Performance Assessment and Aging of Concrete Vaults

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Program Objectives

- **Develop a set of verified and validated (V&V) simulation tools and supporting leaching tests and data to evaluate long-term performance of waste forms and cementitious barriers considering aging, degradation, and leaching mechanisms**.
- **Answer the following framing questions:**
  - How can the assumptions underlying, and uncertainty associated with, the performance of disposal vault concrete in contact with saltstone at Savannah River Site be significantly improved?
  - What is the long-term performance of Cast Stone and similar waste forms for secondary waste, low activity waste (LAW), and non-high level waste (non-HLW) under potential disposal scenarios?
  - How can testing for and the assumptions underlying the performance assessment (PA) of waste forms in near-surface disposal be modified to provide more realistic radionuclide leaching estimates?
  - What is the long-term performance of a closed waste tank under different scenarios?

Applications for Waste Forms and Barriers

- **Hanford Site**
  - Single shell waste tank integrity and closure assessments
  - Waste Management Areas C/A/AX – waste tank closure assessment
  - Integrated Disposal Facility (IDF) performance assessment
  - Source term characterization for Cast Stone (secondary waste, LAW, non-HLW)
  - *In-situ* grouting performance
  - Dry storage of cesium and strontium capsules
- **Savannah River Site**
  - Saltstone assessment (*e.g.*, revision for Performance Assessment, Special Analyses)
  - Disposal vaults and other concrete facilities
- **Oak Ridge Reservation**
  - Treatment and disposal of Y-12 mercury contaminated D&D debris and soils including potential macroencapsulation
- **Nuclear Energy**
  - Dry cask storage performance
  - License extension

Major Activities Related to Waste Forms

Experimental

- Evaluate impacts of oxidation and carbonation on cementitious waste forms and barrier performance
- Evaluate leaching chemistry, density, saturation relationships for Cast Stone materials
- Apply USEPA Leaching Environmental Assessment Framework (LEAF) test methods (in SW-846) to low temperature and low activity glass waste forms
- Evaluate concrete durability under long-term high gamma irradiation

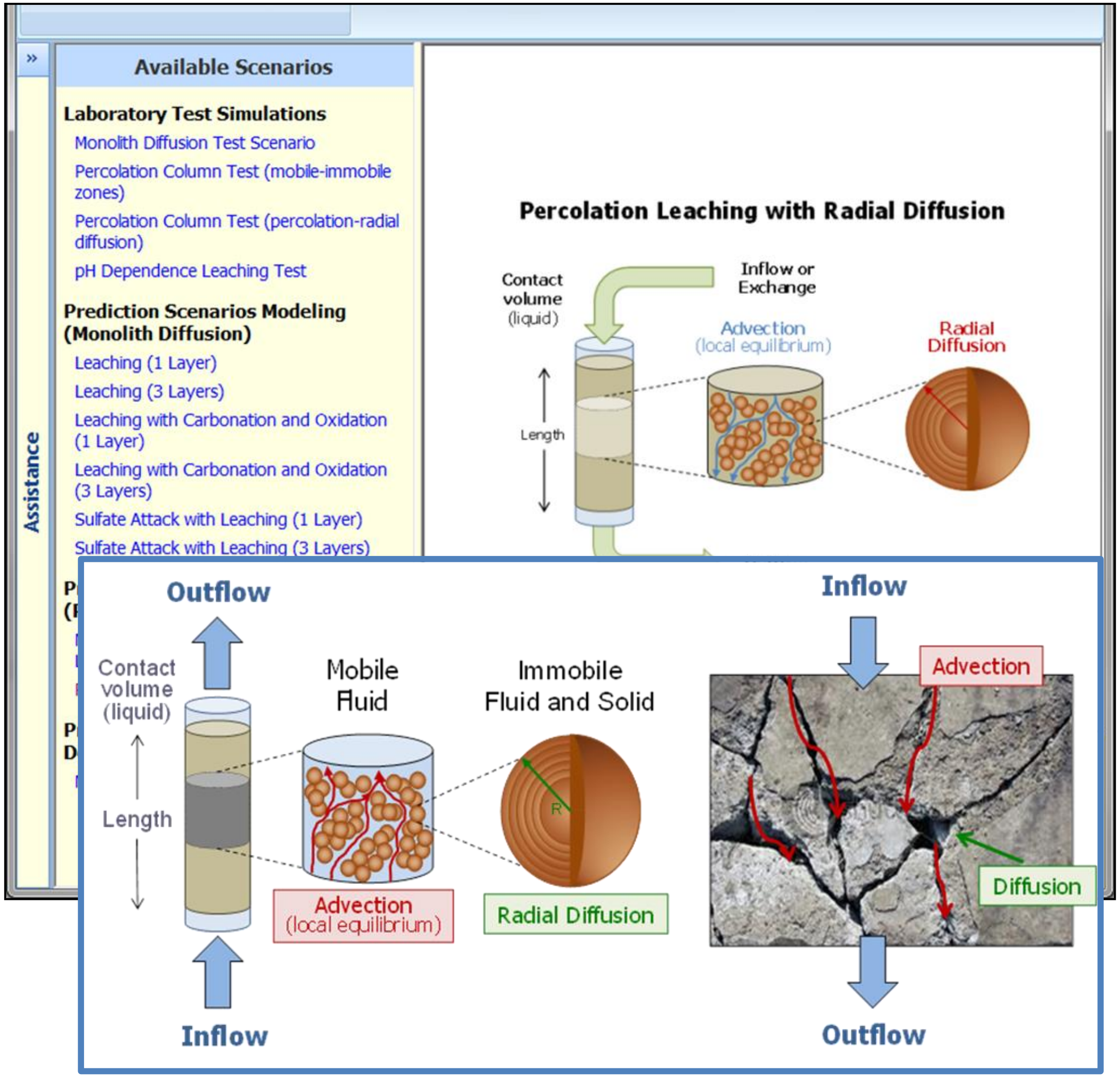
Modeling and Software Quality Assurance (SQA)

