

Observation of a Mesostructure in Calcium Silicate Hydrate Gels of Portland Cement

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Transmission electron microscopy studies of calcium silicate hydrate (C-S-H) gels in portland cement have been performed. This is the first study which unambiguously demonstrates the presence of a mesostructure in the C-S-H gel phase. The mesostructure was found to consist of an amorphous matrix with a strongly variable composition which was embedded with nanocrystalline regions on the scale of ~ 50 Å or less each with a locally homogeneous composition and with short-range ordered regions on the scale of ~ 10 Å with a variable composition and structure. The mesostructure is believed to form due to the inability of normal long-range crystallinity to evolve because of gross fluctuations in the local Ca/Si ratio. [S0031-9007(96)00741-7]

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Many models have been proposed over the years to explain the complex crystal chemical observations which have been reported for calcium silicate hydrate gels (C-S-H) of hardened cement pastes (HCP). Several of the more prominent models include the solid solution model [1] and the nanophasic model [2]. The nanophasic model considers C-S-H to consist of a mixture of tobermorite and jennite structural elements on the nanometer scale. Following this model, sub-crystalline regions would exist; however, they would be confined to small fragments of Ca-O layers (with attached silicate chain fragments) that are several nanometers long. This model can explain many of the crystal chemical observations, macroscopic properties, structural, and compositional trends. In particular, it takes into account the importance of the presence of strong fluctuations in the local Ca/Si ratio. However, the nanophasic model inherently requires that C-S-H is a microheterogeneous system (i.e., local compositional and/or structural order on the nanoscale); however, no investigations as of yet have confirmed the presence of this microheterogeneous nature.

Various transmission electron microscopy (TEM) and electron microprobe analysis (EMPA) studies of HCP have previously made valuable contributions to the compositional and structural understanding of the C-S-H gel phase [3–6]. EMPA studies have revealed the presence of significant fluctuations in the local Ca/Si ratio within the gel phase throughout the specimen [3–6]. The local Ca/Si ratio has been shown to vary widely, between 0.6 and more than 2. Richardson and Groves [6] have reported the presence of a bimodal distribution in the local Ca/Si ratio; however, as specimens matured they found that the degree of bimodality decreased. The early presence of bimodality demonstrates that discrete regions exist which initially have different Ca/Si distributions; however, this study does not establish the presence of short-range compositional and/or structural order.

Evidence of short-range structural order (SRO) in C-S-H gels has previously been reported using selected area electron diffraction (SAED) [7,8] and x-ray diffraction methods [4]. Attempts at obtaining SAED patterns have generally failed; however, there are reports of occasional particles yielding poorly defined patterns [7,8]. In particular, early investigations by Grudemo [7] found the presence of a broadened reflection between ~ 2.7 and 3.1 Å. In addition, x-ray diffraction studies have revealed diffuse peaks between 2.7 and 3.1 Å [4], consistent with Grudemo's results. The purpose of this study was to systematically investigate C-S-H gels by SAED. In order to better characterize any midscale structures associated with SRO, high resolution electron microscopy (HREM) studies were also performed. In addition, a more complete investigation has been performed and will be published separately [9].

White portland cement was hydrated at a water to cement ratio (w/c) of 0.40. All specimens were initially formed by casting. Specimens were hydrothermally cured [100% relative humidity (rd)] at 80 °C for 4 weeks. Subsequently, they were aged in a moist environment (100% rh) at room temperature for approximately 5 yr. Similar results were found on specimens which had not been hydrothermally cured and had only been cured at room temperature for 6 weeks. The cylinders of hardened paste were then cut into disk shaped specimens. TEM specimens were prepared by ultrasonically drilling 3-mm diameter disks which were mechanically polished to a thickness of ~ 100 μm . The center portions of these disks were then further ground by a dimpler to ~ 10 μm , and argon-ion milled to perforation using a liquid nitrogen stage. Care was taken not to damage the specimen, as previously described by Richardson and Groves [6]. Specimens were coated with carbon before examination. Structural investigations were carried out with a Phillips 420 TEM operating at 120 kV and

with a Hitachi 9000 TEM operating at 300 kV. High resolution lattice imaging and high resolution chemical analysis with a probe size of 50 Å were performed using a Hitachi 2000 Field Emission TEM. The results were taken from an inner product area and had a morphology similar to that previously reported for a type 1 gel [6,10,11]; however, similar results were obtained from an outer product area and had a morphology similar to a type 2 gel.

