Assessing the Effects of Gamma Irradiation in Concrete

Elena Tajuelo Rodriguez
William A. Hunnicutt
Paramita Mondal
Yann Le Pape

ANS meeting
June 2018
Outline

- LWRS program and previous work on concrete
- Basics about calcium silicate hydrates
- Viscoelasticity in C-S-H and C-(A)-S-H
- Viscoelasticity and water content in C-S-H
- Synthesis details
- Sample conditioning
- Sample irradiation and characterization
- XRD, TG and TEM results
- Stress relaxation nanoindentation
- Elastic nanoindentation
- Creep nanoindentation
- Conclusions
- Acknowledgements
LWRS program and previous work on concrete

- Extend the life cycle of light water reactors from 40 to 60-80 years
- Need to assess the degradation, integrity and safety of the components in nuclear plants: reactor metals, cables and concrete

LWRS Objectives

- Understand, predict and measure changes in materials as they age
- Develop and demonstrate methods and technologies that support safe and economical long-term operation of existing reactors
- Research new technologies to address enhanced plant performance, economics and safety
The concrete bio-shield of the reactor pressure vessels will withstand unprecedented levels of Gamma and neutron irradiation after 80 years of operation, estimated at $\sim 2-5 \cdot 10^{19}$ n/cm$^2$ and $\sim 100-200$ MGy.

<table>
<thead>
<tr>
<th>Years of Operation</th>
<th>PWR Type</th>
<th>Neutron Fluence (n/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E $&gt; 0.0$ MeV</td>
</tr>
<tr>
<td>40</td>
<td>2-loop</td>
<td>$7.3 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>3-loop</td>
<td>$3.6 \times 10^{19}$</td>
</tr>
<tr>
<td>60</td>
<td>2-loop</td>
<td>$1.1 \times 10^{20}$</td>
</tr>
<tr>
<td></td>
<td>3-loop</td>
<td>$5.4 \times 10^{19}$</td>
</tr>
<tr>
<td>80</td>
<td>2-loop</td>
<td>$1.5 \times 10^{20}$</td>
</tr>
<tr>
<td></td>
<td>3-loop</td>
<td>$7.2 \times 10^{19}$</td>
</tr>
</tbody>
</table>

Remec et al. 2016
LWRS program and previous work on concrete

- A compilation of data on concretes and mortars indicates a decrease in compressive strength, tensile strength and modulus of elasticity with neutron fluence for doses $> 10^{19}$ n/cm$^2$
- Aggregates are mostly affected by neutrons and suffer from RIVE (radiation induced volumetric expansion) that ultimately causes cracking within the aggregates and cement paste
- Gamma rays affect cement paste causing dehydration through hydrolysis $\rightarrow$ Main component of cement paste is C-S-H $\rightarrow$ Lack of understanding on the effects of gamma irradiation on the structure and mechanical properties of C-S-H

Modified from Field et al. 2015

[Graph showing relative compressive strength vs. neutron fluence for different materials, modified from Field et al. 2015]
The onset of damage is reduced with creep for both a free (right) and restrained (left) concrete → the predicted damage decreases for a given fluence taking creep into account.

Creep and hence the viscous behavior were considered independent of fluence → But is that the case?

The creep response of cement paste comes from C-S-H
Basics about calcium silicate hydrates

- CaO central layer with silicate chains attached and interlayer water
- Low C/S ratio $\rightarrow$ long silicate chains (pentamers, octamers and more)
- High C/S ratio $\rightarrow$ short silicate chains and Ca in the interlayer
- When Al substitutes Si in the bridging sites $\rightarrow$ Al substituted C-S-H $\rightarrow$ C-A-S-H

Garbev et al. 2008
Basics about calcium silicate hydrates

- Mean Aluminosilicate Chain length (MCL) can be calculated knowing the percentages of silicate species from $^{29}\text{Si NMR}$:
  \[
  \text{MCL} = \frac{2[\%Q^1 + \%Q^2 + (3/2)\%Q^2(1\text{Al}) + \%Q^3]}{\%Q^1}
  \]