- Complete Verification & Validation test cases for important LeachXS/ORCHESTRA models
  - USEPA Method 1313 – pH Dependence (laboratory) models
  - USEPA Method 1315 – 1-D and 3-D monolith leaching / diffusion (laboratory) models
  - Monolith leaching / diffusion (prediction) models under carbonation and oxidation
  - Column models – begun in 4Q2018

Interfacial Behavior

- Evaluate expected changes in hydraulic and leaching properties of salt waste form in contact with vault concrete
  - Characterize baseline and degraded saltstone and vault concrete behavior
  - Model behavior of degrading saltstone vault concrete during performance period

Multiple, Flexible Base Models Available in LeachXS/ORCHESTRA



Available Scenarios

Laboratory Test Simulations
- Monolith Diffusion Test Scenario
- Percolation Column Test (mobile-immobile zones)
- Percolation Column Test (percolation-radial diffusion)
- pH Dependence Leaching Test

Prediction Scenarios Modeling (Monolith Diffusion)
- Leaching (1 Layer)
- Leaching (3 Layers)
- Leaching with Carbonation and Oxidation (1 Layer)
- Leaching with Carbonation and Oxidation (3 Layers)
- Sulfate Attack with Leaching (1 Layer)
- Sulfate Attack with Leaching (3 Layers)

- **Select general field or laboratory scenario to model**
- **Select materials** from existing reference materials or customize materials
- **Select interface conditions** (*e.g.*, fixed volume, continuous flow or intermittent flow/ exchange and solutions (*e.g.*, “Hanford infiltration”)
- **Resulting models can be transferred to GoldSIM or other for probabilistic or sensitivity analysis**

Software Quality Assurance – Verification & Validation

- **Verification & Validation (V&V) to be consistent with NQA-1** (ASME NQA-1-2015) and DOE Order 414.1D (*Quality Assurance*)
- **Progressing from simpler calculations with analytical solutions to more complex models often using code-to-code comparisons**
  - ORCHESTRA chemical equilibrium versus PHREEQC (code-to-code)
  - Reactive transport system for diffusion of a non-reactive constituent undergoing first-order (radioactive) decay versus analytical solution from Appelo & Postma (2005)
  - International benchmarking studies (code-to-code), including Marty, *et al*. (2015) and Perko, *et al*. (2015)
- **Compare to laboratory and/or field results**
  - Unsaturated carbonation monolith model versus analytical solution from Crank (1975) and compared to results from Hanford 241-C-107 dome core
  - Laboratory monolith models for microconcretes and salt waste forms versus analytical solution from Crank (1975) with comparisons under development
  - Sulfate attack in SRS vault concrete exposed to a high-sulfate waste form compared to microprobe data from Samson & Marchand (2007)

LEAF Leaching Tests*

Equilibrium-based leaching tests

- Batch tests carried out on size reduced material
- Aim to measure contaminant release related to specific chemical conditions (pH, LS ratio)
- Method 1313 – pH dependence & titration curve
- Method 1316 – LS dependence

Mass transport rate-based leaching tests

- Carried out either on monolithic material or compacted granular material
- Aim to determine contaminant release rates by accounting for both chemical and physical properties of the material
- Method 1315 – monolith & compacted granular options

Percolation (column) leaching tests

- May be either equilibrium or mass transfer rate
- Method 1314 – upflow column, local equilibrium (LS ratio)

**Posting to SW-846 as "New Methods" completed August 2013*

Laboratory-to-Field Relationships

- Leaching Assessment Fundamentals
- Ten Cases of Large-scale Field Analyses Coupled with Laboratory Testing For Seven Materials
  - Coal combustion residues (fly ash, scrubber residues
  - Inorganic waste (mixed origin)
  - Municipal solid waste (MSW)
  - MSW incinerator bottom ash
  - Cement-stabilized MSW incinerator fly ash
  - Portland cement mortars and concrete
- Recommendations for Use of LEAF

EPA 600/R-14/061 September 2014 | www.epa.gov/ord

LEAF

Leaching Environmental Assessment Framework

EPA United States Environmental Protection Agency

Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework

Office of Research and Development

EPA 600/R-14/061

Motivation

1. During material aging and degradation, exposure to CO_2 and O_2 from the atmosphere or soil gas may:
   - Impact physical durability of materials (*e.g.*, de-passivation of embedded steel reinforcement (carbonation) leading to eventual cracking)
   - Change the solubility of constituents of potential concern (COPCs) that may impact constituent mobility and release to the environment
2. Supplemental cementitious materials (SCM) (*e.g.*, fly ash) when used in nuclear waste forms and barriers result in different, complex chemistries that can produce significant variability on the ingress and reaction of O_2 and CO_2

Source: cementbarriers.org

Background: CARBONATION

- **Carbonation-induced corrosion primary degradation mechanism for tanks**
- **Alkalinity-based reactions in Portland cement-based cementitious materials during carbonation:**

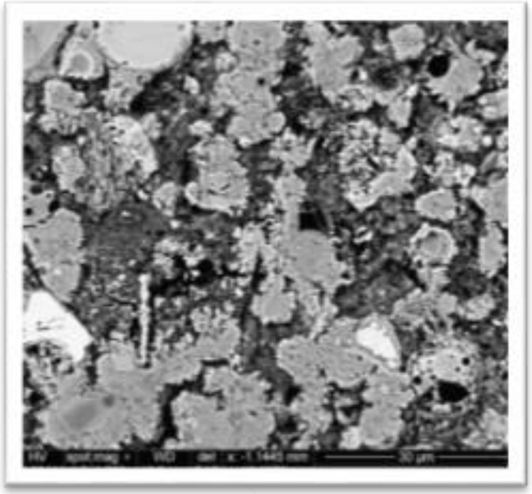
Eq. 1A: $Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

Eq. 1B: $Ca^{2+}(aq) + 2OH^-(aq) + CO_{2\,(g)} \rightarrow CaCO_3(s) + H_2O$

Eq. 2: $xCaO \cdot SiO_2 \cdot nH_2O + yH_2O \rightarrow (x-y)CaO \cdot SiO_2 \cdot nH_2O + yCa(OH)_2$

