Reconstruction of calcium silicate hydrates using multiple 2D and 3D imaging techniques: Light microscopy, $\mu$-CT, SEM, FIB-nT combined with EDX

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Abstract
This study demonstrates the application and combination of multiple imaging techniques [light microscopy, micro-X-ray computer tomography ($\mu$-CT), scanning electron microscopy (SEM) and focussed ion beam – nano-tomography (FIB-nT)] to the analysis of the microstructure of hydrated alite across multiple scales. However, by comparing findings with mercury intrusion porosimetry (MIP), it becomes obvious that the imaged 3D volumes and 2D images do not sufficiently overlap at certain scales to allow a continuous quantification of the pore size distribution (PSD). This can be overcome by improving the resolution and increasing the measured volume. Furthermore, results show that the fibrous morphology of calcium-silicate-hydrates (C-S-H) phases is preserved during FIB-nT. This is a requirement for characterisation of nano-scale porosity. Finally, it was proven that the combination of FIB-nT with energy-dispersive X-ray spectroscopy (EDX) data facilitates the phase segmentation of a $11 \times 11 \times 7.7 \mu m^3$ volume of hydrated alite.

KEYWORDS
cement microstructure, focussed ion beam, micro-CT, tomography

1 | INTRODUCTION

Increasing demands on the performance of cementitious materials, also in connection with the digitalisation process, require a progressive and creative application of different methods to obtain material characteristics across multiple scales. The cross-scale recording of structural characteristics of cementitious materials is still an unsolved, but nevertheless central task. Cross-scale characterisation provides an improved understanding of essential building material properties (strength, fluid and gas transport, durability) on the one hand and is the basis for realistic modelling on the other.\(^1\)

This study combines light microscopy, high-resolution $\mu$-CT, large area SEM imaging and FIB-nT. This enables a cross-scale 3D-representation of the microstructure of hydrated alite using a single specimen. Comparable cross-scale examinations using at least some of these methods were already done, for example, for coal,\(^2\) clay material\(^3\) and hydrated cement.\(^4,5\)
This can be overcome using the FIB-nT, which is already widely adopted in material science. It utilises a gallium ion beam to cut layer by layer of a material volume and then using the various detectors available in a SEM to image and analyse the revealed surface. This allows to reconstruct a detailed 3D-volume of the specimen. While some approaches to image several cubic micrometre small volumes of hydrated alite already exist, none of these approaches were able to provide a detailed 3D geometry of the C-S-H-needle structure due to the sensitivity of the material to the electron and ion beam.

By combining μ-CT with FIB-nT, not only the scale range is significantly extended but also more information becomes available. This includes secondary and backscatter electron (SE, BSE) images but also chemical information from EDX. However, compared to SE and BSE images, the feature resolution of EDX element distribution maps is lower and the scanning rate is rather slow.

2 MATERIALS AND METHODS

In this study, a commercially available tricalcium silicate (alite) (Vustah, Czech Republic) of the MIII polymorph was used. The chemical composition measured by X-ray fluorescence spectroscopy (XRF) is shown in a previous publication. Phase purity of the alite was established at 97.6 wt.-% by X-ray diffraction.

In a CO₂-free atmosphere within a glovebox, the alite was mixed with water (water/solid ratio = 0.5) and cast into 7 × 7 × 50 mm³ prisms. After 28 days of hydration at 100 % relative humidity, the hydration was stopped by rinsing and soaking the specimen with isopropanol and drying the specimen at 60°C for several hours. A 20 mm long specimen was cut from the prism. After taking surface images with a light microscope, a CT-scan of the specimen was performed using a Phoenix Nanotom M | research edition (Baker Hughes Digital Solutions GmbH, Germany). The projections were acquired at 100 kV and 80 μA with a focal spot size of <1 μm and an aluminium filter (0.5 mm) was applied. A region of interest with a volume of 7.47 × 7.24 × 10.6 mm³ was reconstructed with a cubic voxel size of 8.89 × 8.89 × 8.89 μm³. The dataset was reconstructed using the software package phoenix datos | x 2.2, analysed using VGSTUDIO MAX 3.2 and evaluated together with the other image data in Avizo 2020.2, Fiji and custom-written python scripts.

After the μ-CT scan, the specimen was again cut, embedded in epoxy resin, and mechanically polished using diamond oil slurries down to 0.25 μm grain size. To obtain a very clean surface and to reduce scratches from diamond polishing, the specimen was finally polished...
FIGURE 2  PSDs obtained by various techniques. The top diagram shows the PSD histogram, while bottom diagram shows the respective cumulative sum. The pore volumes do not represent absolute values. They were normalised for each technique. To stack the data for the cumulative pore volume, the SEM-BSE image was used to obtain the overall porosity, which was then distributed to the individual techniques.

