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## **3D Nanotomography of Calcium Silicate Hydrates by Transmission Electron Microscopy**

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## Reviewer(s)' Comments to Author:

### Reviewer: 1

#### Comments to the Author

The manuscript by Panod Viseshchitra et al. attempts to investigate the 3D nanostructure of synthetic C-S-H via TEM tomography. To quantify the pores in C-S-H cluster, author utilized various analytic tools (simulation) as well. Although some findings in the manuscript are interesting, I have a couple of major and minor comments that the authors may wish to address:

1. The most important issue in this study is purity of synthesized C-S-H with different C/S. Have you carried out XRD on the C-S-H before performing TEM? Carbonation and the presence of portlandite (in particular C-S-H of C/S 1.6) in C-S-H would significantly alter the pore structure of C-S-H. Please add powder XRD of synthetic C-S-H to present the purity of C-S-H.

The reviewer raises a valid point, so we included XRD measurements to show that the sample did not have portlandite nor showed evidence of carbonation.

The following addition was done on page 7, line 31: "The solid phase for both Ca/Si ratio was analyzed by XRD and only C-S-H was present. There was no evidence of the presence of portlandite nor of carbonation. The XRD results are shown in Figure 2."

2. The schematic of C-S-H (tobermorite 14A) shown in Figure 1 is in atomic-scale which is much smaller scale relative to this study. The authors seem to measure pores between C-S-H globules or clusters in nanoscale. Please specify the special resolutions for TEM tomography since it is directly related to 'the scale' in this study.

Refer to page 11, line 8, we added "The voxel size of both models is 1.14 nm".

3. Page 6, Line 21: What do you mean by 'characterization mechanisms of hydration' ?

Here we refer to reference no. 30 about hydration mechanisms which is not the focus of this study. We have clarified it by removing ", and characterization mechanisms of hydration" on page 6, Line 21.

4. In 2.1, please specify the w/b for each mixture since w/b is also a critical factor affecting the porosity of C-S-H.

Indeed, the w/b can have a significant influence on the C-S-H morphology so we added the following information:

Refer to page 7, line 11, we added "The water to solid ratio of both samples was equal to 45"

5. Page 11, Line 19, what is the reason of selecting 5 particles (I do not think it is 'particle', it seems to be 'ROI' or 'area' in C-S-H)? selected randomly?

We agree with the reviewer, so we changed the term "particle" to "region of interest (ROI)". We selected ROIs that look like a fiber along the original projection direction, but when we rotated, it turned out that they are foil-like. 5 ROIs we selected are not randomly. They are representative

of the entire sample and this supports our finding that all seemingly elongated ROIs are in fact foil-like rather than fiber.

6. For each particles, how did you set the direction vectors in cartesian coordination(axis)?

The particles sit randomly on a TEM grid. The original projection direction with the grid approximately flat (Figure 3 and 4) is arbitrary set as 0-degree rotation. Then we rotate 90° around the parent fiber direction to show that they are not fibers. Here, tomography is absolutely critical because it allows us to observe and slice the object from any arbitrary 3D angle. Otherwise, incorrect conclusions can be drawn from a simple 2D projection along any single direction because features overlap in projection.

Refer to page 11, line 21, we added “The particles sit randomly on a TEM grid. The original projection direction with the grid approximately flat (Figure 3 and 4) is arbitrary set as 0-degree rotation. Then we rotate 90° around the parent fiber direction.”.

7. Please show the visualized pore structures obtained via segmentation using Otsu algorithm. It should be very important.

We agree with the reviewer and a discussion on image segmentation has been added in Appendix B.

8. Page 19, Line 10, intralayer? Interlayer? Have you successfully observed interlayer of C-S-H in this study?

This is a typo. It is interlayer, the pore inside the structure of C-S-H. We didn't focus on interlayer in this study.

## **Reviewer: 2**

Comments to the Author

A fascinating paper, using electron tomography to look at C-S-H pore structure. The authors did a great job generating this very important data. Fits the journal very well. I had some minor comments below, mainly to improve the presentation and impact of the paper for the ACerS audience.

1. Shouldn't “electron tomography” be in the title?

The reviewer has a strong point and we followed the advice of changing the title of the paper to 3D Nanotomography of Calcium Silicate Hydrates by Transmission Electron Microscopy.

2. How did you compare the C-S-H prepared from CaO and silica fume to the C-S-H in Portland cement? i.e., effect of Al impurities, etc.

This comparison is not done in our study. The difference that we reference are from a previous study<sup>37</sup>. However, this is the next step that we plan to do. We plan to compare the 3D structure of synthetic C-S-H and C-S-H from hydration of Portland cement.

3. Any possible effect of not doing a full 180 degree rotation?

The presence of missing rotation angles (known as the missing wedge) leads to an ill-posed inverse problem. This is a well-known limitation of TEM tomography where the maximum range is from about -70 to +70 (total coverage of 140 degrees) due to physical constraints of the sample and microscope<sup>32</sup>. The field of tomography has dedicated great effort to minimize this limitation and significant progress has been achieved with the development of robust reconstruction methods. In this study, we use the SIRT reconstruction algorithm<sup>33</sup>, which improves the resolution and reduces artifacts from the missing wedge. The blurring effect imposed by the limited tilt angles was considered when doing the post-processing but it did not significantly impact our results.

4. What was the resolution, or at least the voxel size, of the reconstructed images? This is an important parameter to give, and especially to compare it to the typical size scale of C-S-H building blocks. How many of these were in one voxel? Also, porosity can scale with voxel size.

Refer to page 11, line 8, we added “The voxel size of both models is 1.14 nm”. This study would be able to measure large pore above the voxel resolution but not below about 2.5 nm (Nyquist sampling resolution). We thus can provide an upper limit on pore size and distribution.

5. Why was a beam dose of 5000 e<sup>-</sup>/(nm<sup>2</sup> s) suitable for this research? Evidence?

We checked the structure stability before and after tomography to confirm that there is no noticeable beam damage. These materials are able to withstand this amount of dose.

Refer to page 10, line 11, we added “The example of effect of beam damage are shown in Appendix A”.

Refer to page 22, where we added Appendix A.

6. The 3D image analysis to extract geometrical information about the C-S-H structures is not obvious to do – I think the reader would appreciate more details about how this was done.

Refer to page 9, line 7, we added “The geometrical information of all particles (ROIs) was obtained from the Tomviz software. The selected ROIs are cropped and object sizes were measured using the ruler function”. We also add the visualized pore structures obtained via segmentation using Otsu algorithm in Appendix B.

7. How did the authors define “elongated particles” of C-S-H? This was not clear. Was foil-like ever quantitatively defined? How was “elongated” defined?

Elongated particles refer to foil-like structures that are perceived as fibers when observing the original 2D projection images of such structures. However, when we rotate such a structure, we see it is extended along the projection direction and looks like flat extended particle. This is what we refer to as foil-like.

Refer to page 11, line 19, we added “Elongated ROIs refer to foil-like structures that are perceived as fibers when observing the original 2D projection images of such structures.”.

8. This statement should have appeared in the front of the paper rather than being left to the discussion: "This research studied synthetic C-S-H instead of hydrated C3S because of the desire to have only one phase in the system."

We appreciate this recommendation as it makes the manuscript clearer for the readers. In page 18, line 29, we moved "This research studied synthetic C-S-H instead of hydrated C3S because of the desire to have only one phase in the system." to page 6, line 46.

The caveat in regards to C-S-H found in portland cement paste or C3S paste should also be mentioned in the conclusions.

It is true that C-S-H can be found in portland cement paste but the Ca/Si ratio of C-S-H is much higher than this research so we can't claim that these C-S-H can be found in Portland cement paste or C3S paste..