Key Considerations:

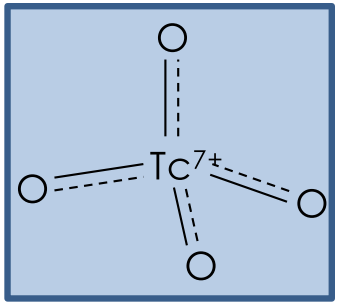
1. **Carbonation decreases "natural pH" of the material (depletion of OH^-)**
   - Depassivation of steel reinforcement
   - Changes in solubility of COPCs
   - Changes in mineralogy
2. **Carbonation changes material pore structure**
   - Impacts gaseous/liquid diffusion
   - Impacts material strength
3. **Limited studies evaluating impact of carbonation in cementitious waste forms containing small quantities of Portland cement**
   - Depending on material, carbonation may decrease or increase porosity



Background: OXIDATION

1. **Oxidation of Tc-99 is key concern for low activity waste disposal**
    - Tc-99 long-lived radionuclide (211,000 years)
    - Oxidation half-reaction:

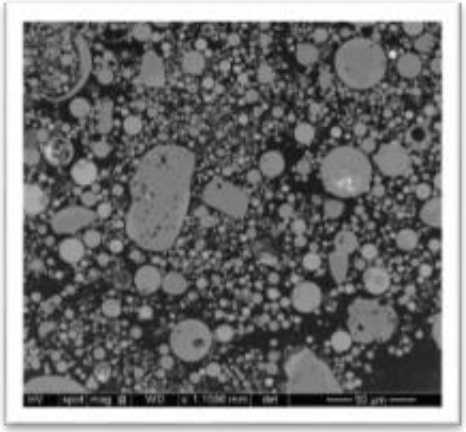
$$^{99}Tc(IV)O_2{\cdot}H_2O + 4OH^- \rightarrow {}^{99}Tc(VII)O_4^- + 3H_2O(l) + 3e^-$$



    - ^{99}Tc(VII) more soluble than ^{99}Tc(IV) → Increased release and water-borne mobility after oxidation
2. **Redox sensitive species are initially in reduced form due to reductive capacity of blast furnace slag, fly ash, Portland cement**
3. **Cr, Fe, and S are redox-sensitive species that may influence rate or extent of oxidation in cementitious waste forms during aging**
4. **Use of an indicator species that is redox sensitive (*i.e.*, Cr) in lieu of Tc-99 is important to better understand oxidation ingress rates**

Background: SCM

- **Cementitious materials used in nuclear waste applications often contain supplemental cementitious materials (SCM) such as fly ash and blast furnace slag**
- **The addition of SCM can improve desired material properties (*i.e.*, refined pore structure, increased reductive capacity), yet significant gaps exist in characterizing evolution of aging mechanisms in materials with SCM**
- **Variability of SCM creates variability in material alkalinity, reductive capacity, and property changes during aging**



Microconcrete Experimental DESIGN

Mix Design

	Control	Blend
Nominal Mix (lb./cy)	866	866
Fly ash replacement (%)	-	45
	Composition (wt%)	
Portland Cement	22.2	12.2
Fly ash	-	10
Water	9.9	10.1
Fine Aggregate	67.9	67.7

Microconcrete = Cementitious material lacking coarse aggregate that serves as surrogate for traditional concrete material

Coding Scheme

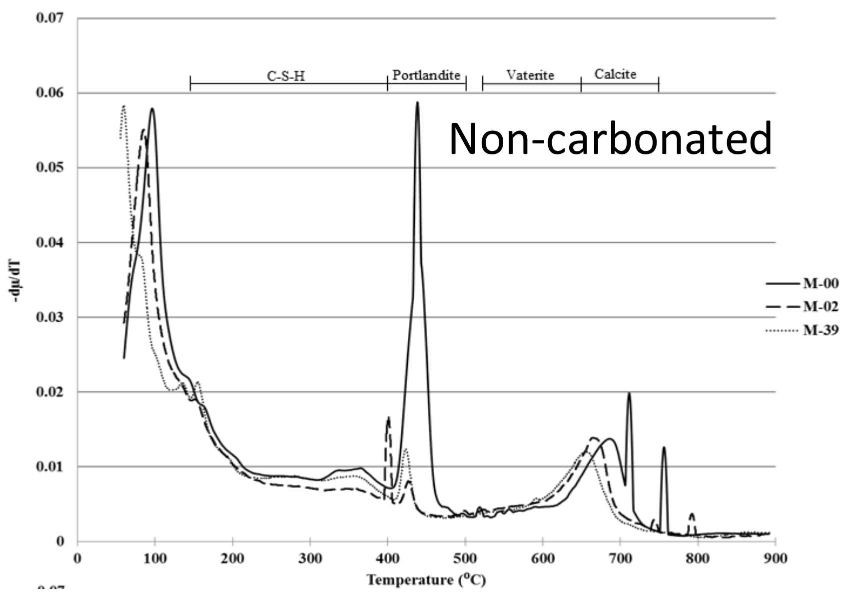
Material Code	Cured	Crushed	Carbonated	Test Method
M-00, M-02, M-39	12 months	No	No	Phenolphthalein, 1315, SEM-EDS
MC-00, MC-02, MC-39	6 months	No	6 months	Phenolphthalein, 1315, SEM-EDS
M-00, M-02, M-39	12 months	Yes	No	Method 1313, TGA, TIC
MC-00, MC-02, MC-39	6 months	Yes	6 months	Method 1313, TGA, TIC

