49-51]. Moreover, since the values of Ca/Si ratio and mean chain length agree reasonably well with the curve in Fig. 3 obtained from leached C₃S paste [17], this constitutes strong evidence that carbonation and leaching affect the silicate structure of C-S-H in a similar way. According to the mechanisms proposed in Section 4.1, carbonation would thus be expected to induce a polymerization-induced shrinkage. In this way, carbonation shrinkage can be interpreted as simply a special case of the more general phenomenon of decalcification shrinkage.

Although the structural changes from carbonation and leaching on the silicate chains of C-S-H are similar, it is important to note that the morphological changes at a larger scale are distinctly different. In the leaching of a cement paste, there is transition in the low-density outer product C-S-H from a particulate (as observed by SANS [20]) or fibrullar morphology (as observed by TEM [23]) at high Ca/Si ratio to a clearly sheet-like morphology at low Ca/Si ratio (as observed by both SANS [20] and TEM [22]). In contrast, during the carbonation of cement paste, the fibrullar low-density morphology, as well as the fine-grained high-density morphology, of C-S-H are largely preserved³ [7,8,52]; sheets do not generally form. The major morphological change during carbonation is the significant deposition of CaCO₃ crystals, which are intimately mixed with, and appear to completely embed, the low-density C-S-H [7]. These observations have several implications for the mechanism of carbonation shrinkage of C-S-H: (1) The contribution of the low-density C-S-H to carbonation shrinkage appears to be small, either via polymerization-induced shrinkage or via local densification through structural reorganization. Both of these mechanisms appear to be hindered due to the physical confinement of the CaCO3 crystals surrounding low-density C-S-H. (2) The contribution of high-density C-S-H to carbonation shrinkage appears to be significant, as previously suggested by Groves et al. [7]. The extensive decalcification of high-density C-S-H [8] and its lack of major structural rearrangement after carbonation suggests that the principle mechanism for carbonation shrinkage is likely a polymerization-induced decalcification shrinkage of C-S-H.

The above interpretation of carbonation shrinkage is similar in some respects to a hypothesis offered by Swenson and Sereda [38], who suggested that carbonation shrinkage was associated with the dehydration and polymerization of the hydrous silica product formed from the decomposition of C– S–H. The formation of hydrous silica, however, need not occur during carbonation. In fact, when conditions for carbonation are relatively mild, such as when carbonating in air, carbonation induces a gradual decalcification of C–S–H (analogous to leaching in NH₄NO₃ solution) without forming hydrous silica until decalcification becomes extensive [8].

It should be noted that polymerization shrinkage cannot account for all the observed phenomena related to carbonation shrinkage, in particular the observation that pure CH compacts shrink during carbonation [38]. Other mechanisms involving the role of CH thus must act concurrently; that proposed by Powers [47], or variations thereof [38], appear most plausible. Nevertheless, the contribution of polymerization shrinkage to carbonation shrinkage would be important, and perhaps dominant, in the carbonation of blended cements, in which the CH content is low, or in extremely aggressive carbonating environments, in which CH has been protected by a coating of $CaCO_3$ [8].

5. Conclusions

Thin cement paste specimens subjected to decalcification by leaching in concentrated solutions of NH_4NO_3 exhibited significant and irreversible shrinkage strains. In contrast to previous studies, net or transient expansive strains were not observed. The marked increase in shrinkage observed when the Ca/Si ratio of C–S–H gel decreased below ~ 1.2 is attributed to structural changes in C–S–H. Three mechanisms for decalcification shrinkage (all of which may occur concurrently) are proposed:

- A polymerization-induced shrinkage can result if a siloxane bond, induced by the removal of interlayer Ca in C−S−H, bridges two adjacent regions or surfaces of C−S−H. This mechanism, analogous to syneresis of inorganic gels, is supported by the simultaneous onset of silicate polymerization and shrinkage at a Ca/Si ratio of ~1.2. Moreover, the enhanced mobility of C−S−H at these low Ca/Si ratios (see mechanism 2, below) facilitates the slight rotations necessary to align the silicate chains of C−S−H on adjacent surfaces before forming a siloxane bridge.
- The loss of cohesion and subsequent increased mobility of C-S-H resulting from the removal of interlayer Ca can also induce shrinkage by encouraging the structural reorganization of C-S-H into dense morphologies, such as a progressively layered sheet-like morphology.

 $^{^2}$ The higher value in this range is measured indirectly from TGA analysis of CH, CaCO₃, and residual C₃S; the lower value was measured from TEM microanalysis of inner product C-S-H.

³ It is possible, however, to form macroporosity in low-density C-S-H during the carbonation of C_3S pastes in air [8]. The same phenomenon has not been observed during the carbonation of OPC pastes [52].

3. At extensive levels of decalcification (i.e., below Ca/Si \sim 0.66), decomposition of the Ca–O sheets of C–S–H generates significant shrinkage due to the precipitation and subsequent polymerization of silica gel.

Since decalcification shrinkage is closely tied to the removal of the interlayer Ca ions (rather than the dissolution of CH or the removal of Ca–OH sites in C–S–H), cement pastes prepared with low bulk Ca/Si ratios are particularly vulnerable to decalcification shrinkage. This conclusion was illustrated by the immediate and significant shrinkage observed during the decalcification of a blended WPC/30% SF paste with a bulk Ca/Si ratio of 1.35.

Based on evidence published elsewhere [4], it is concluded that steep gradients in Ca/Si ratio at a decalcified surface can induce vertical cracks due to differential polymerization shrinkage. This is analogous to the mechanism of cracking produced by drying shrinkage.

Since carbonation of cement paste is known to induce both decalcification and polymerization of C–S–H, without a significant change in morphology, it is argued that carbonation shrinkage, especially when initiated by the carbonation of C–S–H, is largely due to the polymerization-induced decalcification shrinkage (i.e., mechanism 1, above) of high-density C–S–H. The contribution of decalcification shrinkage to carbonation-induced strains would be most important, and perhaps dominant, in systems involving blended cement pastes prepared with low bulk Ca/Si ratios, and in aggressive carbonating environments where reaction with CH is arrested due to the formation of a protective CaCO₃ layer.

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