Conclusions: "TEM tomography shows the capability to determine the 3D nanostructure and pore networks of C-S-H and in the future related cementitious materials such as calcium alumino silicate hydrate (C-A-S-H) should be investigated." The authors said that synthetic C-S-H was chosen so that they had only a binary system, on which the Otsu algorithm works quite well. If they are going to be looking at Portland cement C-S-H and C-A-S-H, the image segmentation will be harder to do accurately. Perhaps some statements about that would also be good to include on their nice list of problems to be overcome, like using Cryo-TEM. The above statement probably belongs more in the Discussion section than in the Conclusions section.

Refer to page 19, line 23, we added "For the 3D nanostructure analysis based on TEM images, These two samples are synthetic samples because of the desire to have only one phase in the system so if the sample of Portland cement is analyzed, the image reconstruction and segmentation will be harder to do accurately because there are many phases in the system. In previous publications<sup>42, 43</sup>, the authors proposed an automated image processing pipeline with machine-learning based classifiers, which achieved accurate multiphase segmentation results for the 3D X-ray micro-tomography images of ancient Roman concrete samples. Similar methods can be used for the image segmentation of TEM tomography of real samples of Portland cement in the future study."

### **Reviewer: 3**

#### Comments to the Author

This manuscript entirely disregards the fact that C3S and C2S hydration generates both CSH and Ca(OH)<sub>2</sub> i.e.e CH or portlandite, and that intimate mix of the two is obtained when mixing CaO and SiO<sub>2</sub>. Due to this, the results provided by the authors relate to the mix of CSH and CH, and not to the sole CSH. Therefore, they cannot claim identifying the pore nanostructure of the CSH.

In the past, we have done the analysis of both synthetic C-S-H and from the C3S hydration<sup>20</sup>. The results showed similar features of morphology. Also, we are developing the protocol to study the nanotomography of cementitious materials so it is wise to start with a homogenous, and yet complex phase, before moving to systems related to the hydration of cements.

We included XRD measurements to show that the sample did not have portlandite nor showed evidence of carbonation. The following addition was done on page 7, line 31: "The solid phase was analyzed by XRD and only C-S-H was present. There was no evidence of the presence of portlandite nor of carbonation. The XRD results are shown in Figure 2."

## **Abstract**

Calcium silicate hydrate (C-S-H), is the principal hydration product of Portland cement that mainly contributes to the physical and mechanical properties of concrete. This paper aims to investigate the three-dimensional structure of C-S-H with Ca/Si ratios of 1.0 and 1.6 at the nanoscale using electron tomography. The 3D reconstructions and selected region of interest analysis confirm that the morphology of both C-S-H materials are foil-like structures. The difference between the two materials is the density of elongated structures. C-S-H with Ca/Si ratio 1.6 is clearly composed of denser particles compared to the other C-S-H material due to overlapping of the foil-like structure. Pore analysis shows that C-S-H 1.0 and C-S-H 1.6 have porosities 69.2% and 49.8% respectively. Pore size distribution also reveals that C-S-H 1.0 has pore size range between 0 – 250 nm and C-S-H 1.6 between 0 – 100 nm. The pore network's size of C-S-H 1.0 is significantly larger than 1.6. This study illustrates the capability of using electron tomography to determine the 3D nanoscale structure of cementitious products and to distinguish between C-S-H 1.0 and 1.6.



## 1. Introduction

Portland cement-based concrete has been used as the primary construction material for the modern infrastructure during the past 65 years <sup>1</sup>. The reasons behind its success are attributed to the low cost and global availability of the raw materials used in Portland cement manufacture and concrete production and to its robust, excellent resistance to water, leading to a controllable and high performance behavior <sup>2</sup>. According to the U.S. Geological Survey, the yearly production of Portland cement has increased dramatically in the past century, with an annual manufacture of 4.1 billion metric tons in 2018 <sup>3</sup>, adding 2.9 billion metric tons of CO<sub>2</sub> into the atmosphere and contributing significantly to global warming. Green concrete contains alternative compounds to reduce the carbon footprint during manufacturing process <sup>4,5</sup>. It uses less energy in its production and may contain industrial by-products such as fly ash or blast furnace slag, reducing the generation of CO<sub>2</sub>. The change in existing technologies to produce efficient green concrete requires optimization of the micro/nano structure such that less cement will be required in its manufacture. Some essential hydration products such as calcium silicate hydrate (C-S-H) consist of particles generally a few nanometers in size <sup>6,7</sup>, which significantly contribute to the concrete mechanical behavior <sup>8,9</sup>. Several imaging techniques have been used to characterize the pore network such as transmission electron microscopy (TEM) <sup>10</sup>, Focused Ion Beam/ Scanning Electron Microscopy (FIB/SEM) <sup>11,12</sup>, and X-ray imaging <sup>13</sup>.

The reactive Portland cement powder, mainly consisting of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>, or C<sub>3</sub>S in the cement notation) and dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>, or C<sub>2</sub>S), can be mixed with water to produce

a hardened material through complex reactions that produce the main binding product: calcium silicate hydrate (C-S-H).

C-S-H formed during the hydration process is the key binding phase and primary contributor to the mechanical properties of most hydrated Portland cement and concretes. The C-S-H phases have poorly ordered crystal structures resembling the mineral tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ )<sup>14</sup>. The crystal structure of 14 Å tobermorite consists of complex layers of central octahedral calcium oxide sheets with tetrahedral silicate chains on both sides, which are attached with a periodicity of three tetrahedra (Figure 1). The space between two complex layers contains additional calcium cations and H<sub>2</sub>O. The poor crystallinity and short-range order character of C-S-H have prevented a satisfactory structural description with X-ray diffraction techniques<sup>15</sup>. To better understand the C-S-H structure, a precise 3-dimensional model of C-S-H at the nanoscale is needed.

