UTILIZING MODERN FIB/SEM TECHNOLOGY AND EDX FOR THREE-DIMENSIONAL IMAGING OF HYDRATED ALITE AND ITS PORE SPACE

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ABSTRACT: The exploration of cementitious materials using scanning electron microscopes (SEM) is mainly done using fractured or polished surfaces. This leads to high-resolution 2D-images that can be combined using EDX and EBSD to unveil details of the microstructure and composition of materials. Nevertheless, this does not provide a quantitative insight into the three-dimensional fine structure of for example C-S-H phases.

The focused ion beam (FIB) technology can cut a block of material in thin layers of less than 10 nm. This gives us a volume of 1000 µm³ with a voxel resolution of down to 4 x 4 x 10 nm³. The results can be combined with simultaneously acquired EDX data to improve image segmentation. Results of the investigation demonstrate that it is possible to obtain close-to-native 3D-visualisation of the spatial distribution of unreacted C_3S, C-S-H and CH. Additionally, an optimized preparation method allows us to quantify the fine structure of C-S-H phases (length, aspect ratio, …) and the pore space.

1 INTRODUCTION

The two-dimensional visualization of specimens using a scanning electron microscope (SEM) is useful in many applications and allows to understand the micro and nano structure of the material observed. In combination with other techniques like energy dispersive X-ray spectroscopy (EDX) or electron backscatter diffraction (EBSD) comprehensive characterisation is obtainable.
However, neither of these methods provide a true volumetric representation of the specimen on their own. The focused ion beam (FIB) technology is used since many decades, especially in the semiconductor industry for imaging or to obtain high-quality cross-sections [1]. Additionally, it can dissect a block of material out of a specimen and cut the block in multiple slices utilizing Ga^+ ions. This allows a three-dimensional reconstruction of this volume.
It was already demonstrated, that the FIB can be used to visualize the nano structure, especially pore structures of hardened cement [2–4]. Nevertheless, none of the published reconstructions show the resolution and needle like structure of C-S-H or are combined with EDX.

2 MATERIALS AND METHODS

For all investigations, commercially available alite (C_3S, M3 polymorph, Vustah, Czech Republic) was used. A nitrogen filled glovebox was used to prevent carbonation. C_3S was mixed with deionized water (w/s = 0.5), filled into silicon sample moulds (7 x 7 x 50 mm) and cured for 28 days in a nitrogen atmosphere. The hydration reaction was stopped by immersing the prisms in ethanol (98 %) for 20 minutes and subsequentially dried at 40 °C. The samples were then cut, embedded in a low-viscosity epoxy resin, polished using diamond paste and an argon broad ion beam polishing device. Surface was sputter coated with carbon to make it conductive.

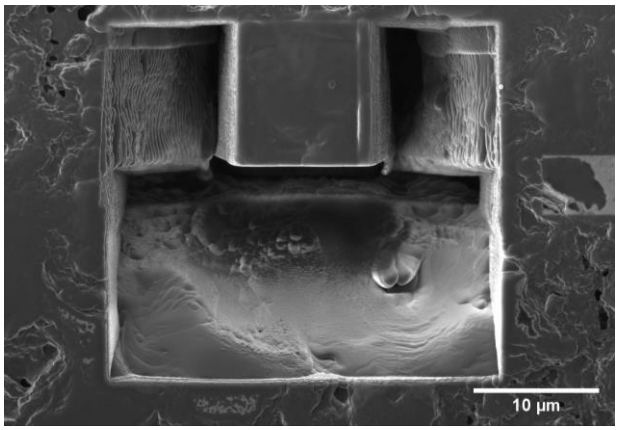

Figure 1: *Ion-image of a cube of 28d hydrated C_3S prepared for the following FIB-SEM tomography.*

The so-prepared sample was transferred in a FIB-SEM (Helios G4 UX DualBeam, thermoFischer Scientific) and a 0.5 µm thin layer of platin was deposited on a 10 x 10 µm² area, to protect the region of interest. As shown in Figure 1, 15 µm deep trenches were cut.
The specimen volume was then cut to 10 nm thin slices. After each cut, a SEM images were recorded at up to 2 kV. Additionally, every 100 nm a EDX mapping was performed at 10 kV.
The image stacks were aligned and prepared using ImageJ and evaluated using Avizo 2020.

