Developments in TEM nanotomography of calcium silicate hydrate

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Abstract

This investigation was designed to explore the possibility of using Transmission electron microscope (TEM) tomography on cement-based systems in order to gain a greater understanding of their nanostructure and pore network. The preliminary results show a clearly a

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well-defined pore network at the nano-scale, with pore size approximately 1.7-2.4nm in diameter and spaced around 5-8nm apart. A comparison of small angle x-ray scattering data with 2-D TEM images analyzed with the Fourier slice theorem documents an excellent structural correlation.

Key words: TEM (C); Calcium-Silicate-Hydrate (C-S-H) (C); tomography (C); Image Analysis (C)

1. Introduction

The main binding phase in all Portland cement based systems is the hydration product, calcium silicate hydrate (C-S-H). As such, the nanostructure and morphology of C-S-H, along with the surrounding pore network which they produce, determines the overall properties and performance of the concrete. The current thrust in research to produce a more durable and resilient concrete, with reduced CO\textsubscript{2} emissions, is not possible without detailed characterization of C-S-H, to define the nanostructure, morphology, and the surrounding pore network. The porosity, determined by the hydration products, plays a key role in the durability-based performance of concrete. The size distribution and connectivity of the pores will determine the ability of fluids and ions to flow through the network, potentially degrading the material. To date, there have been many studies on the nanostructure and morphology of a variety of Portland cement based systems [1-4]. While these answer many questions, the results of these techniques are distilled into 2-dimensional plots that state limited, often inferred, volumetric information of the nanostructure and pore network for a bulk paste. Due to the complex nature of cement hydration and the sensitivity of the products formed, the majority of three-dimensional (3D) information available is not at the nano-scale, or is simulated rather than observed [5-7]. This study aims to empirically investigate and present the localized 3-dimensional structure of C-S-H at the nano-scale using TEM tomography and explore the use of cryo-TEM in an attempt to mitigate beam damage of the sensitive hydration products. TEM nanotomography has been greatly enhanced over the last few decades [8-10] and applied to many porous systems in materials science [11-13] but thus far not used to investigate cementitious materials. This study also includes the analysis of 2-dimensional images from TEM, for the first time using Fourier slice theorem [14] compared with small angle x-ray scattering data (SAXS).
2. Experimental Methods

2.1 Materials

Calcium silicate hydrate (C-S-H) is either amorphous or poorly crystalline, with the hyphens in the notation indicating the variable composition of this phase: for example the Ca/Si ratio can range from 0.6 to 2.0. In this study cryo-TEM and SAXS were performed on a powdered pure synthetic calcium silicate hydrate (I) (CSH(I)) produced by CTL group in Skokie, Illinois (www.ctlgroup.com), with Ca/Si=0.98. The sample was stored in a sealed container flushed with N2 until studied. CSH(I) is a more ordered form of calcium silicate hydrate (C-S-H) than that found in the reaction of Portland cement and water [15] and in this case less variable as the Ca/Si ratio is fixed, making hyphens unnecessary. The reaction of Portland cement with water is complex, producing C-S-H, along with many other phases. As such, Portland cement is not ideal for assessing the validity of a new technique. It is therefore, common practice in proof-of-concept studies such as this to use the simplified hydration reaction of tricalcium silicate (C\textsubscript{3}S), whose hydration products are limited to C-S-H and Ca(OH)\textsubscript{2}. The TEM-tomography was performed on a tricalcium silicate (C\textsubscript{3}S) paste hydrated for approximately one year with a water/cement weight ratio of 0.35.