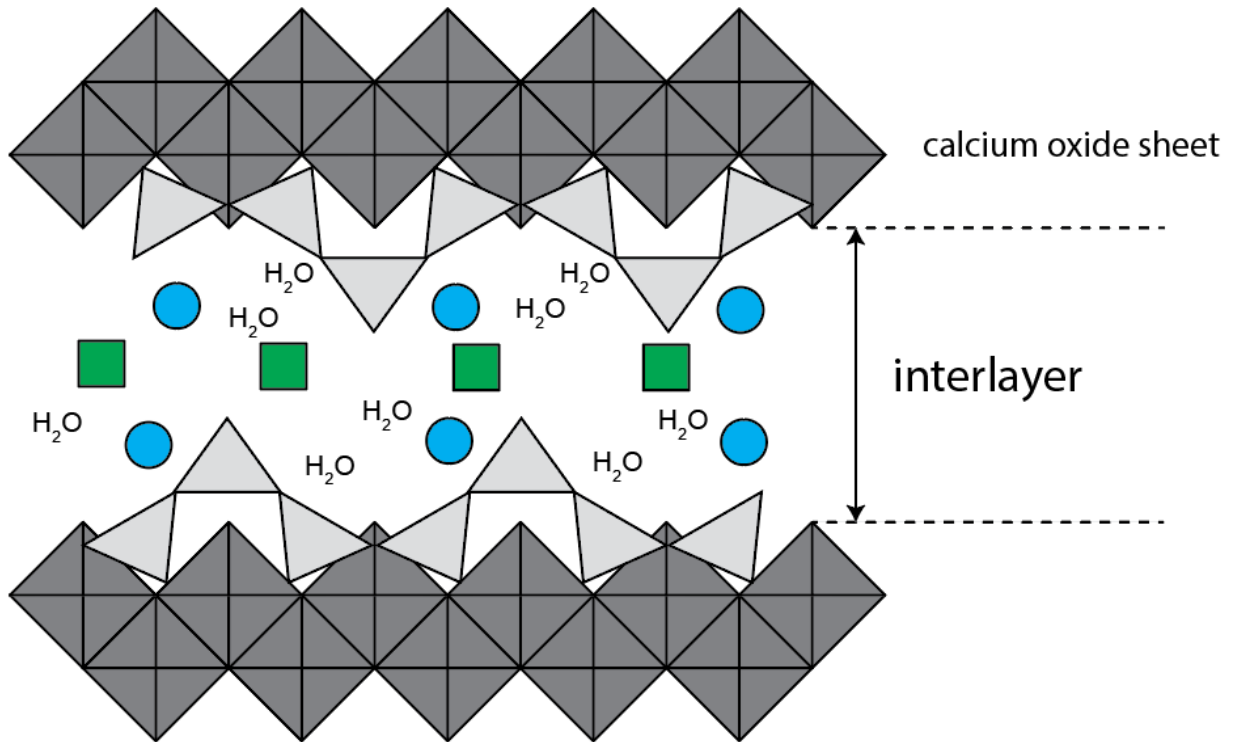


Figure 1. Schematic of the atomic structure of C-S-H. The layers of octahedral calcium oxide sheet are drawn in dark grey, whereas the light grey triangles are  $\text{SiO}_4^{4-}$  tetrahedra. The interlayer contains water and positively-charged species (blue circles and green squares, respectively) that can neutralize the structure (e.g.  $\text{Ca}^{2+}$  and/or  $\text{K}^+$ )<sup>16</sup>

The porosity of C-S-H plays a key role in the durability-based performance of concrete. The size distribution and connectivity of the pores determine the ability of fluids and ions to flow through the network, potentially degrading the material. Both the porosity and the pore size distribution are determined by the nanostructure of C-S-H. To date, there have been several studies on the nanostructure and morphology of a variety of Portland-cement-based systems<sup>17–21</sup>. While such studies answer many questions, such as phase development in the system, the results of these techniques, including scanning electron microscopy are distilled into two-dimensional (2D)

information that provide only limited, often inferred, volumetric information of the nanostructure, and the pore network for a bulk paste. Simulations can also be used for these investigations<sup>22, 23</sup>. Due to the complex nature of cement hydration and the sensitivity of the products formed, only a few studies of the three-dimensional (3D) structure at the nanoscale have been completed<sup>24</sup>.

Transmission electron microscopy (TEM) can image specimens at very high resolution. It is widely used in materials science including observations of cement, for example, to observe the morphology of hydration products of cements<sup>17, 25–28</sup>, to characterize the effect of mineral admixtures, such as metakaolin<sup>29</sup>, on the hydration reactions<sup>30</sup>. Electron tomography uses TEM images to reconstruct the 3D structure of an object from a series of projection images from different viewing angles. This method has been applied to many porous systems in materials science such as in imaging of nanoscale dendrites<sup>31</sup>. A recent study<sup>10</sup> used electron tomography to investigate the nanostructure and pore network of C-S-H and found two separate networks of pores that are most likely attributed to two particles of the same phase in different orientations. Due to sensitivity of C-S-H to the electron beam, beam damage still occurred and improvements are needed to develop a robust protocol for TEM tomographic studies of cementitious materials. To acquire a tomographic tilt series, the sample is rotated and a series of 2D projection images is measured at different tilt angles<sup>32</sup>. This research studied synthetic C-S-H instead of hydrated C3S because of the desire to have only one phase in the system. The 3D reconstruction method used in this experiment is the simultaneous iterative reconstruction technique (SIRT) method<sup>33</sup>. This study aims to investigate and compare the 3D structure of C-S-H with Ca/Si ratios of 1.0 and 1.6

at the nanoscale using 3D electron tomography. The resulting information of pore analysis is critical for the development of a new generation of optimized green cement.

## **2. Experimental Methods**

### 2.1 Materials

The samples in this work is the same materials to this publication<sup>34</sup>. C-S-H was synthesized by mixing calcium oxide (CaO) and silica fume (SiO<sub>2</sub>) at Ca/Si molar ratios 1.0 (C-S-H 1.0) and 1.6 (C-S-H 1.6) with water. The water to solid ratio of both samples is equal to 45. CaO was obtained by burning calcium carbonate (CaCO<sub>3</sub>, Merck, pro analysis) at 1000 °C for 12 hours. SiO<sub>2</sub>, provided by Aerosil 200, Evonik, was chosen for its high specific surface area. The synthesis process and all the sample handling were carried out in a N<sub>2</sub> filled glovebox to prevent CO<sub>2</sub> contamination. The samples were stored in 100 mL high-density polyethylene (HDPE) containers placed on a shaker moving at 100 rpm and equilibrated at 20 °C. For each equilibration time, a separate sample was prepared. After equilibrated for 182 days, the solid and the liquid phase were separated by filtration using a 0.45 µm nylon filter. The solid phase for both Ca/Si ratio was analyzed by X-ray diffractometry (XRD) and only C-S-H is observed. There is no portlandite nor evidence of carbonation. The XRD results are shown in Figure 2.

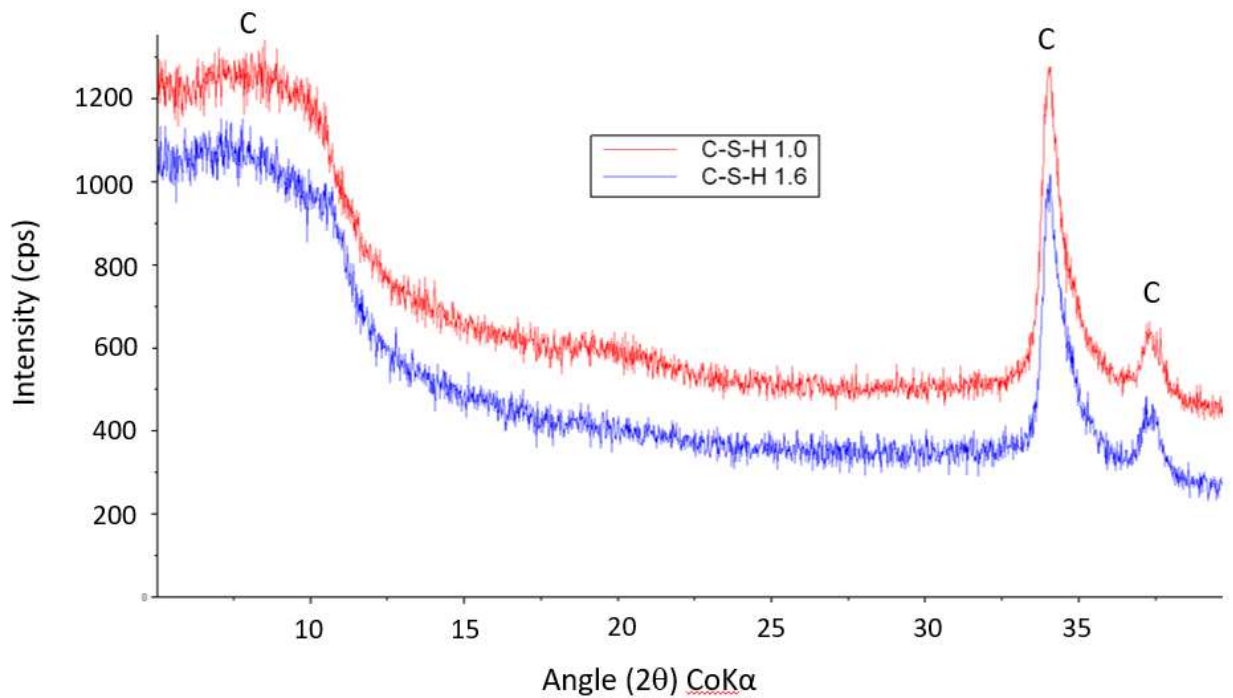


Figure 2. XRD results of C-S-H 1.0 (red line) and C-S-H 1.6 (blue line). Three main peaks of C-S-H are at around 8°, 34° and 37° 2 $\theta$ .