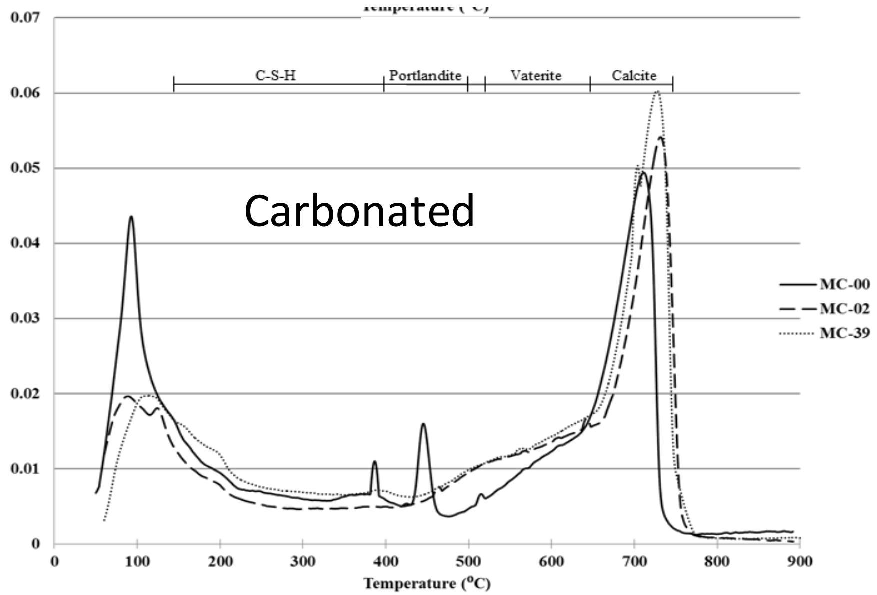
00: Control with no fly ash

02: Bituminous, low Ca fly ash

39: Sub-bituminous, high Ca fly ash

EXTENT of Reaction: TGA





Material	C-S-H (± 3%)	Portlandite (± 6%)	Vaterite (± 10%)	Calcite (± 9%)	% Ca Reacted (± 14%)
M-00	15.2	6.3	1.7	2.3	N/A
M-39	14.6	2.1	1.8	1.1	N/A
M-02	12.8	1.9	1.6	1.4	N/A
MC-00	12.0	2.7	3.4	6.5	26
MC-39	13.0	-	4.0	7.9	54
MC-02	9.3	-	4.0	7.8	58

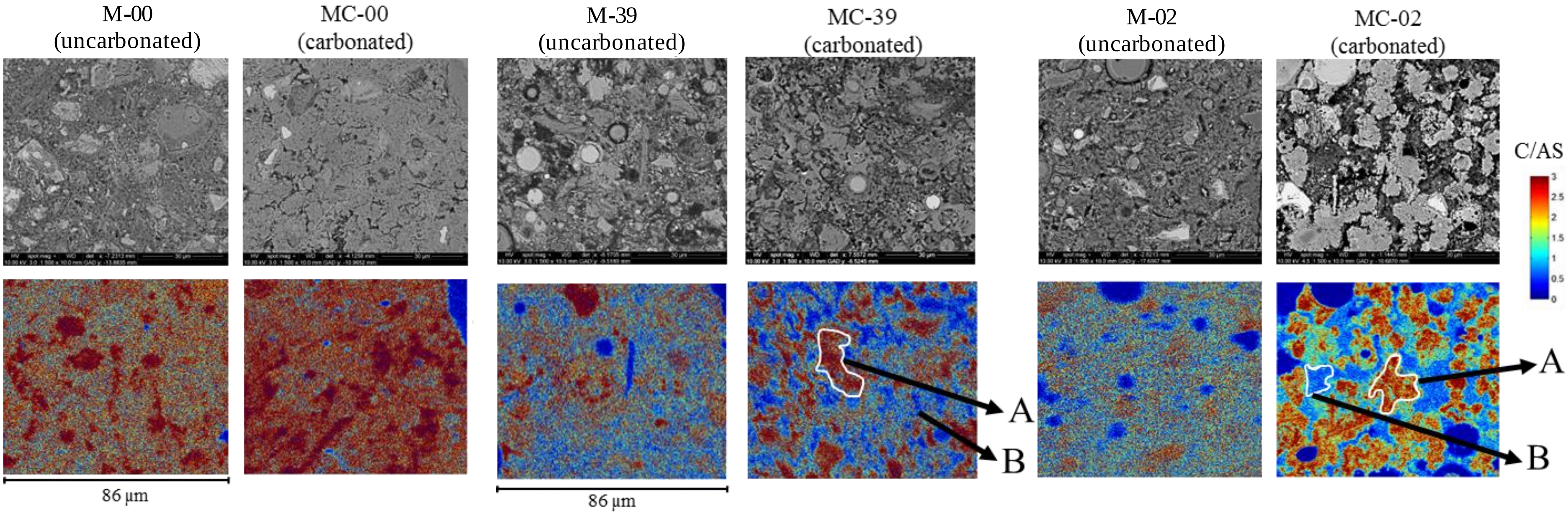
Mass % ± mean CV

Key observations:

% Ca reacted increases as alkalinity decreases

1. C-S-H & portlandite deplete
2. Vaterite & calcite increase

Carbonation: Effect of Fly Ash Addition (Alkalinity) on Microstructure



No Fly Ash
(High Alkalinity)

High Ca fly ash replacement
(Moderate Alkalinity)

Low Ca fly ash replacement
(Low Alkalinity)

A: Calcium carbonate
B: Decalcified C-S-H

<u>Key observations for Microconcretes</u>:

1. Homogenous appearance of BSE image and EDS for MC-00
2. Two distinct regions observed in BSE image and EDS for MC-39 and MC-02

Cast Stone Compositions and Preparation

Compositions:

- LAW Simulant *
  - High pH (pH up to 12)
  - High ionic strength (5M Na)
  - Spiked with 0.2 wt% Cr
- Binder
  - FAF: BFS: OPC= 45:47:8
  - w/b: 0.48

Preparation:

- Casting and Curing
  - 2.5 cm x 12 cm cylindrical molds
  - Cured in 100% N_2 and 100% RH environment for 90 days
- **Preparation for testing**
  - Portion of samples ground to particles with 85 wt% < 2 mm
  - Monoliths prepared for 1-D diffusion reaction

*Russel, R. L., *et al*. "Letter Report: LAW Simulant Development for Cast Stone Screening Tests PNNL-22352 Rev. 0." PNNL, Richland, WA (2013).

