Hard X-ray nanotomography of amorphous aluminosilicate cements

John L. Provis, a,* Volker Rose, b Robert P. Winarski c and Jannie S.J. van Deventer a,d

a Department of Chemical and Biomolecular Engineering, University of Melbourne, Victoria 3010, Australia
b Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne IL 60439, USA
c Center for Nanoscale Materials, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne IL 60439, USA
d The Zeobond Group, P.O. Box 210, Somerton, Victoria 3062, Australia

Received 6 January 2011; revised 16 April 2011; accepted 27 April 2011
Available online 3 May 2011

Nanotomographic reconstruction of a sample of low-CO2 “geopolymer” cement provides the first three-dimensional view of the pore structure of the aluminosilicate geopolymer gel, as well as evidence for direct binding of geopolymer gel onto unreacted fly ash precursor particles. This is central to understanding and optimizing the durability of concretes made using this new class of binder, and demonstrates the value of nanotomography in providing a three-dimensional view of nanoporous inorganic materials.

© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Three-dimensional tomography; Cement and concrete; Nanostructure; Amorphous oxides; Geopolymer

In the push towards designing construction materials with enhanced durability, it is essential to be able to characterize pore network structures on length scales ranging from nanometers to millimeters. The availability of durable construction materials is critical to society, in ensuring environmental sustainability as well as infrastructure safety, because sustainability aspects of infrastructure items must be measured on a life-cycle basis, meaning that a given percentage increase in service life provides environmental benefits approximately comparable to an up-front saving of the same proportion of the environmental cost of construction. Of course, the most desirable outcome would be to generate environmental savings in both areas simultaneously, by designing a material that has both lower up-front environmental cost and higher durability than existing technologies.

By far the most widely used construction material worldwide is Portland cement-based concrete, with more than 1.5 tonnes of concrete produced annually for every person in the world [1]. However, the production of Portland cement leads to the emission of almost 1 tonne of CO2 per tonne of cement [2]. Recently, aluminosilicate “geopolymer” cements have been introduced to large-scale applications in the construction industry [3], offering CO2 emissions savings of approximately 80% when comparing the production of the geopolymer binder to Portland cement production [4]. Geopolymers are synthesized from high-volume aluminosilicate waste materials, including coal fly ashes and metallurgical slags [3,5], resulting in an X-ray amorphous alkali-aluminosilicate gel structure that bears nanostructural similarities to zeolite frameworks [6], and can coexist with higher-calcium gel phases more closely resembling the calcium silicate hydrates formed in Portland cement-based binders if a more calcium-rich raw material is used [7–9].

Although the durability of construction materials can be analyzed by accelerated laboratory testing procedures [10], and some data related to the performance of geopolymers and similar materials in long-term service are beginning to become available [5,11], the ability to predict the performance of a material over several decades relies fundamentally on the ability to directly correlate micro- and nanostructure with chemistry and mass transport properties [12]. Microstructural modeling and microtomography have previously been utilized to provide valuable descriptions of transport properties of Portland cement binders [13–16]. However, the pore networks of all cementitious binders – both Portland cement-based and geopolymer-based – are known to include significant sub-micron porosity with complex geometry [17–20], which can be very challenging to characterize. Conventional X-ray microtomography instruments usually do not provide sufficient resolution for characterization of nanoscale pores, meaning that the
application of nanotomography is important in the analysis of both traditional and novel binder materials for the development of highly durable concretes.

Electron microscopy is almost universally used to provide two-dimensional (2D) information regarding the structure of materials with high spatial resolution. Recently, nanotomography has also been demonstrated in the analysis of complex material structures using electrons as a structural probe [21]. However, the low penetration depth of electrons profoundly limits its application. Generally, samples have to be sectioned in order to access the interior structure, which is not only extremely time-consuming, but furthermore may destroy the structures and introduce artifacts. Likewise, soft X-rays exhibit a relatively small penetration depth [21]. Hard X-ray nanotomography, on the other hand, achieves the required high penetration depth in real materials [22], but to date has suffered from limited spatial resolution. Nevertheless, it has been successfully applied, including in characterizing nanosized objects with complex shapes with a spatial resolution close to 60 nm [23], and observing internal structures within oxide nanoparticles and clay aggregates with voxel dimensions of 50 nm [24-26].

Here we utilize the Center for Nanoscale Materials hard X-ray nanoprobe (HXN) at beamline ID-26 of the Advanced Photon Source, Argonne National Laboratory [27], which can obtain tomographic images with 30 nm voxel resolution. The instrument uses two collinear undulators as a hard X-ray source and a Si(1 1 1) double-crystal monochromator. An elliptically shaped single-reflection glass capillary with a central stop is used as a condenser. Alignment of the beam stop and a pinhole aperture focuses a hollow central cone illumination onto the sample and the objective Fresnel zone plate with a diffraction-limited resolution of 30 nm. The objective zone plate is made by electroplating gold onto a silicon nitride membrane. The condenser and the zone plate, coupled with a phase ring optimized for the specific X-ray energy selected, provide Zernike phase contrast mode, which provides high image contrast even in low-absorbing samples [28], as an alternative to the “zoom tomography” (Kirkpatrick–Baez optics) that is implemented on various other beamlines internationally [22,29]. By acquiring a series of 2D images with the sample rotated stepwise through 180°, 3D tomographic data can be reconstructed and rendered. Our tomographic datasets consist of 1801 images (every 0.1° rotation through a 180° range) with an exposure time of 6 s per step. Positioning of the sample is provided by an active vibration control system based on laser interferometers.