## 2.2 Electron Tomography

The electron tomography requires several steps including sample preparation, data acquisition, data alignment, data reconstruction, and object visualization. The C-S-H sample was suspended in ethanol and deposited on a 200 mesh ultra-thin copper hexagonal grid with carbon film support (CF200H-Cu-UL, Electron Microscopy Sciences). 10 nm gold fiducial markers (Aldrich) were deposited to aid in tilt series alignment. Data acquisition was acquired on a Tecnai 12 TEM, operating at 120 kV. The C-S-H 1.0 was rotated around one axis from -40° to +70° with 1° angle increment producing 111

projection images. The C-S-H 1.6 was rotated around one axis from  $-60^\circ$  to  $+60^\circ$  with  $1.56^\circ$  angle increment, producing 76 projection images. All images were acquired automatically using the SerialEM software.

The alignment, reconstruction were done by using the IMOD software<sup>35</sup>. Visualization of the reconstructed volume was done either by volume or surface rendering. The volume rendering was optimized by manually adjusting the color and the transparency. The visualizations were done using the Tomviz 1.8 software<sup>36</sup>. IMOD and Tomviz are open source software for volumetric data processing and visualization, especially for electron tomography.

### 2.3 Model analysis

The geometrical information of all particles (ROIs) was obtained from the Tomviz software. The selected ROIs are cropped and object sizes were measured using the ruler function". The pore analysis of the reconstructed models was obtained by using the Fiji/ImageJ software. The segmentation, which allows to isolate pores with respect to C-S-H, is based on global thresholding with the Otsu algorithm<sup>37</sup>. The porosity is calculated based on the ratio of the white area (particles) divided by the total area. The continuous pore size distribution (CPSD) and continuous pore size distribution with mercury intrusion porosimetry simulation (CMIP) were determined by using the Xlib plugin<sup>12</sup> in ImageJ. For CPSD, the pore space is separated into regions of different radii that can be filled with objects of different radii<sup>12</sup>. The sizes of these radii are attached to the respective locations. For CMIP, same PSD definition as for the CPSD. However, the balls of different radii are intruded into the pore volume from one of the faces of the 3D image cube or from one of the edges of the 2D image, respectively. This definition of the PSD corresponds to the data that are collected by mercury intrusion porosimetry (MIP)<sup>12</sup>.



### 3. Results

Beam damage is a major problem in electron tomography. Our particles were sensitive to beam irradiation so we were careful to limit the dose and to check for damage before 3D reconstruction. A beam dose of  $5000 \text{ e}^-/(\text{nm}^2 \text{ s})$  is suitable for this research. The example of effect of beam damage are shown in Appendix A.

Brightfield TEM images of two C-S-H particles of each ratio are given in Figure 3. We can see that the C-S-H morphology in the system is a combination of foil-like structures and elongated (fiber-like) structure. The C-S-H 1.6 appears to have a denser structure than C-S-H 1.0. However, these particles have a complex 3D morphology and simple 2D TEM projection images are insufficient to describe the morphology.

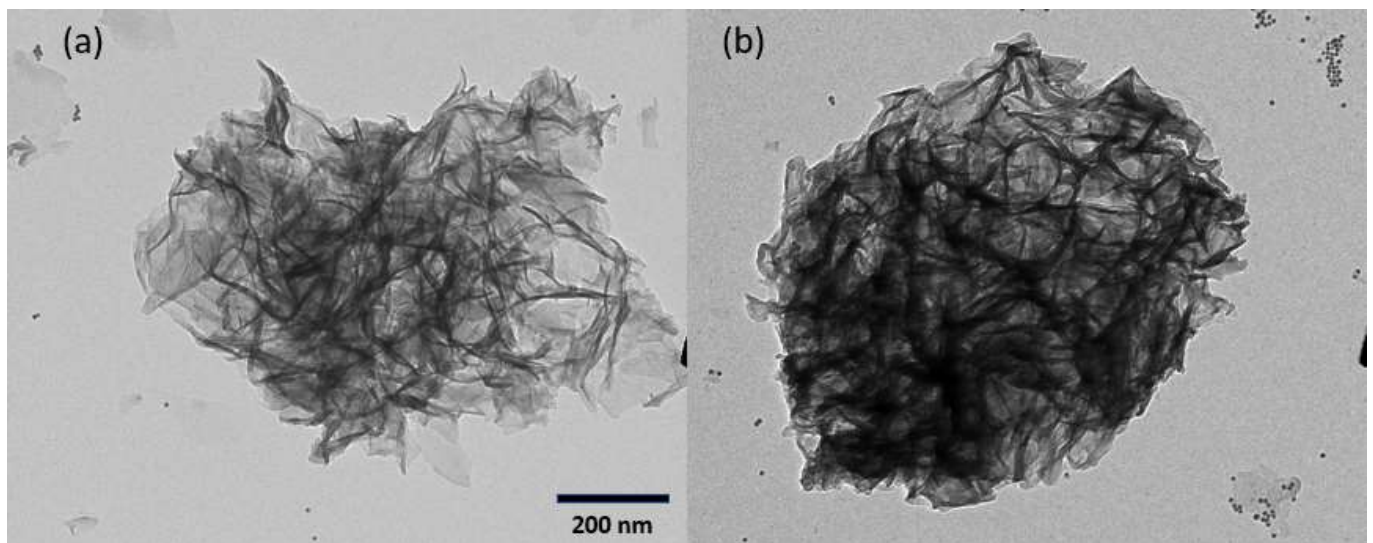


Figure 3. Two 2D images of C-S-H with Ca/Si ratio 1.0 (a) and ratio 1.6 (b) at  $0^\circ$  rotation.

The morphologies of C-S-H are determined by the structure and chemical composition and/or kinetically of the hydration reaction<sup>38</sup>. Figure 4 shows isosurface renderings of the reconstructed 3D structure of C-S-H 1.0 and 1.6. The voxel size of both models is 1.14 nm. The morphologies of both C-S-H are made up of elongated, connected structures with different orientations. The C-S-H 1.6 also shows a higher density of these structures compared to C-S-H 1.0.

Next, we will take a closer look at the elongated regions of interest (ROIs) to investigate the underlying morphology at higher resolution. Elongated ROIs refer to foil-like structures that are perceived as fibers when observing the original 2D projection images of such structures. Five ROIs were selected for each sample (Figure 5). The particles sit randomly on a TEM grid. The original projection direction with the grid approximately flat (Figure 3 and 4) is arbitrary set as 0-degree rotation. Then we rotate 90° around the parent fiber direction. Each ROI is shown in 0° rotation and 90° rotation (Figure 6 for C-S-H 1.0 and Figure 7 for C-S-H 1.6). The actual geometry and aspect ratios of these ROIs are shown in Table 1. The thickness (a) of each ROI can be determined from the orientation looking along the plate. The width (b) and length (c) can be determined from the direction normal to the plate. The thickness (a), width (b) and length (c) are represented by red lines in both Figure 6 and 7. Both 2D aspect ratios have high values (more than 5) indicating that all of them are elongated platelets, not fibers.