<table>
<thead>
<tr>
<th>Type of silicates</th>
<th>Designation</th>
<th>Tetrahedral structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho(mono)silicates</td>
<td>$Q^0$</td>
<td>O-SiO-O</td>
</tr>
<tr>
<td>Disilicates (endchain groups)</td>
<td>$Q^2$</td>
<td>O-SiOSiSi</td>
</tr>
<tr>
<td>Chain middle groups</td>
<td>$Q^2$</td>
<td>SiOSiOSiSi</td>
</tr>
<tr>
<td>Chain branching sites</td>
<td>$Q^3$</td>
<td>Si-O-SiOSiSi</td>
</tr>
<tr>
<td>Three dimensional framework</td>
<td>$Q^3$</td>
<td>O-SiOSiSi</td>
</tr>
</tbody>
</table>

Modified from Garbev et al. 2008

Basics about calcium silicate hydrates

• Typical progression of Q species as the Ca/Si changes

<table>
<thead>
<tr>
<th>Bulk Ca/Si</th>
<th>MCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>18.8</td>
</tr>
<tr>
<td>0.83</td>
<td>10.1</td>
</tr>
<tr>
<td>1</td>
<td>5.5</td>
</tr>
<tr>
<td>1.25</td>
<td>2.7</td>
</tr>
<tr>
<td>1.33</td>
<td>2.5</td>
</tr>
<tr>
<td>1.5</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Viscoelasticity in C-S-H and C-(A)-S-H

• The viscoelastic properties of C-S-H and C-A-S-H are thought to be based on layers/particles moving relative to each other under sustained stress

Hypothesis

• The mean aluminosilicate chain-length and the crosslinking between may have an impact on the viscoelasticity

• Shorter chains and less cross-linking lead to more viscous response

• More particles for a given amount of material that can move relative to each other under sustained stress

Hunnicutt et al. 2016
Viscoelasticity and water content in C-S-H

When C-S-H dries

Water may be removed from the interlayer, thus the interlayer space may decrease, the mean silicate chain length may increase and also certain degree of crosslinking can appear (less number of particles to move relative to each other)

The viscoelastic response is expected to decrease
• Evaluate 3 samples with $C/S = 0.75, 1, 1.33$ to test possible different responses to irradiation when parting from different MCL’s and different interlayer spacing
• Synthesis details:
  ▪ Mix of CaO freshly obtained from roasting CaCO$_3$ at 1000°C overnight with aerosil 200 (nanosilica) with the different Ca/Si ratios and w/s = 8 in a roller mill for 2 days
  ▪ Slurries dried in a container with a continuous N$^2$ flow of 100cm$^3$/min at 50°C for 3 days
  ▪ Sample reduced to powders in a mortar and pestle used inside an N$^2$ filled glovebox and sieved through 75 microns
Sample conditioning

- Powders conditioned at 11%RH over petri dishes in sealed boxes with LiCl solutions and granular soda lime for 4 weeks. The boxes were inside a glovebox with a suppressed CO₂ atmosphere of 1-7ppm provided by granular soda lime.
- Powders compressed into pellets of 25.4 mm diameter and approx. thickness of 2mm. 2g of material were used to press each pellet under a 250 kN load in a 50ton hydraulic press. The pellets were kept in the sealed boxes at 11%RH for 2 weeks until irradiation started.
Sample irradiation and characterization

- Pellets irradiation for 2, 4, 7.5 and 12 months with doses of 0.39MGy, 0.77MGy, 1.39MGy, and 2.24MGy respectively (under Ar flow of approx. 3psi/h to provide inert atmosphere to prevent carbonation) in a Co\textsuperscript{60} gamma reactor (J.L. Shepherd Model 109-68 Co-60 unit) with a dose rate of 0.225 kGy/h
- Use control samples placed in the same containers in the gamma irradiator room out of radiation reach
- Samples were studied with TG, XRD, \textsuperscript{29}Si NMR, TEM and Nanoindentation (3 NSUF RTE proposals funded)
XRD, TG and TEM results

- XRD patterns showed very similar basal spacing distances for control and irradiated samples indicating no water was removed from the interlayer due to irradiation induced drying.
- TG gave water contents in the range of 13-17% for all samples and no correlation was found between water content and irradiation dose.
- TEM revealed no change in morphology (foil-like) with irradiation, and showed similar compositions between samples with the same bulk Ca/Si.

\[
\begin{align*}
\text{2 months dose} & \quad \text{Ca/Si} = 0.81 \pm 0.03 \\
11\%\text{RH control} & \quad \text{Ca/Si} = 0.78 \pm 0.03
\end{align*}
\]
**Stress relaxation nanoindentation**

- The force in indentation is a function of the relaxation modulus, indentation depth, Poisson’s ratio and geometric factors...:
  \[ P = f(E, h, v, \text{geometric factors}) \]

