Multiscale Imaging of Concrete

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Need for multiscale imaging
With Connecticut Foundations Crumbling, ‘Your Home Is Now Worthless’

By KRISTIN HUSSEY and LISA W. FODERARO  JUNE 7, 2016
Combining techniques at the micro/nano scale
Micro-tomography

Marinoni et al., 2015

a) subvolume rendering showing dissolution zone in chert (blue) and debonding (red);
c) rendering of the subvolume with microcracks (red) emanating from the aggregate particle
Mineralogy can be studied with microXRD

Chert near the interface.
Mean peaks $\rightarrow$ quartz

Chert near the interface.
Mean peaks $\rightarrow$ calcite
Quartz has dissolved away
Poro-mechanical model with chemical and mechanical damage
\[(1-d) = \frac{(1-D_{ch}) \left[(1-\omega)K_s + Mb^2\right] - Mb^2}{(1-\omega)K_s}\]
Studies of shales at the nanoscale

(I) a porous, fissurized matrix and
(II) a kerogen inclusion with very low permeability

A mathematical model of fluid and gas flow in nanoporous media

Paulo J. M. Monteiro\textsuperscript{a,b}, Chris H. Rycroft\textsuperscript{c,d}, and Grigory Isaakovich Barenblatt\textsuperscript{c,d,e,1}

\[ \partial_t P = \chi \partial_x (\partial_x P)^{m+1}, \quad \chi = \frac{A \rho_0}{\alpha \mu \phi} \]

for the case of weakly compressible fluid and

\[ \partial_t P = \kappa \partial_x \left( P (\partial_x P)^{m+1} \right), \quad \kappa = \frac{A}{\mu \phi} \]

production rate per unit of area

\[ Q = S j_n \]

\[ = S \rho_0 u_n = \frac{S \rho_0}{\mu} \left( \frac{df(0)}{d\xi} \right)^{m+1} \frac{P^{m+1}}{[\chi(t-t_0)P_m]^{(m+1)/(m+2)}} \]

\[ = \frac{SA \rho_0}{\mu} P^{2(m+1)} [\chi(t-t_0)]^{m+1} \left( \frac{df(0)}{d\xi} \right)^{m+1} \]
Finally, the production rate is given by:

\[ Q = \frac{SA\rho_0}{\mu} P_{m+2}^{m+1}[\kappa(t - t_0)]^{m+1} \left( \frac{df(0)}{d\xi} \right)^{m+1} \cdot Q \sim (t - t_0)^{-\frac{m+1}{m+2}}. \]
Nanoprobe at APS
Preliminary tests for shale

Imaging of shale using hard x-ray at APS. The images were stitched together to have a broad field of view of the particle. The pixel size was 16 nm with a spatial resolution of 30 nm.
Distribution of kerogen in a shale

Determination of the connectivity of organic matter in shales a) absorption image of shale. At this energy it is not possible to identify the various phases in shale; b) Synchrotron radiation allows for the fine-tuning of photon energy so it is possible to create high-resolution mapping of the location of the kerogen. Red: “Kerosene” peak at 286.7, Green: 296eV, Blue: “Shale” peak at 297eV.
Importance of the mesoscale

Fig. 1. (A) PSDs for $\eta = 0.33$ and $\eta = 0.52$. (B) Close-up view of the pore network for a sample with porosity $\phi = 0.48$, where $\phi = 1 - \eta$. The box size is $L = 195.22$ nm. (C) 2D schematic view of C-S-H. Reprinted from ref. 23. (D) Local volume fraction distributions $\eta_{\text{local}}$ for $\eta = 0.33$ and $\eta = 0.52$. (E) Snapshot of a sample with $\eta = 0.33$ and (F) snapshot of a sample with $\eta = 0.52$ (the colors indicate $\eta_{\text{local}}$ and $L = 585.54$ nm).