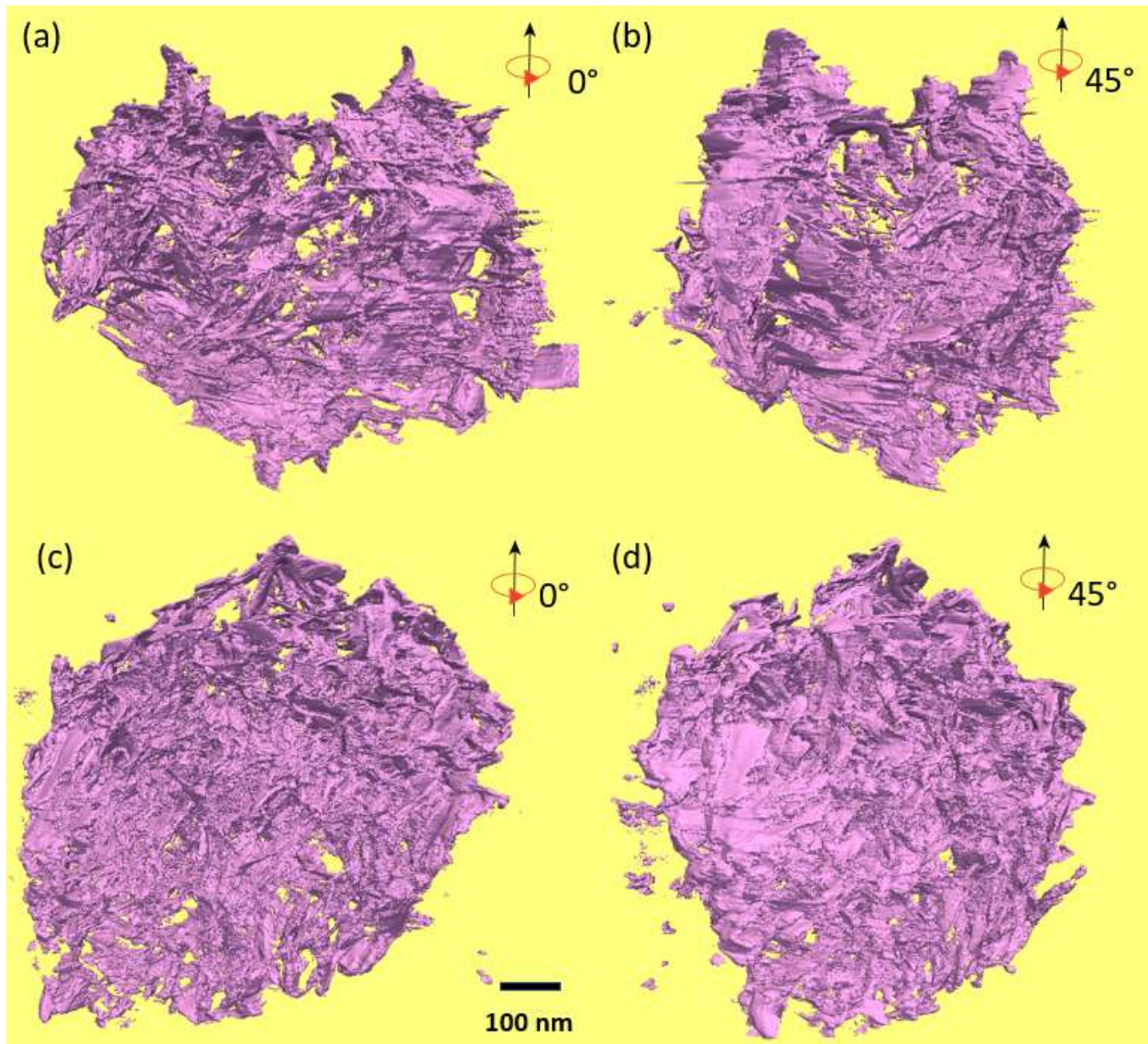


Figure 4. The 3D reconstruction of C-S-H 1.0 (a-b) 1.6 (c-d) at 0° and 45° rotation.

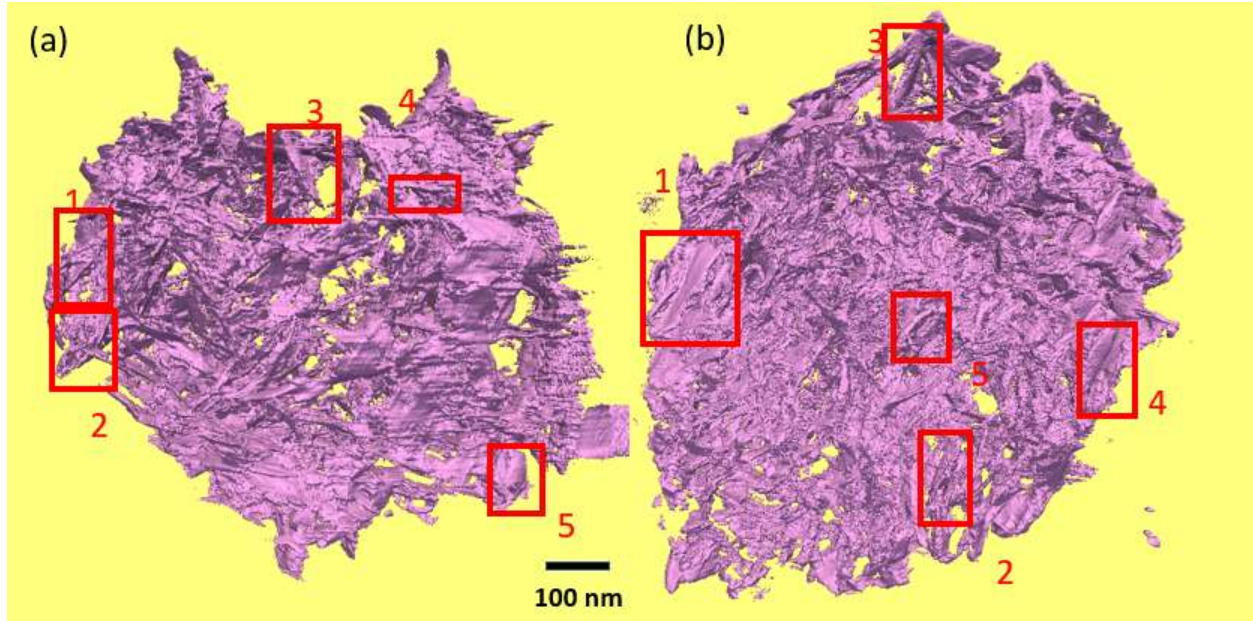


Figure 5. Five selected elongated ROIs of C-S-H 1.0 (a) and 1.6 (b) indicated by red rectangles.

Sample					
C-S-H 1.0	Thickness (a) (nm)	Width (b) (nm)	Length (c) (nm)	2D Aspect ratio (b/a)	2D Aspect ratio (c/a)
Particle 1	7.15	73.00	149.00	10	21
Particle 2	7.76	84.89	171.52	11	22
Particle 3	6.06	76.89	106.24	13	18
Particle 4	6.32	68.11	78.97	11	12
Particle 5	5.46	62.10	99.37	11	18
C-S-H 1.6	Thickness (a) (nm)	Width (b) (nm)	Length (c) (nm)	2D Aspect ratio (b/a)	2D Aspect ratio (c/a)
Particle 1	8.13	58.85	141.06	7	17
Particle 2	4.27	56.05	83.16	13	19
Particle 3	10.19	49.82	156.05	5	15
Particle 4	4.94	42.50	94.80	9	19
Particle 5	3.83	37.63	76.40	10	20

Table 1. Actual geometry and aspect ratio of selected ROIs of both samples.

