Cementitious Barrier Partnership (CBP) Toolsets

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Cementitious Barriers Partnership

Performance & Risk Assessment Community of Practice
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CBP
Cementitious Barriers Partnership

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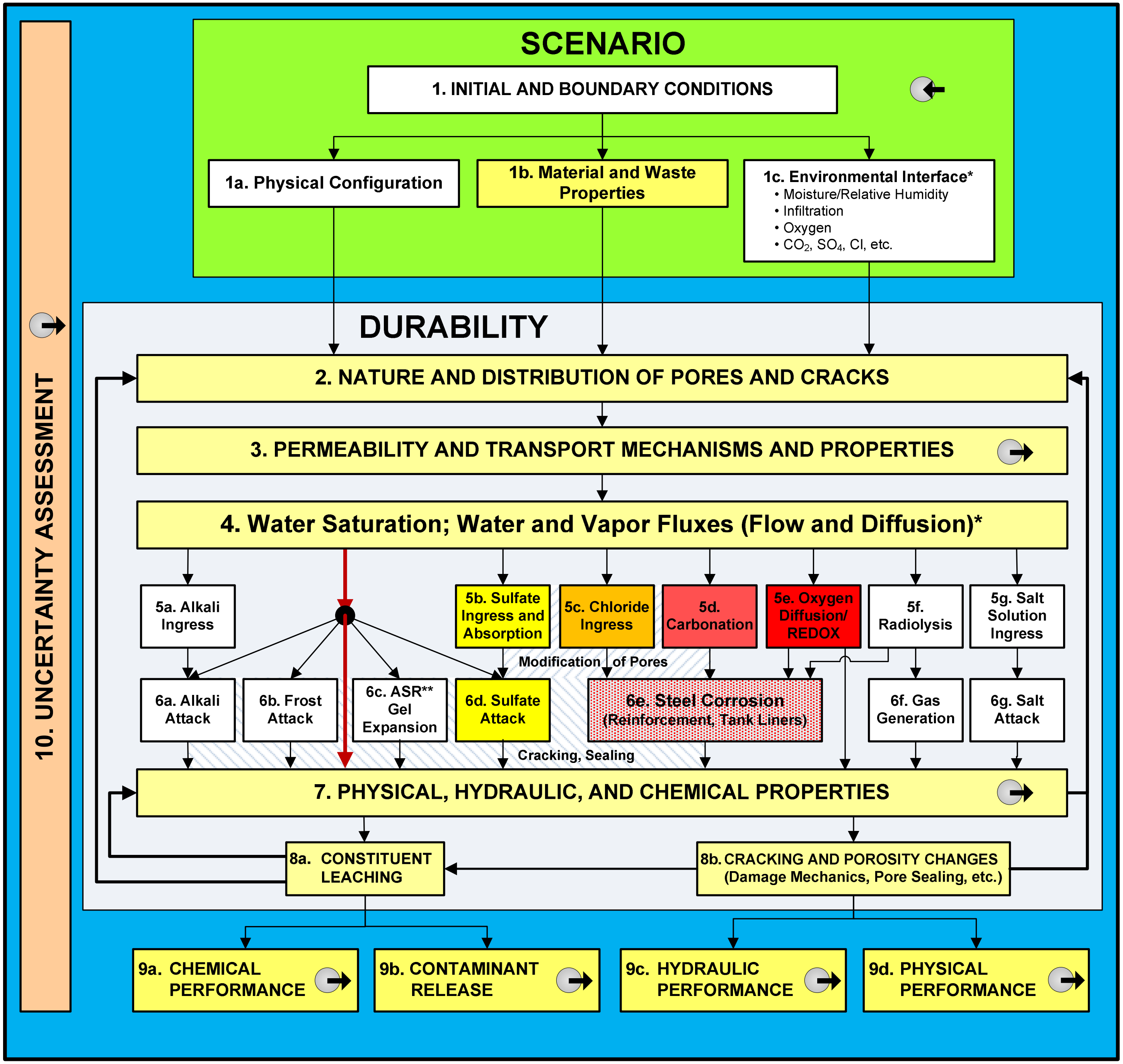
Key Questions

- Waste Forms and Disposal Systems
  - What is the rate of release for hazardous contaminants and radionuclides under a range of scenarios?
  - What is the evolution of system pH and impact on hazardous contaminant and radionuclide release?
  - What is the evolution of pore structure and impact on release and transport?
  - What are the effects of cracking on release and transport? How do we characterize the initial "cracked state"?
  - What is the rate and impact of aging processes (oxidation (Tc-99), carbonation, leaching) on performance?
- Structural Systems Performance
  - What is the remaining service life of the structure?
  - What are the impacts of ingress of aggressive species (chloride, sulfate, CO_2, O_2) on structural performance and service life prediction?

→ CBP Software ToolBox Version 2.0 Release (January 2014)

Primary Near-term Applications

- Hanford Site
  - HLW single shell tank integrity
  - Waste Management Areas C/A/AX – HLW tank closure assessment
  - Integrated Disposal Facility performance assessment
  - Source term characterization for Cast Stone (secondary waste, LAW supplemental treatment)
  - In-situ grouting performance
- Savannah River Site
  - Saltstone performance assessment including special analyses
  - Disposal vaults and other concrete facilities
- Nuclear Energy
  - Dry cask storage performance
  - License extension



Specifications, Properties, and Phenomena for the Evaluation of Performance of Cementitious Barriers

Key Processes

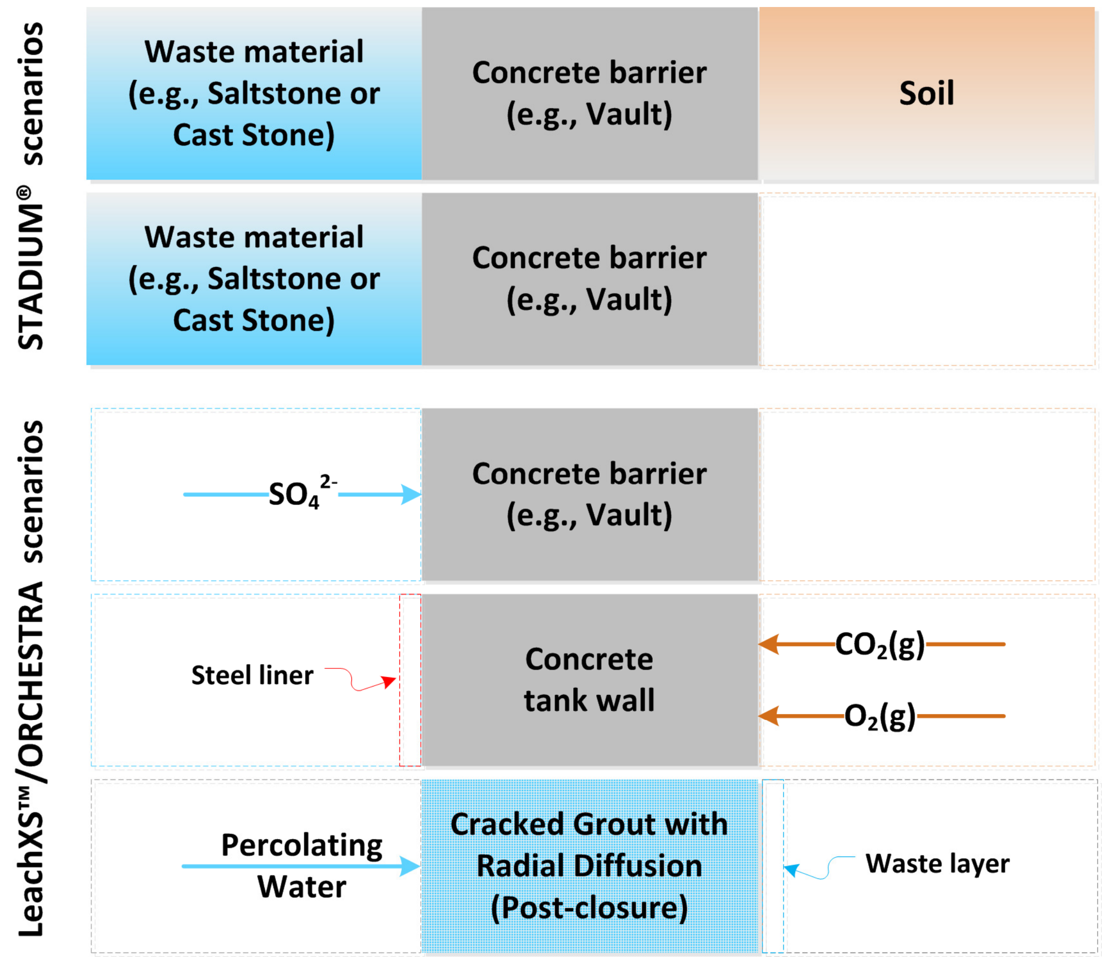
Current

Chloride attack
Sulfate attack
Carbonation
Decalcification
Leaching

In-development

Cracking
Oxidation
Properties estimation
Variable saturation
Alkali-silica reaction

CBP Software Toolbox—Available Scenarios



Multi-layered sulfate ingress or chloride attack case

Simplified two-layer sulfate ingress or chloride attack case

Simplified one-layer sulfate attack case with boundary condition representing salt waste

Simplified one-layer carbonation case ignoring steel liner with boundary condition representing gas ingress of CO_2 and O_2

Simplified one-layer percolation with radial diffusion case ignoring waste layer with boundary condition representing percolating water

Example Applications of the CBP Toolbox

Savannah River Site

- Saltstone sulfate attack, leaching, and uncertainty analysis
- Saltstone characterization and sulfate ingress/reaction
- FY13 Saltstone Special Analysis

Hanford Site

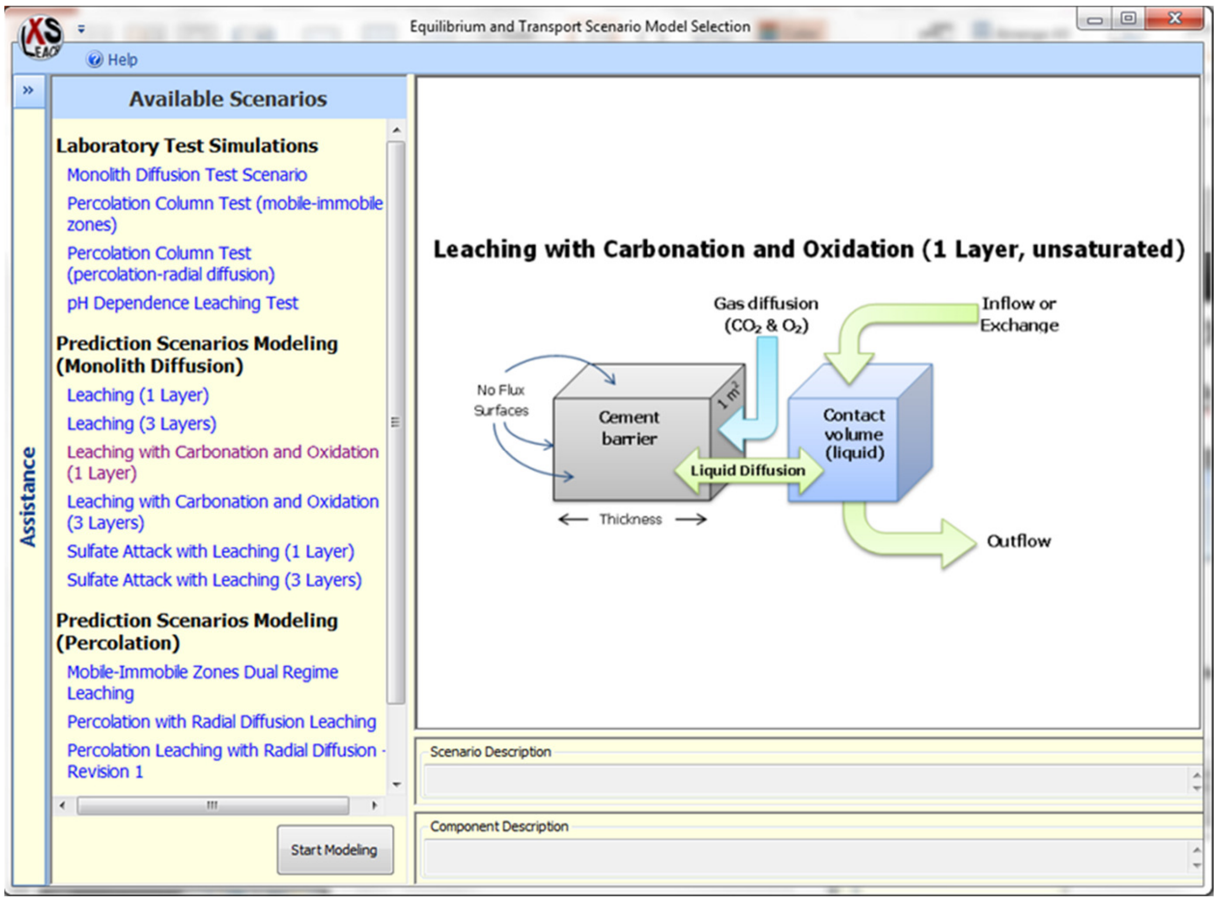
- Low temperature waste form (Cast Stone) development and modeling for Secondary Waste and LAW Treatment

Representative HLW Tank

- Carbonation and leaching for a HLW tank closure scenario
- Probabilistic analysis of flow and leaching through a cracked HLW tank closure grout
- Combined probabilistic analysis of dome carbonation/leaching and then flow/leaching through cracked grout

