ESRF	**Experiment title:** **COMBINED MICRO-TOMOGRAPHY AND MICRO-DIFFRACTION OF CEMENT MATERIALS**	**Experiment number**: MA-648
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Report:

Monitoring the microstructural evolution in cement-based materials during their setting and hardening is a challenging task, due to their intrinsic complexity and the continuously changing character of the system.
The main purpose of this experiment is to investigate non-destructively the 3D evolution of cement samples during hydration, by combining high resolution X-ray micro-tomography (X-μCT) and diffraction tomography (XRD-CT), a recently developed technique at ID22 [Bleuet, P., Welcomme, E., Dooryhée, E., Susini, J., Hodeau, J.-L. & Walter, P. (2008) - *Probing the structure of heterogeneous diluted materials by diffraction tomography.* Nature Materials, **7**, 468-472]. The diffraction enhancement of the tomographic signal allows mapping of the spatial distribution of key phases forming during the hydration process of cements. One fundamental feature of the hydration process is the nucleation and growth of ettringite, a phase developing during the very early stages according to the following reaction:

$$Ca_3Al_2O_6 \text{ (aluminate)} + 3CaSO_4{\cdot}2H_2O \text{ (gypsum)} + 26H_2O = Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O \text{ (ettringite)}$$

A CEM I 52.5R Portland cement (OPC) was used for the preparation of cement pastes and mortar samples. Cement (including a 5% by mass of gypsum, acting as a set retarder) and distilled water were mixed by hand for a few minutes and then injected into thin glass capillaries (internal diameter ~ 500 μm) and sealed with plasticine. In the formulation of two samples, organic additives based on acrylic and methacrylic esters were added in order to modify the kinetics of the reactions and the rheology.
For each of the four samples prepared (three cement pastes and one mortar), several phase contrast tomographies were performed at different times from hydration (1-72 hr) to monitor the microstructural evolution of the reacting material. An example of the modifications occurring in the microstructure of a cement paste during hydration is shown in *figure 1*.
Using a dedicated experimental setup, XRD-CT measures were also carried out on the same samples by scanning them with a 4x2 μm^2 pencil beam at a fixed energy of 18 keV. Due to the longer acquisition time (6-7 hours for the complete scan of a single slice) only one or two XRD-CT scans were performed for each sample.

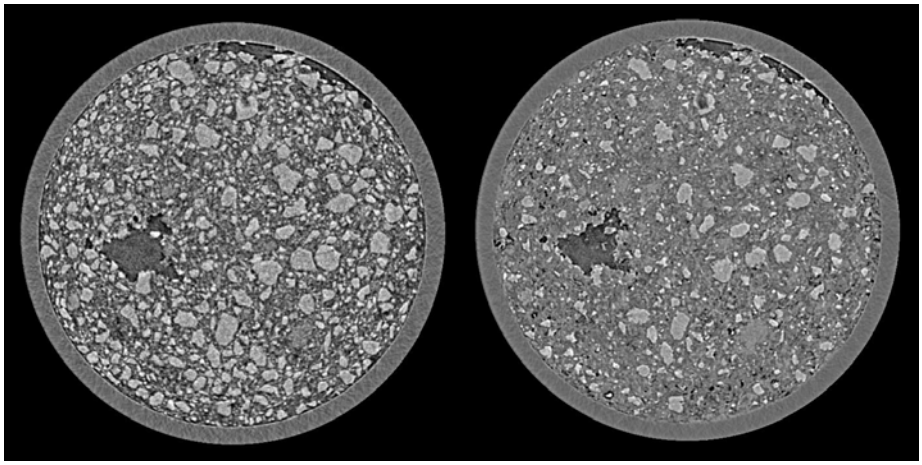

Figure 1: an example of the evolution of the microstructure with hydration time. Two corresponding reconstructed slices of a cement paste (w/c = 0.5) representing a section of the filled capillary after 7 (left) and 70 (right) hours from mixing are showed. The growth of hydration phases (intermediate grayvalues) at the expense of the original clinker grains (lighter GV) and pores (darker GV) is clearly recognizable. The internal diameter of the capillary is approximately 500 µm and the voxel size is ~ 0.7 µm.

For every translation (y) and rotation (ω) of the sample a 2D diffraction pattern was collected by a FReLoN camera, thus obtaining a set of integrated linear diffraction patterns. Regions of interest corresponding to a particular 2θ range (e.g. a single peak) were selected on the linear diffraction patterns to build up sinograms, representing the variations of the diffracted intensity as a function of y and ω. Sinograms were then used to reconstruct cross-sections mapping the spatial distribution of particular phases of interest. The best results were obtained by following the diffracted signal of ettringite, being this phase very fine grained and suitably distributed through the hydrated cement paste. Major difficulties were encountered when trying to map the distribution of the unreacted clinker phases and of the quartz grains included in the mortar sample. As shown in *figure 2*, good agreement was found between the reconstructed images obtained from X-µCT and XRD-CT in spite of the remarkable differences in spatial resolution of the two techniques.
At the same time, by means of an EDS detector placed at 90° to the incident beam, also the fluorescence signal was collected in order to map the distribution of selected elements inside a slice of the sample. Due to the high self-absorption of the fluorescence X-rays inside the sample, good results were obtained only for those elements having higher emission energies (e.g. Rb).
The preliminary results obtained from this experiment clearly show the suitability of XRD-CT for the study of cement-based materials. Persisting problems in the data analysis are mainly due to the scattering signal from large single crystals within the sample (mostly clinker and filler grains). Correction strategies are being developed to overcome the problem.

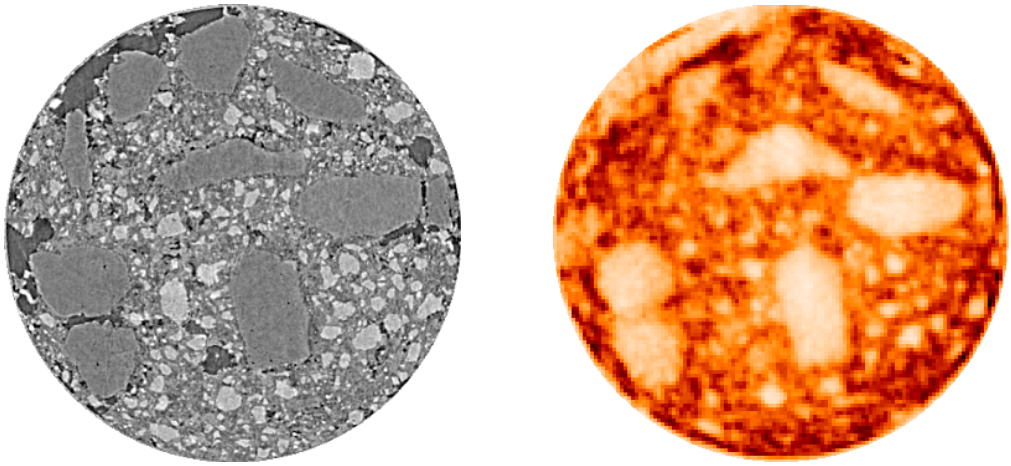

Figure 2: a slice of a mortar sample reconstructed by means of XRD-CT (right) is compared with a roughly correspondant X-µCT slice (left). Only the 2θ range of the (100) ettringite peak was selected for the XRD-CT slice reconstruction. In this image darker areas represent maximum peak intensity while brighter areas correspond to an absence of ettringite (e.g. voids, unreacted clinker and quartz grains). The voxel sizes are ~ 0.7 µm (left) and ~ 5 µm (right). Sample diameter is ~ 400 µm.