2.2 TEM measurements

Cryo-TEM was carried-out on a sample of synthesized CSH(I) taken from the center of the paste to avoid carbonated sections and ground with a pestle and mortar until a powder, then placed on a TEM foil grid with a holey carbon film. Fast freezing was performed using liquid ethane, before the grids were transferred under liquid nitrogen to a Titan CT (FEI Company, Eindhoven, the Netherlands) operating at 300kV, equipped with a 2k x 2k CCD camera (Gatan, Pleasanton, CA, USA); where the nanoparticles were imaged at -170°C. For nanotomography, the fine powder was suspended in ethanol, 2µl of which was deposited on a holey carbon film pre-coated with 10nm gold nanoparticles and dried in air for five minutes before examination. The single axis tilt- series for tomographic reconstruction, performed on tricalcium silicate (C\textsubscript{3}S) hydrated paste, was acquired automatically using the Xplore3D tomography software (FEI Company) on the same Titan CT TEM, without a cooled environment.
Due to the poorly crystalline nature of the material used and the potential formation of highly crystalline Ca(OH)$_2$, diffraction patterns were observed in all areas before tomography was performed. This was done to ensure that the area was amorphous and no strongly scattering phases were present so that the collected images would be a true projection of the structure and the projections criteria were met, while in bright field TEM mode. This is of particular importance when studying C-S-H as nanocrystalline C-S-H(I) is a possible hydration product. A further precaution was taken in not using the objective aperture, as this can increase diffraction effects [16]. The resultant reduction in contrast from not using the objective aperture was overcome by setting the defocus to -1 micron. Before tomography image collection was started, optimal beam dose rate conditions were identified and low-dose settings used, to reduce possible sample damage from the relatively long beam exposure. The sample was rotated from 0 to -65° and from 0 to +65°, following the Saxton scheme [17] for image capture with a starting angle of 2.5°, producing 361 projection images. Using IMOD software [18, 19], the projection images were aligned using the Au nanoparticles as references. A subvolume of the images was reconstructed using the simultaneous iterative reconstruction technique (SIRT) for 17 iterations. Nonlinear anisotropic diffusion, as implemented in IMOD, was applied to the reconstructed subvolume for edge enhancement. Manual segmentation of the reconstructed tomogram was then performed using Avizo® from the Visualization Science Group (VSG). The areas used for reconstruction were selected regarding their features of interests, representative nature of the whole sample and void of carbon film, to eliminate high contrast.

2.3 Small Angle X-ray Scattering (SAXS) measurements

The SAXS was performed at beamline 7.3.3, Advanced Light Source, Lawrence Berkeley National Lab [20]. The sample was sealed inside a polyimide tube with 2.67mm outer diameter and 0.064mm wall thickness. Using an incident monochromatic X-ray at 10keV and a sample-to-detector distance of approximately 2.1m, the data acquisition was optimized with an exposure time of 0.4s, ensuring high counts rate, but no saturation at the Direct Detection Camera CCD detector. The precise sample-to-detector distance and sample tilt were determined during calibration with pure silver behenate (AuB). To reduce the effects of noise, each data set was measured five times and averaged, before subtracting the empty polyimide tube diffraction data as the background. Data calibration and analysis was undertaken with the Fit2D software.

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3. Results and Discussion

3.1 High Resolution TEM Images

The high resolution image of synthesized CSH(I) in figure 1 was taken under cryogenic conditions. When compared with images of cement at the same magnification, cooling was seen to have no noticeable effect on the sample during exposure to the beam. High resolution imaging showed the sample to be generally of an amorphous nature. In a number of areas the amorphous product was interlaced with a small amount of crystalline material, as suggested in earlier work [21]. An example of such a crystalline area is given in Figure 1, where the crystalline phase is evident from the lattice fringes and the selected area diffraction (SAD) pattern (Figure 1c). Figure 1b is an enlargement of the highlighted area which shows finer fringes (vertical), perpendicular to the more prominent, larger fringes. Owing to the observation of these finer fringes, it is assumed that the larger, more defined fringes are rotational Moiré fringes.

Moiré fringes are created when two sets of lines overlap; in this case the lines are lattice planes in a crystal. When two sets of similarly spaced lattices overlap and rotate, the fringes produced are perpendicular to the average direction of the initial lattice plane. Furthermore, the smaller the difference in the initial lattice spacing, the coarser the Moiré fringe spacing becomes, which could result in the initial fringes being harder to distinguish. Moiré fringes are a combination of information, or interference, from two lattice planes, which may or may not be from the same or two different crystals.

As a method of verification, a selected area diffraction (SAD) pattern was taken of the area shown in Figure 1. This was then used to identify phases present by calculating the d-spacing, knowing that the radii of the rings are inversely proportional to the interplanar spacing’s $d_{hkl}$ of a lattice planes of crystals, which follows the same relationship as that of a single crystal given in equation 1, where $D$ is the distance from the center to the dot (in this case radius of the ring), $L$ is the camera length and $\lambda$ is the wavelength of the electron beam. The computed lattice parameter’s from the SAD, given in table 1, are comparable to the d-spacing’s of the semi-crystalline C-S-H(I) phase obtained by previous studies, using synchrotron XRD [22] and TEM diffraction.