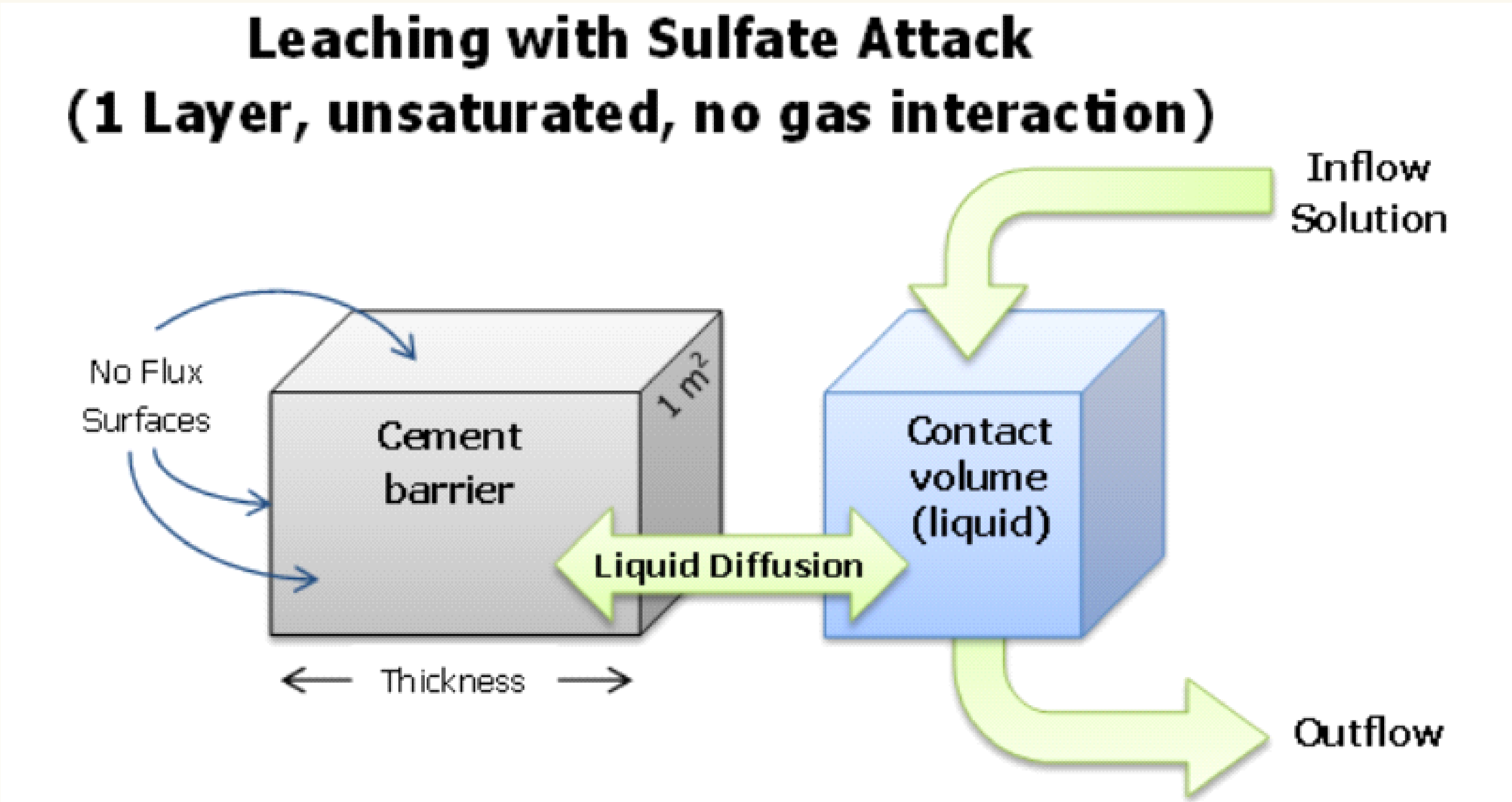
CBP Software Toolbox
Versions 1.0 & 2.0

Multiple, Flexible Base Models Available in LeachXS/ORCHESTRA

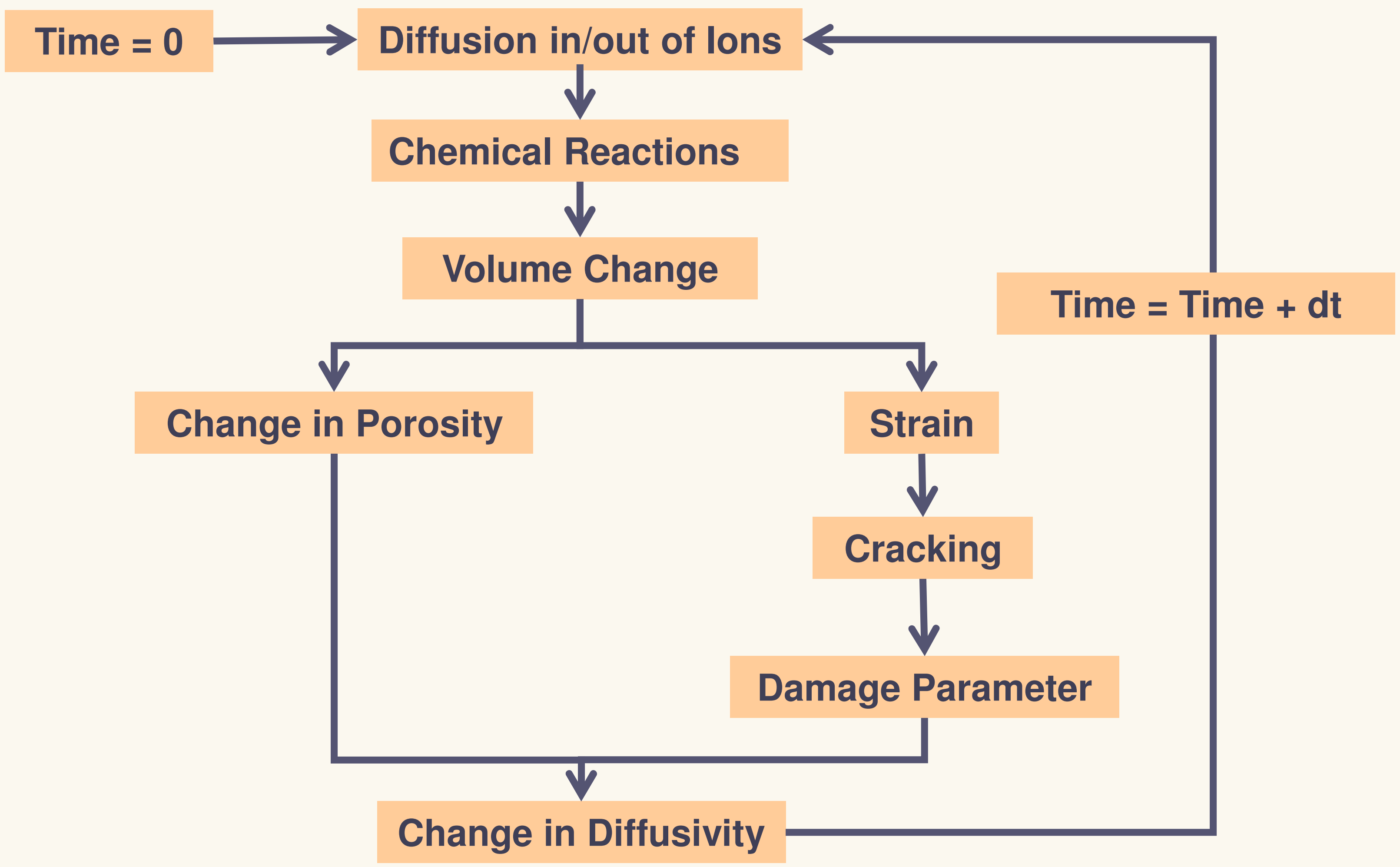


- Select general field or laboratory scenario to model
- Select from existing CBP reference materials or customize materials
- Select interface conditions (e.g., fixed volume, continuous flow or intermittent flow/ exchange & solutions (e.g., “Hanford infiltration” or “saltstone pore water”)
- Resulting model transferable to GoldSIM simulations

LXO Prediction Scenario – Leaching with Sulfate Attack

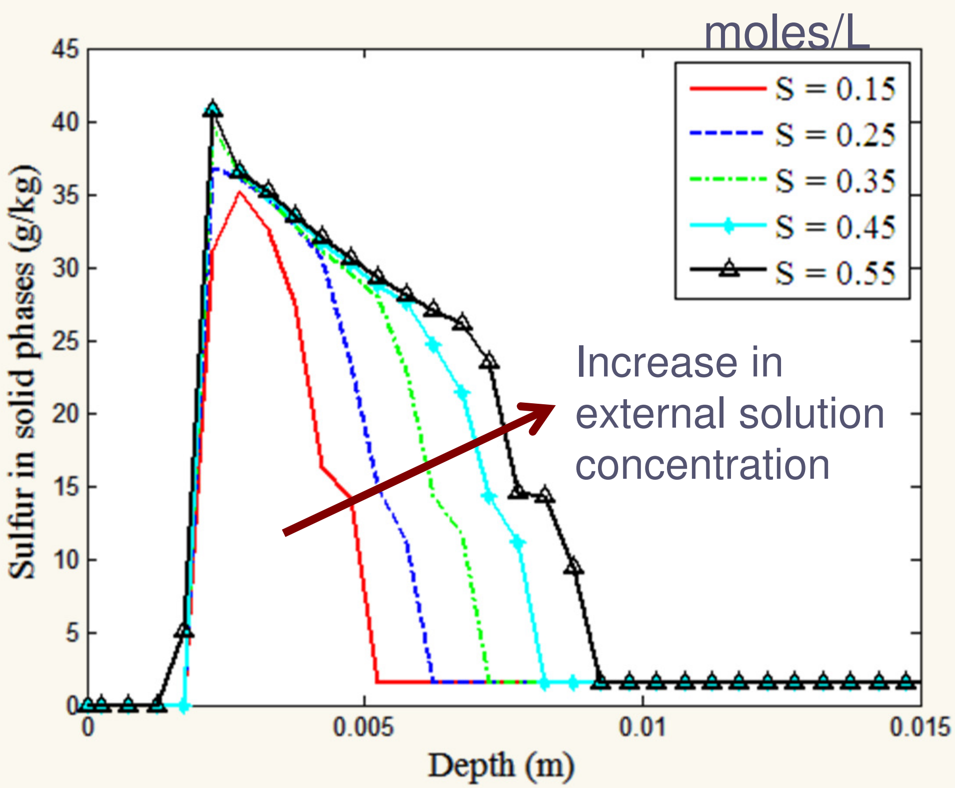


Numerical Modeling Framework

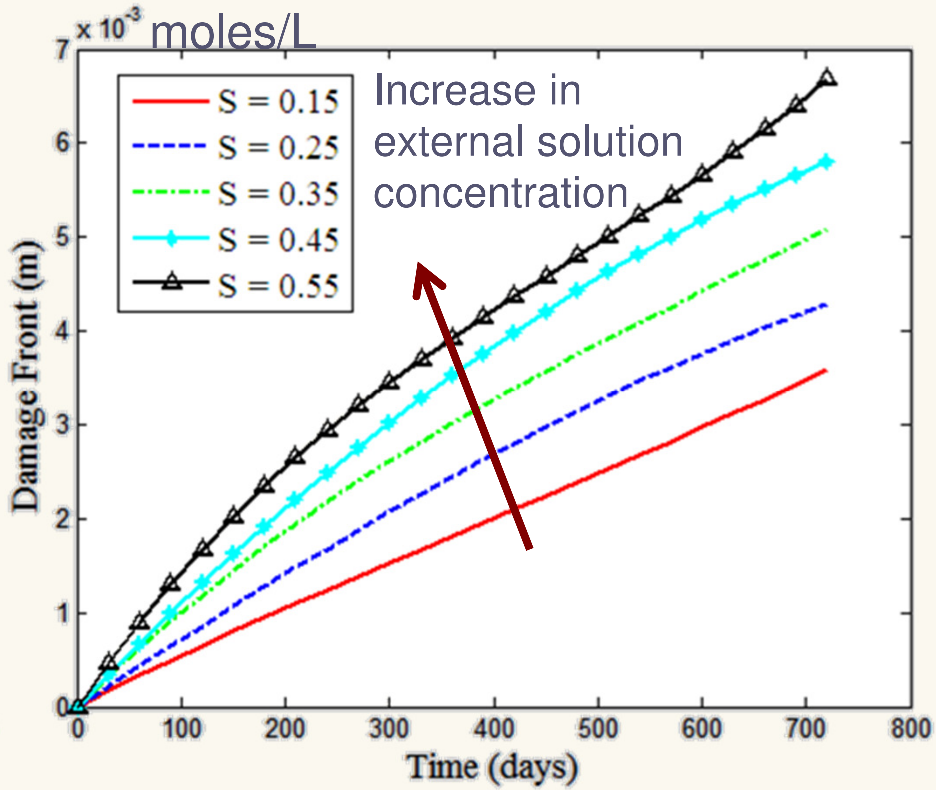


Sensitivity – External Solution Concentration

Sulfur Profile in Solid Phases



Rate of Damage Progression



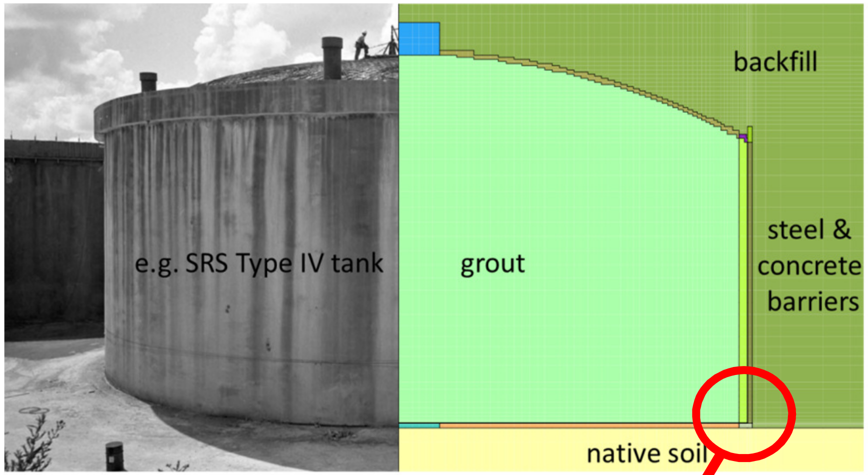
- Rate of damage progression increases with increase in external sulfate solution concentration

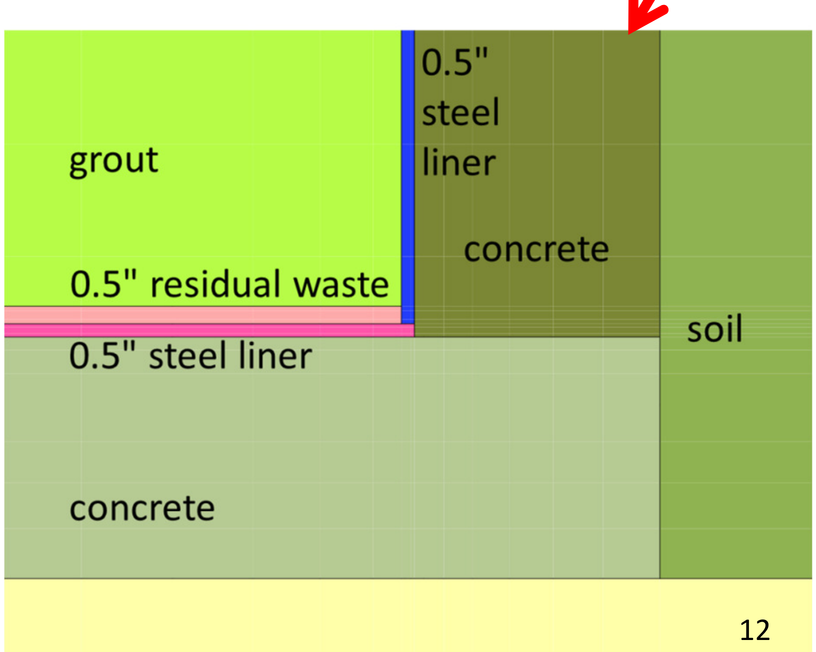
Motivation: Stabilize Residual High-Level Waste