SAED patterns were obtained from various randomly selected regions within the gel, as shown in Figs. 1(a)–1(c). These data were taken using a probe size of 0.5 mm in diameter. Inspection of these patterns will

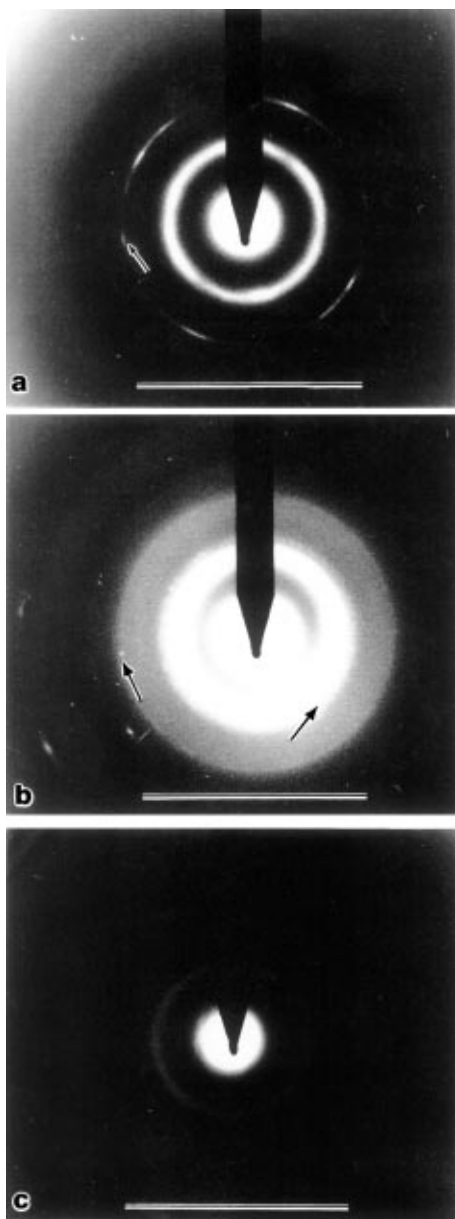


FIG. 1. Selected area electron diffraction patterns taken from various regions of the C-S-H gel, clearly indicating the presence of diffuse rings. The bar on each pattern represents 1 \AA^{-1} .

reveal several interesting features. First, diffuse rings were observed in every pattern. These diffuse rings unambiguously demonstrate that the local structure is not completely disordered, but rather SRO clearly exist. In addition, the diffuse rings were anomalously broad, indicating a wide distribution of d spacings. In Fig. 1(b), the inner edge of the ring had a d spacing of 3.2 Å, whereas the outer edge of the ring had a d spacing of ~ 2.6 Å. Comparisons of the data in Figs. 1(a)–1(c) will reveal that the periodicity of short-range ordering in the diffuse rings varied from region to region within the gel.

In order to get a better understanding of the midscale structural units giving rise to the short-range ordering observed in the diffuse rings of the SAED patterns, HREM studies of C-S-H gels were performed. Figure 2 shows a lattice image taken from the C-S-H gel phase. Figure 2 clearly illustrates the presence of regions of nanocrystallinity, marked as NC in the figure. Inspection of this figure will also reveal regions with some degree of short-range order on the scale of ~ 10 Å, marked as SRO in the figure. Also evident in the figure is the presence of amorphous regions, marked as AM in the figure. Amorphous, short-range ordered, and nanocrystalline regions can be seen to coexist throughout the gel phase. In Fig. 2, the size of the nanocrystalline regions can be seen to be ~ 50 Å or less. Nearly identical mesostructures with 50 Å nanocrystallinities were observed for specimens which had been cured at room temperature for 6 weeks [9]. We believe this indicates that nanocrystallinity develops very rapidly at short times, slowing down drastically for curing times greater than 8 weeks.

