

A Coupled Nanoindentation/SEM-EDS Study on Low Water/Cement Ratio Portland Cement Paste: Evidence for C-S-H/Ca(OH)₂ Nanocomposites

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A low water/cement ratio ($w/c = 0.20$) hydrated Portland cement paste was analyzed by grid-indentation coupled with *ex situ* scanning electron microscope-energy-dispersive X-ray spectra (SEM-EDS) analysis at each indentation point. Because finite element and Monte-Carlo simulations showed that the microvolumes probed by each method are of comparable size (approximately 2 μm), the mechanical information provided by nanoindentation was directly comparable to the chemical information provided by SEM-EDS. This coupled approach provided the opportunity to determine whether the local indentation response was a result of a single- or a multiphase response—the latter being shown predominant in the highly concentrated $w/c = 0.20$ hydrated cement paste. Results indicate that, in the selected microvolumes where C-S-H and nanoscale Ca(OH)₂ (CH) are present, increasing fractions of CH increase the local indentation modulus (and hardness), yielding values above those reported for high-density (HD) C-S-H. Micromechanical analyses show that C-S-H and CH are associated, not merely as a simple biphasic mixture, but as an intimate nanocomposite where nanoscale CH reinforces C-S-H by partially filling the latter's gel pores. The paper discusses the mechanism of forming the C-S-H/CH nanocomposite, as well as the impact of nanocomposites on various macroscopic properties of concrete (e.g., shrinkage, expansion). On a general level, this study illustrates how a coupled nanoindentation/X-ray microanalysis/micromechanics approach can provide otherwise inaccessible information on the nanomechanical properties of highly heterogeneous composites with intermixing at length scales smaller than the stress field in a nanoindentation experiment.

I. Introduction

THE principal binding phase of concrete is a poorly crystalline calcium silicate hydrate gel, denoted as C-S-H.¹ At a scale of tens of nanometers, C-S-H possesses an internal pore structure comprised of pores approximately several nanometers across.² This fine porous structure, akin to that of a colloidal gel, creates a high interfacial surface area between solid and liquid phases, which subsequently gives rise to the characteristic poro-viscoelastic response of concrete to mechanical loading and drying,^{3–5} as well as to the generation of crystallization pressure from the growth of ice or salts in small pores.^{6–8} These mechanisms are critical in determining the long-term performance of concrete structures.

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In a classic study, Powers and Brownyard⁹ showed that the porosity of C-S-H gel was nearly constant over a wide range of cement compositions and water/cement (w/c) mass ratios. Numerous models^{10–13} of C-S-H have attempted to explain this intrinsic and intriguing nature of the C-S-H pore structure. Jennings has proposed¹³ and recently extended¹⁴ a comprehensive model, which envisions C-S-H gel as a particulate colloid comprised of 4–5 nm elementary globules that pack into fractal structures with two preferential morphologies. The low-density (LD) C-S-H structure is believed to have an average packing density of 0.64, and the high-density (HD) C-S-H a value of 0.75; these values suggest packing configurations that approach the theoretical limits for the maximally random jammed state¹⁵ and the hexagonal close-packed arrangement of spheres,¹⁶ respectively. Through an independent experimental route, grid indentation studies¹⁷ on cement paste have yielded nearly identical values for the packing densities of LD and HD C-S-H. From a physical perspective, LD C-S-H forms preferentially in the capillary space (i.e., thus forming outer-product (OP) hydrates), where crystal growth can occur in a relatively unimpeded manner. In contrast, HD C-S-H forms in more confined regions located within the original boundaries of the cement (i.e., thus forming inner product (IP) hydrates) or within confined capillary spaces.

Recent nanoindentation studies by Vandamme and colleagues^{18,19} on low w/c ratio pastes have illustrated an additional complexity to the above model of C-S-H. Upon decreasing the w/c ratio of a series of cement pastes from 0.40 to 0.15, it was shown that, in addition to the increase in HD C-S-H at the expense of LD C-S-H (a trend originally proposed by Tennis and Jennings²⁰), there is the formation of a mechanical phase with elevated indentation modulus, M , and indentation hardness, H . The (M , H) values for this so-called “ultra-high density” (UHD) phase were reported to be (47.2, 1.6 GPa),¹⁸ compared with (29.1 \pm 4.0, 0.83 \pm 0.18 GPa)¹⁶ and (18.2 \pm 4.2, 0.45 \pm 0.14 GPa)¹⁶ for HD and LD C-S-H, respectively. Under the assumption that the UHD phase is comprised of the same elementary C-S-H particle as in LD and HD C-S-H, it was proposed that the improved mechanical properties of this UHD phase were achieved by a random packing of two particle classes, yielding a packing density of $\eta = \eta_1 + (1 - \eta_1)\eta_2 = 0.87$ (assuming $\eta_1 = \eta_2 = 0.64$).

The aim of this study was to determine the chemical nature of the UHD phase identified by grid indentation. This method has been reviewed elsewhere,^{21,22} and so only points pertinent to the current study are discussed below. Grid indentation involves the application of a large array of nanoindentation experiments, each with a characteristic indentation depth, h , which elicits a mechanical response from a subsurface microvolume (Fig. 1). From the simultaneous measurement of indentation load and displacement, M and H can be computed²³ at each point. When applying this procedure over a large array of indents, a deconvolution method^{17,21} can be applied to the resulting cumulative frequency M and H histograms to identify the mean

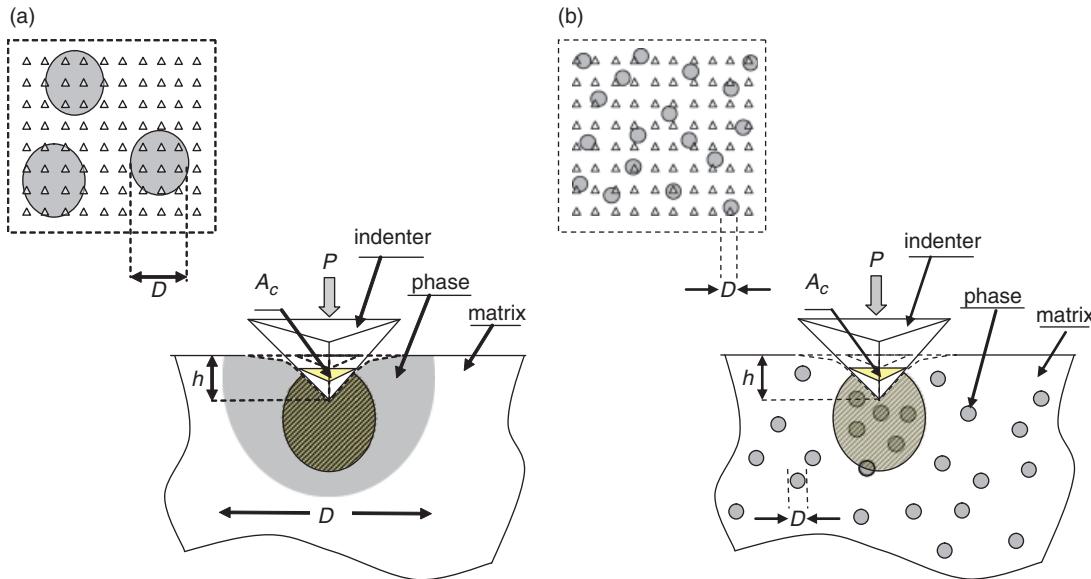


Fig. 1. Grid indentation on a heterogeneous system where the probed microvolume (cross-hatched regions below the indenter) is either (a) smaller or (b) larger than the characteristic length scale, D , of the phase of interest. Symbols are defined in the text.

