

X-ray Characterization of Cement-based Materials: Previous Applications & New Opportunities

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Challenges Associated with Characterization of Cement-based Materials

Many challenges are intrinsic to the characterization of cement-based materials. First, cement-based materials are typically hydrated systems whose structure will be altered with removal of water. In addition to altering the structure, any reactions requiring water (e.g., cement hydration, pozzolanic reaction, alkali-silica reaction, sulfate attack, freeze/thaw) will be halted upon its removal. This presents a challenge for *in situ* observation of ongoing reactions. Thus, it is often desirable to characterize these materials in the presence of water.

When observing ongoing reactions, data acquisition must be fast. For observation of early hydration, for example, imaging times in the seconds to fractions of seconds is desirable. In addition, it is important to acquire images without destroying the sample or altering the rates and/or mechanisms of ongoing reactions. For tracking damage evolution during deleterious reactions, a non-destructive method which allows for sample indexing (i.e., precise locations within a sample can be characterized on multiple occasions as damage progresses) advantageous.

The complex physical structure of cement-based materials presents an additional challenge to their characterization. These materials are heterogeneous on multiple scales, from the nano- and micro-scale to the meso-scale. The inherent challenge, then, is to resolve the finest detail in the structure (i.e., nanoscale C-S-H), while maintaining a representative concept of the whole. A technique which allows for a wide magnification range would, then, be quite useful. Recognizing that these desires for high resolution while maintaining a broad field of view (or large sample) may be practically difficult to achieve within the same instrument, the ability create a larger montage or tiled image composed from smaller images to give a larger field of view would be beneficial.

A final challenge is that these materials are generally optically opaque; however, often sub-surface characterization is desired. This may be to avoid near-surface alterations to the physical or chemical structure, which occur during sample preparation (e.g., cutting, polishing, epoxy impregnation) or environmental exposure (e.g., carbonation, leaching). In some cases, the surface may not be representative of the bulk features. This is often the case with fracture surfaces, which are inherently among the weakest regions in a sample. Also, features such as phase connectivity and size distribution (in complex structures) cannot be discerned with accuracy from a two-dimensional image. Thus, techniques, such as x-ray methods, which afford sub-surface and/or volumetric characterization, are likely to be useful.

Review of Applications of X-ray Characterization

For ease of presentation, applications of synchrotron x-ray imaging will be discussed as they relate to cement production, cement hydration, mechanical behavior, and durability.

Cement Production

Opportunities for research exist in the identification and quantification of phases existing in unhydrated cement and clinker, as well as the characterization of phase structure as influenced by the introduction of hazardous and non-hazardous (introduced for improved production or hydration) impurities. Studies to date in this area have almost exclusively relied upon synchrotron powder diffraction, rather than imaging. For instance, De La Torre *et al.* [2002] describe the MIII structure of alite ($3\text{CaO}\cdot\text{SiO}_2$ or Ca_3SiO_4) achieved through Al and Mg doping using Rietveld-refined synchrotron (at ESRF) and neutron diffraction data; their data shows both techniques to be far more accurate than the commonly-used Bogue equations for cement composition. Peterson *et al.* [2002] found synchrotron diffraction (at KEK Japan) results to be superior to neutron diffraction for phase quantification in cement clinker. *In situ* studies of phase evolution at temperatures up to 230C have been performed by Shaw and co-workers [2001] at SRS. Such *in situ* studies at high temperature are very interesting and useful for optimizing cement production; the value of imaging in addition to diffraction data, however, for these types of studies is not clear.

Cement Hydration

Cement hydration studies have also been undertaken with synchrotron diffraction, spectroscopy, and imaging. With both, fast data acquisition is essential to adequately capture the complexities of the system. In a single phase

(Ca₃SiO₄) hydration study, Clark and Barnes [1995] report better precision with energy-dispersive powder diffraction performed at Daresbury, as compared to neutron and lab diffraction. Barnes *et al.* [2000] provides an excellent survey of their group's work, including time-resolved hydration studies of C₃A (where a short-lived intermediate phase was observed using 6s time steps) and oil well cements (under ambient and autoclave conditions). Subsequently, Jupe *et al.* [2001] combined synchrotron x-ray and neutron diffraction with EXAFS to examine the relative activity of pure and Mg-doped Brownmillerite (Ca₂FeAlO₅), finding the pure form to be more active within the first 100 minutes. Biernacki and co-workers [2003] showed synchrotron XRD to provide a broader range of detectability and greater accuracy than lab XRD, and to offer a viable alternative to thermogravimetric analysis for determining calcium hydroxide content.