Ioannidoua et al., PNAS 2016
Nanoscale Characterization

• Spectromicroscopy

• Very high spatial resolution nanoCT
Scanning Transmission X-ray microscopy (STXM)

much lower cost for better interferometers, these days

removable sample-scan piezo-stack
K-edge: 1s→2p
L-edge: 2p→3d
Absorption Edges
Cement Chemistry at Nanoscale

SCANNING MODE

Image Scan  Element Mapping  Line Scan  Stack Scan
Image Scan

Element Mapping
Study of the Ca-edge

![Graph showing normalized intensities vs energy for Anhydrous C_3S](image)
Study of the Ca-edge
Study of the Ca-edge
Study of the Si-edge for reference materials
Hydrated C$_3$S (17day old sample)
Older $C_3S$ samples

1.5 years

Geng et al., CCR, 2015

50 years
Energy difference, $\Delta E$, between minor and major peak at Si K-edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X (eV)</th>
<th>Y (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Hydration time (years)</th>
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<tbody>
<tr>
<td>$C_3S$</td>
<td>1847.7</td>
<td>1858.9</td>
<td>11.2</td>
<td>0</td>
</tr>
<tr>
<td>Ip C–S–H-1</td>
<td>1848.1</td>
<td>1860.9</td>
<td>12.8</td>
<td>1.5</td>
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<td>Ip C–S–H-2</td>
<td>1848.1</td>
<td>1860.9</td>
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<td>Op C–S–H-1</td>
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<td>Op C–S–H-2</td>
<td>1848.1</td>
<td>1861.1</td>
<td>13.0</td>
<td>1.5</td>
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<tr>
<td>$C_3S50$</td>
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<td></td>
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<tr>
<td>C–S–H-3</td>
<td>1848.3</td>
<td>1864.8</td>
<td>16.5</td>
<td>50</td>
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<tr>
<td>C–S–H-4</td>
<td>1848.3</td>
<td>1864.8</td>
<td>16.5</td>
<td>50</td>
</tr>
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Quantity of Si anions in each environment as a percentage obtained from integration of the peak areas.
Data from 12 h to 26 years are from Rodger [9].

<table>
<thead>
<tr>
<th>Age</th>
<th>$Q^0$</th>
<th>$Q^1$</th>
<th>$Q^2$</th>
<th>MCL</th>
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<tr>
<td>12 h</td>
<td>89</td>
<td>11.0</td>
<td>0.0</td>
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<tr>
<td>1 day</td>
<td>68</td>
<td>30.0</td>
<td>2.0</td>
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<td>7 days</td>
<td>48</td>
<td>43.0</td>
<td>9.0</td>
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<td>14 days</td>
<td>33</td>
<td>52.0</td>
<td>15.0</td>
<td>2.58</td>
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<tr>
<td>1 month</td>
<td>30</td>
<td>53.0</td>
<td>17.0</td>
<td>2.64</td>
</tr>
<tr>
<td>3 months</td>
<td>18</td>
<td>62.0</td>
<td>20.0</td>
<td>2.65</td>
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<tr>
<td>6 months</td>
<td>14</td>
<td>65.0</td>
<td>21.0</td>
<td>2.65</td>
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<td>1 year</td>
<td>10</td>
<td>55.0</td>
<td>35.0</td>
<td>3.27</td>
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<tr>
<td>2 years</td>
<td>6</td>
<td>52.0</td>
<td>42.0</td>
<td>3.62</td>
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<td>26 years</td>
<td>0</td>
<td>42.0</td>
<td>58.0</td>
<td>4.76</td>
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<tr>
<td>50 years</td>
<td>0</td>
<td>47.9</td>
<td>52.1</td>
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Interactions between bi-polymer fiber/matrix

D. Hernández-Cruz et al. / Cement & Concrete Composites 48 (2014) 9–18

(a) 

(b) 

(c) 