M , H values, as well as the respective volume fractions for each “mechanical” phase in the system. In order to directly correlate the mechanical phase with a unique chemical phase, the size of the probed microvolume must be sufficiently smaller than the characteristic size, D , of the chemical phase of interest (Fig. 1(a)): calculations²¹ indicate that h_{\max} must be less than approximately $D/10$ for this condition to hold. If, on the other hand, h_{\max} is greater than approximately $D/10$, then a composite mechanical response will inevitably be observed (Fig. 1(b)). Because of the roughness of a polished cement paste surface,²⁴ indentation depths in the hydrated cement paste are generally limited to values of $h_{\max} \approx 200$ nm, which correspond to probed microvolumes with linear depths of approximately 2 μm . Because scanning electron microscope-energy-dispersive X-ray spectra (SEM-EDS)²⁵ and TEM²⁶ studies often show intermixing of hydrated mineral phases in a hydrated cement paste on a submicrometer scale, the mechanical phases detected in the probability density plots of M and H are potentially a composite response of multiple phases. In favor of this conjecture are recent results from small-angle neutron scattering measurements that provide evidence for nanoscale $\text{Ca}(\text{OH})_2(\text{CH})$ in hydrated cement paste.²⁷

The specific goals of the experimental study were to develop a methodology that could (1) determine whether a local composite mechanical response was present, and (2) if so, quantify the influence of the individual chemical phases on this composite mechanical response. *Ex situ* SEM-EDS spot analyses were therefore performed at each nanoindentation point in the grid of points on the low $w/c = 0.20$ cement paste. Because the microvolumes probed in each technique are similar (Section III(1)), the chemical information from SEM-EDS was directly related to the mechanical information obtained by nanoindentation. While this general approach has been followed in another study,²⁸ the sizes of the microvolumes probed by SEM-EDS and nanoindentation in the study were of a significantly different magnitude, and, as a result, the results could only be compared in a qualitative fashion. The results in the current study, coupled with micromechanical analysis, demonstrate that the UHD phase is, in fact, an intimate nanocomposite of HD C-S-H and nanoscale CH that resides in the gel pores of C-S-H. On a general level, the study illustrates the utility of coupling SEM-EDS, nanoindentation, and micromechanics to study mechanical behavior in highly heterogeneous materials at the nanometer scale.

II. Experimental Procedure

(1) Materials

The cement paste was prepared with a Type 1 Portland cement and with deionized water at a w/c ratio of 0.20. Rietveld XRD analysis showed the cement to be rich in calcium silicates (alite, 71.1%; belite, 15.0%), moderately rich in the ferrite phase (7.0%), and low in the aluminate phase (1.2%). XRF showed the following oxide composition: CaO , 67.2%; SiO_2 , 22.1%; Al_2O_3 , 3.1%; Fe_2O_3 , 2.5%; SO_3 , 2.1%; loss on ignition, 1.7%. The blaine-specific surface area of the cement was measured as 2940 cm^2/g .

The cement paste sample was cast and cured sealed at 20°C in plastic cylinders of 10 mm internal diameter and several centimeters’ length. The predominance of the calcium silicate phases (together representing over 85% of the cement), combined with the low reactivity of the ferrite phase, caused the hydrated cement paste to be comprised largely of C-S-H and CH. The composition of the alite and belite phases were measured by SEM-EDS (Section II(3)) as $\text{Ca}_{2.93}\text{Si}_{0.96}\text{Al}_{0.06}\text{Fe}_{0.01}\text{Mg}_{0.05}\text{S}_{0.01}\text{O}_5$ ($\text{Ca}/\text{Si} = 3.07$) and $\text{Ca}_{1.96}\text{Si}_{0.86}\text{Al}_{0.08}\text{Fe}_{0.02}\text{Mg}_{0.02}\text{S}_{0.05}\text{O}_5$ ($\text{Ca}/\text{Si} = 2.28$), respectively. After approximately 1 year of sealed hydration, a polished cross section of the sample was prepared as described below.

(2) Nanoindentation

A nanoindentation test consists of maintaining contact between a solid and a rigid indenter (typically diamond), while simultaneously measuring changes in the applied load, P , and the penetration depth, h .²⁹ The properties extracted from a $P-h$ curve are the indentation modulus, M , and indentation hardness, H .²³

$$M \stackrel{\text{def}}{=} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_C}} \quad (1)$$

$$H \stackrel{\text{def}}{=} \frac{P_{\max}}{A_C} \quad (2)$$

where S is the unloading indentation stiffness and A_C is the projected contact area (Fig. 1). The latter is estimated from the maximum penetration depth, h_{\max} , using the Oliver and Pharr method.²³ For a homogeneous isotropic linear elastic material, M reduces to the plane-stress elastic modulus $M = E/(1-\nu)^2$

where E is the Young modulus and ν is the Poisson ratio of the indented material. Similarly, the hardness H can be related to the indenter cone angle and to the strength properties of a cohesive-frictional material by means of limit analysis.^{30,31} Recently, the application of the technique has been extended to heterogeneous materials such as cementitious materials, bones, and shales.¹⁷

In this work, nanoindentation was performed over a grid of 20×12 points, evenly spaced by $20 \mu\text{m}$. During each test, the load was linearly increased up to a maximum load of 4 mN in 10 s , kept constant for 5 s , and linearly decreased in 10 s . The mean measured maximum indentation depth h_{\max} was approximately 310 nm . The Berkovich indenter with a three-sided pyramidal shape and a semivertical angle of 65.3° was chosen to minimize the pile-up phenomena. A quartz standard of known mechanical properties was used to calibrate the contact area function of the indenter.²³

To prepare the flat surface required for nanoindentation, the sample was fixed on a steel support, coarsely ground with Si-C paper, and then polished on a lapping wheel impregnated with a $1 \mu\text{m}$ diamond paste.²⁴ The sample was subsequently cleaned with n -decane in an ultrasonic bath for 5 min . Because the sample was not supported with epoxy as in conventional methods to prepare polished samples for SEM analyses, some surface defects were observed (e.g., cracks, pop-outs). These points were excluded from the coupled nanoindentation/SEM-EDS analysis. No evidence for pore filling by surface detritus³² was observed.

(3) SEM-EDS and BSE/SE Imaging

EDS were collected on a JEOL 840 SEM (Tokyo, Japan) on the same specimen tested by the grid indentation method. Spot analyses were performed just adjacent to the indentation imprint to avoid errors introduced by the local surface roughness. Analyses were conducted with an accelerating voltage of 15 kV , a beam current of 1 nA (measured using a Faraday cup), and a 15 mm working distance. Calibrations were made on a range of standard specimens, including Ca_2SiO_4 , $\text{Ca}_3\text{Al}_2\text{O}_6$, Fe_2O_3 , MgO , CaSO_4 , $(\text{K},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$, InP, Mn, and Ti. Ca/Si ratios were calibrated with Ca_2SiO_4 . Matrix corrections were made using the PhiRhoZ method.

Each indentation zone was imaged in the back-scattered electron (BSE) mode, as well as in the secondary electron (SE) mode. The former facilitated visualization of the unreacted cement grains (which yield a high atomic number contrast), while the latter facilitated visualization of the small indent impressions ($\approx 1 \mu\text{m}$) left by the Berkovich indenter. To aid in isolating microvolumes elicited solely from hydrated phases, each imprint was assigned to one or four “phases”: (1) surface defect (e.g., void, crack, pit), (2) residual clinker grain, (3) IP hydrates or hydrates formed within several micrometers of cement grains grain, and (4) OP hydrates.

