NEW APPROACHES IN MICROSTRUCTURE ANALYSIS OF CEMENTITIOUS MATERIALS: FROM MICRO TO NANO, FROM 2D TO 3D AND FROM QUALITATIVE TO QUANTITATIVE CHARACTERIZATION

L. Holzer, B. Münch and Ph. Gasser

Empa, Materials Science and Technology, 3D-Mat group, Dübendorf, Switzerland

Abstract

FIB-nanotomography is a new method for high resolution 3D-microscopy that was recently developed by the 3D-Mat group at Empa. With a resolution below 20nm, FIB-nt opens new possibilities for microstructure analysis of the complex cementitious materials, which can not be achieved with any other microscopy method at present.

In this paper the potential of FIB-nt for quantitative microstructure analysis is demonstrated for porosity in hardened cement pastes and, in combination with cryo-preparation methods, for agglomerations and early hydration products in fresh cement pastes.

In combination with modern computational analysis, important topological and statistical information can be obtained from the high resolution 3D-data. As discussed in this paper, the new approaches of microstructure analysis will considerably improve our understanding of the micro-macro-link such as the relationship between porosity and the corresponding transport properties in hardened cementitious materials or the mechanisms of particle agglomeration and the influence on rheological properties in fresh cement pastes.

Keywords: high resolution tomography, quantitative microstructure analysis, porosity, skeletonization, early hydration, cryo-microscopy.

1. INTRODUCTION

Microstructural information represents a key to the profound understanding of macroscopic materials properties (eg. mechanical or durability properties) and of the corresponding physico-chemical processes (eg. fracture mechanics or chemical degradation). However, although extensive microstructure analyses have been performed over the last decades, the micro-macro-link is still not established on a quantitative level. Analytical problems arise,
because the structural features range over several orders of magnitudes (from $\text{<} \text{nm}$- to $\text{> cm}$), the materials are heterogeneous and they tend to form artifacts during sample preparation and image acquisition.

Above the $\mu\text{m}$-scale, very valuable information can be obtained from backscattered electron (BSE) imaging [1-3]. However, a considerable volume fraction of microstructural features (e.g., gel-porosity) is beyond the resolution of the BSE-method. Therefore, quantitative data from BSE-imaging must be treated with great caution, because all nanoscale components of the cementitious matrix are disclosed from these analyses due to the insufficient resolution.

In addition, important geometrical aspects such as the connectivity of pores can not be deduced from 2D-imaging (SEM/BSE, TEM), because the cementitious microstructures are strongly disordered. Hence, for a geometrical and topological characterization of the microstructure, high resolution 3D-information is required. For microstructure analysis of hydrated cements, conventional 3D-methods such X-ray tomography or confocal scanning microscopy do not provide sufficient resolution and hence, these methods are restricted to coarse microstructural features above the $\mu\text{m}$-scale (coarsest fraction of capillary porosity, air voids, fractures, unhydrated particles and aggregates). Thus, in order to establish the important relationships between the fine-grained microstructure and the macroscopic properties of cementitious materials, new methods are required which provide 3D-information at nano-scale resolution.

In this paper we are presenting a new approach for 3D-microstructure analysis using Focused Ion Beam-nanotomography (FIB-nt). This method, which has recently been developed by the 3D-Mat group at Empa (www.empa.ch/3D-Mat), is described in more detail in a separate publication [4]. FIB-nt provides an excellent resolution in the 10nm range and consequently, it enables the acquisition of unique microscopic data, which serves as a basis for quantitative microstructure analysis and image based modelling such as topological characterization of the pore network and subsequent simulation of capillary condensation (and shrinkage). In this paper we are briefly presenting two examples of FIB-nt applications from our ongoing research with cement based materials:

- 3D-analysis of the pore network in hardened cement pastes.
- Early hydration products and particle agglomeration in fresh cement pastes investigated by a combination of FIB-nt and cryo-preparation methods.