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3 RESULTS AND DISCUSSION

The combination of the EDX and the BSE data allow the identification of the phases. Figure 2 shows the raw BSE image and the segmented C-S-H phase of the acquired data set after removing the curtaining effect and applying a Non-Local-Means denoising filter.

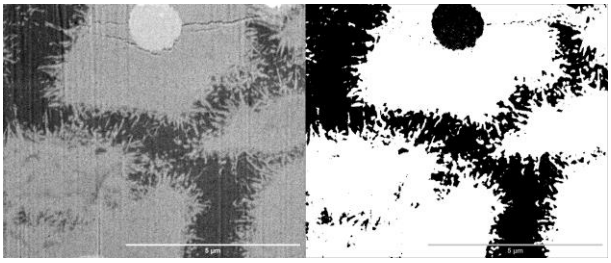

Figure 2: *Raw image with a pixel size of 3.8 nm next to a binarized version, selecting C-S-H of a 28d hydrated C_3S specimen (7.8 x 7.4 µm).On the top centre, a unhydrated C_3S grain is visible.*

In this case, only up to five possible phases (C-S-H, alite, portlandite, resin and air) can be found within the specimen. Therefore, the necessity of an EDX mapping is not obvious. However, more complex specimens like hydrated cement paste may profit from this method. The segmentation of the SEM image set allows a complete three-dimensional reconstruction of the volume as shown in Figure 3.

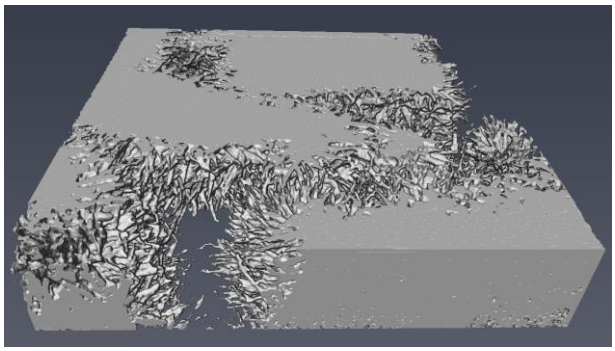

Figure 3: *3D-reconstruction of C-S-H (solid, grey) of a 28d hydrated C_3S specimen (7.8 x 7.4 x 1.6 µm³).*

The reconstructed volume clearly shows the typical needle-like structure of C-S-H phases.

Utilizing a higher resolution, within a smaller volume, reveals pores (52 nm³ and above) within the dense inner C-S-H as shown in Figure 4. In this illustration, the solid C-S-H is made semi-transparent, while the pores are rendered solid.

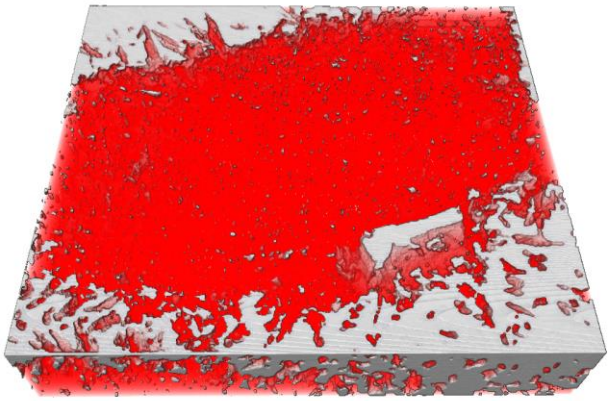

Figure 4: *3D-reconstruction of pores (solid, grey) within dense inner C-S-H (semi-transparent, red) of a 28d hydrated C_3S specimen (3.7 x 3.3 x 0.74 µm³).*

Nevertheless, it is still challenging to acquire a full dataset of the whole cube in the demonstrated resolution without major artifacts after a couple hundred slices due to charging issues.

4 CONCLUSIONS

It is possible to differentiate the phases utilizing a FIB-SEM in combination with EDX for high resolutions. It could be shown that C-S-H needles of hydrated C_3S can be visualized with a resolution of down to 4 x 4 x 10 nm³ for a large volume. Smaller volumes allow resolutions of down to 1.6 x 1.6 x 10 nm³. This allows the visualization of nano-pores within dense inner C-S-H.

ACKNOWLEDGEMENT

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