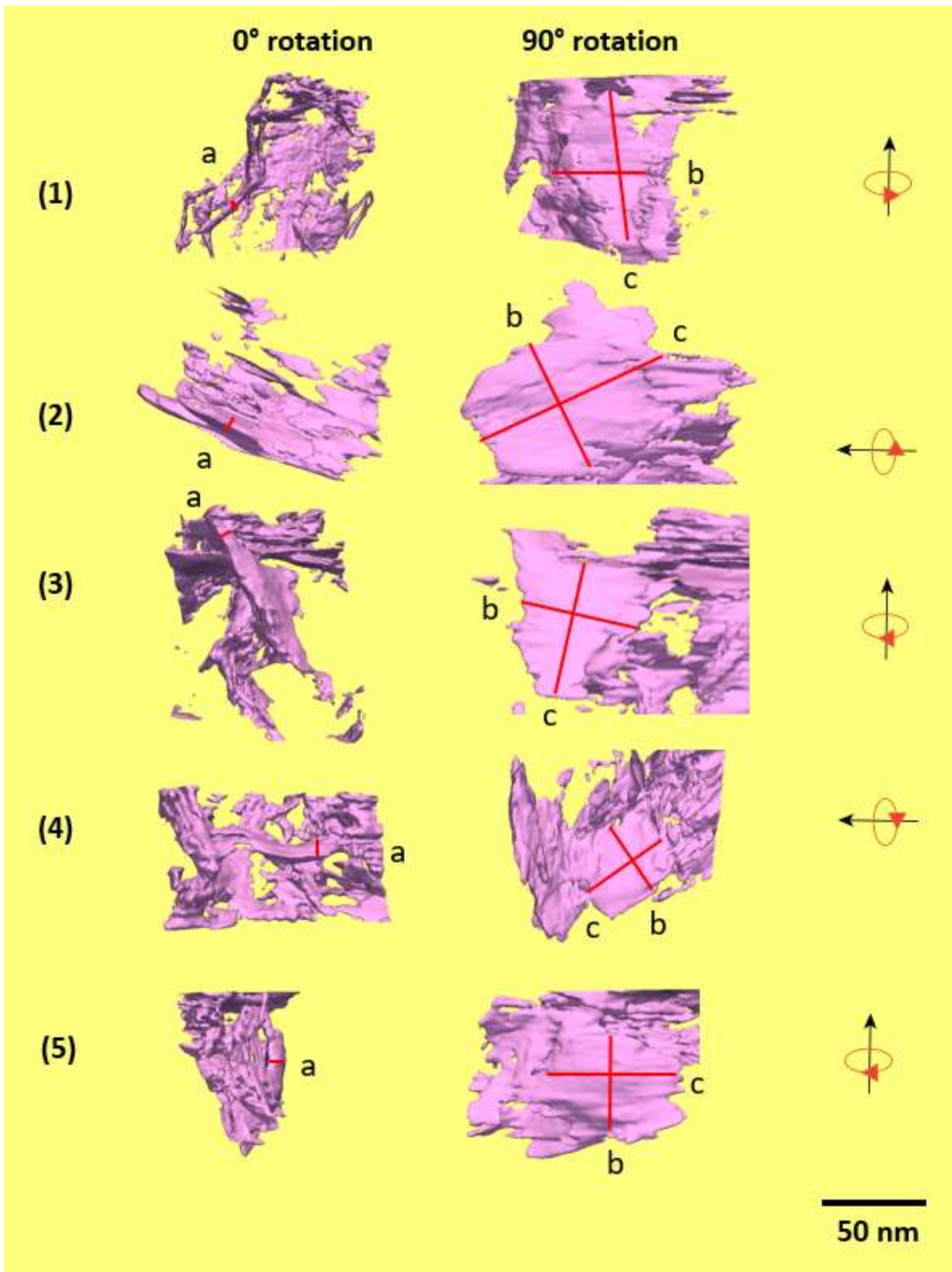


Figure 6. Morphologies of five selected elongated ROIs of C-S-H 1.0

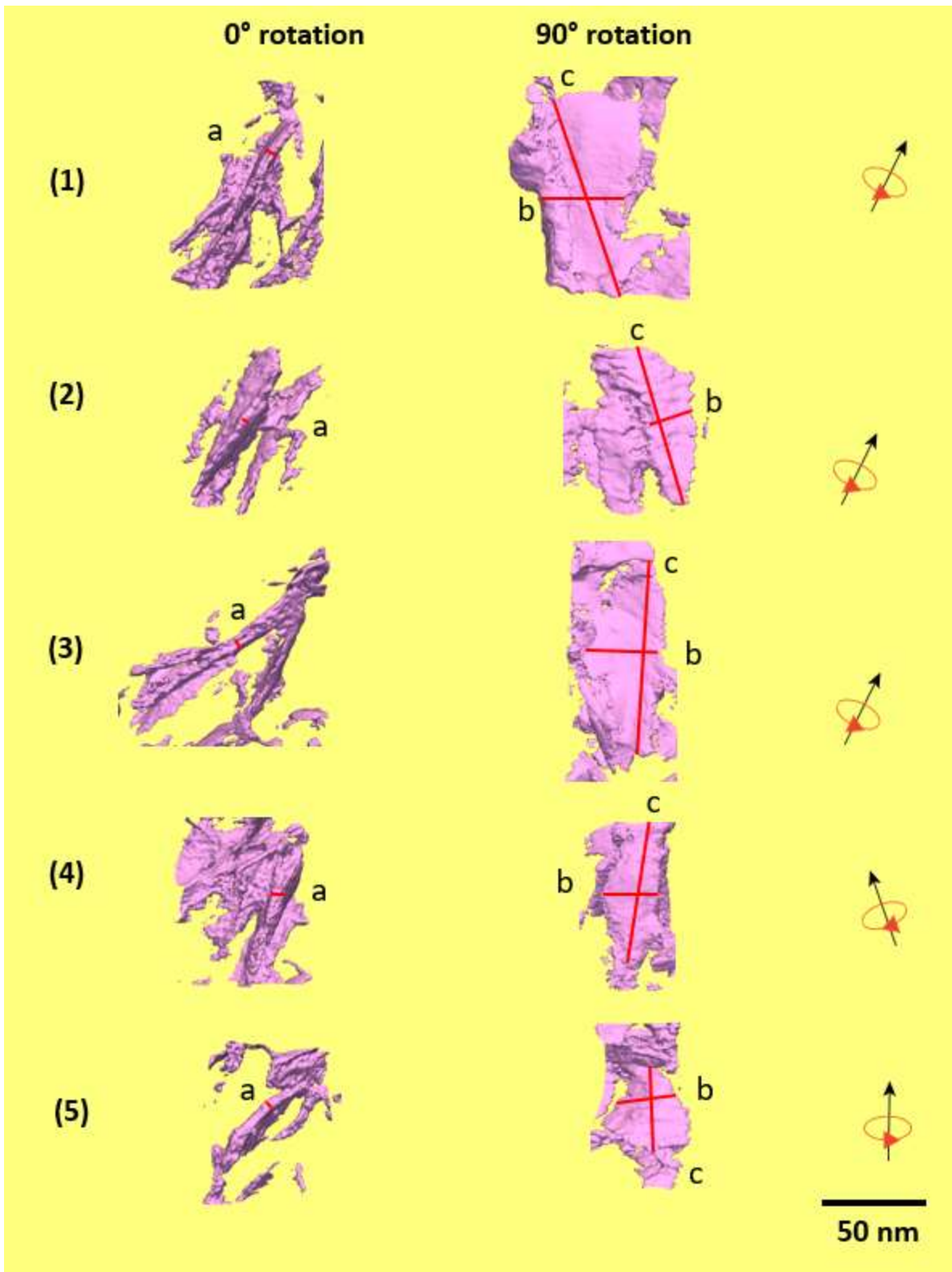


Figure 7. Morphologies of five selected elongated ROIs of C-S-H 1.6

The pore analysis shows that C-S-H 1.0 and C-S-H 1.6 have porosities 69.2% and 49.8% respectively. Continuous pore size distribution (CPSD) and Continuous pore size distribution with MIP simulation (CMIP) was analyzed in this research (Figure 8). Both CPSD and CMIP reveal that C-S-H 1.0 has pore size range between 0 – 250 nm and C-S-H 1.6 between 0 – 100 nm. For CPSD (Figure 8a), the average pore size of C-S-H 1.0 and 1.6 are 72.0 nm and 26.4 nm respectively. However, C-S-H 1.6 has a high number of small pore volume less than 50 nm. For CMIP (Figure 8c), The average pore size of C-S-H 1.0 and 1.6 are 57.1 nm and 16.0 nm respectively. C-S-H 1.0 has 3 dominant peaks at 24.2, 28.6 and 41.8 nm. while C-S-H 1.6 has only one dominant peak at 13.2 nm.