2. 3D-ANALYSIS OF THE PORE NETWORK IN CEMENT PASTES

Porosity is a fundamental microstructural feature in cementitious materials which can be correlated with macroscopic properties such as permeability, durability, strength, elasticity and shrinkage behaviour. However, there are still no methods available which allow a reliable quantitative or geometrical characterization of the pore network. The most widely used method, mercury intrusion porosimetry (MIP), is now considered as "an inappropriate method for measuring pore size distributions in cement based materials" [5]. For a realistic representation of the pore network, high resolution 3D information is necessary, because the connectivity of pores can not be reconstructed from 2D images. Two ears ago, this task was the main motivation for us to start with the development of the FIB-nt method.

First results are now available from cement pastes of OPC CEM I (w/c ratio 0.35, impregnated with epoxy resin), which have been investigated at magnifications of 5kx, 20kx
and 35kx after 2, 7 and 28 days of hydration. The corresponding Øvoxel resolutions are 74, 20 and 12nm. Fig. 1 represents 3D-visualizations from a 2 days old paste at 20kx magnification (left) and from a 28 days old cement paste at 5kx magnification (right), respectively. On a qualitative level, it can be observed that the capillary porosity originates from two different microstructural domains: a) from the initial intergranular pore space, which is continuously filled with outer product C-S-H during hydration and b) from the hollow hydration shells, which are internally fragmented by relatively coarse ettringite needles and portlandite flakes.

![Figure 1: 3D-reconstructions of 2 days and 28 days old cement pastes (adapted from [6])](image)

As shown in Fig 2, even the 3D-structure of the fibrous outer product C-S-H can be extracted from the FIB-nt image volumes. Thereby, the very fine pores within the dense intergrowth of C-S-H are considered as pore necks which represent potential pathways between the larger capillary pores. For these pore necks, neither capillary-porosity nor gel-porosity are suitable terms. Thus, based on the detailed information from FIB-nt, the terminology for the pore system will have to be adapted in future to the real structural facts.

The topological characterization of these pore necks is of major importance, when dealing with aspects of connectivity, permeability and transport of water and dissolved chemical species. For the extraction of realistic pore network properties, 3D-algorithms for skeletonization and associated statistical analysis (eg. nr. of pathways linking 2 distinct points, dimensions of pore necks and pore bodies, pore size distribution, free distance histogram etc.) are currently being developed and refined. First results from the skeletonized porosity at resolutions of 20nm indicate that the entire pore network is almost completely connected. The skeletonized network in Fig. 3 (left) illustrates the extraordinary complexity of the pore structure with very fine branches at the 50nm to 100nm-scale. At a four-fold reduction of the resolution, some of the porous domains disappear or they become disconnected (Fig. 3 right). Depercolation of the pore network, as it is postulated from simulated 3D-microstructures or from X-ray tomography, is thus probably an artificial feature.
which originates from a lack of resolution. This observation raises the need for a more thorough resolution sensitivity analysis.

Figure 2: 3D-reconstruction of a sub-volume from 2 days old cement paste. Left cube: orthoslices from raw data after alignment. Right cube: semitransparent 3D-visualization with orthoslices (adapted from [6]).

Figure 3: Detail of the skeletonized pore structure from a 2 days old cement paste, representing a sub-volume of 4x4x3µm. Left cube: skeletonization based on original voxel resolution (15x19x30 nm). Right cube: skeletonization based on a 4-fold reduction of the voxel resolution (59x75x120 nm) (adapted from [6]).

Our current activities on pore structure analysis are focusing on the improvement of topological and statistical characterization of the pore network in order to establish the
quantitative relationship with the corresponding mechanical and transport properties. From the skeletonized network a geometrical pore model can be reconstructed which shall serve as a more realistic basis for modeling of capillary condensation related to shrinkage or liquid flow related to transport and chemical degradation of cement based materials.