In addition to diffraction, x-ray absorption spectroscopy (XAS) has been used to examine the immobilization of chromium during hydration [Tsuyumoto and Uchikawa, 2003], and lead (at the Pb-LIII edge) [Rose *et al.* 2000] and zinc (at the Zn K-edge) [Rose *et al.*, 2001] during and after hydration. And, Winslow *et al.* [1995] used small angle scattering (performed at Cornell University) to examine the effect of drying on the fractal types and dimensions in cement pastes.

Most relevant to imaging, a small number of synchrotron microtomography studies to examine cement hydration have been reported. Using the microtomography BL X27A at NSLS with electron probe microanalysis and NMR spectroscopy, Butler *et al.* [2000] found that the introduction of toluene during mixing produced large voids or vesicles in the hardened material, likely initially filled with the hazardous organic waste. Very small (~1mm) samples of calcium phosphate (bone) cement on bone have been examined by Weiss *et al.* [2003] by phase-contrast microtomography at BL ID22 at ESRF. While not a synchrotron technique, medical CT was used with acoustic emission to monitor calcium aluminate cement hydration [Chotard *et al.*, 2003].

Transmission soft x-ray microscopy (TXRM), performed at BL 6.1.1 at the Advanced Light Source (ALS), has been used to characterize the pozzolanic reaction and product formation [Gartner *et al.*, 2000] and cement hydration. Kurtis and Rodrigues [2003] examined the effect of Ba-doping and hydrothermal treatment on hydration of β-C₂S cement. Juenger *et al.* [2003] examined alite hydration in gypsum and calcium hydroxide solutions. These TXRM studies have typically been performed at much higher water-to-cement ratios than would be used in practice

Effect of Loading

Landis has reported the application of microtomography at BL X2B (NSLS) to examine internal cracking in 4x8 mm cylindrical mortar samples under compression. Landis's use of mortar (i.e., cement paste with fine aggregate) is rather unique among the synchrotron research performed. The technique was used to monitor, in three-dimensions, internal damage and cracking in a single specimen under load [Landis *et al.*, 1997] and to relate damage to fracture energy [Landis *et al.*, 2003].

Durability Studies

A variety of synchrotron methods have been applied to a wide range of durability issues associated with cement-based materials. X-ray absorption spectroscopy (XAS) was used to study ingress of iodine species into cement paste and C-S-H; XANES indicated that C-S-H does not itself uptake iodine [Bonhoure *et al.*, 2002]. Castellote *et al.* [2002] monitored accelerated leaching, induced with an electrical field, in cement pastes by SXRD.

The first synchrotron imaging of cement-based material found in the literature reports sulfate damage to an epoxy-impregnated 3.5mm-diameter sample cored from a standard mortar bar, as examined by Bentz *et al.* [1995] at BL X-2B at NSLS. Stock and co-workers [unpublished data] have subsequently examined small (1-2 mm) diameter cement paste cylinders exposed to sulfate attack, using facilities at APS. Related to durability as a measure of permeability, Landis *et al.* [2000] characterized three-dimensional pore structure by synchrotron microtomography.

TXRM has been used to examine *in situ* the alkali-silica reaction [Kurtis *et al.*, 2002, 1999, 1998], products of sulfate attack, and reinforcing steel corrosion [Kurtis *et al.*, 2000].

Hall *et al.* [2000] have described a technique TEDDI (tomographic energy-dispersive diffraction imaging) which uses diffraction to provide direct compositional/structural data with resolution of about a micron. Tests performed at station 16.4 at SRS (Daresbury) demonstrated the identification of calcite, dolomite, calcium hydroxide, and ettringite in a 13x6mm region cut from a concrete block, subjected to conditions meant to produce the deleterious

delayed ettringite formation. This technique, which provides spatial phase identification, could be used for a wide range of durability investigations.

Concluding Remarks

X-ray imaging affords some clear benefits for the characterization of cement-based materials, including:

- Non-destructive examination and/or sectioning of opaque cement-based materials
- High (nanoscale) resolution
- Rapid data acquisition
- Characterization of hydrated samples at normal temperature and pressure, if desired.

Developments which would be beneficial for researchers in the cement-based materials community include:

- Coupling of imaging and diffraction or spectroscopy
- Dedicated beamlines for imaging, avoiding complicated and time-consuming set up and break down
- User support for imaging and reconstruction
- Ability to image larger samples, even at lower resolution

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