- Assuming a time-independent Poisson’s ratio and using a Heaviside function for displacement, the solution is independent of porosity and other geometric factors (Cao et al. 2010):
  \[ \frac{P(t)}{P_0} = \frac{E(t)}{E_0} \]

- 175 nm displacement chosen because non-linear viscoelastic regime appears for deeper depths
- 10x10 grid, 5\( \mu \)m spacing
- Minimized drift using:
  - Piezo automation
  - > 3 hours settle time before indenting
  - 1 min settle time between each indent

- A mean relaxation curve and confidence intervals of 95% were calculated with bootstrap analysis
Stress relaxation nanoindentation results

0.77 MGy

CSH 1.33

Normalized force vs. Time (seconds)

Normalized force vs. Dose (MGy)

BS Mean Fit - 4m dose
BS Mean Fit - 4m ctrl
BS Mean Lower 95% CI
BS Mean Upper 95% CI
BS Mean Lower 95% CI
BS Mean Upper 95% CI

Ca/Si = 1.33 control
Ca/Si = 1.33 irradiated

Stress relaxation nanoindentation results
Stress relaxation nanoindentation results

- **Ca/Si = 0.75 control**
- **Ca/Si = 0.75 irradiated**

- **Ca/Si = 1 control**
- **Ca/Si = 1 irradiated**
Stress relaxation nanoindentation results

- No apparent relationship between normalized force and MCL or Q^3 contradicting previous hypothesis by Hunnicutt et al., but the range of proven MCL is lower in this case (C-A-S-H MCL for Hunnicutt was 28.3)
Elastic nanoindentation

- The reduced modulus and Young modulus can be calculated as:
  \[ E_r = \frac{\sqrt{\pi} \frac{dP}{dh}}{2\sqrt{A_c}} \] and \[ E \sim E_r(1 - \nu^2) \]

- 4000 μN load
- 10x20 grid, 10μm spacing
- 60s settle time between each indent
The Young’s modulus values present no trend with irradiation dose. The dependence on Ca/Si has to be looked out with CAUTION, it is an effect of the porosity and packing samples of different densities at the same pressures. Young’s modulus should decrease with Ca/Si according to Manzano et al (2009).
Creep nanoindentation

- 1000μN load
- 10x10 grid, 5μm spacing
- Minimized drift using:
  - Piezo automation
  - > 3 hours settle time before indenting
  - 1 min settle time between each indent
- Displacement data versus time were fitted to (Jones and Grasley 2011):
  \[ h(t) = 1.21 \sqrt{P_{max}(J(t))} \cot \theta \]

  Where \( P_{max} \) is the max load, \( J(t) \) is the creep compliance as a function of time, and \( \theta \) is the equivalent half-angle of the indenter tip.

  The creep compliance was taken as a stretched exponential function:
  \[ J(t) = \frac{1}{E_0} + \frac{1}{E_1(1 - e^{-1})} \left(1 - e^{-(t/th)^\beta}\right) \]

- A mean creep compliance curve and confidence intervals of 95% were calculated with bootstrap analysis.
Creep nanoindentation: Creep compliance results

2.24 MGy

Ca/Si = 0.75

Ca/Si = 1.33
Conclusions

- Gamma irradiated C-S-H to doses up to 2.24 MGy present no significance difference in stress relaxation and creep behavior to unirradiated samples.
- The normalized force for stress relaxation tests showed no dependence on MCL over the range of MCL’s studied (from 2 to 16) or the degree of cross-linking (from 0 to 30%).
- The Young’s modulus values showed no trend with respect to irradiation dose.
- Further conclusions regarding the observed trends need the planned examination of irradiated samples at higher doses. Experiments to reach 25 and 200 MGy are being performed at SNL.
Acknowledgements

- Thanks are due to the U. S. Department of Energy, Office of Nuclear Energy, Light Water Reactor Sustainability (LWRS) Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC / Oak Ridge National Laboratory and the NSUF for funding through four RTE proposal calls.

- Thanks to all the staff at ORNL for support: Yann Le Pape, Tom Rosseel, Alain Giorla, Jim Kiggans, Kevin Field, Zachary Burns, Chris Stevens, Chinthaka Silva, Jake McMurray, Andres Marquez-Rossy, Edgar Lara-Curzio

- Thanks to the ASTRO student: William Hunnicutt
Load (μN) vs. Time (s)