Cast Stone Material Aging and Analysis

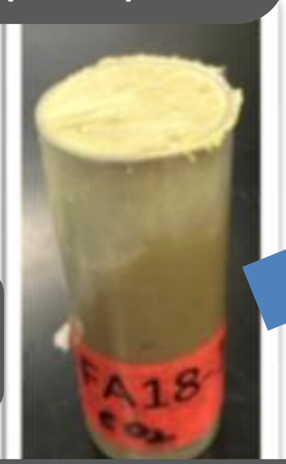
Cured 100 days 100 % RH and 100 % N_2

Hydrate samples before exposure to degradation

Aged 60 days 65 % RH:

1. **100 % N_2 (CS-N)**
2. 100% air, no CO_2 (CS-O)
3. 95% N_2 + 5% CO_2 (CS-C)
4. **95% air + 5% CO_2 (CS-OC)**

Granular material (1313, TGA, XRD, TIC)



1-D gaseous diffusion (SEM, 1315)

1-D Monolith Leaching

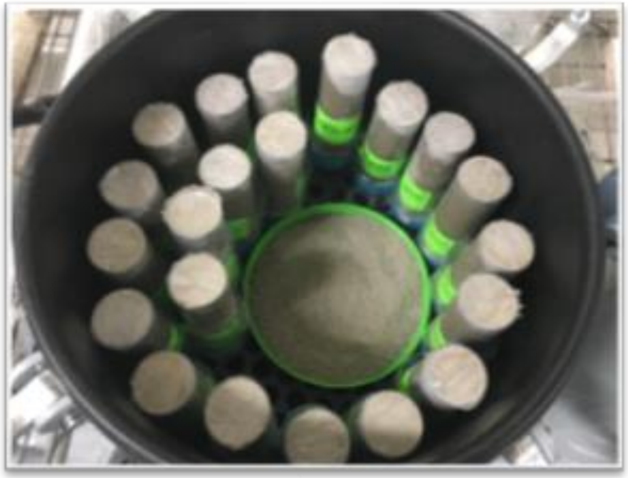
Caste Stone Materials Aging Conditions

- 3 Gaseous compositions
- 4 Relative Humidity (RH) levels
- Various aging times →

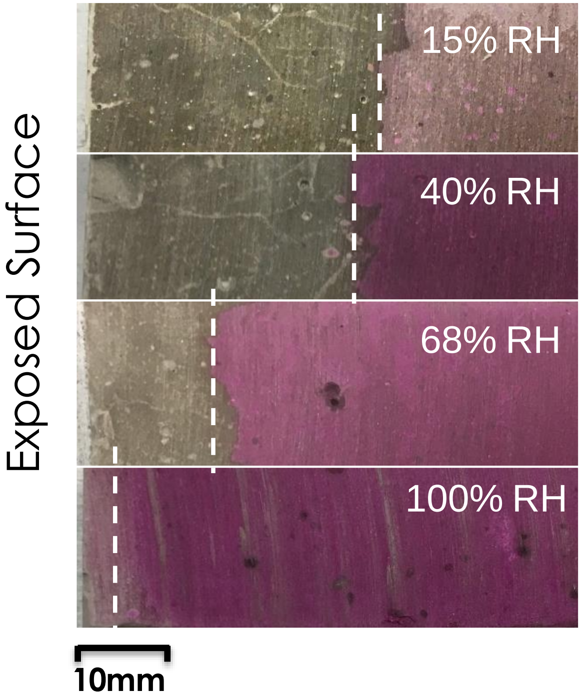
Sample aging times in different aging scenarios (weeks)

RH Conditions (Gas)		15%	40%	68%	100%
Control (CS-N)	N_2	16/32	16/32	16*/32	16/32
Oxidizing (CS-A)	Air	16/32	16/32	16*/32	16/32
Accelerated carbonation (CS-C)	2% CO_2	16/28	16/28	16*/28	16/28

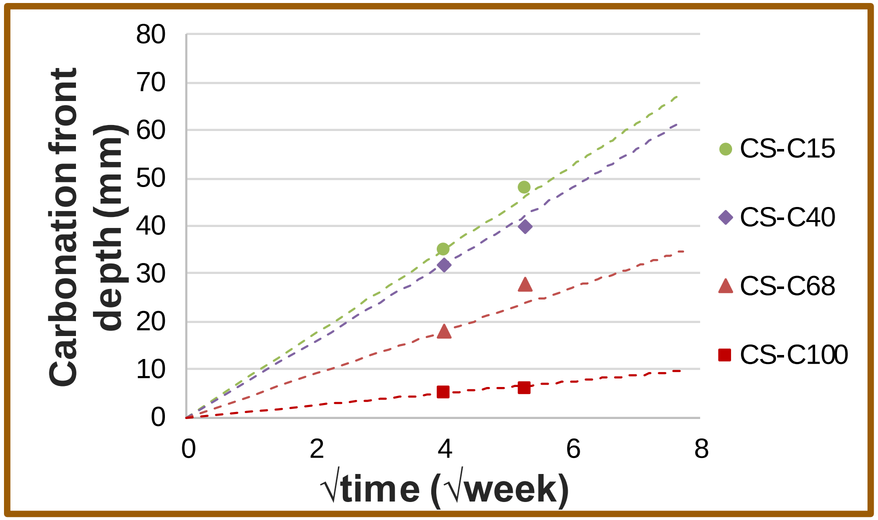
*** Monoliths and Granular samples**



Effect of Relative Humidity (RH) on Carbonation



Phenolphthalein test results. Samples aged for 16 weeks in accelerated carbonation condition.