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Unlike other studies, however, no d-spacing was observed at 0.16nm in the TEM diffraction pattern. When the 0.16nm d-spacing has been observed in TEM and XRD, the intensity is noted as ‘weak’ (Table 1). It is therefore assumed that the selection of a larger SAD aperture than required, reduced the contrast in the diffraction pattern, making the already weak 0.16nm signal imperceptible. This, and not the absence of crystallinity, causes the 0.16nm d-spacing to be absent from the SAD image. Figure 2 shows high resolution images of C₃S paste, on which TEM tomography was performed. Generally throughout the samples the morphology tended to be featureless (Figure 2a), with the exception of small regions of the previously reported fibril morphology [1]. This is unexpected for C₃S at one year of hydration, as longer fibril features should be clearly visible throughout the sample [23].

It is possible the limited number of images taken were of only inner product C-S-H, which at one year hydration would remain featureless. Another explanation for the lack of features could be the presence of large calcium hydroxide (CH) crystals, which are featureless when observed at low magnification and form relatively early in the reaction of C₃S. However, this theory has been dismissed as CH crystals tend to form in large irregular, angular plate-like shapes, several microns across, which were not seen anywhere in this sample, at any magnification. In addition, the fringes seen at higher magnification in Figure 2d indicate small crystals, with no correlation to known CH d-spacings. Therefore, it is assumed that CH is not responsible for the fringes, and the small amount of crystalline phase present in selected areas is C-S-H(I), agreeing with the x-ray diffraction measurements of the same sample [24].

### 3.2 2-D images and structural correlation

A TEM image is a projection image that captures the electron beam attenuation through the sample slice. For the image analysis performed here, the electron beam attenuation generally follows a Beer-Lambert law. The logarithm transform of the projection image, with a change of sign, gives an attenuation 2D map. Each pixel grey level located in (x,y) is proportional to the attenuation integral along the optical axis, z. The (x,y) plane is parallel to the detector plane and the yy axis is perpendicular to the zz axis. A generally accepted hypothesis is to consider that the electronic absorption in (x,y,z), noted $\mu(x, y, z)$, is proportional to the electronic density at this

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point. In fact, this hypothesis is one of the key points allowing building a 3D reconstruction of the object using a series of projections taken at various angles. In this study only one projection is used, $A(x,y)$. First the 2D Fourier transform of $-\ln(A(x,y))$ is performed to obtain the complex function $A_c(q_x,q_y)$. The spectral density, $P(q_x,q_y)$, of $-\ln(A(x,y))$ is written as:

$$P(q_x,q_y) = A_c(q_x,q_y)A_c^*(q_x,q_y)$$

Under the former hypothesis and using the so-called Fourier slice theorem [14], it has been shown that this spectral density is a good approximation of the small angle scattering pattern, $I(q_x,q_y,q_z=0)$ [25]. The image of the synthesized CSH shown in Figure 1 exhibits an anisotropic long range texture along the x axis. As a consequence, the 2D $I(q_x,q_y,q_z=0)$, shown in Figure 3, exhibits a strong anisotropy along the $q_y$ axis with an angular distribution of around $\theta=+/\pm 20^0$. In order to retrieve the small angle scattering of powdered CSH, $I(q)$, an angular average of the pattern shown in Figure 3 was performed, using an angular mask centered along the $q_y$ axis, having an angular aperture of $\theta=+/\pm 20^0$.

The computation is shown in Figure 4 and compared to the experimental SAXS data from the same sample. The ordinate scale is normalized in arbitrary unit. There is good correlation between the two sets of data, with an overlap in a limited q-range from $10^{-2}$ Å$^{-1}$ to $4 \times 10^{-2}$ Å$^{-1}$. The computed $I(q)$ exhibits some interesting features which can be compared to the numerous investigation of cement pastes by SAXS or SANS started in the mid-eighties [26-33]. Regardless of the precise composition or the age of the hardened cement paste, the scattering intensity $I(q)$ invariably behaves as a fractional power of $q$ in a low and very low q range. The resulting spectrum found in the literature clearly shows the existence of two power-law regimes, with a transition around $q=0.03-0.05$ Å$^{-1}$ such as:

$$I(q) \propto q^{-(3+\gamma_1)}$$

for $q<0.03$ Å$^{-1}$ with $\gamma_1$ around 0.2 and

$$I(q) \propto q^{-(2+\gamma_2)}$$

for $q>0.03$ Å$^{-1}$ with $\gamma_2$ slightly above 0.
In our case this last regime ends above $q=0.3 \text{ A}^{-1}$ where we start to observe a diffraction centered around $q=0.53 \text{ A}^{-1}$. This peak is followed by its harmonic at $q=1.05 \text{ A}^{-1}$.