3. **EARLY HYDRATION PRODUCTS AND PARTICLE AGGLOMERATION IN FRESH CEMENT PASTES INVESTIGATED BY A COMBINATION OF FIB-NT AND CRYO-PREPARATION METHODS**

   Workability, rheological properties and the setting of fresh cement pastes, mortars and concrete are related to interparticle forces and the corresponding formation of particle networks during the early stages of cement hydration [7]. Modeling of rheological processes and the corresponding particle interactions allows the prediction of viscous properties, for example by means of dissipative particle dynamics [8]. Nevertheless, the modeling approaches are based on considerations of simplified systems (e.g. spherical particles) and they can not account for the entire complexity of real cement systems. Major uncertainties are due to the lack of chemical and microstructural data from the hydration layer on the particle surfaces and from agglomerates and particle networks which are formed within the suspension. Until now, these microstructural aspects could hardly be characterized with conventional microscopy methods (ESEM, Cryo-SEM, X-ray tomography). A new approach for 3D-microstructure analysis of granular textures in fresh cement pastes is based on FIB-nt in conjunction with high pressure freezing and cryo-transfer, whereby the loose particle systems in the suspensions are stabilized by cryo-vitrification. In this chapter, first results are presented from our experiments with high-pressure frozen samples that were analyzed with FIB-nt in combination with new cryo-transfer facilities.

![Figure 4: Particle structure of a high-pressure frozen cement paste after 24 minutes of hydration (CEM I, w/c: 0.5). Left side: 3D-reconstruction from a data volume of 13x13x9µm, based on a voxel resolution of 31 nm. Right side: Detail showing an unhydrated grain (bright) with a discontinuous hydration layer (intermed.) in frozen water (dark). Image width: 5 µm.](image)
Considering the structure of particle surfaces, the thickness, homogeneity and chemical composition of the AFm/organoaluminate layers are of major interest, because this layer potentially acts as a sink for superplasticizers [9] and its quantitative characterization is crucial for the optimization of dispersed cement systems. Fig. 4 shows a 3D-reconstruction of the particle structure in a cement paste after 24 minutes of hydration. As can be seen on the right side of fig. 4, the hydration products covering the particle surfaces do not form a continuous layer. Locally, the layer reaches a thickness of 200nm, but on many surface sites the hydration layer is not detectable at all. Based on the 3D data volumes that are currently acquired for different cement types and for different time steps, the volume fraction and the surface area of the hydration layer shall be quantified by means of image analysis. This information is used to improve our understanding about the mechanisms how admixtures are distributed among the different potential "reservoirs" (dissolved in pore solution, adsorbed on particle surfaces or incorporated in the hydration layers) and how saturation and/or undersaturation of admixtures are evolving during the early hydration period.

![3D-reconstruction of particle structure](image)

**Fig. 5:** The two examples illustrate the extraordinary potential of FIB-nt to detect individual particles in complex granular textures. The upper series of images shows an agglomerate which consists of 19 distinct particles (left: FIB-SEM grayscale image, middle: same image after segmentation, right: 3D-reconstruction of the agglomerate). The lower series represents a strongly fragmented domain with 37 subgrains (left: FIB-SEM grayscale image, middle: same image tilted, right: 3D-reconstruction of fragmented domain superimposed on segmented and tilted image). Both, agglomeration and fragmentation, are frequently observed features in cement powders (adapted from [10]).
The nr of contacts between particles and the contact curvatures represent crucial parameters for the calculation of interparticle forces and for the corresponding prediction of viscosity and yield strength. These calculations are based on the assumption that the cement particles are homogeneously distributed in the suspension. Agglomeration, which has a large impact on viscosity and yield strength, leads to a restructuring of the homogeneous particle packing and to a change of the nr of interparticle contacts. On a larger scale, attractive particle forces related to the agglomeration processes may lead to the formation of a loose but percolating granular network structure which, in combination with new hydration products, invoke an increase of viscosity and yield strength.