FIGURE 3  3D visualisation of an EDX dataset of 28-day hydrated alite acquired by FIB-nT (volume: $11.2 \times 11.0 \times 7.68 \mu m^3$, EDX voxel size: $26.9 \times 28.2 \times 96 \text{nm}^3$). (A) Raw EDX-dataset of calcium, (B) 2D SEM-BSE image and (C) segmentation by phase using EDX and BSE data.

using a triple argon ion beam milling device (EM TIC 3X, Leica Microsystems GmbH, Germany) on a rotating specimen holder at 4 kV, 2 mA for 2 h. For BSE imaging, the sample was carbon coated (approximately 10 nm layer thickness). Hereafter, the specimen was transferred to a FIB-SEM (Helios G4 UX, ThermoFisher Scientific, MA, USA) to obtain a high-resolution BSE image of the specimen surface. The image was stitched out of $10 \times 10$ smaller images with a pixel size of 202.3 nm and was used to find a suitable area for FIB-nT.

The FIB-nT-cube of about $10 \times 10 \times 10 \mu m^3$ was prepared onsite for BSE only and lifted out of the bulk material and welded on a copper grid for simultaneous BSE and EDX analysis. The lift-out helps to improve the signal quality and reduces charging artefacts. The slices were cut in 10 nm steps at 30 kV and 0.75 nA, while the EDX
mapping was performed every 10th slice to avoid damaging the hydrate phases. This and the pretilt of the specimen in respect to the electron beam leads to cuboid voxel shapes. The BSE images were acquired at 2 kV, 0.20 nA and the EDX mappings at 6 kV, 0.40 nA.

Initially the data were segmented using trainable Weka segmentation function available in Fiji17 (for μ-CT), manual thresholding (for SEM-BSE and FIB-nT) and pixel classification within software tool ilastik18 (applied to FIB-nT-EDX data). The large-scale SEM-BSE image was used to segment air voids (mostly circular and larger) and capillary pores. The PSD was obtained by using the chord-length density function (CDF)19 for every image/slice in two directions.

The PSDs obtained from image analysis were combined and compared with results from MIP using a prism, dried at 40°C. MIP was carried out using an AutoPore IV 9500 (Micrometrics Instrument Corporation, GA, USA). With this device, pore sizes within a range from 5 to 6000 nm can be detected.

3 RESULTS AND CONCLUSIONS

It was possible to apply all techniques to a single specimen. Results in Figure 1A–C show the images obtained by light microscopy, μ-CT, SEM-BSE and FIB-nT. The μ-CT dataset was used to segment the spherical air voids (Figure 1B) and the surrounding matrix. Furthermore, the CT data quality also allows to distinguish the hydrate matrix and unhydrated alite grains. It was possible to automatically segment these phases in the 2D-slices after manually training a Weka algorithm, while it was not possible to distinguish between C-S-H and portlandite (CH) (results not shown here).

Due to the nearly rectangular saw-cut to reveal the area for the SEM-BSE image and the good contrast of the air voids within the μ-CT data and the large SEM-BSE image, it was possible to manually register both datasets. Since the location of the FIB-nT volume was determined via the SEM-BSE image, it was possible to link all the acquired images to form a spatially correct dataset over a scale range of several millimetres down to the nano-level in 2 and 3 dimensions. Figure 1A–C shows the subsequent increase of the achieved image resolution. The combined dataset as shown in Figure 1 allows a cross-scale pore analysis as demonstrated in Figure 2. The μ-CT dataset contained 2.9 vol.-% pore space (mainly air voids, > 50 μm), which is similar to the 2.1 area-% found in the SEM-BSE image. Additionally, 27.1 area-% pore space (mostly capillary pores, 50 μm < x < 50 nm), 36.3 area-% C-S-H, 19.1 area-% CH and 17.5 area-% of unhydrated alite were segmented in this image based on the different contrast obtained from BSE imaging. The FIB-nT dataset contained 9.3 area-% porosity.

To obtain the stacked cumulative sum diagram of the PSD (Figure 2, lower diagram), a total of 30 vol.-% of porosity was assumed due to the SEM-BSE image. The porosity was distributed as follows: 3 vol.-% μ-CT/SEM-BSE (air voids), 22 vol.-% SEM-BSE (capillary pores) and 5 vol.-% FIB-nT. This distribution should only be understood as a rough approximation.