200+ High-level waste (HLW) tanks require waste removal and closure:

- Tanks in service
  - Capacity up to ca. 4 million liters
  - Carbon steel liner within a reinforced concrete shell
- Tank closure
  - HLW retrieved to extent practical and filled with grout
  - Grout – cement mixed with supplementary materials
  - Grout intended to provide structural stability and to retain residual radionuclides

Challenge – predict timeframe and radionuclide rate of release





Source: SRNL-STI-2012-00372

Modeling Approach

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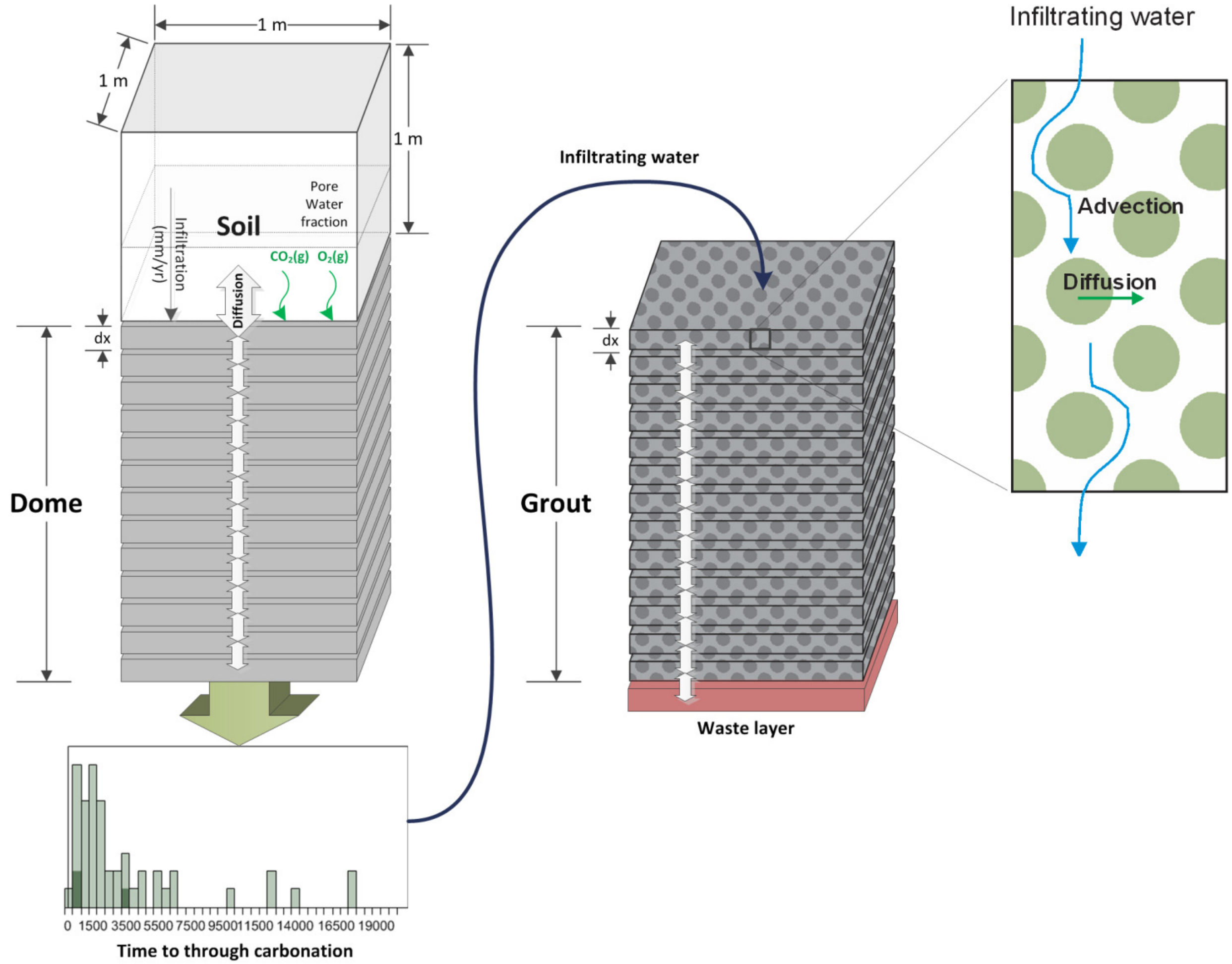
Decouple carbonation of the dome from transport in the grout (dual regime reactive transport) model

- Carbonation of dome is a very slow process (e.g., << 1mm/yr)
- Transport in the grout assumed negligible until dome is carbonated and cracked (allowing infiltration)
- Stochastically model dome carbonation to generate distribution of times until cracked
- Time distribution then used to delay impact on cracked grout pH using dual regime model



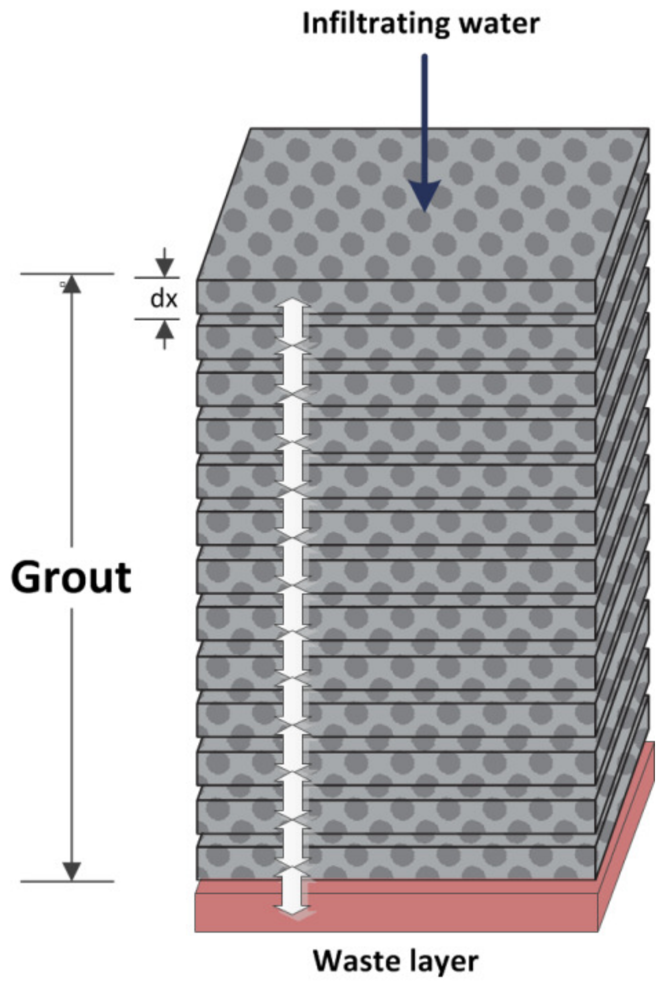
Probabilistic Grout Analysis

Non-Stochastic Parameters

- Grout thickness 10.5 m (SRS Type IV Tank)
  - Varies between 9 and 16 m (Sites, et al. 2006)

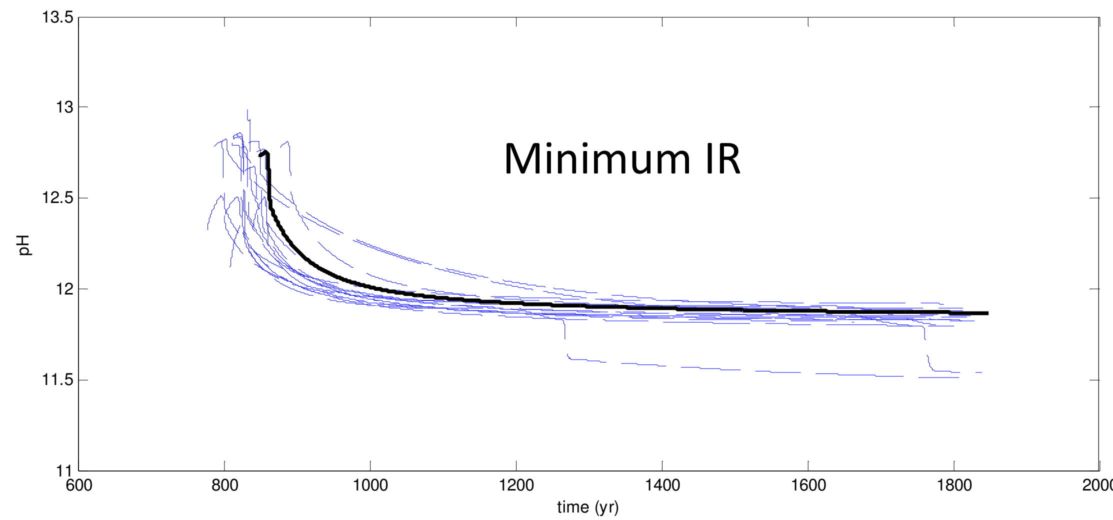
Stochastic Parameters

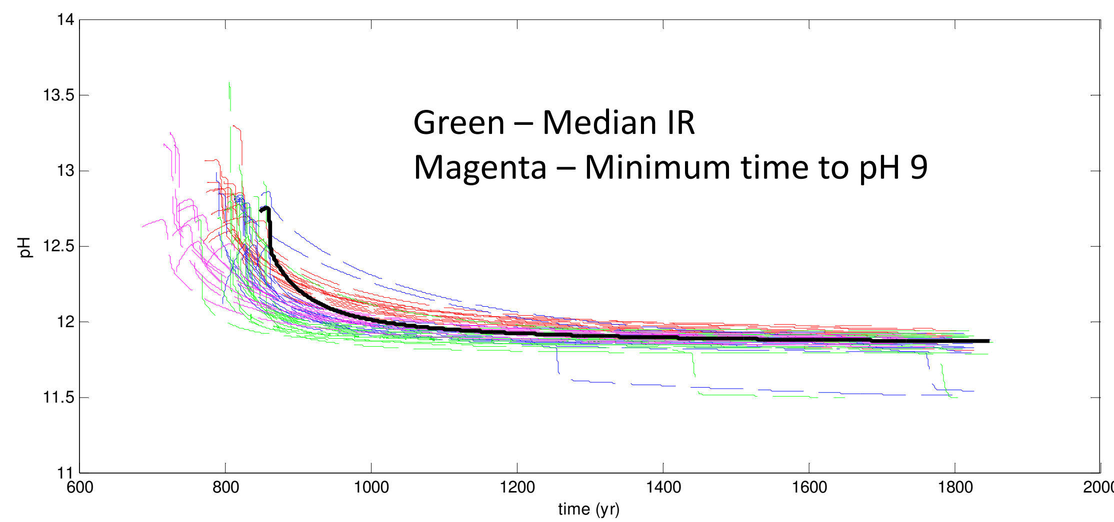
- Crack spacing – U(1,2) m
  - Sarkar, *et al.* (2013)
- Infiltration Rate – N(0.18, 0.051) m/yr
  - Distribution of 1,000-yr rates (WSRC-STI-2007-00184)
- Total porosity: ϕ_t – U(0.20, 0.30)
  - Sarkar, *et al.* (2013)
- Immobile zone porosity: ϕ_{im} – N(0.221, 0.013)
  - Information from WSRC-STI-2006-00198
- Mobile volume fraction: U(0.10,0.20)
  - Sarkar, *et al.* (2013)
- Solid composition: N(mean, ±10%)
  - Sensitivity evaluation



Coupled Analysis Results

- Simulated pH response at grout – waste layer interface
- Upper graph (blue) indicates sensitive pH response *at minimum infiltration rate*
- Lower graph indicates sensitive pH response *depending on infiltration rate*
  - Similar sensitive response found at median (green) infiltration rate
  - Waste layer not impacted until after 700 years (and likely much longer)
- Significant pH effects over the first two millenia tend to be observed as the infiltration rate is lower
  - Longer simulations may be required to better evaluate assumptions and results





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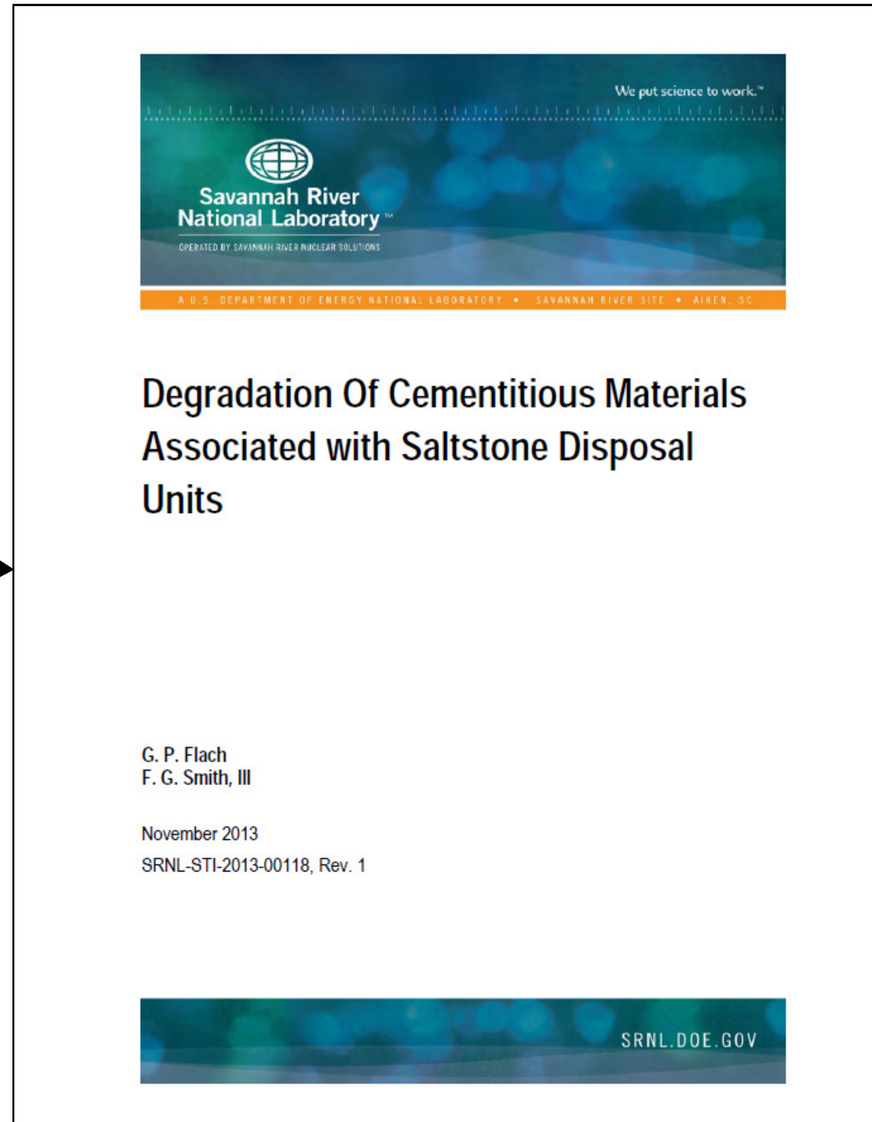
FY13 Saltstone Special Analysis