III. Results

(1) Comparison of Microvolumes in Nanoindentation and SEM-EDS Experiments

To directly compare the results from nanoindentation and SEM-EDS, it was necessary to verify that the microvolumes probed by each method were of a comparable size. Figure 2 shows a cross section of an indented region, where the results of Monte Carlo (MC) and finite element (FE) simulations are superimposed. The MC simulation, performed in CASINO³³ and using as input parameters the SEM operating conditions noted in Section II(3), showed electron trajectories reaching a normalized depth of $z/h_{\max} \approx 6-7$ or a real depth of $\approx 2.0 \mu\text{m}$ ($h_{\max} = 310 \text{ nm}$). The maximum depth at which characteristic X-rays are generated in SEM-EDS will be slightly smaller than this value, due to the fact that the most deeply penetrating electrons will have insufficient energy to promote inner shell electron ionizations.³⁴ The results of FE simulations, performed in ABAQUS,³⁵ are represented in Fig. 2 as isocontours of the nor-

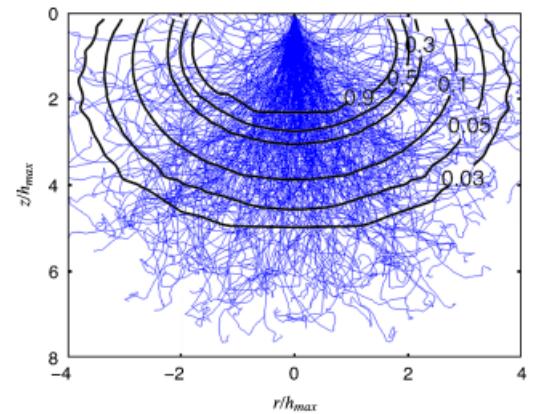


Fig. 2. Comparison of microvolumes probed by nanoindentation and by SEM-EDS. The volume probed by nanoindentation is estimated from the isocontours (black lines) of the normalized local strain energy density calculated by finite element analysis. The volume probed by SEM-EDS is approximated by the zone demarcated by the electron trajectories (blue lines) in the specimen, calculated here by Monte Carlo simulation. In both cases, the interaction volume has a linear dimension of $\approx 1.5-2.0 \mu\text{m}$.

malized local strain energy density field. The calculation assumed axisymmetrical conditions. The Berkovich tip was approximated by a cone of half-angle 70.3° . The strength properties of the indented material (assumed elastoplastic, with a yield strength-to-modulus ratio of $10^{-1.5}$) were chosen such that the computed contact depth-to-indentation depth ratio, h_c/h_{\max} , was close to that measured experimentally on cement pastes ($h_c/h_{\max} \approx 0.88$). Results show that the microvolume probed by nanoindentation has a characteristic size of $z/h_{\max} \approx 5$ or approximately $1.5 \mu\text{m}$. These results thus illustrate that the microvolume probed by nanoindentation was comparable to that probed by SEM-EDS.

(2) Nanoindentation Coupled with BSE Imaging

After performing a grid indentation analysis, the indented sample was analyzed in the SEM. Figure 3 shows a SEM-BSE image of a typical zone of the hydrated cement paste subjected to the grid indentation test; 16 indents are shown, each marked by an triangle, enlarged in size for visibility. As described in Section II(3), each indent was located and visually classified in the SEM as either (1) a surface defect, (2) a residual clinker grain, (3) an IP or an near-grain hydrate, and (4) OP hydrate. Surface

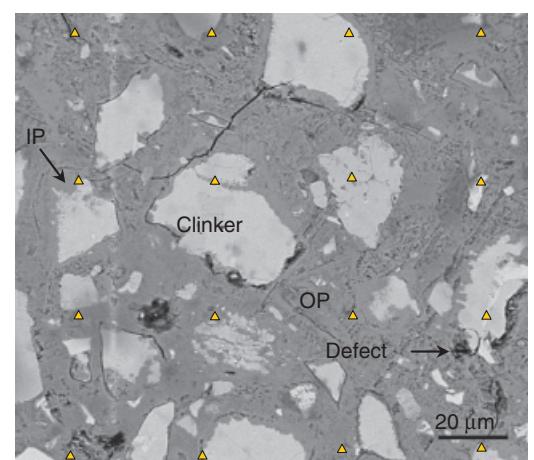


Fig. 3. BSE-SEM image of a typical zone of the $w/c = 0.20$ hydrated cement paste specimen, showing a grid of 16 indent impressions (triangles, enlarged in size for visibility). An example of the clinker, inner product (IP), outer product (OP), and defect regions is also shown.

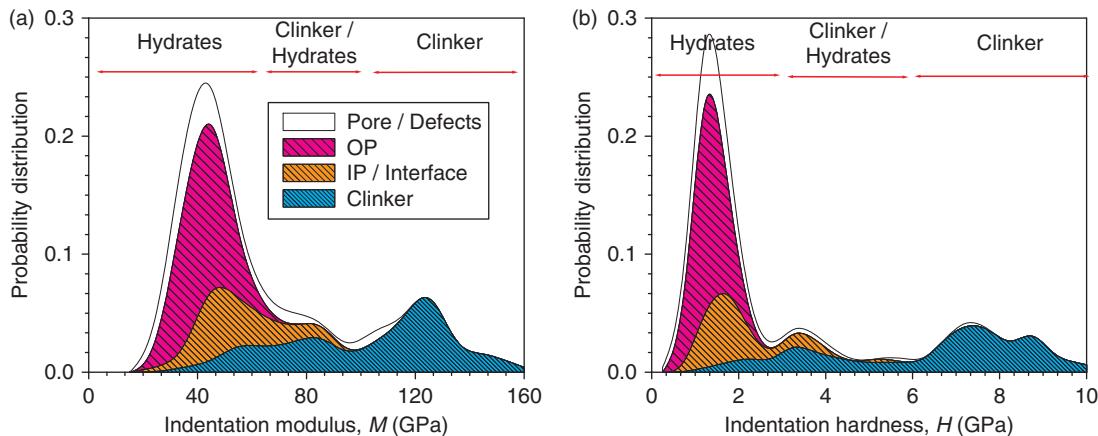


Fig. 4. Probability density distributions of (a) indentation modulus (M) and (b) indentation hardness (H) for the $w/c = 0.20$ hydrated cement paste. The distributions are decomposed by phase: clinker, inner product (IP), outer product (OP), and pore. The cross-hatch density increases with the stiffness of the phase.

defects, generated during the polishing process to prepare the flat specimens, were present as cracks and pop-outs of hydrated paste regions adjacent to clinker grains (see Fig. 3). Of the 240 indents analyzed, 15% represented surface defects, 32% residual (unhydrated) clinker grains, 25% OP hydrates, and 18% IP/near-grain hydrates. The degree of hydration for the hydrated paste, calculated as $\alpha = 1 - f_{\text{cem,resid}}(\rho_c w/c + 1) = 0.48$ (assuming $\rho_c = 3.15$, $f_{\text{cem,resid}} = 0.32$), is in good agreement with Powers' model of hydrated cement paste.⁹

Because each point in the nanoindentation grid was assigned a phase as defined above, it was possible to decompose the total frequency distribution curves for indentation modulus (M) and indentation hardness (H) into their respective phases (Fig. 4). Both the M and the H distribution curves show three major peak families. (1) The peak at low M and H , centered around 40–45 and 1.2–1.3 GPa, respectively, and spanning 30–55 and 0.7–2.0 GPa, respectively, represent hydrated phases—comprising both the IP and the OP variety. Note that these values exceed the reported nanoindentation values of LD and HD C–S–H,^{16–18} and yet they are close to the characteristic elasticity values of portlandite, $M = 38.0 \pm 5$ GPa, as obtained from nanoindentation on large CH crystals³⁶ and from molecular dynamic simulation on CH ($M = 39$ GPa).³⁶ From purely mechanical evidence, the hydrates formed in this $w/c = 0.20$ cement paste appear to resemble a chemical phase intermediate between portlandite and HD C–S–H. There is little to no evidence for LD C–S–H or for “spurious” peaks³⁷ produced artificially by averaging the mean values of a mix of hydrated phases characterized by an indentation modulus of $M \leq 65$ GPa and a hardness of $H \leq 3$ GPa.^{38,39} (2) The peaks at high M and H , centered around 120 and 7–9 GPa, respectively, are clearly associated with the residual clinker grains, as demonstrated in earlier studies.¹⁶ (3) The intermediate shoulder centered on $M = 80$ –90 GPa and $H = 3.0$ –3.5 GPa displays properties well above the particle properties of hydrated phases (i.e., $M \leq 65$ GPa and a hardness of $H \leq 3$ GPa³⁸). Thus, this peak is not representative of a hydrated phase, but is clearly identified as mixtures of clinker and hydrated phases in the probed microvolume. This peak—a result of the unusually high concentration of a residual clinker—can legitimately be considered a “spurious” peak. Thus, a combination of nanoindentation and knowledge of the intrinsic hydrate solid properties allows us to assign this mechanical “phase” as a hydrate–clinker composite phase.³⁹ This phase is not considered in subsequent analyses.

