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Micro- and nano-X-ray computed-tomography: A step forward in the characterization of the pore network of a leached cement paste

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ABSTRACT

Pore structure of leached cement pastes (w/c = 0.5) was studied for the first time from micro-scale down to the nano-scale by combining micro- and nano-X-ray computed tomography (micro- & nano-CT). This allowed assessing the 3D heterogeneity of the pore network along the cement profile (from the core to the altered layer) of almost the entire range of cement pore size, i.e. from capillary to gel pores. We successfully quantified an increase of porosity in the altered layer at both resolutions. Porosity is increasing from 1.8 to 6.1% and from 18 to 58% at the micro-(voxel = 1.81 μm) and nano-scale (voxel = 63.5 nm) respectively. The combination of both CT allowed to circumvent weaknesses inherent of both investigation scales. In addition the connectivity and the channel size of the pore network were also evaluated to obtain a complete 3D pore network characterization at both scales.

1. Introduction

For many years, cement-based materials have been used as structural or filling materials in a great variety of applications, not only as building materials but also as radioactive waste disposal matrices. The durability of these materials is affected as they are altered in contact with water (percolating water such as rain or sea water) and exposed to various climatic conditions (e.g. freezing–thawing cycle). This dissolution-induced alteration is considered to be one of the major factors that alter the physico-chemical properties of cement such as strength, permeability, barrier properties and ion diffusion coefficient [1–5].

Cement-based materials are porous with a large pore size distribution ranging from few nanometers (nm) up to tens of micrometers (μm) [6]. Pore structure of hardened cement paste is usually divided into gel pores (from a few nm to 0.2 μm), capillary pores (from 0.2 μm to 10 μm) and air voids (above 10 μm) [7,8]. Gel pores are intrinsic to calcium silicate hydrates (designed as C–S–H in cement notation). Capillary pores are created by chemical shrinkage, i.e., by the reduced of volume occupied by the hydrated phases compared to the volume of the anhydrous phases plus water. Air voids correspond to the air trapped during hydrated cement paste formation [6,9,10].

It is well established that cement leaching and dissolution of cement hydrates (i.e. primary cement phases) result in an increase of the porosity and changes in the pore structure. These phenomena result in a porosity gradient from the cement core to the surface altered layer [1]. Cement pore structure plays a fundamental role in the transport processes of elements (major and trace elements, e.g. metals) within the cement matrix and hence their potential release in the environment. Accurate description of the heterogeneity of the cement pore structure of the altered layers remains a challenging goal, but necessary to help understanding the cement long-term performance.

A variety of experimental techniques such as mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM) and gas adsorption techniques have been used to characterize the pore structure of cement-based materials whether freshly hydrated, or altered [5,9,11–13]. MIP is able to quantify almost all cement pore size range from few nm to 375 μm [6]. All these techniques provide basic information (porosity, pore sizes) but are too constraining to assess precisely pore connectivity and spatial heterogeneity of the porosity. For instance MIP is not able to characterize the porosity heterogeneity along the altered profile and therefore, is usually used to characterize the porosity of unaltered core [5].

The ideal methodology to assess spatial heterogeneity of internal pore structure would reach the following performances: three-dimensional (3D), non-destructive and spatially-resolved investigation (non-bulk dependent), no constraining specific specimen preparation requirement (e.g. drying), direct measurement without interpolation

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or hypothesis on pore geometry and a sufficient high spatial resolution to detect all size range of cement pores including gel pores, i.e. a nano-scale resolution. Considering all this, X-ray computed tomography (CT) appears to be a good candidate that reaches most of these requirements. This non-destructive technique provides 3D images that can be processed and analyzed to get morphological information of the cement pore network such as pore shapes, sizes and pore connectivity and tortuosity [14–17]. Micro-CT has been used for many years to assess the pore structures of various materials such as soils, bones, ceramics and even cements [18–22].

Over the last years, spatial resolution of the technique improved and reached values lower than 1 μm as the capabilities of the optics used to focus the beam have increased. The resolution of the CT images depends on the spot size of the X-ray source, the optics used for the magnification and the resolution of the detector.

A recent study revealed the efficiency of synchrotron-based micro-CT (i.e. CT with a spatial resolution of the order of a micron and an effective voxel size of 500 nm) to characterize the porosity profile within leached cements [23]. The authors quantified porosity and pore connectivity of altered cements at various deterioration states. They also extracted the tortuosity of the pore network by random simulation.

However, spatial resolution reached by micro-CT remains insufficient to visualize gel pores and a majority of capillary pores. As a result, porosity of cement is generally largely under-estimated in studies based on micro-CT compared to porosity determined using MIP for instance [14]. This is due to the fact that the spatial resolutions used were usually much larger than the smallest pores [24].

Gallucci et al. reported that porosity and pore connectivity of cement measured by micro-CT strongly depend on the voxel size (spatial resolution) [25]. Indeed they showed that a decrease in the voxel size (from 2.67 to 2, 1.34 and 0.67 μm) induces an increase of the calculated pore network connectivity (from 0 to 66, 82 and 95% respectively) and calculated porosity (from 5.03 to 6.63, 11.48, and 18.6% respectively).