CBP Software Toolbox Version 1.0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Degradation Of Cementitious Materials Associated with Saltstone Disposal Units

G. P. Flach
F. G. Smith, III

November 2013

SRNL-STI-2013-00118, Rev. 1

SRNL.DOE.GOV

Material Properties and Conditions

Saltstone Disposal Unit Concrete

Table 9 – Initial solid phases in the concrete mixtures

Properties	Concretes Vault 1/4	Vault 2
Hydration (%)		
Cement	80	75
Slag	75	65
Fly Ash		
Silica Fum		
Mineral phases (g		
C-S-H		
Portlandite		
Monosulfo (AFm)		
C_4FH_{13}		

Table 11 - Chemical analyses of pore fluids extracted after 28 days of curing

Species	Vault 1/4 (mmol/L)	Vault 2
OH^-	244.4	113.9
Na^+	73.9	26.5
K^+		
SO_4^{2-}		
Ca^{2+}		
Cl^-		

Table 13 - Diffusion properties estimated from migration test analyses

Properties	Vault 1/4	Vault 2
OH diffusion coeff. (E-11 m^2/s)		
28 days	4.29	2.80
97 days	3.69	0.41
Cl diffusion coeff. (E-11 m^2/s)		
28 days	1.65	1.08
97 days	1.42	0.16
Tortuosity (-)		
28 days	0.0081	0.0053
97 days	0.0070	0.0008

SIMCO Technologies inc.

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Multi-Step Outflow Extraction

Dixon, K. L. and R. L. Nichols, *Method Development for Determining the Hydraulic Conductivity of Fractured Porous Media*, SRNL-STI-2013-00522, September 2013

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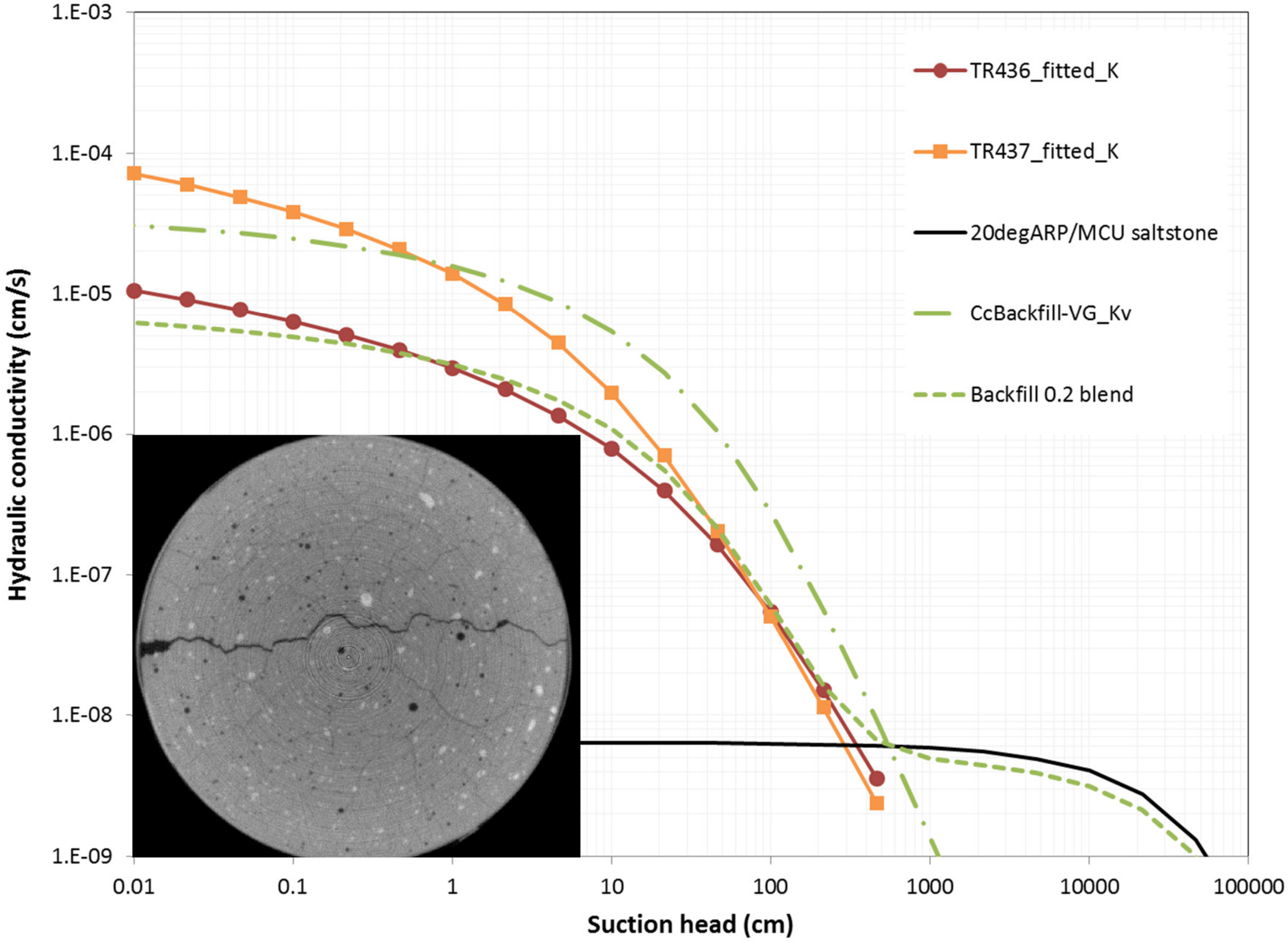
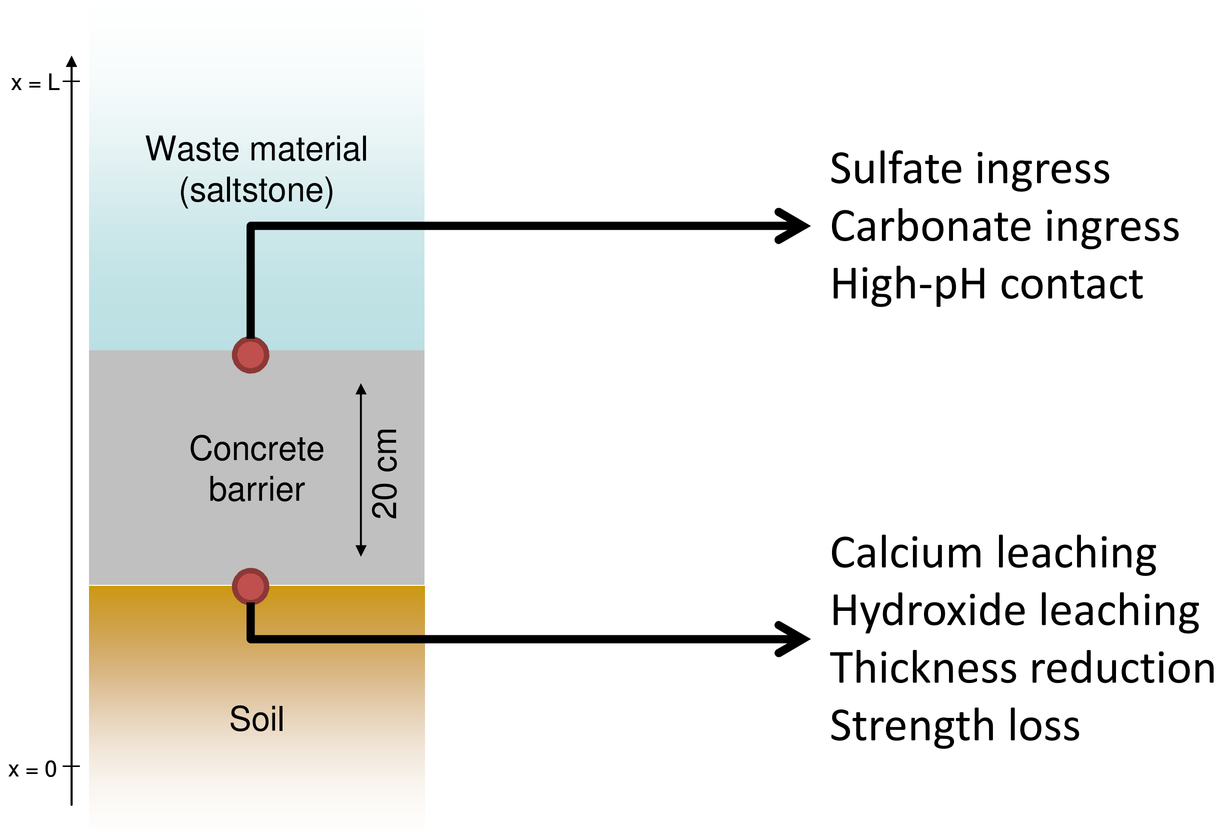
Conceptual Model Validation



CBP Test Case

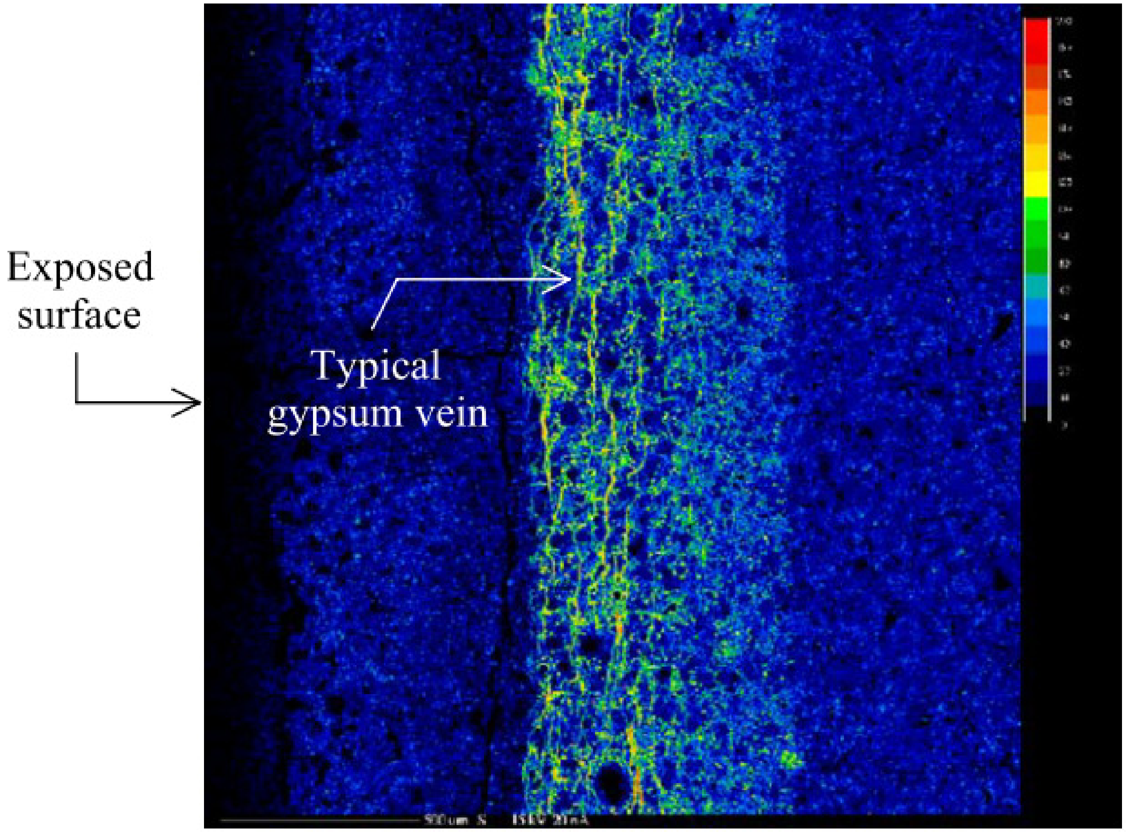
Two critical interfaces:



Previous work on sulfate attack

Sulfate exposure

Sulfur content mapping – 3 months



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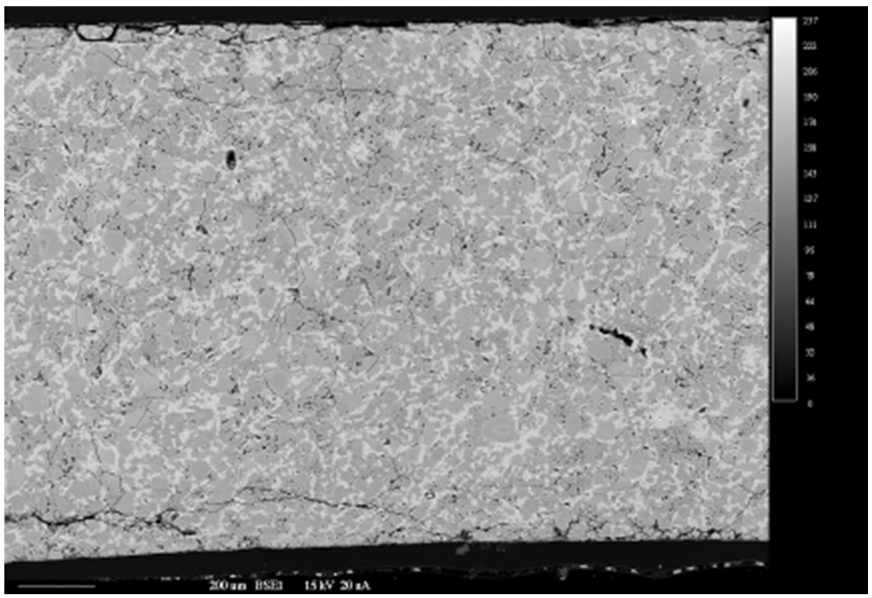
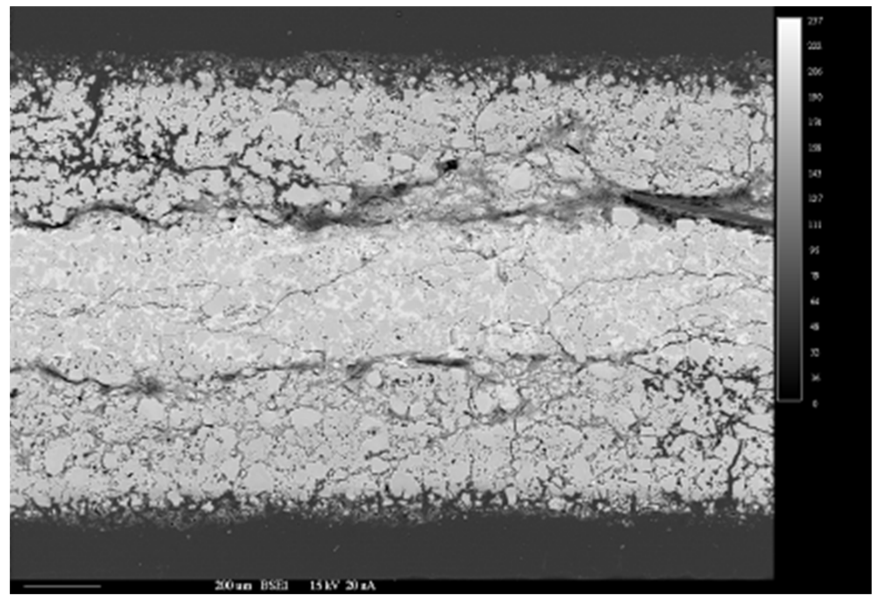
Previous work on calcium leaching