(3) Nanoindentation Coupled with SEM-EDS

The objective of coupling the nanoindentation data with the SEM-EDS results was to shed light on the chemical nature of

the UHD mechanical phase. As discussed in Section III(2), the UHD phase showed unexpectedly high M and H values, suggesting mechanical properties intermediate between those of HD C–S–H and portlandite. It was thus decided to isolate only those indents whose microvolumes comprised solely C–S–H and CH. This was done in a series of steps. (1) First, all points associated with surface defects (e.g., pop-outs near grain boundaries) and clinker grains were removed from the analysis. (2) All microvolumes whose SEM-EDS oxide totals exceeded 0.76 (i.e., the theoretical value for portlandite) were then removed, as they represent admixtures of clinker and hydrated phases. Similarly, all microvolumes whose SEM-EDS oxide totals were <0.68 (i.e., corresponding to C–S–H compositions with water contents exceeding that represented in the formula, $1.8\text{CaO} \cdot \text{SiO}_2 \cdot 4.2\text{H}_2\text{O}^{\dagger\dagger}$) were removed, as they represent admixtures of C–S–H and either high water-content hydrates such as ettringite (ETT, oxide content ≈ 0.54), capillary pores, or both. The points remaining in the analysis, representing microvolumes comprised largely (but not exclusively) of C–S–H and CH, were thus bound between $0.68 < \text{oxide total} < 0.76$; this can be visualized on the Si/Ca versus oxide total plot as the filled points between the two dashed vertical lines (Fig. 5). (3) These selected points were further analyzed to eliminate any points with small amounts of admixed ferrite clinker phase or of hydrated calcium sulfoaluminate phases (e.g., ETT, monosulfoaluminate (MON)). This was accomplished by plotting Si/Ca versus (Fe+Al)/Ca (Fig. 6(a)) and Si/Ca versus S/Ca (Fig. 6(b)) and taking only those points scattered closely around the CH/C–S–H tie lines in both graphs (shown as filled points within the dashed curves). The lack of points clearly on the MON/C–S–H or ETT/C–S–H tie lines most likely indicates that, when present, MON and ETT are closely admixed with both C–S–H and CH.

The remaining points after the above treatment yield microvolumes with differing amounts of CH and C–S–H. The volume fraction of CH in each microvolume, f_{CH} , was measured as $f_{\text{CH}} = x_{\text{CH}}\rho_{\text{paste},i}/\rho_{\text{CH}}$, where x_{CH} is the mass fraction of CH in the microvolume (measured by EDS), ρ_{CH} is the density of portlandite (i.e., 2.24 g/cm^3), and $\rho_{\text{paste},i}$ is the density of the hydrated paste. The latter was calculated in two ways (see Appendix A). In case 1, a microcomposite of C–S–H and CH was assumed, where the latter was assumed to precipitate outside the gel pores of C–S–H. In case 2, a nanocomposite of C–S–H and CH was assumed where CH precipitates within the gel pores of C–S–H. The average value and standard deviation of f_{CH} were computed from the two values for $\rho_{\text{paste},i}$ calculated at each indentation point. This calculation allowed to formulate a plot of f_{CH} versus

^{††}This composition is consistent with the generally accepted composition of water-saturated C–S–H (i.e., C–S–H with minimum oxide content), $1.8\text{CaO} \cdot \text{SiO}_2 \cdot 4.0\text{H}_2\text{O}$.¹

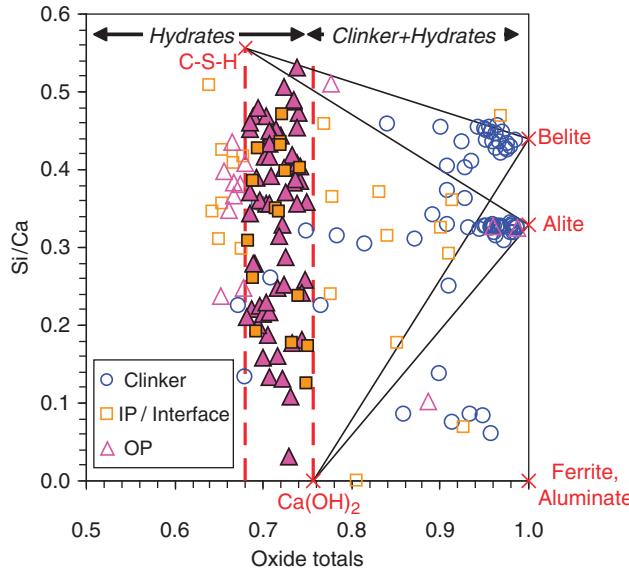


Fig. 5. Si/Ca versus total oxide content measured by SEM-EDS. Theoretical oxide totals for clinker phases, portlandite, and C-S-H are shown. Filled points represent microvolumes rich in C-S-H and CH with oxide totals between 0.68 and 0.76.

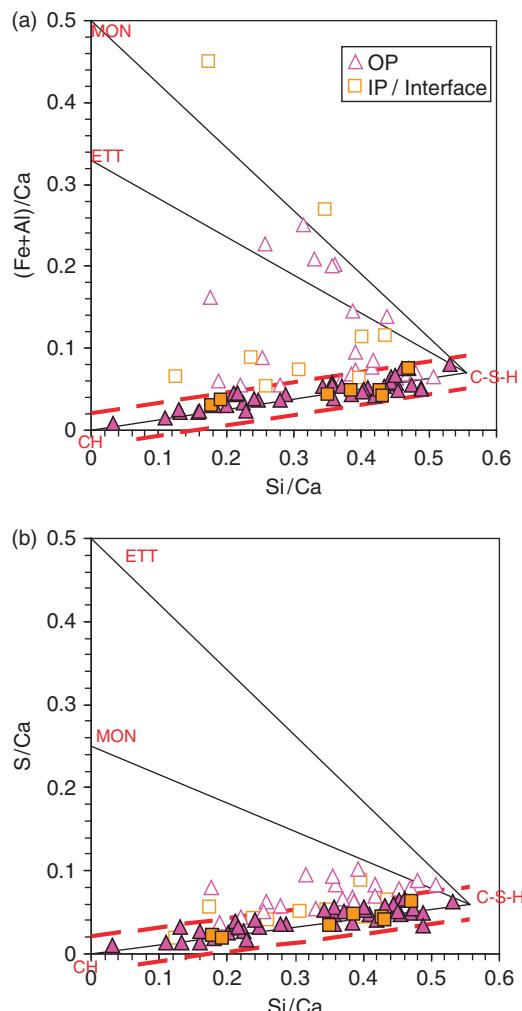


Fig. 6. Si/Ca versus (a) $(\text{Fe}+\text{Al})/\text{Ca}$ and (b) S/Ca obtained by SEM-EDS. Filled points, representing microvolumes containing varying proportions of C-S-H and CH, are those that lie within the dashed curves scattered around the C-S-H/CH tie lines in both (a) and (b).

