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In situ tomographic investigation on the early hydration behaviors of cementing systems

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ABSTRACT

The early hydration of three cementing materials has been investigated *in situ* by Synchrotron X-ray Tomographic Microscopy thanks to an automatic sample exchanger recently integrated at the TOMCAT beamline at the Swiss Light Source in Villigen (CH). Hydration has been investigated by following the three dimensional evolution of pastes up to 12 h, with particular attention to the consumption of anhydrous phases, the formation of hydrates and to changes in microstructure. A lecture key for the interpretation of the tomographic images is proposed, based on the relationship between the linear attenuation coefficient μ-function of the density and elemental composition of each mineral phase- and the corresponding grey tone experimentally observed. Some examples of application of the technique are proposed, such as: a comparison among the reaction kinetics of the three investigated cements, the study of morphological evolution of mineral phases, the analyses of the three-dimensional evolution of the pore network.

1. Introduction

The investigation on the early hydration behavior of cements and cementing systems has been for a long time a very important area of research: understanding the chemical reactions that lead to hardening is fundamental for the prediction of performances and durability of the materials.

Tomographic methods, i.e. 3D computed reconstructions of a sample from 2D projections, are known since more than 50 years and have quickly become important tools for investigation in different scientific fields. It is however only in the last decades that, thanks to new tomographic beamlines in third generation synchrotron facilities, 3D investigations with micrometer resolution have become routine [1]. The application of the technique to cementing materials and in construction field [2–9] demonstrated its effective usefulness in the investigation of internal distribution of different phases: for example gravel or sand in concrete and fillers or water in cement paste.

In some cases, Synchrotron X-ray Tomographic Microscopy (SRXTM) has been proposed for the evaluation of the pore network [6–8] as an alternative method to more conventional and well-known techniques such as mercury intrusion porosimetry (MIP) or backscattered electron scanning microscopy (BSE-SEM). SRXTM shows the obvious advantage of being a non destructive technique which does not require sample pretreatment; moreover, it supplies information on the 3-dimensional phase distribution and on the pore network otherwise inaccessible, such as topology, tortuosity or connectivity.

Another advantage in the use of this technique for the study of hydration behaviors is that amorphous phases can also be detected: X-ray Powder Diffraction (XRPD), the most conventionally used technique for the study of hydration mechanisms of cementing materials, has the strong limitation that only crystalline structures can be detected, while many hydration products are partially or totally amorphous.

A limitation of the SRXTM is the limited spatial resolution: the best resolution routinely reached is about 0.7 μm, while it is well known that porosity of cements can extend from tens of micrometers down to few nanometers [10].

A novel SRXTM *in situ* set up, recently developed at Swiss Light Source in Villigen (CH) [11], allows measurement of evolving samples, such as freshly hydrated cement pastes. Thanks to the help of a robotized arm integrated at the TOMCAT beamline [12], it was possible to exactly re-position the sample in the same place with micrometrical precision at each successive measurement. In this

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Table 1
Mineralogical composition of the three investigated materials as obtained by Rietveld semi-quantitative XRD analyses (% in weight).

Mineral phase	OPC	CSA	MIX
C_3S	57.4	–	23.1
C_2S	10.2	21.7	16.1
C_3A	4.5	9.3	7.0
C_4AF	9.4	3.9	3.8
$C_4A_3\overline{S}$	–	42.4	23.6
Gypsum	3.6	11.3	12.3
Anhydrite	-	4.9	0.4
Calcite	13.5	6.0	12.8
Residual phases	1.4	0.5	0.9

way the evolution of the same region of a sample could be followed for the whole investigation period, allowing one to directly observe the changes of microstructure of the cement paste during hydration, a target impossible to achieve with any other conventional technique.

In the present study, the multiple investigation possibilities supplied by SRXTM have been evaluated and applied to the investigation of hydration mechanisms of three different binders: an Ordinary Portland Cement (OPC), investigated as a reference material; a Calcium Sulfoaluminate Cement (CSA) and a mixed sample (later on named MIX) obtained from the blending of the two cements.

Portland cement is the most common material in the construction field. Portland clinker is essentially constituted by four mineral phases: dicalcium silicate (belite, C_2S[1]), tricalcium silicate (alite, C_3S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (ferrite, C_4AF); gypsum ($C\overline{S}H_2$) is normally added during clinker grinding. Main physical, chemical and mechanical properties of cement arise from the interaction of these minerals with water: hydration of silicates results in the formation of a hydrated calcium silicate (CSH), an amorphous gel having variable stoichiometry, and calcium hydroxide (portlandite, CH). Calcium sulfoaluminate cement is a special cement having unique properties like high early compression strength, well tunable time of workability depending on the addition of different additives, high frost and corrosion resistance. Its clinker is essentially based on tetracalcium trialuminate sulfate or yeelimite ($C_4A_3\overline{S}$), belite and calcium sulfate or anhydrite ($C\overline{S}$); the main hydration product is ettringite ($C_6A\overline{S}_3H_{32}$) produced from the reaction between yeelimite (or C_3A), calcium sulfate and water.