C3S paste exposed to pure water

Sound C_3S paste



Leached C_3S paste



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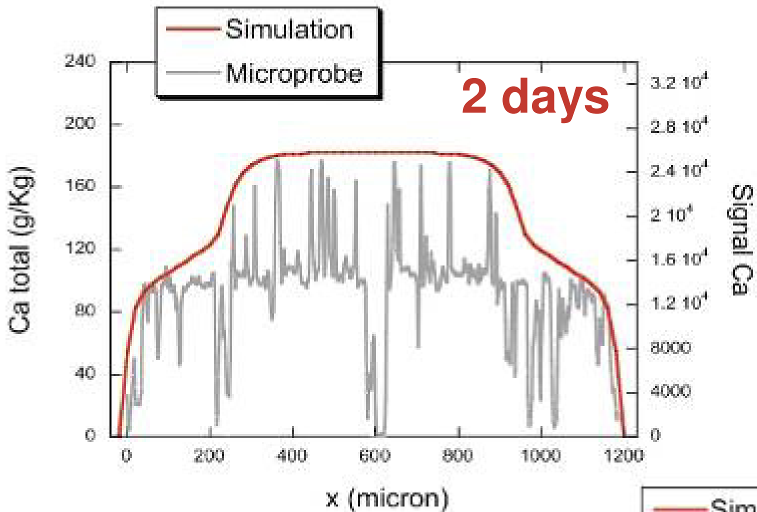
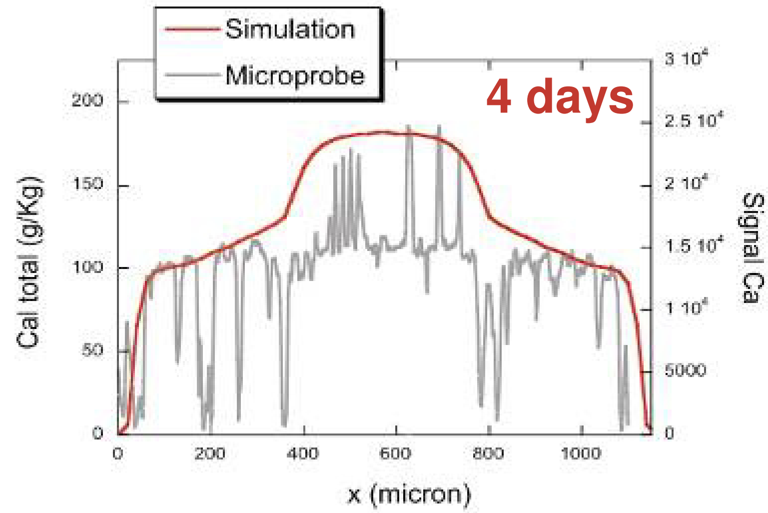
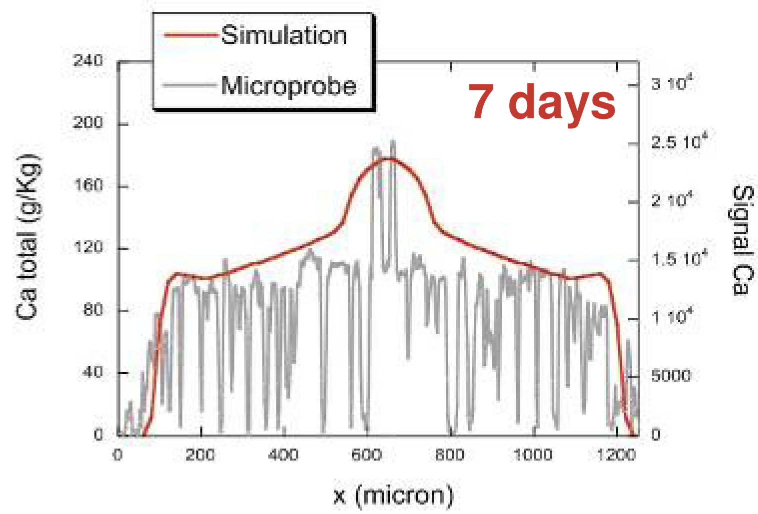
Previous work on calcium leaching

C3S paste exposed to pure water – Ca profiles







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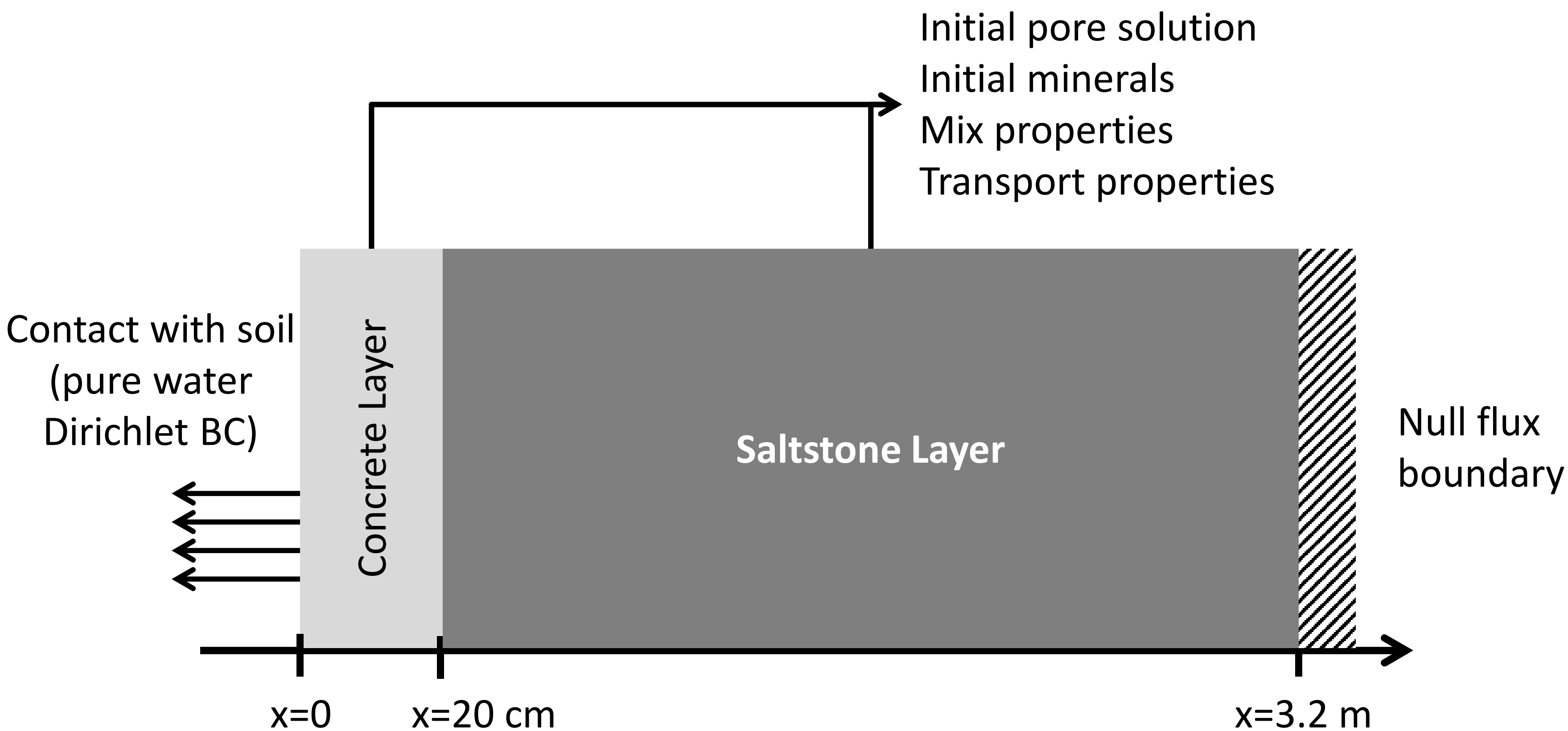
CBP Test Case

Modeling a two-layer system:



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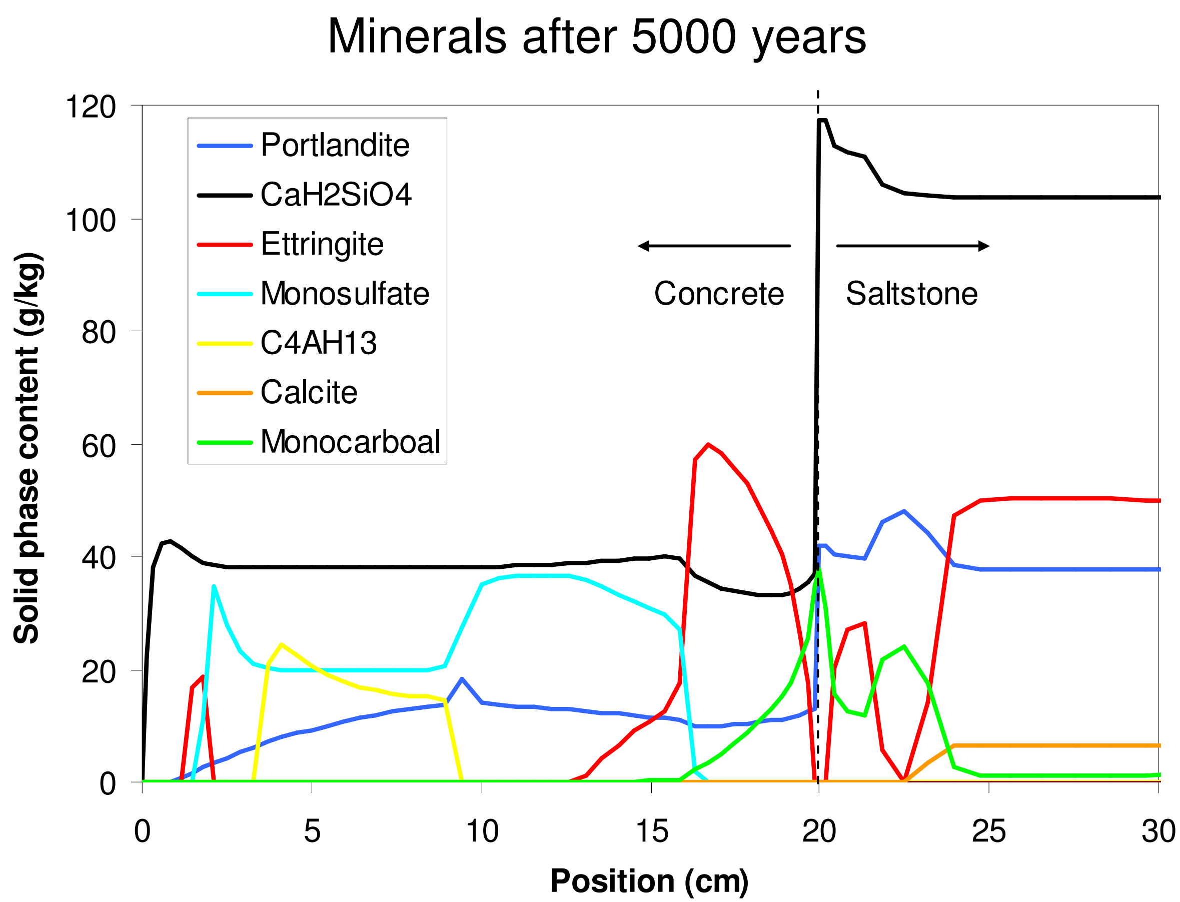
CBP Test Case