In order to understand the link between the particle structure and the corresponding viscous properties (eg. before setting), the agglomeration and formation of the granular networks within the suspension need to be characterized. This is a very demanding task for 3D-microscopy as well as for the subsequent image based modeling. In order to set up suitable methods for a quantitative characterization of such granular microstructures, samples of unhydrated cement pastes were analyzed with FIB-nt [10] and special segmentation techniques and stereological correction procedures for measurement of particle size distributions were developed [11]. Based on the imaging and modeling techniques developed in these studies, agglomeration and interface topology from particle networks cement pastes can now be characterized, as illustrated in figs. 5 and 6.

Fig. 5 represents two examples with agglomerations of 19 cement grains (top) and desintegration of a clinker grain into 37 fragments (bottom). Both processes, agglomeration and fragmentation, represent a prominent feature in the suspensions and in the cryo-stabilized samples, respectively. In both cases, the dimensions of the subgrains are predominantly in the sub-µm range, which can only be resolved with high resolution 3D-microscopy. In future studies, the processes of agglomeration and fragmentation, and their impact on "active" particle size distribution, nr of interparticle contacts and related viscous properties of fresh cement pastes shall be investigated by means cryo-FIB-nt and image based modeling.

Fig. 6: Topological characterization of particle-particle interfaces based on 3D-analysis with FIB-nt: a) Selected subvolume (6x8x6 µm) with a dense particle structure (150 particles). b) Interfaces within volume a. c) Selection of 30 particles. d) Superposition of interfaces with selected particles (adapted from [10]).
Of particular interest for the modeling and understanding of flow properties in viscous systems is the geometry and frequency of (potential) interfaces between the particles. Fig. 6 shows an example of the reconstruction of the interfaces between neighboring particles in a grain-supported texture. The left cube (a) represents a selected subvolume from a larger cube which contains 150 particles. The red, curved areas in (b) show the contact surfaces between the particles. In order to illustrate the relationship of the contact surfaces with the granular textures, 30 particles were selected (c) and superimposed on the contact surfaces (d). The example illustrates the potential of FIB-nt to describe topological details of particle interfaces. This is of particular interest, since macroscopic properties of granular materials are strongly related to the microscopic interface characteristics, i.e. the particle bonding sites. Future research activities with FIB-nt in the field of granular materials (suspensions and solids) will focus on the quantitative description of the particle network, the interfaces and the agglomerations. This is considered as a basis for the elaboration of quantitative relationships with macroscopic materials properties, such as the flow properties of cement suspensions.

4. CONCLUSIONS

At the current stage of research, microstructure analysis of cement based materials has hardly reached a quantitative level. Therefore the correlations between microstructure and macroscopic properties are not yet well established. New approaches are needed in image acquisition, image based modeling and in linking this information with experimental data.

For image acquisition, FIB-nt opens new possibilities to evolve from 2D- to 3D- and from micro- to nano-scale characterization. The current FIB investigations give promising results for the microstructure analysis of the pore network in hardened cement pastes and, in combination with cryo-microscopy, for the topological and morphological characterization of early hydration products and agglomerations in fresh cement pastes.

For image based modeling, algorithms are currently being developed (see e.g. [11]) to extract quantitative and topological data from porous and granular structures. This will certainly help to improve our understanding of the micro-macro link in cementitious materials. In addition to the empirical micro-macro link, the 3D-microstructural data from FIB-nt can be used as a basis for the simulation of physico-chemical processes such as simulation of viscous flow in suspensions including more realistic particle morphologies [8], 3D microstructure modeling of cement hydration based on more realistic granular textures [12] and/or simulation of capillary condensation (and shrinkage) in more realistic pore systems. The lack of realistic structural data was one of the most serious shortcomings in these models, which can now be improved due to the high quality data from FIB.

The main challenge for future research in this area will be to merge the new possibilities of 3D-microscopy and image based modeling with sophisticated experimental work and correspondingly improving the real world materials properties.
ACKNOWLEDGEMENTS

A. Käch (BALTEC) and M. Müller (ETHZ) are thanked for help with the implementation of the cryo-preparation method. A. Zingg, F. Winnefeld and R. Flatt are thanked for fruitful discussions about particles, admixtures and rheology.

REFERENCES