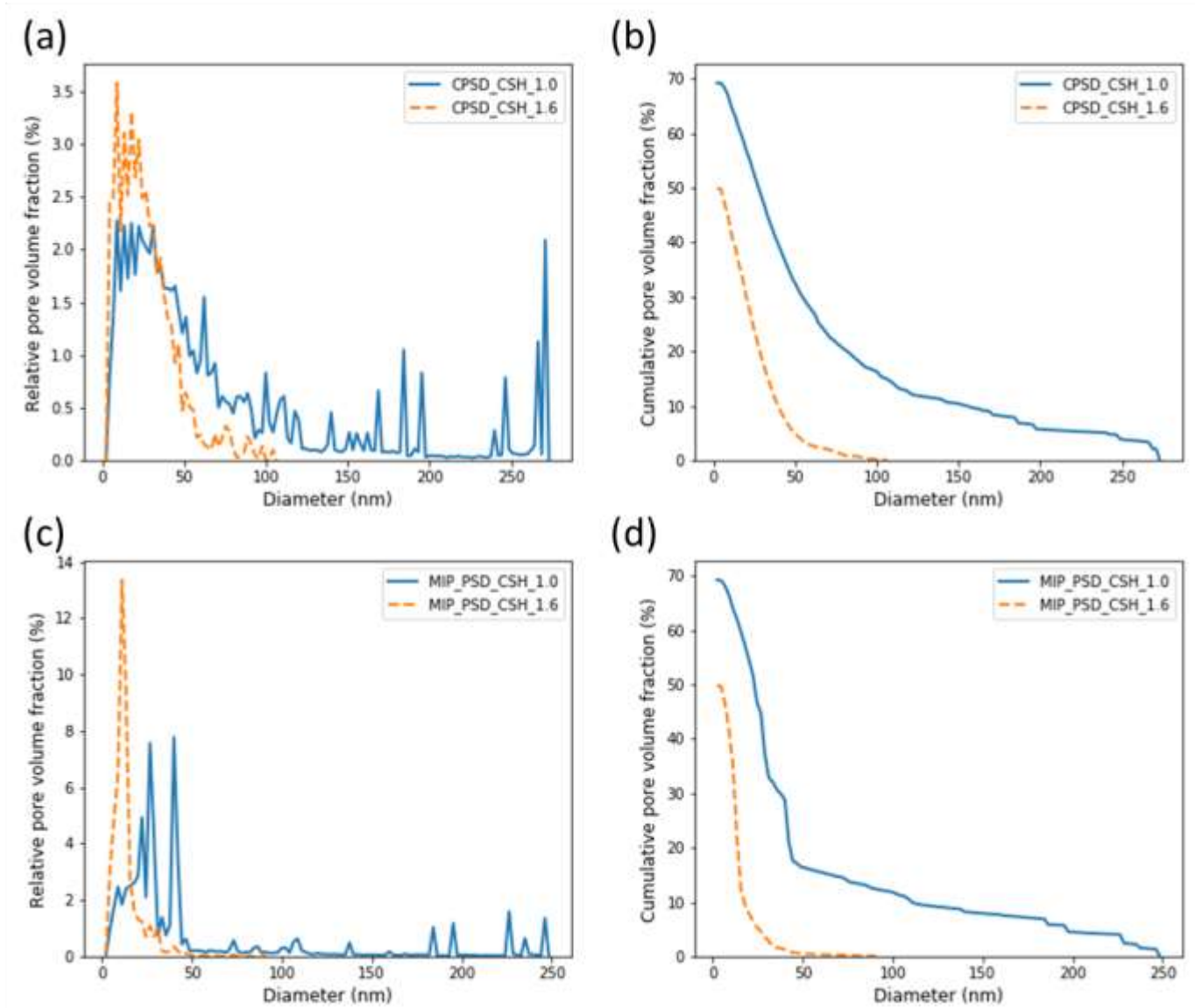


Figure 8. Pore size distributions of both samples: (a) Continuous pore size distribution (CPSD), (b) Cumulative continuous pore size distribution (CCPSD), (c) Continuous pore size distribution with MIP simulation (CMIP),(d) Cumulative continuous pore size distribution with MIP simulation (CCMIP).



## Discussion

From overviews of 2D images and 3D reconstructions, both samples have morphologies of elongated and foil-like structures. However only when the selected elongated structures were tilted, they clearly display that the elongated structures are also foil-like structures and not fibers. The real C-S-H morphologies for both Ca/Si ratio 1.0 and ratio 1.6 in the system are all foil-like structures, with no evidence for fibrous structures in the both samples. The C-S-H 1.6 sample had denser particles than C-S-H 1.0. The denser structures of C-S-H 1.0 come from the overlapping of the foil-like structure. However, the morphologies of C-S-H that came from cement paste or hydrated  $C_3S$  depend on the lime concentration. Low lime concentrations (Ca/Si ratio  $< 1.4$ ) during synthesized will yield foil-like structures. High lime concentration (Ca/Si ratio  $> 1.6$ ) will yield fibrous structures<sup>39</sup>.

The pore analysis in ImageJ, which was based on segmentation by Otsu algorithm, reveals that C-S-H 1.0 has higher porosity than C-S-H 1.6. The cumulative pore size distribution for both CPSP and CMIP (Figure 7b, 7d) also indicate that C-S-H 1.0 has higher porosity than C-S-H 1.6. The peak pore size for C-S-H 1.6 (Figure 7a, 7c) ranges from 0 to 50 nm while for C-S-H 1.0 it ranges from 0 to 250 nm. There are also peaks with pore size larger than 100 nm for C-S-H 1.0 (Figure 7a, 7c) which means, the pore network's size of C-S-H 1.0 is significantly larger than of C-S-H 1.6.

TEM tomography is a powerful technique to illustrate the 3D reconstruction of microstructures. However, there are some limitations. First, fiducial markers are required. To align the data set, high-contrast reference points are needed. In this experiment 10 nm gold particles were used as a fiducial marker. Second, we can reach the magnification 18,500X with equal to the beam dose

of is  $5000 \text{ e}^-/(\text{nm}^2 \text{ s})$  for both C-S-H 1.0 and 1.6. For these magnifications, it is difficult to analyze the very small intralayer pore structure. To go to higher magnification, Cryo-TEM is suggested because it can reduce the beam damage. Scanning transmission electron microscope (STEM) is another method that may work. STEM satisfies the incoherent imaging approximation in which diffraction and phase contrast is decreased, and the image intensity depends on the sample thickness and the atomic number<sup>40</sup>. Also, the digital control of the beam in STEMs can minimize radiation damage<sup>41</sup>.

For the 3D nanostructure analysis based on TEM images, These two samples are synthetic samples because of the desire to have only one phase in the system so if the sample of Portland cement is analyzed, the image reconstruction and segmentation will be harder to do accurately because there are many phases in the system. In previous publications<sup>42, 43</sup>, the authors proposed an automated image processing pipeline with machine-learning based classifiers, which achieved accurate multiphase segmentation results for the 3D X-ray micro-tomography images of ancient Roman concrete samples. Similar methods can be used for the image segmentation of TEM tomography of real samples of Portland cement in the future study.