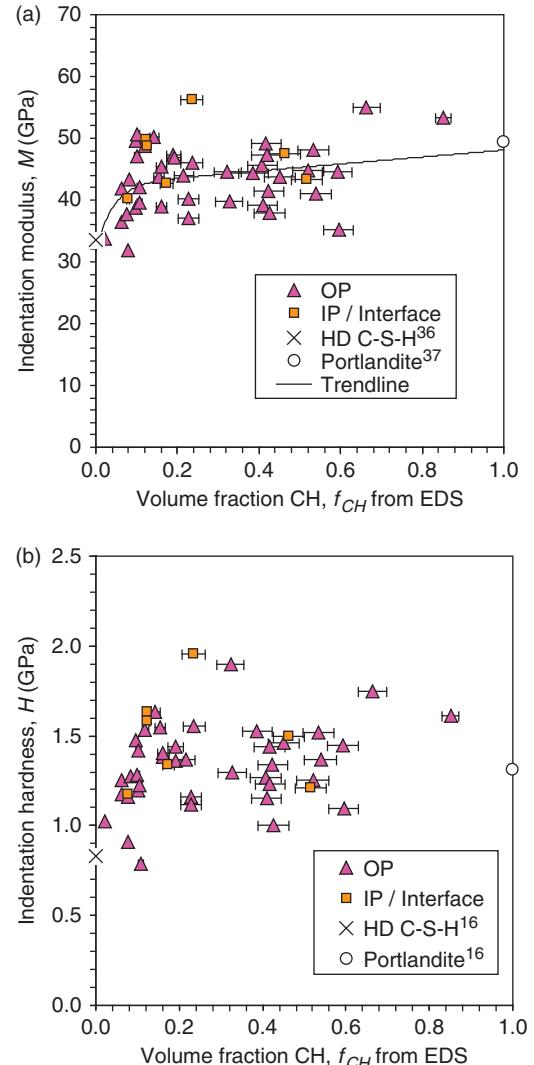


Fig. 7. (a) Indentation modulus M and (b) indentation hardness H plotted as a function of the volume fraction of CH in microvolumes containing CH and C-S-H. The arbitrary trendline in (a) follows the general trend of the M data.

indentation modulus, M , and f_{CH} versus indentation hardness, H , as shown in Figs. 7(a) and (b), respectively. Also present are the respective (M , H) values for HD C-S-H ($f_{\text{CH}} = 0$) and portlandite ($f_{\text{CH}} = 1$); M values were taken from atomistic simulations^{40,41} and H values from nanoindentation.¹⁶ Figure 7 shows two important observations. First, the range of observed values for M and H (spanning 30–55 and 0.8–2.0 GPa, respectively) corresponds to the values associated with the UHD phase. Second, as is somewhat more apparent in the indentation modulus data (Fig. 7(a)), increasing the amount of CH from pure HD C-S-H (i.e., $f_{\text{CH}} = 0$) sharply increases M , up to $f_{\text{CH}} \approx 0.15$ –0.20; at this point, subsequent increases in CH show no significant change in M , with values scattered around $M \approx 45$ GPa. This value is close to that of pure portlandite.⁴¹

IV. Discussion

(1) Micromechanical Analysis: Evidence for C-S-H/CH Nanocomposites

To understand the influence of microstructure on the mechanical response observed in Fig. 7, we computed via micromechanics the elastic response of two plausible structures for the C-S-H/CH mixture. In both cases, we assume, for the $w/c = 0.20$ cement paste, the presence of HD C-S-H (with

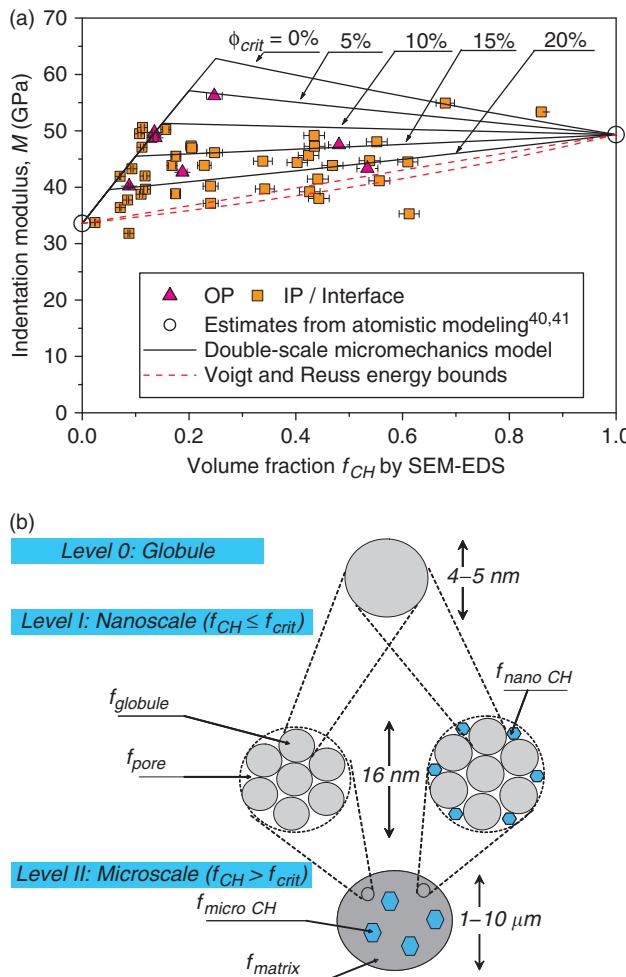


Fig. 8. (a) Computed curves for indentation modulus, M , versus the volume fraction of CH, f_{CH} , calculated for two different microstructures where a C–S–H/CH nanocomposite structure is either assumed to be absent (dashed lines) or present (solid lines) with varying amounts of residual porosity, ϕ_{crit} (b) Schematic of the double-scale micromechanics model used in the calculation.

intrinsic porosity ($\phi_0 = 0.25^{14,17}$), CH, and no capillary pores (consistent with the Powers model⁹). See Appendix B for further details on micromechanics theory.

Case 1: Microcomposite. CH precipitates outside the gel pores of C–S–H. Regardless of the spatial arrangement, the homogenized stiffness of the C–S–H/CH bicomposite must fall between the following energy bounds of Voigt and Reuss^{42,43}:

$$0 \leq f_{CH} \leq 1 : \begin{cases} \mathbf{C}_{hom}^{\text{UB}} = \langle \mathbf{c}_r \rangle_v \\ \mathbf{C}_{hom}^{\text{LB}} = \langle \mathbf{c}_r^{-1} \rangle_v^{-1} \end{cases} \quad \text{with} \quad r = \{1 : \text{CH}, 2 : \text{HDC–S–H}\} \quad (3)$$

where \mathbf{c}_r is the isotropic elastic stiffness of the r th phase and the brackets represent volume averages.

Case 2: Nanocomposite. CH precipitates within the gel pores of C–S–H. At a low f_{CH} , CH nanocrystals fill the C–S–H gel porosity, ϕ_0 , thus forming an intimate C–S–H/CH nanocomposite (see Fig. 8(b), “Level I”). This filling, assumed to occur to varying extents, increases up to a critical CH volume fraction, f_{CHcrit} (which ranges from 0 to ϕ_0). In the general case, where there is partial filling of the gel porosity, there will be a residual porosity, ϕ_{crit} , defined as $\phi_{crit} = \phi_0 - f_{CHcrit}$. For $f_{CH} < f_{CHcrit}$, the homogenized stiffness is estimated by the mean average theory as follows:

$$0 \leq f_{CH} \leq f_{CHcrit} : \quad \mathbf{C}_{hom}^I = \left\langle \mathbf{c}_r : \mathbf{A}_r^{\text{SC}} \right\rangle_v \quad (4)$$

$r = \{1 : \text{nano-CH}; 2 : \text{globule}; 3 : \text{pore}\}$

where \mathbf{A}_r^{SC} is the Self-Consistent localization tensor of spherical inclusions.^{44,45}