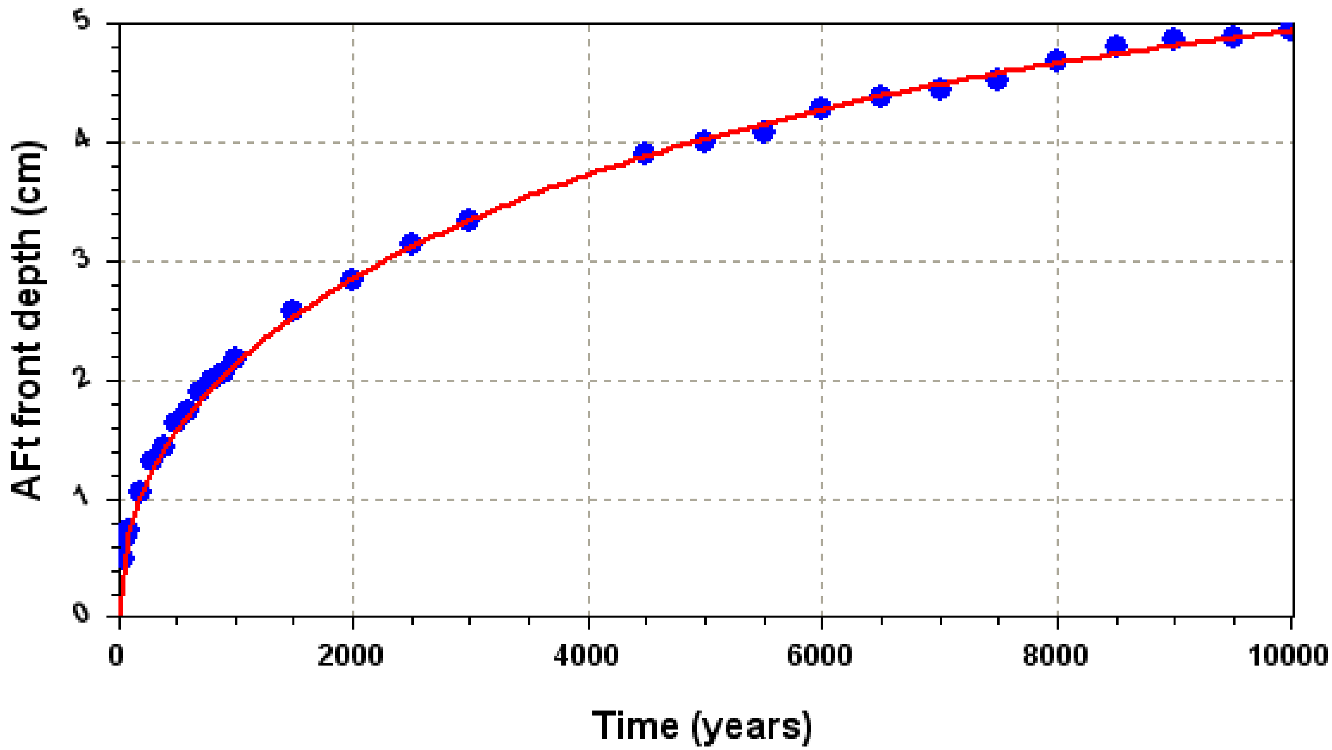
Concrete in contact with saltstone



CBP Test Case

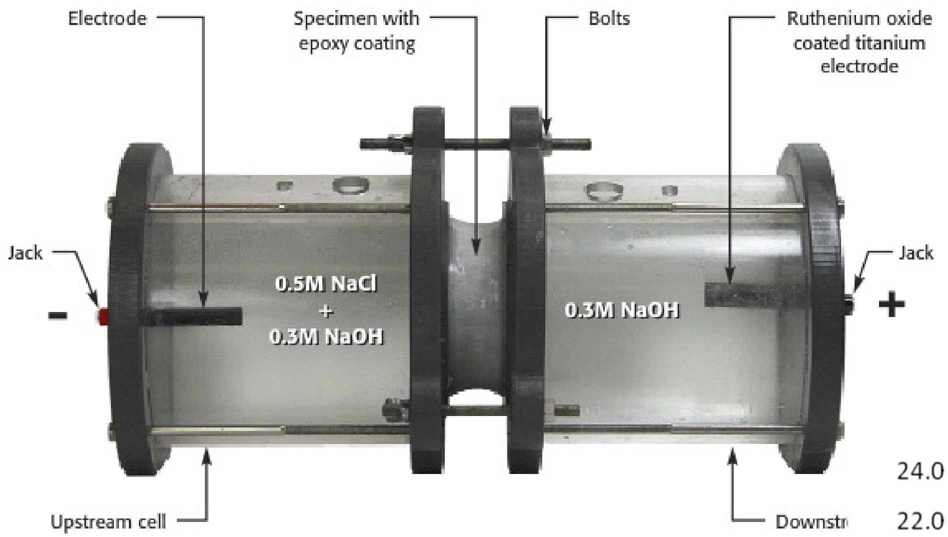
Concrete in contact with saltstone

Position of the ettringite front

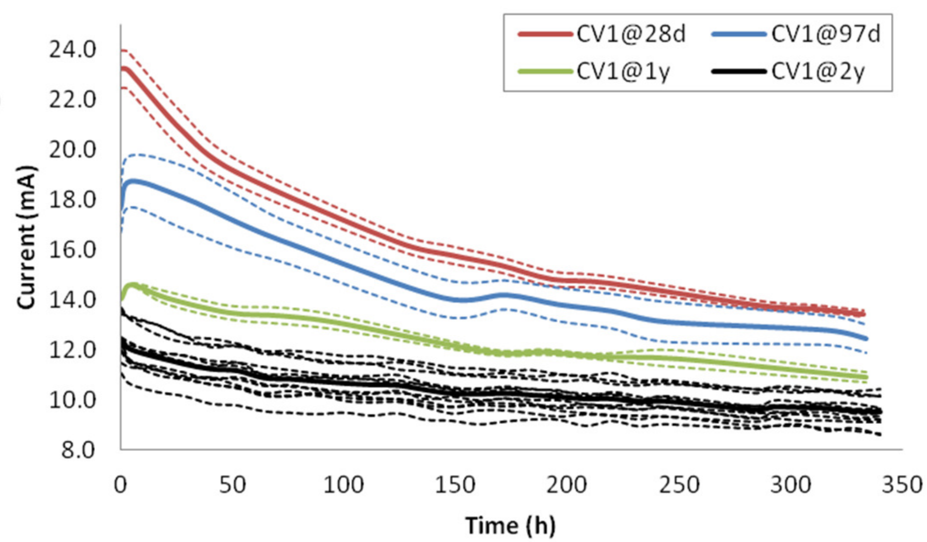


Concrete characterization

Diffusion coefficient measurements (migration test)



Vault 1/4



Concrete characterization

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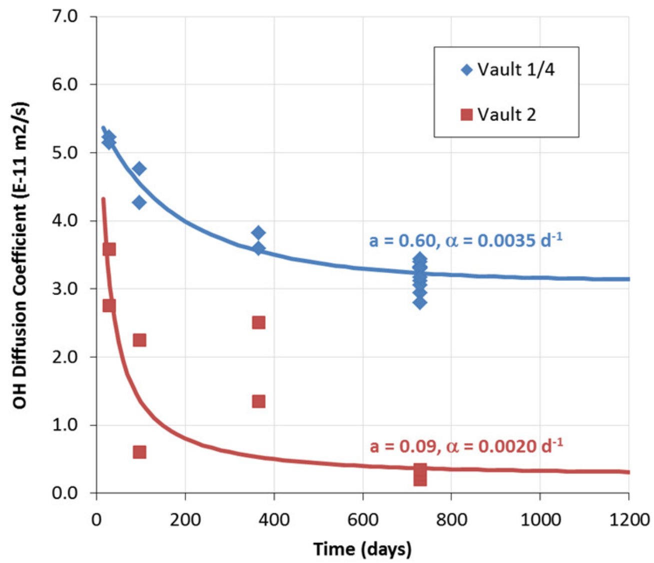
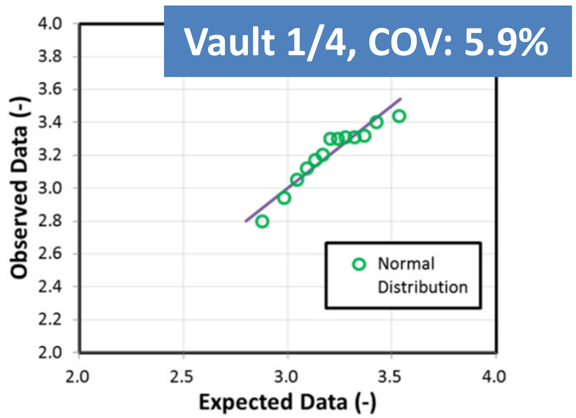
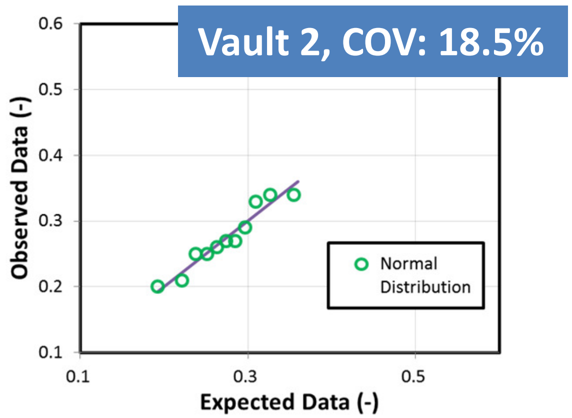
Diffusion coefficient measurements (migration test)



Avg. τ @ 2 yrs: 0.0061

Avg. τ @ 2 yrs: 0.0005





Carbonation of Microconcretes

Microconcrete sample types:

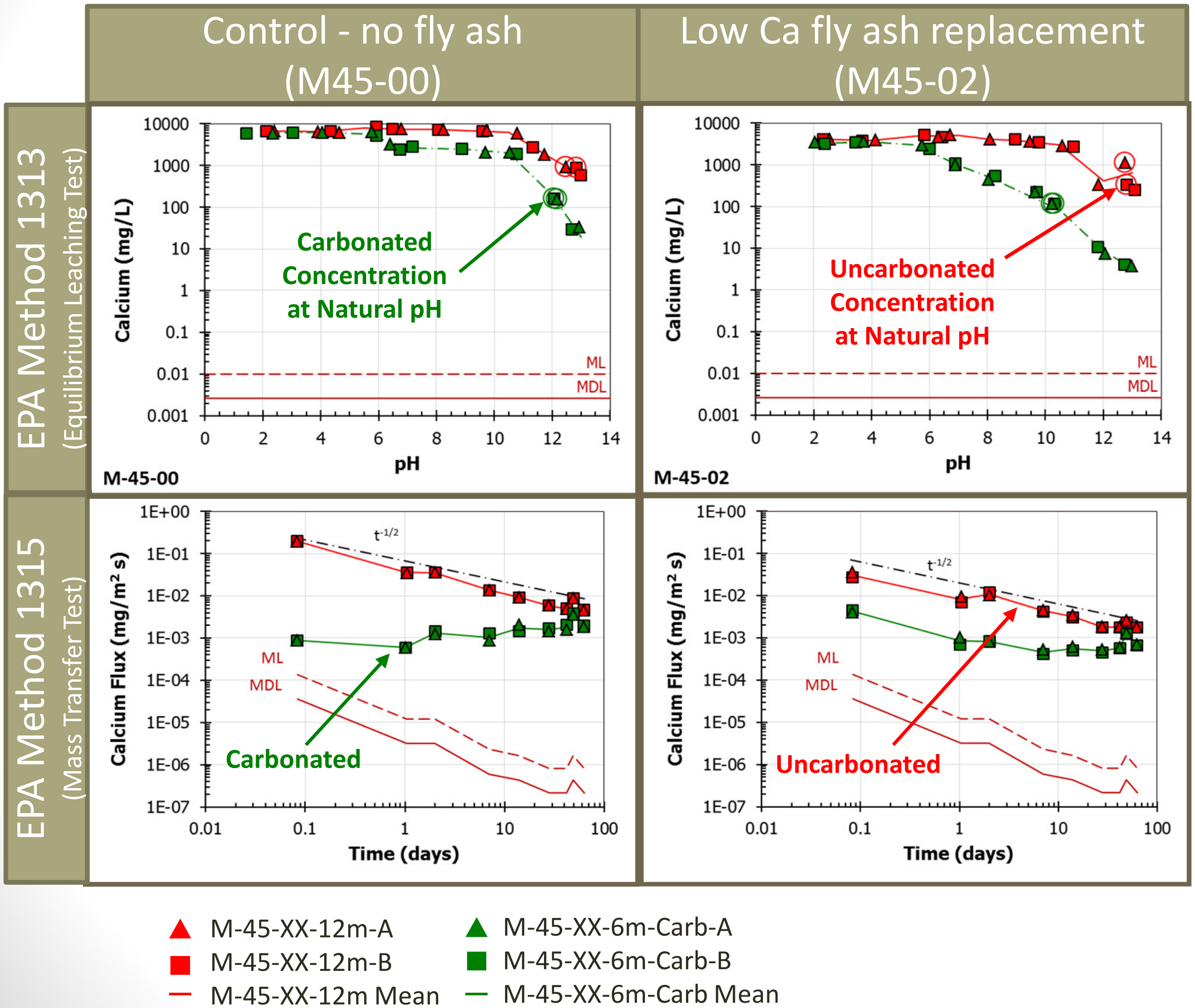
- Microconcrete with no fly ash (Control)
- Microconcretes with 45% fly ash replacement using either
  FA02 (bituminous coal, low calcium fly ash, ~4 wt% Ca) or
  FA39 (sub-bituminous coal, high calcium fly ash, ~23 wt% Ca)

Sample preparation:

- 6-month cured (100% RH)
- 6-month accelerated carbonation ($5\% CO_2$, 65% RH)

	Control	Blend
Nominal Mix (lb/cy)	866	866
Fly ash replacement (%)	N/A	45
Composition (wt%)		
Portland Cement	22.2	12.2
Fly ash	N/A	10.0
Water	9.9	10.1
Fine Aggregate	67.9	67.7
Fly ash used (Sample code)	N/A	FA02
		FA39
Microconcrete Sample Code	M45-00	M45-02
		M45-39