Samples were mounted on tungsten tips using an adhesive obtained from strips of Scotch® Tape, aligned using the vibration-controlled HXN stage and analyzed. Images were obtained by the use of a PIXIS-XF X-ray camera with 1024 × 1024 pixels, with an incident X-ray energy of 10 keV. Images were corrected using background images collected after every tenth scan image. Tomographic reconstruction was carried out using the XRadia TXMReconstructor software package.

Data were collected for more than ten individual micron-sized particles of geopolymer binder; the results presented here are representative of the data obtained across this sample set. The sample analyzed here was synthesized by mechanically mixing fly ash (Gladstone Power Station, Queensland, Australia; Class F according to ASTM C618, detailed characterization information presented in Ref. [30]) with a potassium silicate solution of composition H2O/K2O = 11, K2O/SiO2 = 1.0, at a mass ratio of 0.56. The sample was cured in a sealed polymeric mold at 40 °C for 7 days, then aged (still sealed) at room temperature for 24 months before being crushed by hand to enable analysis of micron-sized specimens.

Figure 1 presents an overview of the whole sample as reconstructed, showing that it consists of a spherical fly ash particle, with a piece of geopolymers gel binder attached (top of the particle as seen in Fig. 1). The morphology of the gel binder here is consistent with previous observations showing that it is composed of sub-micron sized clusters of smaller gel particles, which can show varying levels of adhesion to unreacted fly ash particles depending on the chemistry of the fly ash glasses and the selection of alkaline solution used to react with the ash [31-33].

The texture of the geopolymer gel is clearly visible in the reconstruction, and is much more evident here than in the individual transmission images because the reconstruction has utilized data from all 1801 images collected to accurately reconstruct the nanometer-scale pore structure of the geopolymer gel. Supporting information available online includes a video of the reconstructed particle passing through a full 360° rotation, as well as a video showing the progression through a stack of reconstructed slices through the sample, similar to the cross-section shown in Figure 2.

It is particularly interesting to note that taking a section through the center of the specimen (Fig. 2) shows that the original fly ash particle was hollow, a “cenosphere”. Such particles have been observed in Australian and

![Figure 1.](image-url)
The fact that the fly ash particle studied here remained connected directly to a piece of geopolymer gel after (manual) crushing of the original monolithic sample indicates that there was not a reaction rim between the particle and gel, showing strong adhesion of the geopolymer binder to the particle. Such close adhesion between the gel and an Fe-aluminosilicate particle is clearly important in the development of a strong and impermeable geopolymer gel, but probably even more important in the development of geopolymer concretes. The porous “interfacial transition zone” that forms between binder regions and aggregate particles in Portland cement-based concretes is a primary factor in determining the strength and durability of the concrete [1]. Analysis of the interfaces between geopolymer binders and various silicate minerals has shown a generally dense (and therefore desirable) interfacial region [36,37], and the results presented here show for the first time that similar behavior would also be possible for the case of the basalt (Fe-aluminosilicate) aggregates that are widely used in concrete.

Figure 3 shows a higher-magnification image of the reconstructed geopolymer gel region of the specimen, highlighting the pore network of the geopolymer gel. The size range of the pores that are visible in this region of gel is around 100–400 nm, and the porosity of the gel region is identifiable as being around 30–50%, although this computation is subject to significant uncertainty due to the need for binary thresholding of the grayscale density data [20]. This is consistent with the observations of Lloyd et al. [19], who studied geopolymers synthesized from the same fly ash as is studied here and showed that, although a significant fraction of the porosity in the geopolymer gel appears in the <10 nm size range via N₂ sorption analysis, Wood’s metal intrusion porosimetry instead shows a significant pore volume in the 10–1000 nm size range. This discrepancy was attributed to difficulties related to “ink-bottle”-shaped pores in the gas sorption analysis, and the results presented here – which give a direct measure of the pore network structure rather than relying on an indirect probe technique such as gas sorption – support that proposition. The pores are visibly non-cylindrical, even in the very small gel region shown in Figure 3. Dense geopolymer gel clusters of size generally not more than 200 nm, and closer to oblate than spherical in shape, are seen to be accreted together...
to form a gel structure that percolates in 3D space and provides good mechanical strength.

This is the first ever image of a geopolymer gel generated directly on this length scale other than by transmission electron microscopy (TEM), and the interpretation of images of geopolymers obtained by TEM is problematic due to the very rapid and extensive degradation of the samples that is induced by both ion beam milling during preparation, and also the effects of the electron beam itself. By comparison, the manual crushing and X-ray tomographic analysis conducted here provides for the first time a 3D view of an intact section of the geopolymer gel, where globular particles of aluminosilicate gel are visible in conjunction with an undisturbed pore network. Future work in nanotomographic analysis of geopolymer binders will build from these initial outcomes, with a view towards developing a more rigorous understanding of the geometry of the nanoscale pore network of geopolymer binders.

This communication has therefore demonstrated the applicability and value of nanotomography in the analysis of complex porous inorganic samples, and specifically geopolymer gels. The 3D structure of a section of geopolymer gel that has adhered to an iron-containing fly ash cenosphere has been established, and essential information regarding the likely adhesion of geopolymer gel to iron-containing basalt aggregates has been obtained.

Use of the Advanced Photon Source and Center for Nanoscale Materials was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This work was funded by the Australian Research Council (ARC), including partial funding from the Particulate Fluids Processing Centre, a Special Research Centre of the ARC, and by the Australian Synchrotron International Access Program. We thank Dr C. Shi, P.V. Krivenko, D.M. Roy, Alkali-Activated Cements and Concretes, Taylor & Francis, Abingdon, 2006.