The CH occurring above f_{CHcrit} is assumed to be present as microscale CH crystals located outside the gel pores. Thus, for $f_{CH} > f_{CHcrit}$, we assume a mixture of the C–S–H/CH nanocomposite and of microscale CH crystals. The homogenized stiffness of such a double-scale microstructure, represented in the “Level II” structure in Fig. 8(b), is expressed as:

$$f_{CH} > f_{CHcrit} : \quad \mathbf{C}_{hom}^{II} = \left\langle \mathbf{c}_r : \mathbf{A}_r^{\text{MT}} \right\rangle_v \quad (5)$$

$r = \{1 : \text{matrix with } \mathbf{C}_{hom}^I \text{ at } \phi = \phi_{crit}; 2 : \text{micro CH}\}$

where \mathbf{A}_r^{MT} is the Mori–Tanaka localization tensor of spherical inclusions.⁴⁶ The volume fractions of the phases vary linearly with f_{CH} :

$$0 \leq f_{CH} \leq f_{CHcrit} : \quad \begin{cases} f_{pore} = \phi_0 + (\phi_{crit} - \phi_0) \frac{f_{CH}}{f_{CHcrit}} \\ f_{globule} = 1 - f_{pore} - f_{nano\ CH} = 1 - \phi_0 \\ f_{nano\ CH} = f_{CH} \end{cases} \quad (6)$$

$$f_{CH} > f_{CHcrit} : \quad \begin{cases} f_{micro\ CH} = (f_{CH} - f_{CHcrit}) / (1 - f_{CHcrit}) \\ f_{matrix} = 1 - f_{micro\ CH} \end{cases} \quad (7)$$

where f_{matrix} is the volume fraction of the matrix (“Level 1”) with homogenized stiffness expressed in Eq. (5) at $\phi = \phi_{crit}$. As in the previous work,^{16,47} the Self-Consistent scheme and the Mori–Tanaka scheme are adopted for the granular-like structure of C–S–H and for the matrix-inclusion microstructure of the cement paste, respectively. Note that the assumption of spherical localization tensor is justified by the fact that the shape effect of randomly oriented C–S–H inclusions is a secondary effect for porosity $< 30\%$.^{47,48}

Table I. Cited and Model Values for the Elastic Constants of the C–S–H Solid (Globule) and of CH

Property	Model values	Cited values
E_{Globule}	63.5	Simulation: 63.5 ⁴⁰ (EM); 35.6–56.0 ⁴⁰ (EM); 51.90 ⁴⁹ (DFT, 14 Å Tobermorite), 53.55 ⁴⁹ (DFT, Jennite) Experiment: 58–61 ⁵⁰ (N, with $v = 0.3$); 60.0 ² (N)
v_{Globule}	0.26	Simulation: 0.25–0.26 ⁴⁰ (EM) Experiment: 0.27–0.31 ⁵⁰ (N)
E_{CH}	46.0	Simulation: 35.7, 46.0, 56.2 ^{41,\dagger} (DFT); 41.5, 54.6, 67.8 ⁵¹ (EM); 35.4 ⁴⁰ (EM) Experiment: 38.9, 44.9, 50.9 ^{51,\dagger} , 39.7, 40.3, 44.2 ⁵² (B); 35.2 ⁵³ (C); 48 ⁵⁴ (C); 36.0 ⁵⁵ (N); 38 ^{16,56} (N)
v_{CH}	0.26	Simulation: 0.22, 0.23, 0.23 ^{51,\dagger} (EM); 0.24, 0.26, 0.28 ^{41,\dagger} ; 0.31 ³⁶ (EM) Experiment: 0.32, 0.33, 0.35 ^{51,\dagger} ; 0.30–0.32 ⁵² (B)

^{\dagger}Reported as lower bound, average value, and upper bound, respectively. Codes: N, nanoindentation; C, measured on pressurized compacts, then extrapolating to zero porosity; B, brillouin light scattering; EM, force field, energy-minimization; DFT, density function theory.

Table I reports the input parameters for the micromechanics model, as well as data from the literature. The elastic properties of the C–S–H solid phase, called the “globule” here, were identified by inverse analysis of nanoindentation results³⁶ and recently confirmed by atomistic modelling^{36,38,40} and by the quantum mechanics density functional theory.⁴⁹ The porosity of HD C–S–H is taken to be $\phi_0 = 0.25$ in accordance with previous works, which cite values between 0.24 and 0.26.^{14,18,56} The elastic constants of portlandite, calculated using density functional theory,⁴¹ were taken as $C_{11} = 99.39$ GPa, $C_{12} = 30.78$ GPa, $C_{33} = 36.29$, $C_{44} = 7.88$, and $C_{66} = 34.31$ GPa. For the sake of simplicity, the Voigt–Reuss–Hill (VRH) estimates of isotropic elastic properties for the portlandite are calculated using the full elastic tensor of the single crystal and the arithmetic mean of the Voigt and Reuss averaging schemes.⁵⁷

Figure 8(a) compares the experimental results with the micromechanics predictions for the two microstructural cases. The energy bounds of “Case 1,” representing a pure microcomposite of CH and C–S–H (dashed lines), underestimate most of the experimental data. These bounds are narrow due to the low stiffness contrast between CH and HD C–S–H. The curves for “Case 2,” which assume a CH/C–S–H nanocomposite with different values of ϕ_{crit} , capture the data notably better, especially at a low f_{CH} , where there is a steep increase in M . Note that the assumed value of the elastic modulus of CH has little influence on this conclusion, as it only influences the curves at a high f_{CH} . The calculations also show that the majority of the data are consistent with ϕ_{crit} values between 0.10 and 0.20, suggesting that CH fills 40%–80% of the initial HD C–S–H porosity. The fact that nearly all the data lie within the envelope created by the curves for the pure microcomposite and those for the nanocomposite suggests that the dispersion in the data results from the coexistence of the two microstructural arrangements in the system.

(2) Implications of Nanoscale CH for the Structure and Properties of Cement Paste

A central finding of the study is that the UHD phase identified in earlier nanoindentation studies^{17,18} is, in fact, a nanocomposite of HD C–S–H and nanoscale CH. Micromechanical analyses presented in Section IV(1) show that the latter occupy a variable fraction of the total HD C–S–H gel porosity.

While CH is conventionally thought to precipitate in the capillary space as relatively large crystals of tens of micrometers or larger, the CH nanocrystals proposed to reside in the pores of C–S–H are over an order of magnitude smaller, approximately several nanometers across. The existence of nanoscale CH is supported in the literature.^{27,37,58,59} For example, Groves,⁵⁸ using TEM on a low w/c ratio cement paste (prepared at $w/c = 0.25$, and then compressed to an effective $w/c = 0.15$), showed the presence of CH with lamella thicknesses of ≈ 10 nm. These crystals were intimately embedded in the C–S–H gel, which led the author to speculate that the CH inclusions were mechanically reinforcing the gel. This supposition has been directly confirmed in the current study. Small amounts of nanoscale CH have also been observed at higher w/c ratios (e.g., $w/c = 0.40$) by TEM⁵⁹ and SANS.²⁷ The intermixing of nanoscale CH with C–S–H is also consistent with models of C–S–H at the crystal chemical level, where a defective tobermorite C–S–H structure admixed with nanoscale CH has been found to best describe certain systems.^{59,60}

The introduction of nanoscale CH into the gel pores of C–S–H will have a strong influence on the volumetric changes in cement paste. For example, the replacement of evaporable water for solid CH in the C–S–H gel pores will increase the stiffness of the solid, as well as decrease the volume of gel pores that can generate high capillary pressures during drying (arising from the high curvature of the liquid–vapor menisci). Both of these effects should reduce the driving force for drying shrinkage and potential cracking.⁶¹ The increased solid density of the C–S–H/CH nanocomposite

would furthermore expect to decrease creep due to the greater resistance against the sliding of C–S–H particles.¹⁸

