



## Investigating the pore structure of the calcium silicate hydrate phase

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### ABSTRACT

The physical properties of the calcium silicate hydrate phase (C-S-H) greatly impact material strength and durability of cement-based materials. However, despite its widespread use and influence on material stability, there is still debate concerning its nanostructure. In this paper, the pore structure of C-S-H was characterized by analyzing focused ion beam prepared lamellas from a model tricalcium silicate clinker cement paste using scanning transmission electron microscopy (STEM) performed with a scanning electron microscope (SEM) for measurements at 30 keV and a transmission electron microscope (TEM) operating at low primary electrons energy (80 keV). The composition was mapped in the SEM using energy-dispersive X-ray spectroscopy (EDX). These investigations were accompanied by argon adsorption measurements using non-local density functional theory (NLDFT) models to calculate the pore size distribution. Mercury intrusion porosimetry (MIP) was used to investigate macropores. The STEM investigations performed at 30 and 80 keV both reveal a sponge-like pore structure built up by 0.7–4.0 nm thin C-S-H foils. The pore sizes range between 2 and 10 nm with a dominance of 5 nm wide pores. These results are in line with the pore size distribution determined with argon adsorption, which predominantly found 4.6 nm wide pores. The similar pore width distributions in STEM and gas adsorption validates the gas adsorption measurements and points towards minimal electron beam damage occurring during observation and analysis.

### 1. Introduction

The calcium silicate hydrate phase (C-S-H), along with calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), is largely responsible for material strength and durability of cement-based materials. It is the hydration product of calcium silicate clinkers, which are the major components of Portland cement. Concrete made from this cement is the most widely and diversely used material in our infrastructure today. Here, it has to endure varying application and environmental impacts, which can cause structural and chemical changes that affect material performance often in the first decades of service-life. The processes at work are closely linked to the nanostructure of this complex composite material [1]. For example, the pore structure of C-S-H, as well as its relationship with pore water, is suggested to play a part in shrinkage and creep of cement paste [2,3]. Understanding and evaluating these processes is detrimental for materials that are more durable. This, however, requires fundamental and detailed information on the structure of C-S-H on the nanoscale in order to develop materials with greater performance and

increased durability, as well as innovations based on functionalizing the C-S-H's interface. As of now, the nanostructure has not been fully resolved [4]. Mercury intrusion porosimetry (MIP), a common approach to characterize the pore structure of cement-based materials, can theoretically analyze nanometer ( $\sim 3$  nm) to almost millimeter wide pores given the appropriate mercury pressure [5]. However, these MIP results appear to be dependent on the relative humidity of the material [6,7]. Some authors have called pore size distributions measured with MIP into question because there is evidence to suggest the required conditions for this method cannot be met [8,9]. Furthermore, it might be more reliably for the larger meso- to macropores since high pressures often cause damage to the pore structure [10,11]. Gas adsorption measurements are frequently used to gain insight into the nanometer small micropores (0.35 nm) as well as small macropores (100 nm), which covers the necessary range of pore sizes for C-S-H [4]. However, this technique requires validation since it cannot distinguish between the porosities of various phases present in a multi-component sample.

Many models have been put forth throughout time in order to

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explain the chemical and structural properties of C-S-H, as well as the interactions with water [12–17]. These models are in part based on gas adsorption measurements with water, nitrogen and other gases, as well as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). Most models show C-S-H to have a gel porosity on the nanoscale. Experimental research, however, is hindered by C-S-H's heterogeneous structure, nanoscale morphology and short-range order. Transmission electron microscopy (TEM) is one of the few techniques where textural, structural and chemical characteristics can be analyzed with the required resolution. In conventional TEM (CTEM), the gel porosity is not visible, which is in conflict with the previously mentioned gas adsorption measurements. Instead, the nanostructure has a fine-fibrillary texture consisting of nanometer sized intertwined foils, which can be locally denser packed [18–22]. Henderson and Bailey [23] observed a honeycomb-like microstructure. Their micrographs of the interfacial C-S-H consist of 5 to 110 nm wide spherical and oval pores, which are built by curved or straight foils of 1 nm and 2 nm thicknesses. Richardson and Groves [24] analysis of tricalcium silicate paste found regions with low and high density C-S-H. They described C-S-H in large pores as having a fibrillary directional character whereas C-S-H in small pores is more tightly packed, fine and homogeneous. They also saw a coarsening during preparation and observation and attribute this to partial dehydration. Others have also debated whether some aspects are preparation and observation artefacts or, indeed, intact material features. Further, doubts have in the past arisen in related fields such as thin crystal analysis about the reliability and reproducibility of results due to possible damage during observation [25]. Especially C-S-H is reported to have a low stability in the electron beam [26]. Some discussed artefacts are rounding of edges and formation of bubbles [27,28]. The latter of the two is supposed to cause a coarsening of the pore structure and was reported to occur when volatiles are hindered in their escape.

These possible artefacts and the discrepancies between gas adsorption measurements and CTEM show that there still is a lack of knowledge concerning the pore structure of C-S-H. Therefore, this study focuses on the analysis of C-S-H with scanning transmission electron microscopy (STEM) and argon adsorption measurements using non-local density functional theory (NLDFT) models to gain insight into the pore structure and to validate in particular pore size distributions determined with gas adsorption.