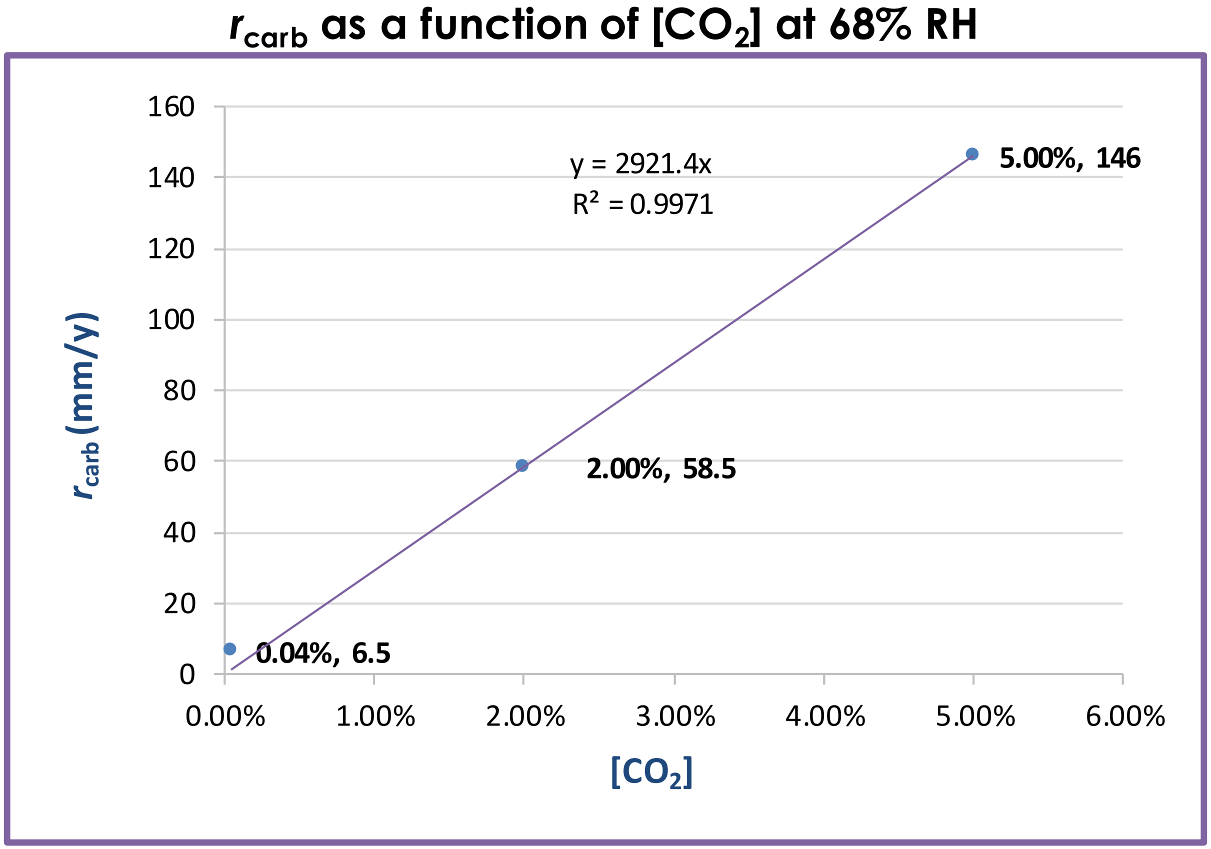


- RH ↓, depth ↑
  - Evaporation of pore solution facilitates gas penetration
  - $2OH^{-}+CO_2 \rightarrow CO_3^{2-}+H_2O$

    Water generated during carbonation
- Carbonation rate coefficient *A* (L/t)
  - $x = A\sqrt{t}$ *
  - Constant *A* is a function of RH

*Papadakis & Fardis, AIChE Journal, **35**, 10 (1989)