If we assume a surface energy, γ_{CL} , and curvature, κ_{CL} , of the nanoscale CH crystal, the equilibrium solubility, C , of the nanoscale crystal increases with respect to that of a micrometer-sized (flat) crystal according to Scherer⁶

$$\kappa_{\text{CL}} \gamma_{\text{CL}} = \frac{R_g T}{V_c} \ln(C/C_0) \quad (8)$$

where R_g is the ideal gas constant, V_c the molar volume of CH, and C_0 the solubility of a flat crystal. This phenomenon has several important implications. First, we conclude that nanoscale CH must form under conditions of high supersaturation. Because high supersaturations most likely occur near the interface between the dissolving cement grain and liquid pore solution, we can expect that the loci of nanoscale CH crystals will be found precisely here; this argument is further extended in Section IV(3). Second, if we encounter the possible scenario where the solution composition is undersaturated with respect to the nanoscale CH crystal, but supersaturated with respect to the micrometer-scale CH crystal residing in the capillary space (which could occur just after precipitation of nanoscale CH from a transient supersaturated solution), we would expect the growth of the micrometer-scale CH crystals at the expense of the nanoscale CH crystals (i.e., Oswald ripening). This process would logically degrade the mechanical properties of the nanocomposite, provided there is sufficient capillary space for the growth of micrometer-sized CH crystals. This condition would be possible in a (porous) high w/c ratio paste, but unlikely in a (dense) low w/c ratio paste, where the Oswald ripening mechanism would thus be strongly impeded. Lastly, we could encounter the scenario where a sustained supersaturation exists. This situation could arise near a dissolving cement grain that lacks local space for precipitating new CH crystals. To maintain equilibrium of the existing nanoscale CH crystals (i.e., to prevent them from growing), the surrounding matrix needs to apply a counterbalancing pressure on the crystals. This pressure, p_c , which arises from the push of the crystal on the pore wall, is directly related to the supersaturation in the liquid:

$$p_c = pl + \frac{R_g T}{V_c} \ln(C/C_0) \quad (9)$$

where pl is the pressure in the liquid. This crystallization pressure induced by nanoscale CH provides a viable mechanism for the poorly understood expansion observed in low w/c ratio cement pastes.^{62,63}

(3) Mechanism of Forming C–S–H/CH Nanocomposites During Cement Hydration

The scatter in the f_{CH} versus M data in Fig. 7 between the extreme bounds of the micromechanical analysis suggests that, in addition to being able to form a C–S–H/CH nanocomposite, C–S–H and CH can also form a pure microcomposite, whereby micrometer-scale CH crystals precipitate outside the gel pore volume of C–S–H. The coexistence of both structures in a cement paste leads to the fundamental question: under what conditions do C–S–H/CH nanocomposites form? From nanoindentation experiments at different w/c ratios,¹⁸ it is clear that the formation of the nanocomposite is encouraged at low w/c ratios, especially for w/c ratios below 0.3, and very markedly below 0.2. This w/c range coincides with the range in which (unhydrated) cement particles in a fresh cement paste initially begin to impinge due to a deficiency in water to fill the pores of a dry cement pack (which has a representative packing fraction of 0.55–0.60). From this evidence, we hypothesize that the C–S–H/CH nanocomposite is a direct consequence of a local deficiency of water and space. Such a lack of water would occur in regions where cement particles are in close proximity, separated by films or wedges of water as small as tens of nanometers thick

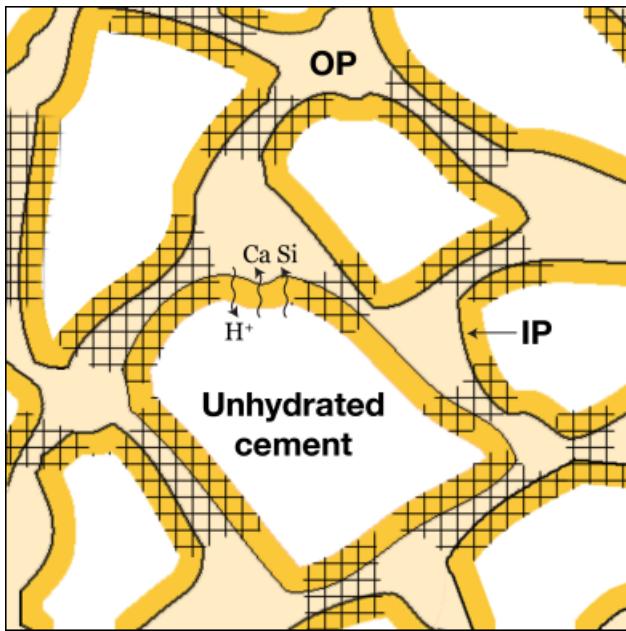


Fig. 9. Schematic of a hydrated, low *w/c* cement paste. It is hypothesized that the C–S–H/CH nanocomposite structure forms in IP regions and in thin films separating cement grains, where there is a local deficiency in water and space (denoted by crosshatched regions). Inner product (IP) (dark), outer product (OP) (light), and unhydrated cement grains (white) are shown. The influx of H^+ to the anhydrous clinker core and the efflux of Ca and Si ions to the capillary space are also shown.

(Fig. 9). In these highly confined reaction zones, where supersaturation in the liquid is presumably high (as argued above), there will likely be a tendency to favor reaction paths that minimize atomic transport; calculations of atomic fluxes presented below support this hypothesis. In regions where there is a local excess of water for hydration, such as in the interstices between cement particles (Fig. 9), there is a greater facility for CH to precipitate as micrometer crystals, thereby forming a microcomposite with C–S–H. By these above mechanisms, we can thus account for both the nanocomposite and the microcomposite structures observed in the *w/c* = 0.20 paste. The above mechanism also suggests that if the interstices between cement grains are filled with ultrafine fillers, such as in ultra-high-per-

formance concretes,⁶⁴ we may expect a greater potential for forming a nanocomposite structure due to the reduction in available capillary space.

Table II shows the number of Ca, Si, O, and H atoms in a 1 cm³ volume of C₃S, HD C–S–H, and the C–S–H/CH nanocomposite. The atomic densities in the reactant and product phases yield an insight into the flux of atoms across interfaces. For example, the observation that the O densities of C₃S, HD C–S–H, and C–S–H/CH nanocomposite are nearly equal suggests that there is little, if any, long-range movement of the oxygen anions during hydration.⁶⁵ This process would suggest an efficient mechanistic pathway, whereby, upon contact of the hydrated surface with water, H diffuses through the IP (instead of the bulkier water molecule), while Ca and Si atoms diffuse out to the capillary space (to form OP hydrates). Compared with an equal volume of HD C–S–H, the C–S–H/CH nanocomposite (with an assumed $f_{CH} = 0.15$) reduces the required efflux of Ca atoms to the capillary space by 25%, as well as the required influx of H by 12%. As argued above, both of these trends would be favored in the highly confined reaction conditions in a low *w/c* ratio cement paste.

V. Conclusions

This study provides the first direct evidence for the mechanical reinforcing effect of nanoscale CH crystals embedded in a C–S–H/CH nanocomposite structure. This nanocomposite structure is particularly prone to form during the hydration of a low *w/c* ratio cement paste. In these concentrated systems, it is believed that the numerous near-contact points separating cement grains create confined reaction zones that are characterized by high supersaturations in the aqueous phase and by a lack of available space—two factors that should encourage nanocomposite formation. In contrast, in the interstices between grains where there is ample space for microscale CH to crystallize, microcomposites of CH and C–S–H are believed to preferentially form, which experiment and micromechanical modeling show to have lower elastic moduli compared with those of the nanocomposites. This reasoning furthermore suggests that ultrafine fillers, which fill the interstices between cement grains, should promote nanocomposite formation. On a general level, this study illustrates the great potential in coupling X-ray microanalysis, nanoindentation, and micromechanics to advance our understanding of the relationships between chemistry, nanostructure, and mechanics in highly heterogeneous materials.