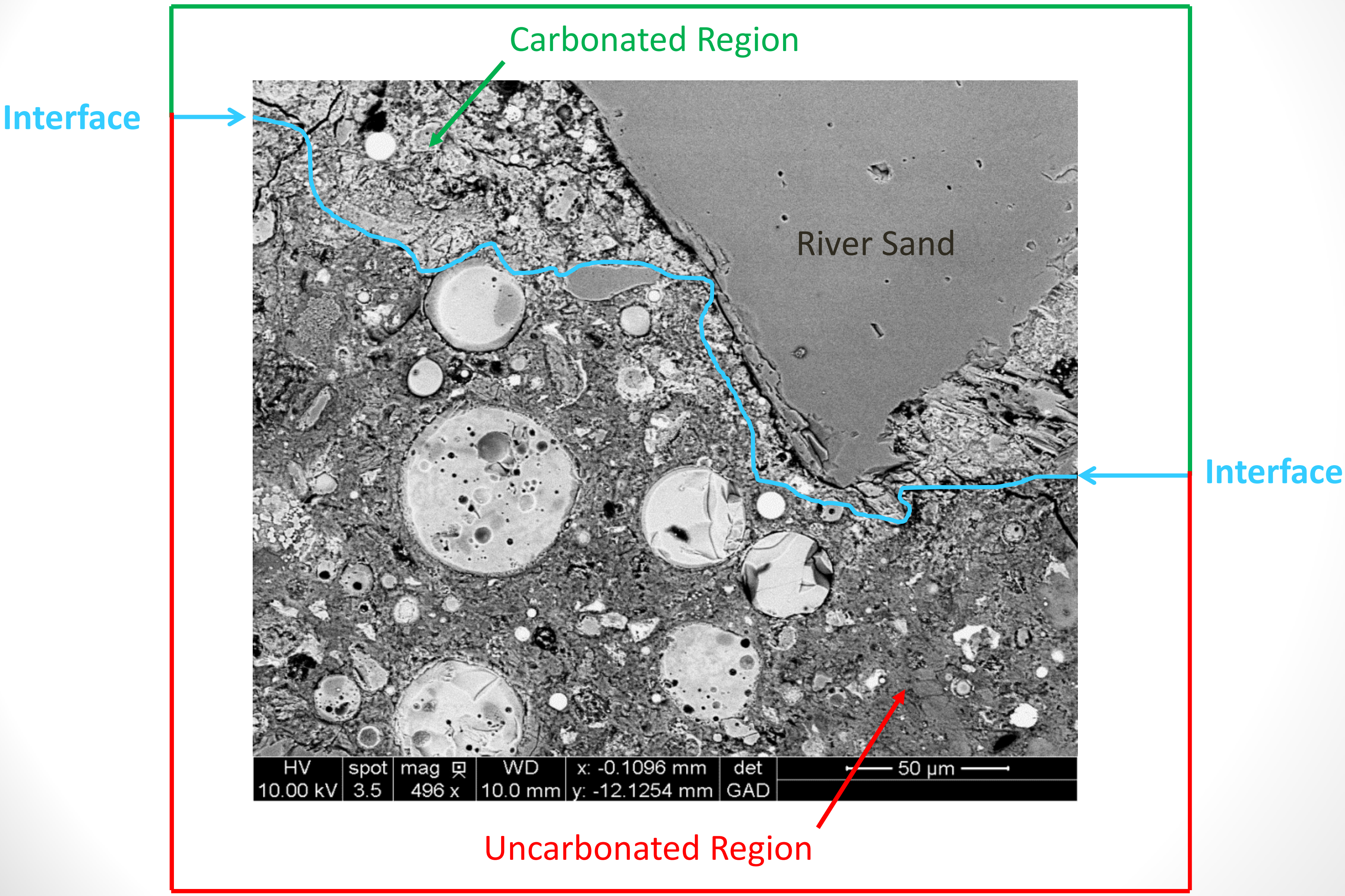
Results from LEAF Methods



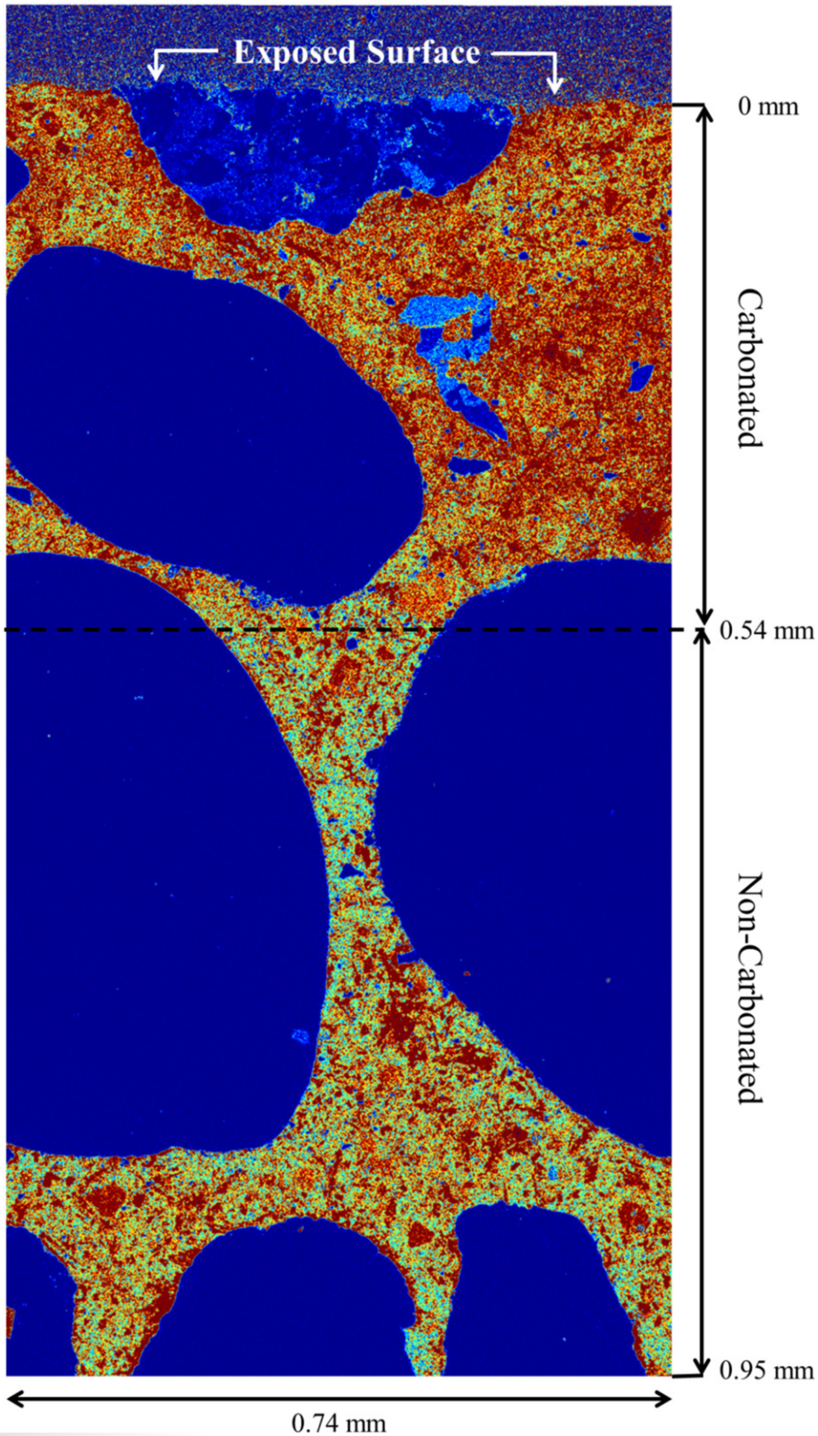
1. Solubility of Ca is lowered in carbonated materials compared to non-carbonated materials at their respective natural pH

2. Initial flux of Ca is lower for carbonated materials but approaches the non-carbonated flux as the leaching front surpasses the carbonated front

Carbonation Microstructure



*Ex: M45-02 (low Ca FA replacement)

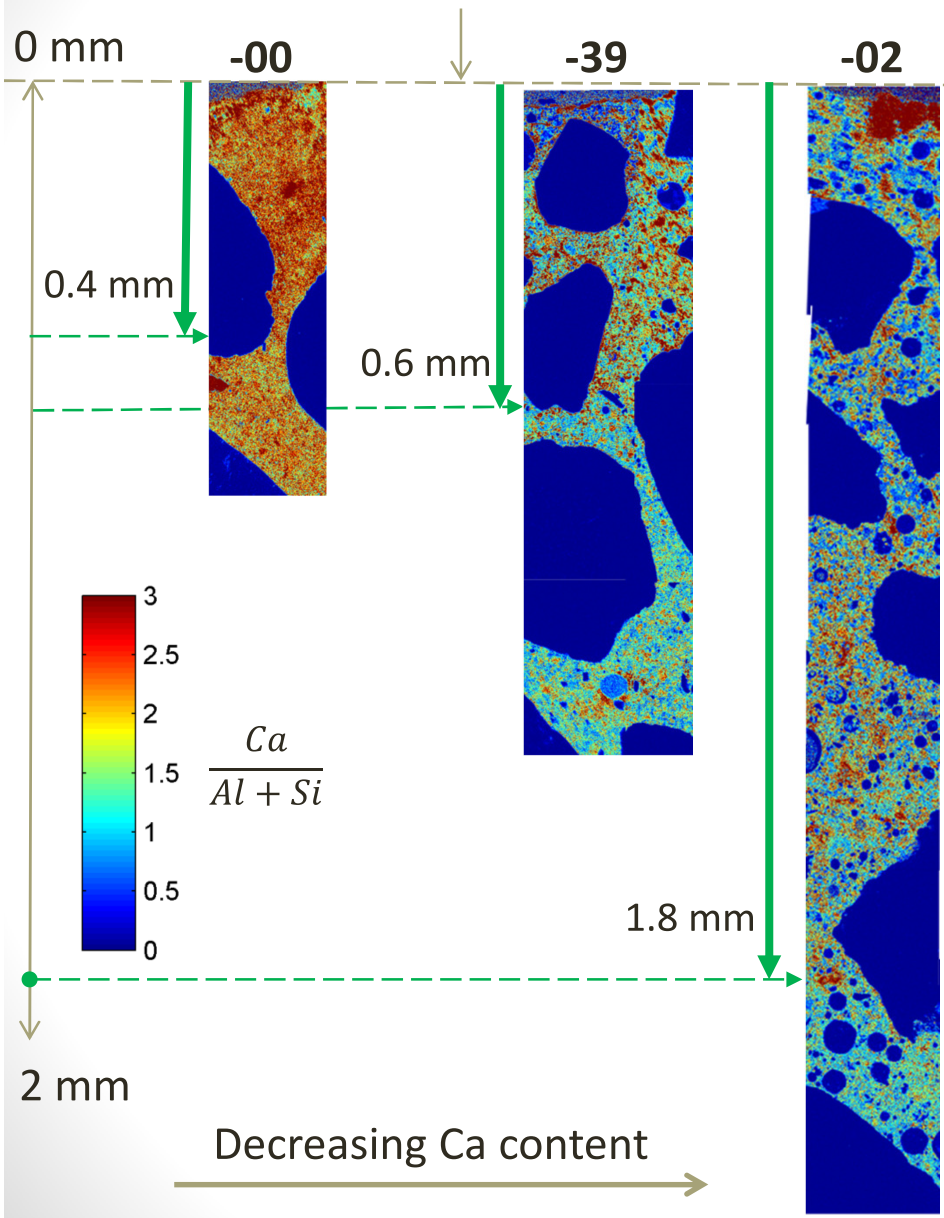


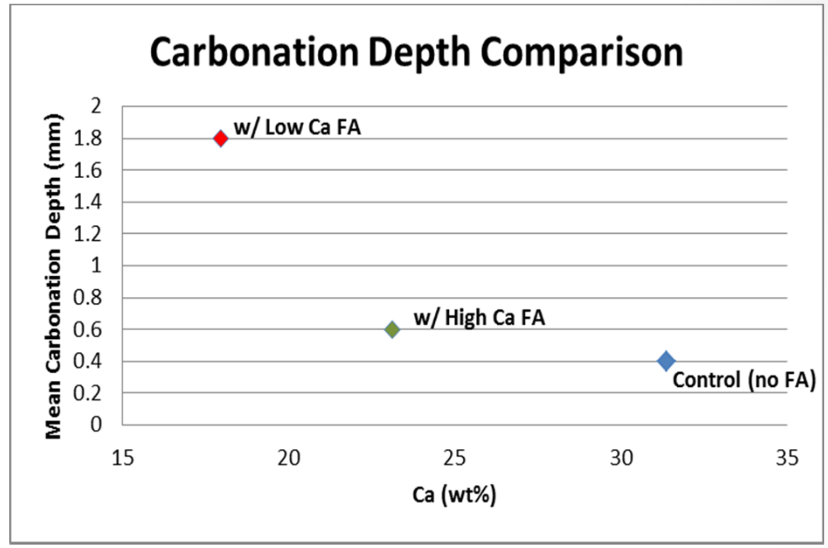
Carbonation Profile

The material is not homogeneous

- Different layers / preferential pathways for the carbonation
- Large blue areas are the fine aggregate and the little blue ones are the epoxy from the sample preparation
- Migration of constituents to the carbonation interface based on their solubilities
- Accumulation of calcium
- *Analogous behavior for pH & redox sensitive species*