(d)
Fig. 7. (a) An OD image showing the area where a Ca image stack was obtained; (b) the OD image extracted from the image stack showing the three areas where the NEXAFS spectra were extracted; (c) the NEXAFS spectra extracted for the three areas representing the PP core (1), the EAA sheath (2), and the clear and strong spectra of the HCP area (3); and (d) the RGB composite map showing the PP core in red, the EAA sheath in green, and the HCP in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
What about Afm and Aft?
STXM images of NaCl-reacted monosulfoaluminate samples
Effect of chemical admixtures

C₃S (reference)  C₃S + PCE-Sil  C₃S + PCE
Towards very high spatial resolution nanotomography
Soft X-ray nanotomography work done at BESSY, Berlin

Jackson et al. JACers, 2013.
Soft X-Ray Nanotomography

Work done at BESSY, Berlin

Bridging the gap from nano to micro length scales

Application of the 2D Fourier slice theorem:

Consider one projection $A(x,y)$;
1. Take the 2D Fourier transform of $-\ln(A(x,y))$ to obtain the complex function $A_c(q_x,q_y)$;
2. The spectral density $P(q_x,q_y)$ of $-\ln(A(x,y))$ is

$$P(q_x,q_y) = A_c(q_x,q_y) \cdot A_c^*(q_x,q_y)$$

The spectral density is a good approximation of the small angle scattering pattern, $l(q_x,q_y,q_z=0)$
Portland cement paste

Log Fourier transform

SAXS experiment

Brisard et al., Am. Min., 2012
Soft X-ray microscopy at a spatial resolution better than 15 nm

Weilun Chao¹,², Bruce D. Harteneck¹, J. Alexander Liddle¹, Erik H. Anderson¹ & David T. Attwood¹,²

Figure 3 | Scanning electron micrograph of a zone plate with 15 nm outermost zone. Shown in the inset is a more detailed view of the outermost zones. The zonal period, as indicated by the two black lines, is measured to be 30 nm. The zone placement accuracy is measured to be 1.7 nm.
Ptychography
A major breakthrough in high resolution x-ray imaging
Advantage of redundant data

Object is split into frames with known centers
Each frame is illuminated separately
Neighbors overlap

From David Shapiro
Nanosurveyor 1.0 – ALS
Beamline 5.3.2.1

- 7 s / $\mu$m$^2$ measurement time
- 5-10 nm resolution
- 2 nm RMS stability
- Open geometry, EASY TO USE
- 25-250 nm zone plate
- Up to 25 mm focal length, 100 $\mu$m depth of field
- No cryo
Ptychography with soft x-rays (work done at the Advanced Light Source)

Log Fourier transform

\[ I(q) \propto q^{-3} \]

Bae et al., JACers, 2015

\[ I(q) \propto q^{-4} \]
With such high spatial resolution it is possible to probe the inner product.
Chemistry?

XANES with Soft X-Ray Transmission Microscopy

[Graph showing energy vs. intensity with peaks labeled as 'Op' and 'CH']

[Image of a biological sample with arrows indicating specific areas]
Final Question:

Is it possible to obtain nanoCT with extremely high spatial resolution?
<table>
<thead>
<tr>
<th>Collaborators</th>
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<tbody>
<tr>
<td>Pierre Levitz</td>
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<tr>
<td>G.I. Barenblatt</td>
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<td>S. Brisard</td>
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<tr>
<td>K. Kurtis</td>
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<td>G. Geng</td>
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<tr>
<td>C. Bae</td>
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<tr>
<td>D. Shapiro</td>
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<td>C. Ostertag</td>
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<tr>
<td>Rossella Pignatelli</td>
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<tr>
<td>Claudia Comi</td>
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<tr>
<td>M. D. Jackson</td>
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<td>S. Yoon</td>
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<tr>
<td>Daniel Hernandez Cruz</td>
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<tr>
<td>David A. Kilcoyne</td>
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<tr>
<td>P. Guttmann</td>
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