The mixed sample is a commercial product made by mixing Portland cement and Sulfoaluminate clinker, calcium sulfate (mainly gypsum) and other additives.

2. Experimental

2.1. Materials and sample preparation

All materials were supplied by Buzzi Unicem: main mineral phases, detected by Rietveld semi-quantitative X-ray diffraction, are listed in Table 1.

Cement pastes were prepared by manually mixing the binder with distilled water in a water-to-cement ratio of 0.4 by mass.

For *in situ* SRXTM, Lindemann glass tubes (∅ = 600 μm) were used as sample holders: the glass tube was used like the needle of a syringe in order to fill it up with the cement paste. The glass tubes were rapidly prepared and mounted on the stage as shown in Fig. 1, so as to minimize the delay between the sample preparation and the first measurement.

2.2. Synchrotron measurements

Micro-tomographic synchrotron measurements were performed at the TOMCAT beamline at the Swiss Light Source (SLS) at Paul Scherrer Institut in Villigen, Switzerland [11]. All samples have been scanned with an energy of 14 keV, so as to obtain high contrast between the different phases. For conversion of the X-rays into visible light, a 18 μm thick LAG scintillator, doped with Ce has been used. Projections have been magnified by a diffraction limited microscope optics (20× objective) and digitized by a high-resolution CCD camera (pco.2000, PCO AG, Kelheim, Germany) with 14 bit dynamic range. Twofold "on-chip binning" has been used to decrease the acquisition time and therefore reduce artifacts due to the evolution of the samples during the time of each single analysis. These settings resulted in an isotropic pixel size of 0.74 μm, a field of view of 0.75 mm and an exposure time of 200 ms. For each dataset, 1001 projections over 180° have been acquired in about 4½ min and each sample was scanned every 36 min, for about 12 h.

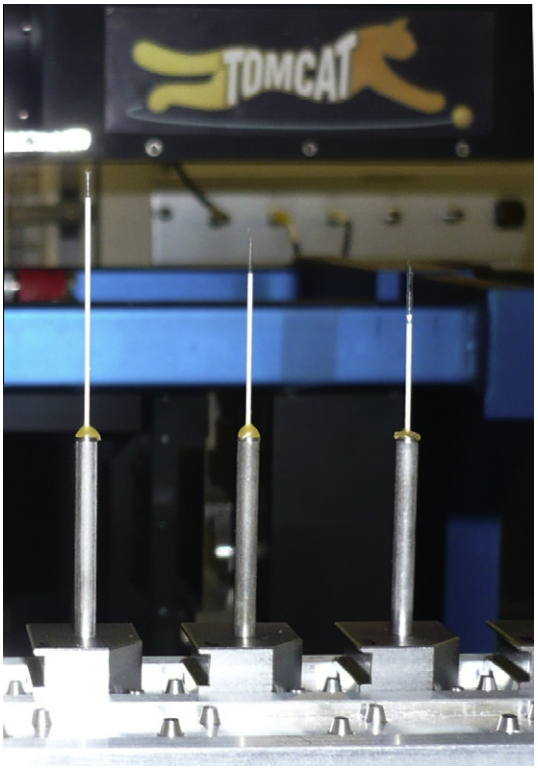

Fig. 1. Sample holder stage: the three glass tubes are filled with the three investigated cement pastes.

The samples were automatically exchanged at fixed intervals using a Stäubli RS40 Robot Arm (Staubli, Pfaeffikon, Switzerland), integrated into the beamline control system to move samples from the tray to the measurement position [12]. The beamline control system is scripted to load the samples, perform the scan, and then switch the sample at fixed time intervals. The time the arm takes to load a single sample is under 15 s, but the total time required for sample change is closer to a minute as the sample must be moved away from the detector and other beamline components before the robot can pick it up or drop it off. The reproducibility of the entire process was determined to be less than 5 μm (in most cases much better), corresponding, at the highest resolution (20× Objective), to seven pixels out of 2048: this means that the sample remains entirely within the field of view, and image processing algorithms such as cross-correlation are efficient for aligning the samples.

For each scan, the optimal parameters for the 3D reconstruction of the dataset have been determined with a user-friendly Web-based application [13]. The data have then been reconstructed on a 20 node PC-cluster in a few minutes using a highly optimized algorithm based on the Fourier Transform method [14].

2.3. Image processing

32-bit float reconstructed slices were firstly processed through the Fit2D software [15–17]. Singular binary images of 1024 × 1024 pixels were input in real 4-byte unsigned integers without byte swapping and subsequently exported in TIFF 8-bit per pixel format. The obtained outputs were images of 1024 × 1024 pixels with 255 output grey levels: in this paper, the convention was chosen that grey level 0 corresponds to white and 255 to black.

The reduction to 255 levels of grey from the original binary input required a deep investigation on the exportation scale limits, being the grey intensity function of the linear attenuation coefficient of a specific mineral phase. In addition, to be able to directly compare slices, it was necessary to identify a common scaling range for the grey scale normalization of all samples/images; scaled images were then managed using the free software ImageJ [18].

[1] Note that standard cement nomenclature is followed here, whereby C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\overline{S}$ = SO_3 and H = H_2O.