The PSD-histograms (n_{PSD}(d), where d is the pore diameter) were calculated using CDF (n_{CDF}(d)) and the cumulative sums were calculated using the following equation and then normalised using the maximum value of n_{PSD}(d) and \sum n_{PSD}(d), respectively.

\[ n_{PSD} = \frac{\pi}{6} d^3 \times n_{CDF}(d). \]

There is a significant difference between the MIP and the CDF/PSD of the stacked porosimetry of all three image sources. Foremost, the MIP showed a total of 26.2 vol.-% of porosity. The reasons of the deviation in the curve progression can be manifold. There are dimensional differences between CDF (line) and MIP (hydraulic volume), which were only partially compensated for by the above equation. Furthermore, large statistical errors are
expected, especially in the FIB-nT dataset due to the small volume. Also, there is only a small overlap in the data of the FIB-nT and the SEM-BSE imaging method as already described by Desbois et al.\textsuperscript{20} Incidentally, the MIP shows the most pore volume in exactly this area. This is especially obvious in the PSD-histograms (Figure 2, top diagram). Additionally, it is noticeable that the MIP provides imprecise results for pore diameters larger than 6 μm (dotted progression).

Furthermore, it is known that MIP may alter the pore geometry due to high pressures and can only characterise connected pores. Additionally, the bottleneck effect can distort the final pore size distribution.\textsuperscript{21} Nevertheless, there are some similarities in the curve progressions of MIP and the image-based CDF for the air voids.

The most significant finding is that the SEM-BSE (air voids) and μ-CT PSD progressions are very similar. The same may be achieved for FIB-nT and SEM-BSE by increasing the resolution of the SEM-BSE dataset or the FIB-nT volume.

As visible in Figure 1C, the segmentation of C-S-H phases and CH based on BSE image contrast can be difficult. This is especially true for FIB-nT BSE images. Therefore, EDX mappings were recorded during FIB-nT. Thereby the EDX count rate need to be sufficiently high while avoiding sample deformation due to extended electron beam interaction. As a compromise, a medium voltage and beam current (6 kV, 0.4 nA) were applied for EDX analysis. While this does not allow to quantify the phase composition, it leads to an increased EDX mapping resolution and thus to an approximation of the resolution of the BSE image. Results of FIB-nT BSE-EDX analysis reveal that the obtained resolution of EDX element distribution maps (Figure 3A) allow a good segmentation of alite, C-S-H and CH (Figure 3C). Compared to the BSE image (Figure 3B), more phases can be segmented using the combined techniques. Nevertheless, the EDX feature resolution remains lower than possible with BSE imaging.

Figure 4 demonstrates, that by using FIB-nT it is possible to obtain a voxel resolution down to $4 \times 4 \times 10$ nm$^3$, allowing to observe nano-scale pores and the close-to-native 3D-shape of all phases contained in a sample of 28-day hydrated alite. This 3D data can be further segmented so that quantification of solids (e.g. specific surface of C-S-H phases etc.) and pores at nano-scale dimension is possible. While the contrast between the hydration products CH and C-S-H in the BSE is low and therefore they are hard to segment (Figure 3B), the EDX data can support the segmentation (Figure 3C).

4 | CONCLUSION AND OUTLOOK

This research demonstrated the possible benefits of combining different imaging techniques (μ-CT, 2D-SEM and FIB-nT combined with EDX). This combination enables the visualisation of feature sizes from a few mm down to the nano-scaled structure of cementitious materials. This allows, for example, to calculate a pore size distribution and to identify otherwise indistinguishable phases. Compared to the imaging of fractured surfaces the flat, sectioned surfaces provided by FIB allows to record BSE images that can be used to quantify phase fractions including porosity and fractures. Especially for irregular and connected structures such as fractures and porosity, 3D imaging is seen as the only way for a quantitative characterisation.

A requirement for close-to-native imaging and analysis of, for example, porosity in hydrated cementitious materials is the preservation of the microstructure through all steps of sample preparation and imaging. Here we demonstrate that the applied protocol does allow the image the fibrous structure of C-S-H as previously described by low-vacuum SEM\textsuperscript{22}, where the process of drying and beam damage are reduced to a minimum. This allows us to conclude that the expected structural loss is relatively low, that is limited to structures below image resolution. Nevertheless, in future studies, we will investigate if additional cooling of the sample during FIB sectioning is beneficial.

However, the segmentation and localisation of the images is a very labour-intensive task. Furthermore, there is still a lot of potential to improve the image quality and resolution, both for μ-CT and FIB-nT. This may be achieved by improved preparation and imaging parameters. But also, by more elaborated segmentation algorithms. In future work, the SEM-EDX segmentation will be used to improve segmentation of μ-CT data.

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