Relationship Between $[CO_2]$ and Carbonation Rate

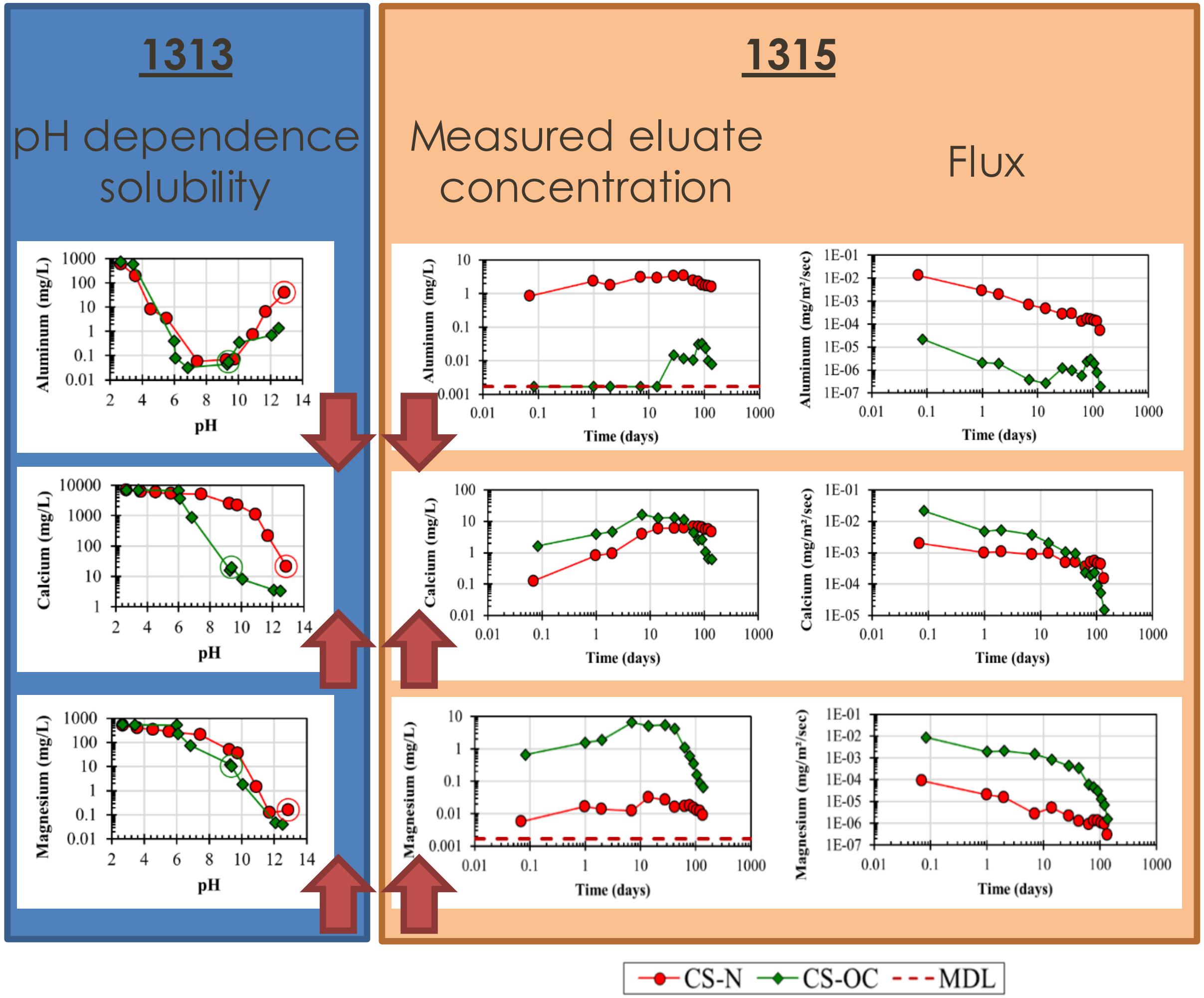


- Apparent linear relationship between $[CO_2]$ and observed r_{carb}
  - Suggesting a high reaction capacity with CO_2 in Cast Stone materials

Leaching Behavior for Carbonation-Sensitive Constituents

Key Observations:

1. Solubility at natural pH impacts mass transfer release in initial exchanges
2. After 63 days of leaching, shift in mass transfer release likely due to position of leaching front relative to carbonation depth and corresponding shift in eluate pH



1313

pH dependence solubility

1315

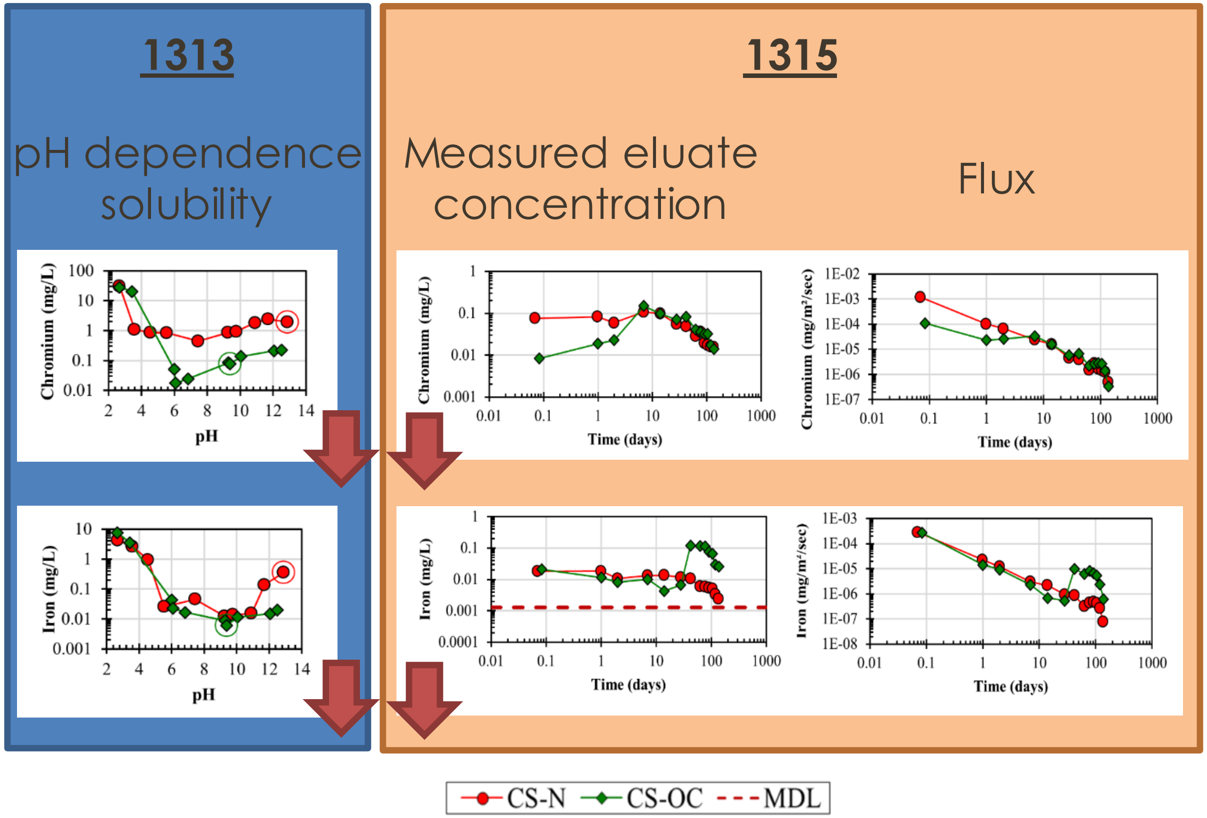
Measured eluate concentration

Flux

Leaching Behavior of Oxidation-Sensitive Constituents

Key Observations:

1. Solubility at natural pH impacts mass transfer release in initial exchanges
2. After ~21 days of leaching, shift in mass transfer release likely as a result of position of the leaching curve relative to the oxidation curve
3. Shift in mass transfer release in earlier exchanges compared to shift for carbonated sensitive species suggests smaller oxidation front compared to carbonated front