In Fig. 2, the d spacing within the nanocrystalline regions can be seen to be quite uniform. In consideration of the correlation between compositional and structural variabilities in C-S-H, we believe that these results indicate that locally the Ca/Si ratio is nearly uniform within each nanocrystalline region, as any significant

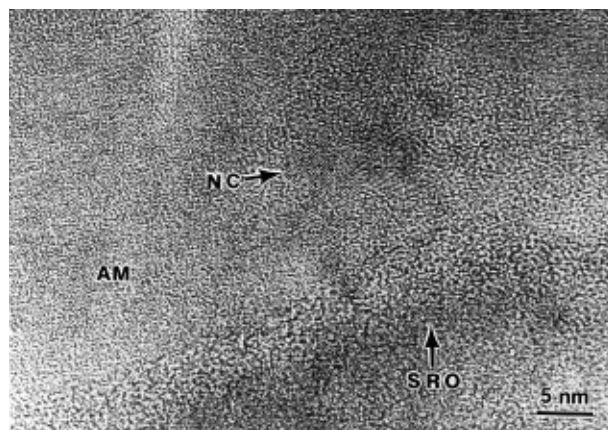


FIG. 2. Lattice image of C-S-H gel. Arrows indicate regions of nanocrystallinity.

fluctuations in the Ca/Si ratio within a nanocrystalline region would be expected to give rise to corresponding fluctuations in the d spacing. To estimate the local composition of single nanocrystalline regions, the beam was focused to a spot size of ~ 50 Å and centered on a nanocrystalline region. Quantitative analysis showed that the Ca/Si ratio varied between 0.4 and 2.0 between various nanocrystallinities. In general, amorphization was not found to occur during the EDAX or lattice imaging studies. However, when the electron beam was focused on a single nanocrystalline region to determine the local compositional order, amorphization was observed. In addition, we did not seemingly have significant trouble with selective evaporation during the investigations, as the EDAX count rate was constant with time. These results demonstrate that the nanocrystalline regions have a distribution of compositional order parameters. It would appear that a multitude of local compositional order parameters may be "frozen-in," where different nanocrystalline regions have different Ca/Si ratios. In a system where global homogenization of the Ca/Si ratio is limited by thermal diffusion, the development of longer range crystalline order may be prevented. However, short-range diffusion can occur quite rapidly over the distance of several tens of angstroms. Consequently, coarsening of the nanocrystalline regions may occur up to a scale of ~ 50 Å, but the process is eventually rate limited by the diffusion kinetics. Rather, the system becomes long-time metastably trapped into a sequence of near degenerate C-S-H states with various Ca/Si ratios and d spacings.

Figures 3(a)–3(c) show optical diffraction patterns obtained by using a laser beam to cover various nanocrystalline regions in the corresponding negative of a lattice image. Optical diffraction patterns were taken from the individual nanocrystalline regions, identified as areas A through C in the lattice image given in Fig. 3(d). These figures clearly reveal sharp diffraction spots associated with crystallinity. Various periodicities could be identified in the optical diffraction patterns. For example, in Fig. 3(a), d spacings of 2.8, 2.5, 1.8, and 1.3 Å were found. In addition, the values of the d spacings were found to vary over a considerable range between regions, as can be determined by comparisons of the results for the various optical diffraction patterns. The 2.5 Å periodicity is consistent with the repeat unit of the CaO part of the jennite structure, whereas the 2.8 Å periodicity is approximate to the repeat unit of the CaO part of the tobermorite structure [10]. In addition, the 1.8 Å periodicity would be found in any structure containing dreierketten, including both tobermorite and jennite [12]. These results give strong evidence demonstrating that the nanocrystalline regions have both tobermorite-like and jennitelike structural elements, supporting the central concepts of the nanophasic model conjectured by Taylor [2].

Following the results above from the optical diffraction patterns, the broad diffuse rings in the SAED patterns between 2.6 and 3.2 Å would seemingly reflect the presence of an intimate mixture of tobermoritelike and jennitelike structural elements. The broadness may reflect