SEM-EDS Carbonation Profile

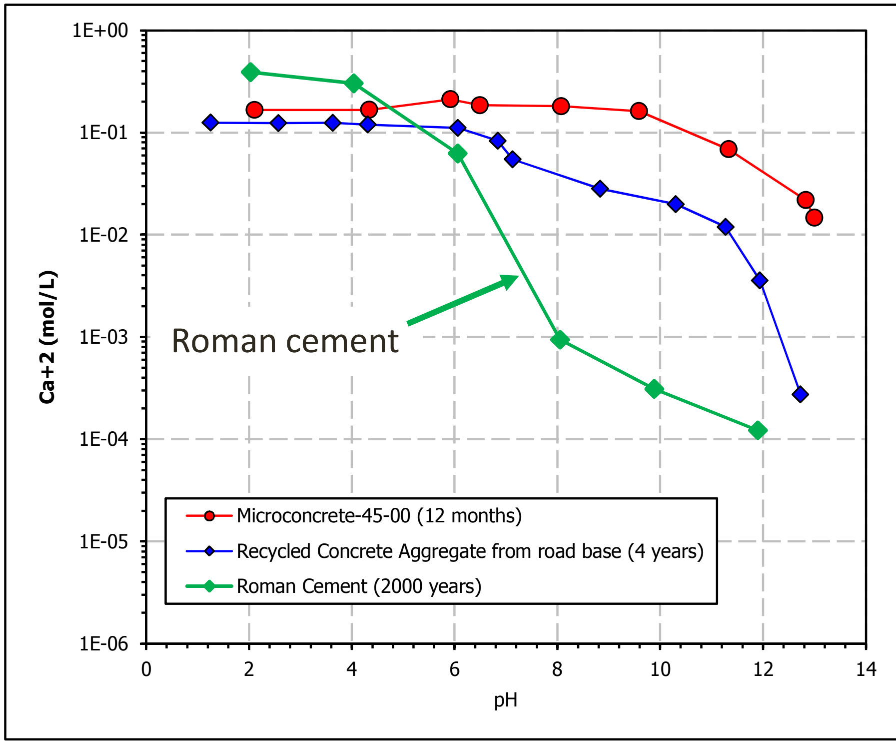


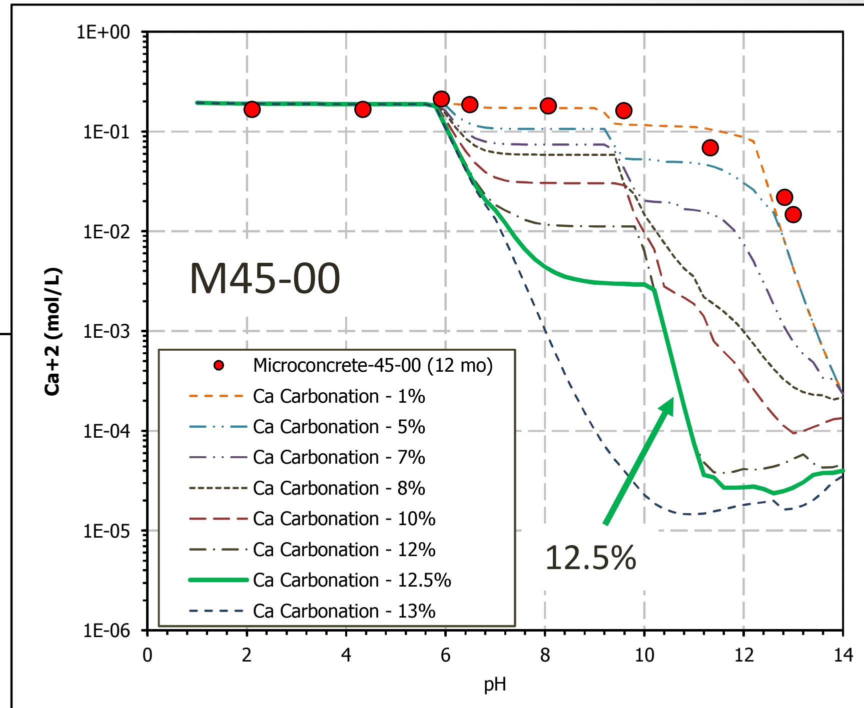


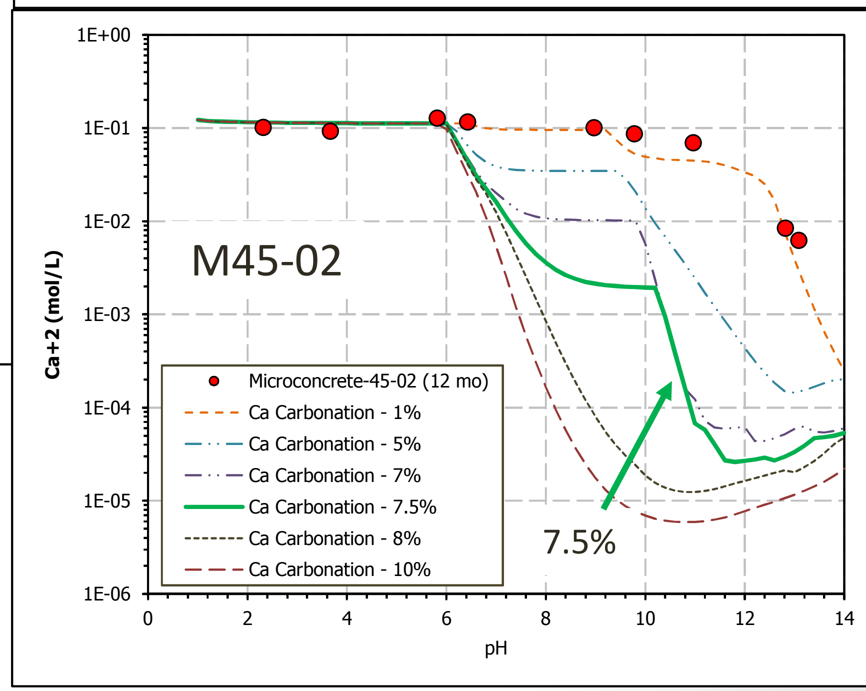
Type	Mean Depth (mm)
Control	0.4
w/ High Ca FA	0.6
w/ Low Ca FA	1.8

- Ca wt% is of the unhydrated Portland cement and fly ash (excluding fine aggregates)
- Ca wt% estimated by Method 3052B, test does not include C

Carbonation of Cement Materials





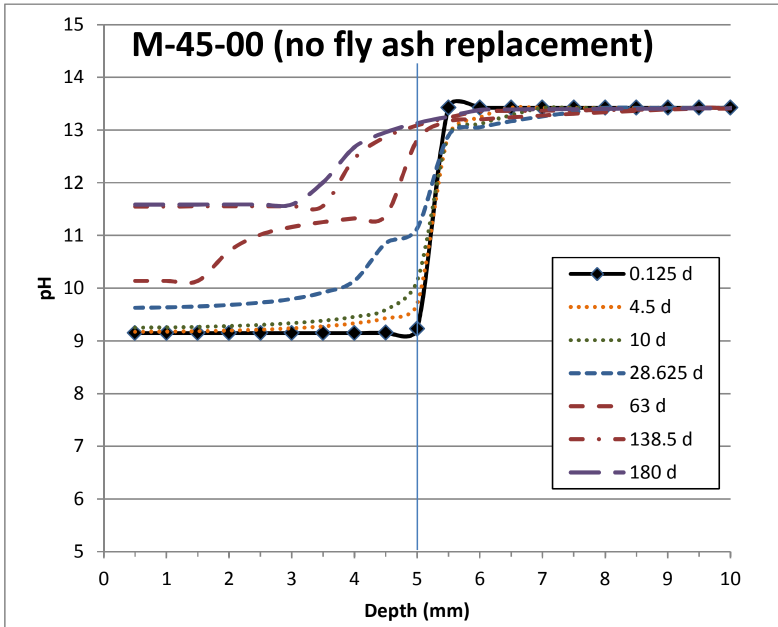


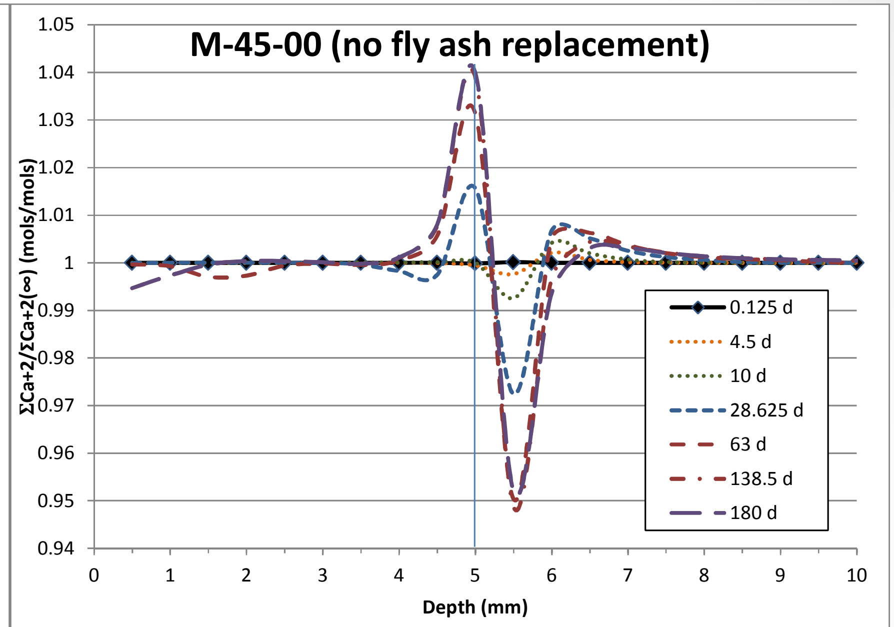
Degree of Carbonation

- Modeled by input CO_3 content
- 2000-yr-old Roman Cement (green diamonds) – completely carbonated

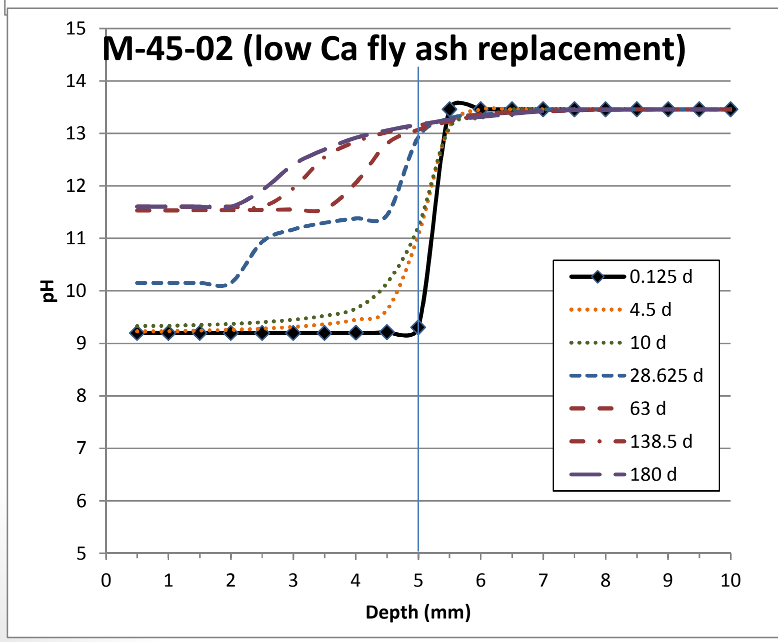
Monolith Diffusion Results

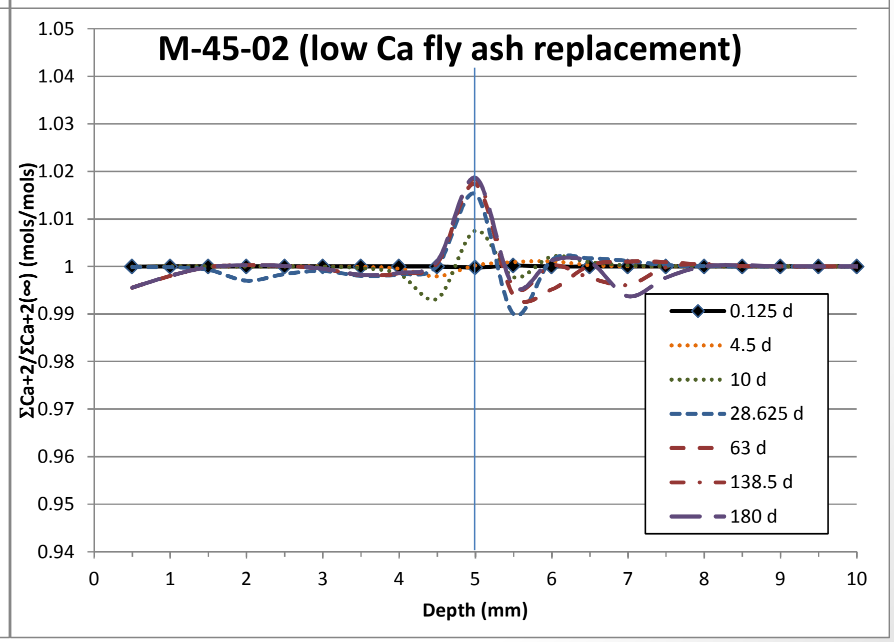
M45-00 (no FA)





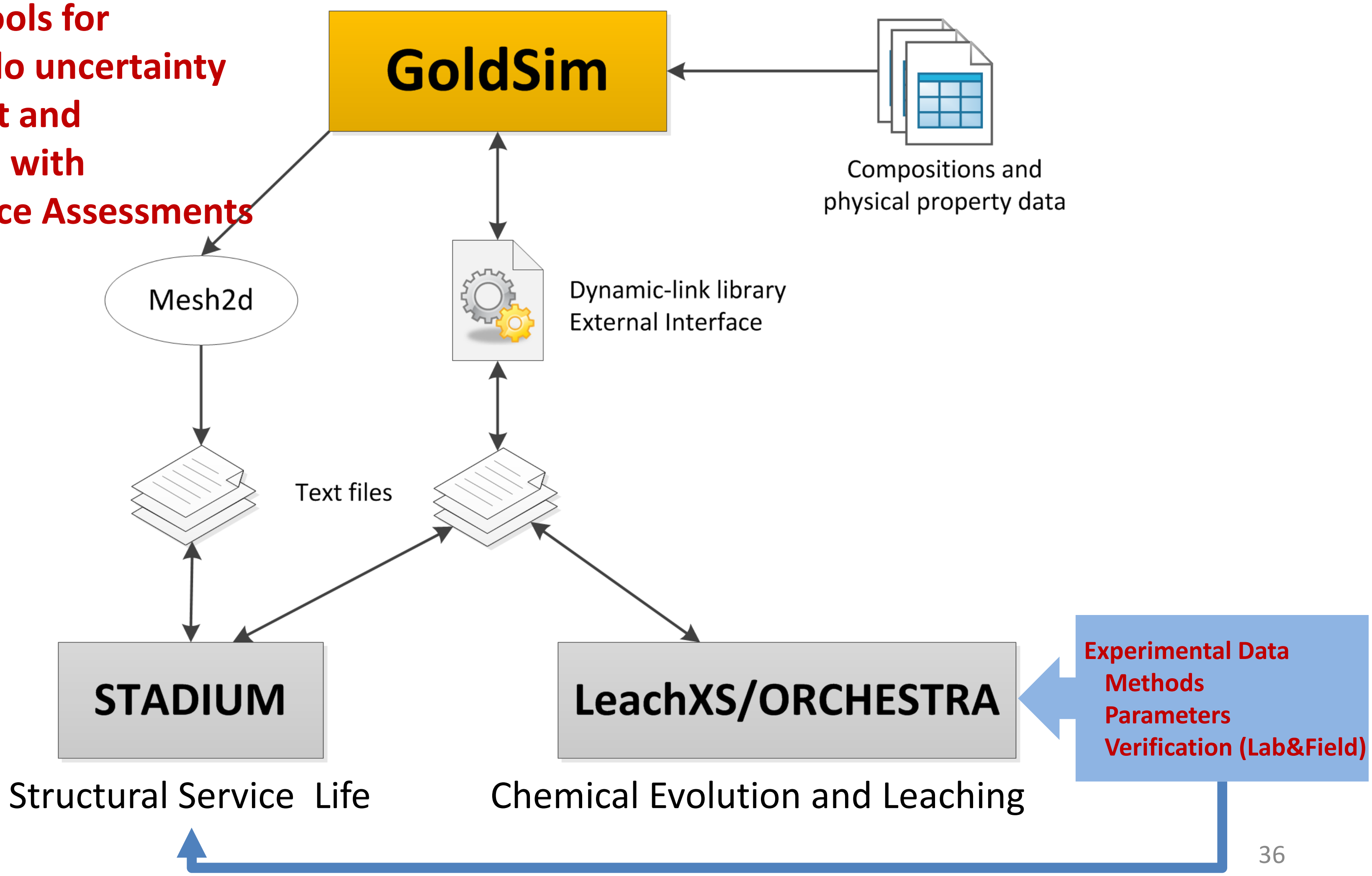
M45-02 (low Ca FA)





Summary of the CBP Software ToolBox

Provides tools for Monte Carlo uncertainty assessment and integration with Performance Assessments



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SRS PA Support Summary

- **CBP software data and tools can engage the PA process in multiple ways**
  - **Provide higher fidelity models for particular phenomena**
  - **Support model abstraction**
  - **CBP tools are 'GoldSim-ready'**
  - **Material characterization**

- **CBP data and software have proven to be useful in the Savannah River Site Saltstone PA**
  - **Cementitious material degradation**
  - **Material characterization**
  - **Conceptual model validation**