## 2. Experimental

For this study, a model cement paste was made from tricalcium silicate clinker and deionized and degassed water ( $w/s = 0.5$ ). The clinker was sintered from a mixture of silica gel (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and calcium carbonate (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) with a ratio of 1 g: 5 g. This mixture was filled and pressed into a platinum crucible and placed into a blast furnace four times. The first burn process was at 1000 °C for 10 h. The following three burn processes were performed at 1550 °C for 12 h. At the end of each burn process, the crucible was taken out of the hot blast furnace and as soon as possible mortared and pressed again into the crucible for the next burn cycle. The final product consisted of triclinic tricalcium silicate  $\text{Ca}_3\text{SiO}_5$  (PDF 31-0301), some dicalcium silicate  $\text{Ca}_2\text{SiO}_4$  (PDF 33-0302) and low amounts of calcium oxide CaO (PDF 82-1690) as determined with powder X-ray diffraction (Bruker D8 Advance with a LynxEye Position Sensitive Detector). The cement paste was hydrated in plastic  $7.0 \times 1.5$  cm tubes. The samples were sealed with plastic paraffin film in order to protect the cement paste from drying and carbonation and stored at room temperature in the laboratory. After 10 days, 1 mm discs were cut from the middle of the hardened cement paste cylinder. One of the disks was gold coated for focused ion beam preparation (FIB). Using the FIB technique in a FEI Dual Beam Strata 400S, two  $15 \mu\text{m} \times 10 \mu\text{m}$  electron transparent lamellae were cut from this sample. On top of the lamella 1  $\mu\text{m}$  thick

platinum frames was deposited for stability and protection during the milling and thinning process. After preparation, one lamella was studied in the FEI Dual Beam Strata 400Sat 30 kV using STEM with the high-angle annular dark-field detector (HAADF). This detector is sensitive to the atomic number and local density in the sample [29]. The second lamella was analyzed with the aberration corrected transmission electron microscope (TEM) FEI Titan 80-300 (FEI) with HAADF-STEM at an acceleration voltage of 80 kV. The C-S-H morphology as well as its pore width distribution was studied and measured out of STEM images made at 30 and 80 kV. The composition was investigated with energy-dispersive X-ray spectroscopy (EDX) mapping with a Quantax silicon drift detector (Bruker) in the Strata 400S with a measurement time of 6 min. These electron microscopic studies were accompanied by argon adsorption using Quantachrome's Autosorb-1 MP. In preparation for gas adsorption measurements, samples were in the outgassing station at 95 °C for 16 h. The determined absorption isotherms were modelled with nonlocal density functional theory (NLDFT) analysis using the zeolite/silica equilibrium transition kernel at 87 K based on a spherical and cylindrical pore model. Further, mercury intrusion porosimetry (MIP) was performed with the Pascal 140/440 (ThermoFinnigan) at 200 MPa to gain insight into the capillary pores. For MIP, the samples were dried at 50 °C until they reached a constant mass. Higher mercury pressures for small mesopores were not applied due to the risk of material damage.

## 3. Results

### 3.1. Low Energy STEM in SEM and EDX Analysis

Multiple phases can be distinguished by their morphology in the  $15 \mu\text{m} \times 10 \mu\text{m}$  FIB lamellas. The sample, which is shown in Fig. 1, consists of a homogeneous dense phase in the lower part of the lamella, whereas the top part is made up of a porous phase. Six pores spanning 1–4  $\mu\text{m}$  are at this boundary. A few macropores are visible within the porous phase, too. Further, vertical grooves, called curtaining, which are areas where the ion beam cut more deeply into the material, can clearly be seen. In HAADF-STEM images of the thin area of the lamella, the morphology of the porous phase appears molten together in these lines. A  $1.5 \times 1.0 \mu\text{m}$  large area was analyzed with EDX. It features the boundary of these two phases. In the bright field STEM image, which was taken after the EDX measurement in Fig. 1a), the mapping area is indicated by the black rectangle. The dashed line marks the interface of the two phases. The highly porous material consists of Si and Ca (c.f. Fig. 1b) and c)) and can, based on this, be identified as C-S-H. The lower phase only consists of Ca (c.f. Fig. 1c)), which points towards portlandite ( $\text{Ca}(\text{OH})_2$ ).

### 3.2. STEM Analysis with TEM at Reduced Energies

HAADF-STEM analysis of the lamella in the Titan 80–300 shows the complex pore structure of the cement paste. The lamella consists of two 4 and 5  $\mu\text{m}$  large macropores in the middle, which are surrounded by mostly C-S-H and portlandite. The portlandite grains range in size from 1 to 2  $\mu\text{m}$ . Their boundary with C-S-H is marked by a wavy shape. Some individual sword-shaped needles of C-S-H can be seen at the edge of the macropores with a length of 100 to 400 nm. Behind this rim zone of the capillary pores, in multiple areas of the lamella, the C-S-H morphology changes to a more heterogeneous structure. There is a predominance of a honeycomb or sponge-like pore structure, which is built up by mesopores. Pores close to the boundary with portlandite stretch 50–200 nm resulting in a low-density pore structure. This is contrasted by the dense fine meshed pore structure visible in other areas. These dense regions span approximately 100 nm. Fig. 2 shows an area consisting of C-S-H at the edge of a large macropore. The pores have a round and oval shape when viewed in a cross section (Fig. 2). From other directions, they appear to be more elongated (c.f. top left area in

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