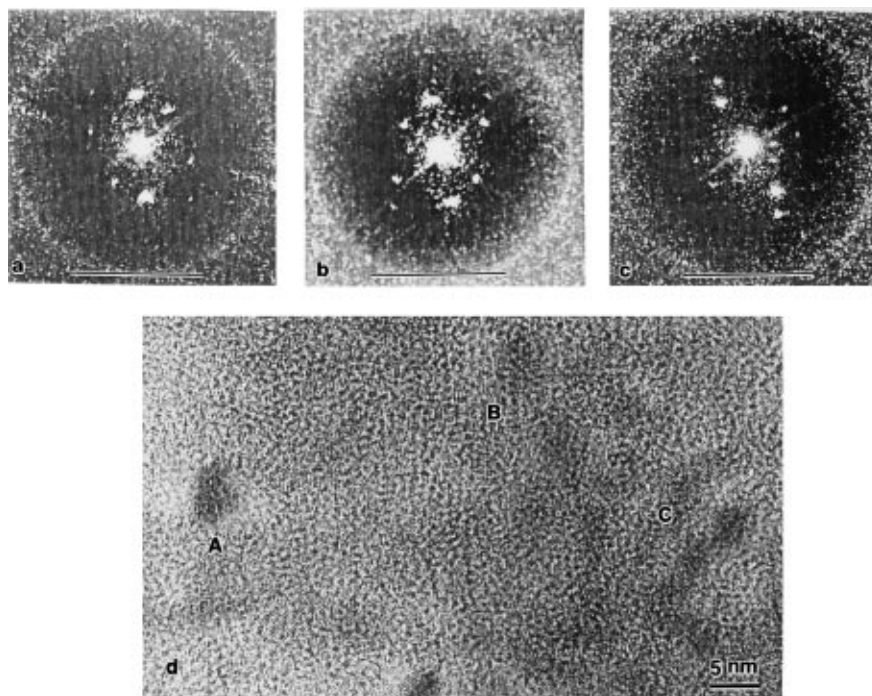


FIG. 3. Optical diffraction patterns for C-S-H gel (a)–(c) taken from various regions in the lattice image (d). The bar on each optical diffraction pattern represents 0.5 \AA^{-1} .

fluctuations in the local Ca/Si ratio, which then result in fluctuations in the lattice parameter locally, as both the local Ca-occupancy and tilting of the silicate tetrahedra could lead to significant changes in the distortion of the Ca-O layer. In consideration of the wide range of Ca/Si ratios which is possible in the nanocrystalline regions, the structure might be able to adapt its lattice parameters over a relatively wide range. Consequently, a near continuous sequence of metastable C-S-H states could exist with varying degrees of tobermoritelike and jennitelike characteristics.

The important conclusions of the present study can be summarized as follows: (i) The mesostructure of C-S-H gels has been identified for the first time. The mesostructure consisted of an amorphous matrix with a strongly variable composition which was embedded with nanocrystalline regions on the scale of ~ 50 Å or less each with a locally homogeneous composition and with short-range ordered regions on the scale of ~ 10 Å with a variable composition and structure. (ii) As a consequence of a wide variation in local Ca/Si ratios between the nanocrystalline regions, the system would seemingly be able to form a near continuous sequence of metastable C-S-H states. The evolution of normal long-range crystallinity with curing time is then prevented by gross fluctuations in Ca/Si ratios, which would require long-range diffusion in order to homogenize the composition.

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- [1] K. Fujii and W. Kondo, *J. Am. Ceram. Soc.* **66**, C220 (1983).
 - [2] H. F. W. Taylor, *J. Am. Ceram. Soc.* **69**, 464 (1986).
 - [3] K. Mohan and H. F. W. Taylor, *Cem. Concr. Res.* **12**, 25 (1982).
 - [4] K. Mohan and H. F. W. Taylor, *J. Am. Ceram. Soc.* **64**, 717–719 (1981).
 - [5] G. Groves, P. LeSueur, and W. Sinclair, *J. Am. Ceram. Soc.* **69**, 353 (1986).
 - [6] I. Richardson and G. Groves, *J. Mater. Sci.* **28**, 265 (1993).
 - [7] A. Grudemo, in *Proceedings of the Fourth International Symposium on the Chemistry of Cement, 1960* (U.S. GPO, Washington, DC, 1962), pp. 615–647.
 - [8] L. E. Copeland, E. E. Bordor, T. Chang, and C. H. Weise, *J. PCA Res. Dev. Labs* **9**, 61 (1967).
 - [9] D. Viehland, J.-F. Li, L.-J. Yuan, and Z. Xu, *J. Am. Ceram. Soc.* (to be published).
 - [10] H. M. Jennings, N. J. Dalgleish, and P. L. Pratt, *J. Am. Ceram. Soc.* **64**, 567–571 (1981).
 - [11] S. Diamond, in *Hydraulic Cement Pastes: Their Structure and Properties* (Cement and Concrete Association, Slough, UK, 1976), pp. 2–30.
 - [12] H. F. W. Taylor, *The Chemistry of Cement* (Academic Press, London, 1992).