Table II. Atomic Density of Selected Atoms in C₃S, HD C–S–H, Nanoscale CH, and a C–S–H/CH Nanocomposite (with $f_{CH} = 0.15$)

Phase	Volume (cm ³)	Atomic density (1000 N _A ⁻¹)					
		Ca	Si	O	H	Ca/Si	H ₂ O/Si
(1) Ca ₃ SiO ₅ [†]	1.00	42.2	14.1	70.4	0.0	3.0	0.0
(2) HD C–S–H [‡] (including saturated gel pores)	1.00	18.1	10.0	70.6	64.9	1.8	3.2
(3) Ca(OH) ₂ (in nanocomposite)	(0.15) [§]	4.5	0.0	9.1	9.1	—	—
(4) C–S–H/Ca(OH) ₂ nanocomposite	1.00	22.6	10.1 [¶]	71.4	57.3**	2.3	2.9
(5) Remaining atoms ^{††}	—	19.6	4.0	−1.0	—	4.9	—

[†]Assuming $\rho = 3.21$ g/cm³. [‡]Assuming composition, 1.8CaO · SiO₂ · 3.2H₂O, $\rho = 2.20$ g/cm³. [§]Because we assume CH resides in the pores of HD C–S–H, this volume does not contribute to the apparent volume of the nanocomposite (row 4). [¶]Calculated by adding values from rows (2) and (3). ^{||}Calculated as

$$\rho_o^{\text{nanocomposite}} = f_{C-S-H} \frac{\rho_{C-S-H}}{MW_{C-S-H}} f_O^{C-S-H} + f_{C-S-H} \left[\frac{\rho_{CH}}{MW_{CH}} f_O^{CH} - \frac{\rho_{H_2O}}{MW_{H_2O}} f_O^{H_2O} \right]$$

where f_O^j is the oxygen density in phase j . **Calculated as

$$\rho_o^{\text{nanocomposite}} = f_{C-S-H} \frac{\rho_{C-S-H}}{MW_{C-S-H}} f_H^{C-S-H} + f_{CH} \left[\frac{\rho_{CH}}{MW_{CH}} f_O^{CH} - \frac{\rho_{H_2O}}{MW_{H_2O}} f_O^{H_2O} \right]$$

where f_H^j is the hydrogen density in phase j . ^{††}Calculated by subtracting values from rows (1) and (4).

Appendix A. Calculation of Cement Paste Density from SEM-EDS Data

As described in Section III(3), 2 density values were calculated at each SEM-EDS spot analysis.

For “case 1,” a microcomposite of C–S–H (including empty gel pores) and CH was assumed, and the density was thus calculated as

$$\rho_{\text{paste,micro}} = \left[x_{\text{CH}}(1 - x_{\text{CH}})^{-1} + 1 \right] / \left[x_{\text{CH}}(1 - x_{\text{CH}})^{-1} \rho_{\text{CH}}^{-1} + \rho_{\text{CSH,dry}}^{-1} \right] \quad (\text{A}-1)$$

where $\rho_{\text{CSH,dry}}$ is the bulk dry density of HD C–S–H, computed as, $\rho_{\text{CSH,dry}} = \rho_{\text{globule}} / (1 + \phi_0(1 - \phi_0)^{-1})$. Thus, assuming $\rho_{\text{globule}} = 2.6 \text{ g/cm}^3$ and $\phi_0 = 0.25$, $\rho_{\text{CSH,dry}} = 1.95 \text{ g/cm}^3$.

For “case 2,” a nanocomposite of C–S–H and CH was assumed where the CH was assumed to precipitate in the gel pores of C–S–H. This substitution increases with x_{CH} , until $x_{\text{CH}} = 0.22$, when the pores of HD C–S–H (with $\phi_0 = 0.25$) are theoretically full; subsequent increases in x_{CH} thus translate into a composite of the C–S–H/CH nanocomposite (with complete replacement of CH for gel pores) and of microscale CH. The density for this case thus reads as follows:

$$\rho_{\text{paste,nano}} = \rho_{\text{CSH,dry}}(1 - x_{\text{CH}})^{-1} \text{ for } x_{\text{CH}} \leq 0.22 \quad (\text{A}-2\text{a})$$

$$\begin{aligned} \rho_{\text{paste,nano}} = & [(1 - x_{\text{CH}})x_{\text{CH}}^{-1} + 1] / \\ & [(1x_{\text{CH}})\rho_{\text{CSH/CH}}^{-1} + \rho_{\text{CH}}] \text{ for } x_{\text{CH}} > 0.22 \end{aligned} \quad (\text{A}-2\text{b})$$

where $\rho_{\text{CSH/CH}}$ is the density of the “CH-saturated” C–S–H/CH nanocomposite, equal to 2.51 g/cm^3 .

Appendix B. Basics of Continuum Micromechanics

In linear elastic continuum micromechanics, the macroscopic strain E and the macroscopic stress Σ applied to the representative elementary volume V are simply defined as the averages of the microscopic counterparts $\varepsilon(x)$ and $\sigma(x)$:

$$E = \langle \varepsilon(x) \rangle_V \quad (\text{B}-1)$$

$$\Sigma = \langle \sigma(x) \rangle_V = \langle \mathbf{c}_r : \varepsilon(x) \rangle_V \quad (\text{B}-2)$$

where \mathbf{c}_r is the stiffness tensor of the single phase and $\langle y \rangle_V = 1/V \int y dV$ denotes the volume average of quantity y over the domain V . The concept of localization tensor $\mathbf{A}(x)$ is used to relate the microscopic strain $\varepsilon(x)$ at point x with the macroscopic strain E as follows:

$$\varepsilon(x) = \mathbf{A}_r(x) : E \quad (\text{B}-3)$$

The localization tensor \mathbf{A}_r is a key concept as it gathers all the information about the microstructure morphology. Substituting Eqs. (B-1) and (B-3) into the stress average of Eq. (B-2) yields the homogenized stiffness of the composite:

$$\mathbf{C}_{\text{hom}} = \langle \mathbf{c}_r : \mathbf{A}_r \rangle_V \quad (\text{B}-4)$$

For a matrix-inclusion morphology, the Mori-Tanaka localization tensor is frequently used

$$\begin{aligned} \mathbf{A}_r^{\text{MT}} = & [\mathbf{I} + \mathbf{S}_m : (\mathbf{c}_m^{-1} : \mathbf{c}_r - \mathbf{I})]^{-1} \\ & : \left\langle [\mathbf{I} + \mathbf{S}_m : (\mathbf{c}_m^{-1} : \mathbf{c}_r - \mathbf{I})]^{-1} \right\rangle_V^{-1} \end{aligned} \quad (\text{B}-5)$$

where \mathbf{S}_m is the Eshelby tensor of the inclusion within the matrix.^{45,66} In contrast, for a granular morphology, the General Self-Consistent localizer tensor⁴⁴ is used

$$\begin{aligned} \mathbf{A}_r^{\text{SC}} = & [\mathbf{I} + \mathbf{S}_{\text{hom}} : (\mathbf{C}_{\text{hom}}^{-1} : \mathbf{c}_r - \mathbf{I})]^{-1} \\ & : \left\langle [\mathbf{I} + \mathbf{S}_{\text{hom}} : (\mathbf{C}_{\text{hom}}^{-1} : \mathbf{c}_r - \mathbf{I})]^{-1} \right\rangle_V^{-1} \end{aligned} \quad (\text{B}-6)$$

where \mathbf{S}_{hom} is the Eshelby tensor of the inclusion within a matrix that coincides with the homogenized material. In the case of randomly oriented C–S–H fibers, the Eshelby tensor \mathbf{S} obtained from a geometric procedure of orientation averaging is still isotropic.⁴⁵

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