## **Conclusion**

This study uses TEM tomography with simultaneous iterative reconstruction technique (SIRT) to generate the 3D reconstruction of C-S-H 1.0 and 1.6 microstructures which can be found in Portland cement paste or C<sub>3</sub>S paste. The projection images were aligned using the 10 nm gold nanoparticles as references. The highest beam dose that can achieve this with a little beam damage is 5000 e<sup>-</sup>/(nm<sup>2</sup> s) for both Ca/Si ratio 1.0 and 1.6. To obtain higher magnification and improve the quality of the reconstruction, Cryo-TEM or STEM may provide better results. The 3D reconstructions and selected ROI analysis confirm that the morphology of both C-S-H 1.0, and 1.6 are foil-like structures. The difference between two Ca/Si ratios is the density of particles. The C-S-H 1.6 shows clearly more densely packed structures compared to C-S-H 1.0 due to the overlapping of the foil-like structure. The pore analysis shows that C-S-H 1.6 has lower porosity than C-S-H 1.0. The CPSD and CMIP reveal that C-S-H 1.0 has pore size between 0 – 250 nm and C-S-H 1.6 between 0 – 100 nm and C-S-H 1.0 has pore network's size larger than C-S-H 1.6. TEM tomography shows the capability to determine the 3D nanostructure and pore networks of C-S-H and in the future related cementitious materials such as calcium alumino silicate hydrate (C-A-S-H) should be investigated.

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## Appendix A. Example of beam damage

Figure 9b shows the serious beam damage. The whole particle is almost destroyed. Figure 9d shows almost no beam damage. The particle is almost the same.

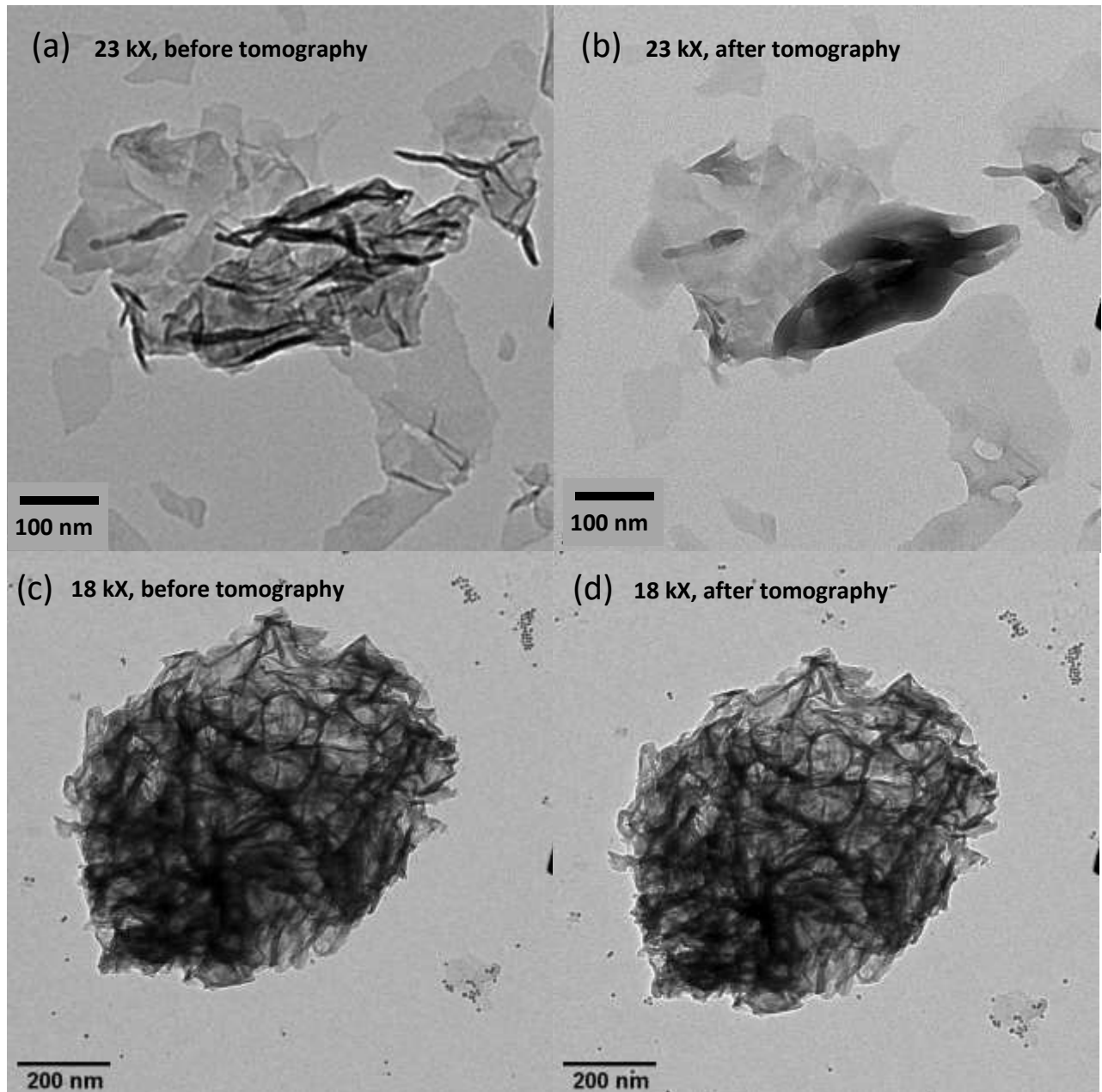


Figure 9. Compare the 2D images of C-S-H 1.6 at 0° rotation (a) before and (b) after tomography at 23 kX magnification. (c) before and (d) after tomography at 18 kX magnification.

**Appendix B. Example of image segmentation from otsu algorithm**

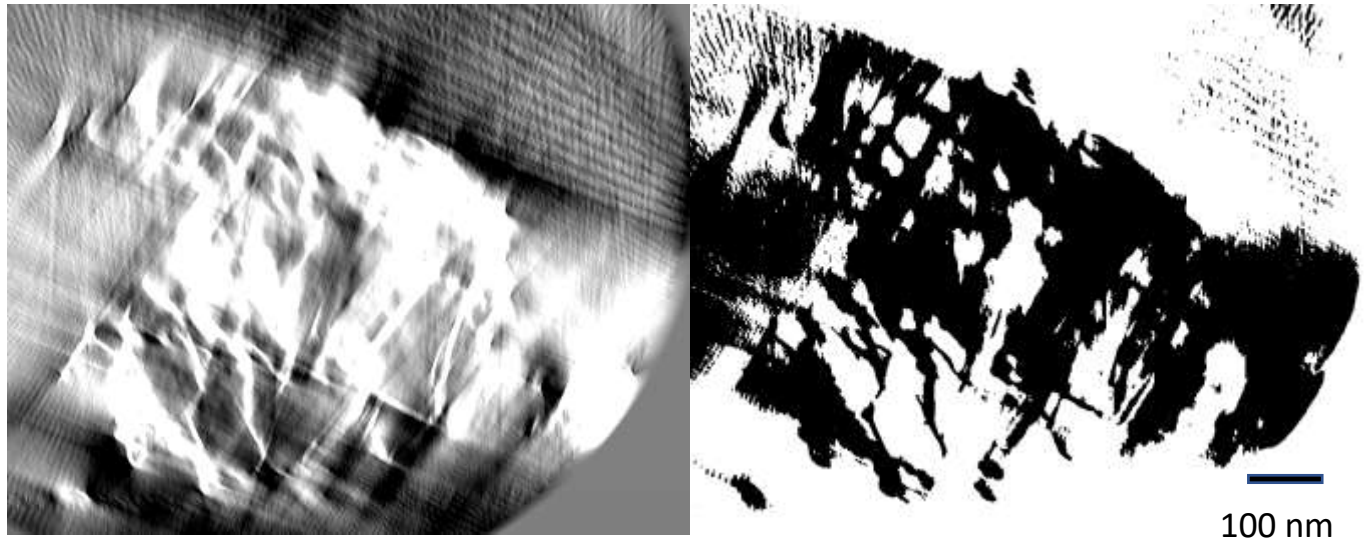


Figure 10. Example of segmentation of a greyscale image (left) of C-S-H 1.0 with otsu algorithms (right). The segmented black phase in the segmented image is C-S-H (solid phase) and the segmented white phase is pore phase.

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