1313

pH dependence solubility

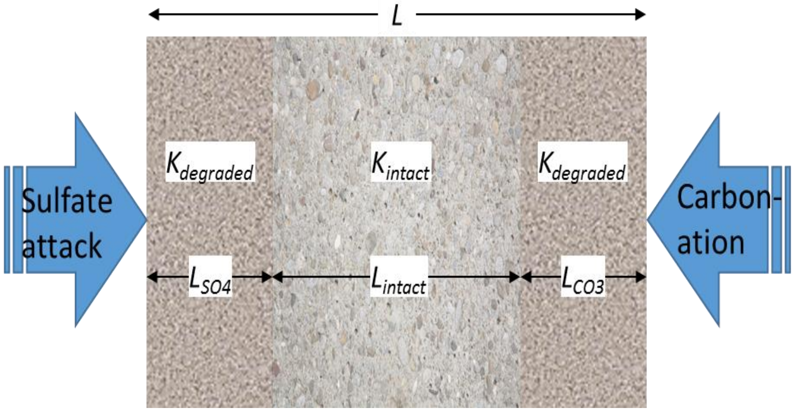
1315

Measured eluate concentration

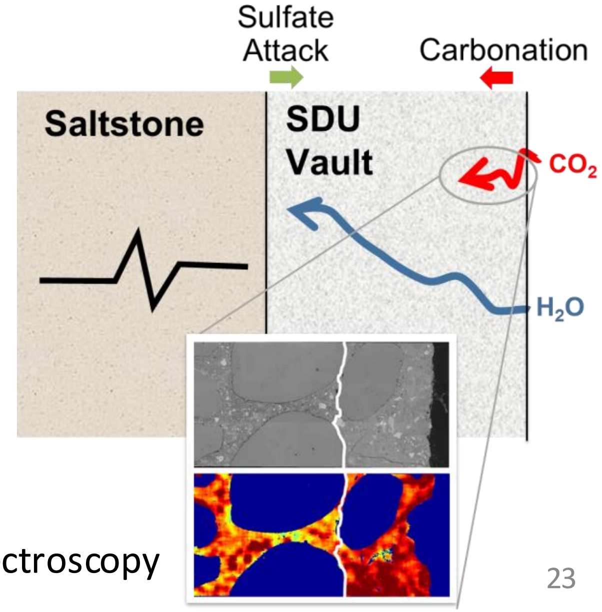
Flux

Savannah River SDF PA Support

- **Addressing conservative assumptions**
  - Worst-case linear degradation profile for hydraulic conductivity currently assumed
  - Recommended effective hydraulic conductivity be based on weighted *geometric* mean
  - More realistic and defensible estimate that decreases effective hydraulic conductivity by up to several orders of magnitude



- **Degradation at interfaces**
  - Simulate interfacial layered system within LeachXS/ORCHESTRA
  - Supplement model with analysis of interfaces using SEM/EDS
  - Potential for degradation of SDU vault concrete after contact with saltstone



SDF = Saltstone Disposal Facility SDU = Saltstone Disposal Unit
SEM/EDS = Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy

Development of a Nano-Modified Concrete for Next Generation of Storage Systems

Motivation

- Need to extend the service life and performance of used nuclear fuel (UNF) and other dry cask storage systems
    - Extend concrete performance under gamma radiation, high temperatures/gradients, and environmental weathering

http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/dry-cask-storage.html

Vertical casks

- Nanomodification of concrete through incorporation of nano-sized particles might be a viable solution
- Effect of gamma radiation alone on the performance of concrete under dry state conditions has largely been ignored

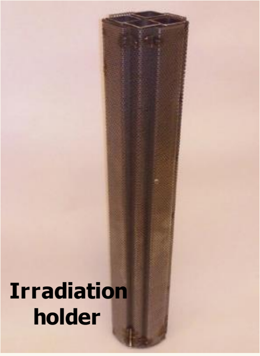
NSUF - Gamma Irradiation at ORNL HFIR

Development of a Nano-Modified Concrete for Next Generation of Storage Systems

Gamma Irradiation at ORNL

Goal: Address current knowledge gaps of the effects of gamma irradiation (without neutron radiation) under dry state conditions

- Materials
  - Conventional concrete formulations
  - Nano-modified concrete formulations
- Irradiation holder
  - Fully instrumented
- Irradiation conditions
  - Up to 50 MGray, simulates ~100 years
  - High temperature run ~250 ºC
  - Low temperature run ~80 ºC



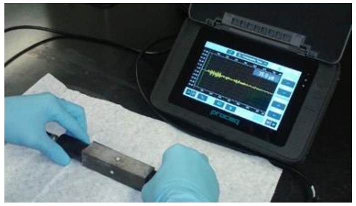
Irradiation holder

Development of a Nano-Modified Concrete for Next Generation of Storage Systems

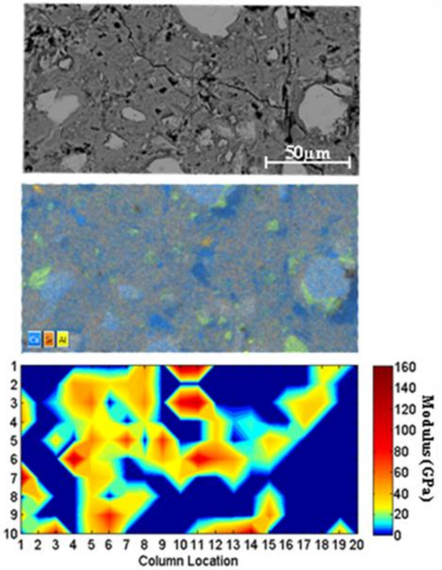
Gamma Irradiation at ORNL

Post irradiation evaluation at Vanderbilt Univ.

- Non-destructive mechanical testing
  - Ultrasonic pulse velocity measurements
- Chemical and microstructural characterization
  - SEM-EDS mapping
- Local nano/micromechanical characterization
  - Grid nano-indentation coupled with SEM-EDS analysis
- Micro-macro upscaling methods



Ultrasonic pulse velocity test



Grid nanoindentation coupled with backscatter SEM-EDS analysis