It is important to remember when comparing data calculated using the Fourier slice theorem with experimental data that the Fourier slice theorem accounts for all the information found in the image. Therefore, the prominent Moiré fringes identified in Figure 1 will have the largest intensity after the application of the Fourier slice theorem, despite being an artifact. Taking this into consideration, the d-spacing calculated from TEM SAD, are also indicated on Figure 4 for comparison. As predicted, the relative intensities of the peaks do not agree with experimental data, but there is a good alignment of the d-spacing obtained through both methods.

3.3 Nanotomography

3-D reconstruction of the voids in the powdered C$_3$S is given in Figure 5 and 6. All reconstruction images show only the voids present and not the C-S-H itself. As such, the images in Figures 5 and 6 can be considered to be the inverted representations of the TEM images seen in Figures 1 and 2, where the highlighted areas are the pores and the space between is the hydration product C-S-H. The image reconstructions were performed in Avizo® with no automatic gray scale application. The image shows what could be described as ‘sheets of voids’ with two distinct sets as indicated by the arbitrarily applied colors. Considering the high resolution TEM of synthetic CSH (Figure 1b) showed areas of C-S-H(I) overlapping to produce rotational Moiré fringes, it is assumed overlapping is also the case here, but not of the crystalline C-S-H(I) phase. Using basic analysis and the discussion of the 2D images, the two separate networks of pores are therefore mostly likely attributed to two particles of the same phase in alternate orientations. The diameter of the voids is estimated at around 1.68-2.4nm (8-11 pixels), with the distance between voids being approximately 5-8nm. Due to the preliminary nature of this investigation, the results obtained here should be seen as a ‘proof of concept’ and, as such, a direct relation between these results and theoretical models on the nature of C-S-H has not been made here.

4 Final Remarks

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For the first time, we have imaged and resolved the 3-D network of hydrated C-S-H and its pore network in single digit nanoscale spatial resolution using TEM. In addition, we have shown that computed quantitative morphological analysis of TEM transmission images correlate strongly with SAXS measurements and expected XRD features. Despite the sensitivity of cement paste to the electron beam and the potential damage this can cause, the initial investigation using cryo-TEM, showed beam damage could still occur. The primary investigation presented here clearly shows, in optimal dose rate conditions, that it is possible to obtain TEM tomography of C-S-H. Furthermore, nanoscale void structure is imaged in 3-D, which provides detailed information on void size, spacing, and orientation; and potentially an additional insight in void connectivity. TEM provides an increased resolution when compared to other tomography techniques. This preliminary study has proven the TEM tomography of cement pastes to be possible. TEM tomography opens a wide range of possibilities, when developed alongside quantitative image reconstruction, to study cementitious materials. Development of this technique will aid research in internal nanopore structure and packing density of C-S-H which, will provide a better understanding of this complex and widely used material.

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References

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TABLE AND FIGURE CAPTIONS

Table 1: C-S-H(I) d-spacing (nm) comparisons.
**Figure 1:** High resolution images of synthesized CSH taken under cryo-conditions with (b) an enlargement of the highlighted area to show finer lattice fringes (right) and (c) selected area diffraction.

**Figure 2:** High-resolution TEM images of C₃S paste.

**Figure 3:** I(qₓ,qᵧ,qₜ=0) computed from Figure 1.

**Figure 4:** A composite graph: SAXS plot of hydrated synthesized CSH (solid line), and quantified morphology calculations from the 2-D TEM images (round dots). Expected d-spacing extracted from TEM SAD image for synthesized CSH (from Figure 1) is shown in dashed lines, in angstroms.

**Figure 5:** 3D reconstruction of C-S-H interstitial pore network formed in hydrated C₃S, with original slices inset. (512x 488 pixels)

**Figure 6:** Enlarged 3D reconstruction of C-S-H interstitial pore network formed in hydrated C₃S. (512x 488 pixels)

**Tables**

**Table 1:** C-S-H(I) d-spacing (nm) comparisons.

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<th>Taylor [34]</th>
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<th>Synthesized CSH From XRD [22]</th>
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1

2 Table 1:
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