To the best of our knowledge the smallest voxel size used to characterize cement porosity by X-ray CT is 500 nm [23,25] which is not small enough to detect the smallest pores (i.e. gel pores). It is then clear that the spatial resolution of the X-ray micro-CT represents a key issue in characterizing the cement pore network. The best resolutions are generally achieved using synchrotron-based CT [23,25,26]; however access to synchrotron beamlines is highly competitive and can be a strong limitation to many users. Recently a new generation of laboratory-based nano-CT has been developed and provides nanometer-scale resolution [27,28]. Despite the fact that these lab-based setups do not benefit from a monochromatic beam and high X-ray coherency, potentially causing some artifacts such as beam hardening, lab-based nano-CT represent a valuable complement to synchrotron-based X-ray CT.

In this paper, we present results of cement pore structure investigation carried-out on leached cement paste. A multi-scale approach coupling X-ray micro- and nano-CT was used to characterize the heterogeneous spatial distribution of porosity from an altered surface layer to an unaltered cement core. This approach allows visualizing and quantifying in 3D the pore network at large observation scale from tens of nanometers to few micrometers. Image processing and thresholding step (to isolate void phase from solid phase) previously published for micro-CT study have been adapted to nano-CT scans. The quantification of the porosity, pore connectivity and pore size distribution was performed using a 3D morphological software (iMorph) [29].

2. Materials and methods

2.1. Materials

Anhydrous white Portland Cement (PC) was hydrated with Ultra Pure Water (UPW) at a water-to-cement weight ratio of 0.5 and molded in a cylindrical tube. High water-to-cement weight ratio was selected to increase the porosity of the initial cement paste and therefore enhance leaching effects on the pore network. The tubular unsealed molds were placed in a sealed container and cured for 28 days at ambient temperature in the dark. Cylindrical pellets of cement paste (diameter × height = 20 × 10 mm) were then obtained by cutting with a diamond wire saw and polishing the edges to remove specific border surface crystallization and defects.

2.2. Chemical and mineralogical characterization of the hardened cement paste

The chemical composition of PC was obtained by ICP-AES (inductively coupled plasma atomic emission spectroscopy) after mineralization (alkaline digestion). The crystallized phases of the cement unaltered core and altered layer at the cement surface (isolated from unaltered core by sanding) were identified by X-ray diffraction (XRD) using an X'Pert-Pro PANalytical X-ray diffractometer equipped with a cobalt source ($\lambda = 1.79$ Å) and operating at 40 kV and 40 mA. Each sample was previously ground in an agate mortar and scanned over a 2θ range of 5–80° with a counting time of 10 s per 0.033° step.

2.3. Aging protocol

A static leaching test (batch test) was used to simulate high level of cement alteration to obtain an altered layer with a significant porosity gradient from the surface to the unaltered cement core [1]. Batch tests were performed during seven days at liquid-to-solid-weight ratio (L/S) of 100 with UPW. Altered cement pellets were dried under glove box in N_2 atmosphere to avoid secondary surface carbonation [5]. Samples were then embedded in epoxy resin (araldite AY 103 mixed with hardener Hy 956) to preserve the structure of the very porous and friable altered surface layer.

Two samples with different sizes were prepared for micro- and nano-CT to allow sufficient X-ray transmission. Embedded leached cement pellets were cut perpendicularly to the cement surface into two sticks (5 × 5 × 15 mm for micro-CT scans and 0.4 × 0.4 × 15 mm for nano-CT scans). Obtained sticks are cross-sections of the sample including three layers: the resin, the altered layer at the cement surface and the unaltered core (Fig. 1).

2.4. X-ray micro- and nano-CT

Micro-CT scans were performed with a microXCT-400 X-ray microscope (Zeiss Xradia) to determine the cement porosity in a large field of view (LFOV) of mm size range, i.e. a representative sample volume including the unaltered core, the altered layer and the resin. Such LFOV enables to measure the thickness of the altered layer characterized by a lower material density (i.e. lower X-ray attenuation) due to higher porosity compare to the core region. Scans were performed at 60 kV (W target) and 150 μA with 1601 projections (angle step of 0.225° from −180 to 180°) and a 6 s exposure time per projection. Data were acquired with a 10× magnification optical objective for a total scan time of 4 h including the collection of reference images. The voxel size achieved under these conditions was 1.81 μm ($x = y = z$) and the FOV was 1.85 mm ($x = y = z$).

The nano-CT scans of the leached cement were obtained using an UltraXRM-L200 3D X-ray microscope (Zeiss Xradia). Four nano-CT scans were recorded at various positions from the surface to the core to assess the porosity heterogeneity along the cement profile as detailed below. The spatial resolution of this equipment is unique at the laboratory scale and reaches 150 nm using a Fresnel zone plate to focus the transmitted beam on a scintillator plate in front of a 20× optical device (SI. Fig.2). A copper X-ray source (rotating anode) produces a polychromatic beam with a maximum intensity at energy of 8.048 keV (Cu Kα X-ray emission). Scans were recorded with 901 projections from −90 to 90° with an angle step of 0.16° and an exposure time of 40 s per