Technical Basis for Cementitious Barriers Partnership Models

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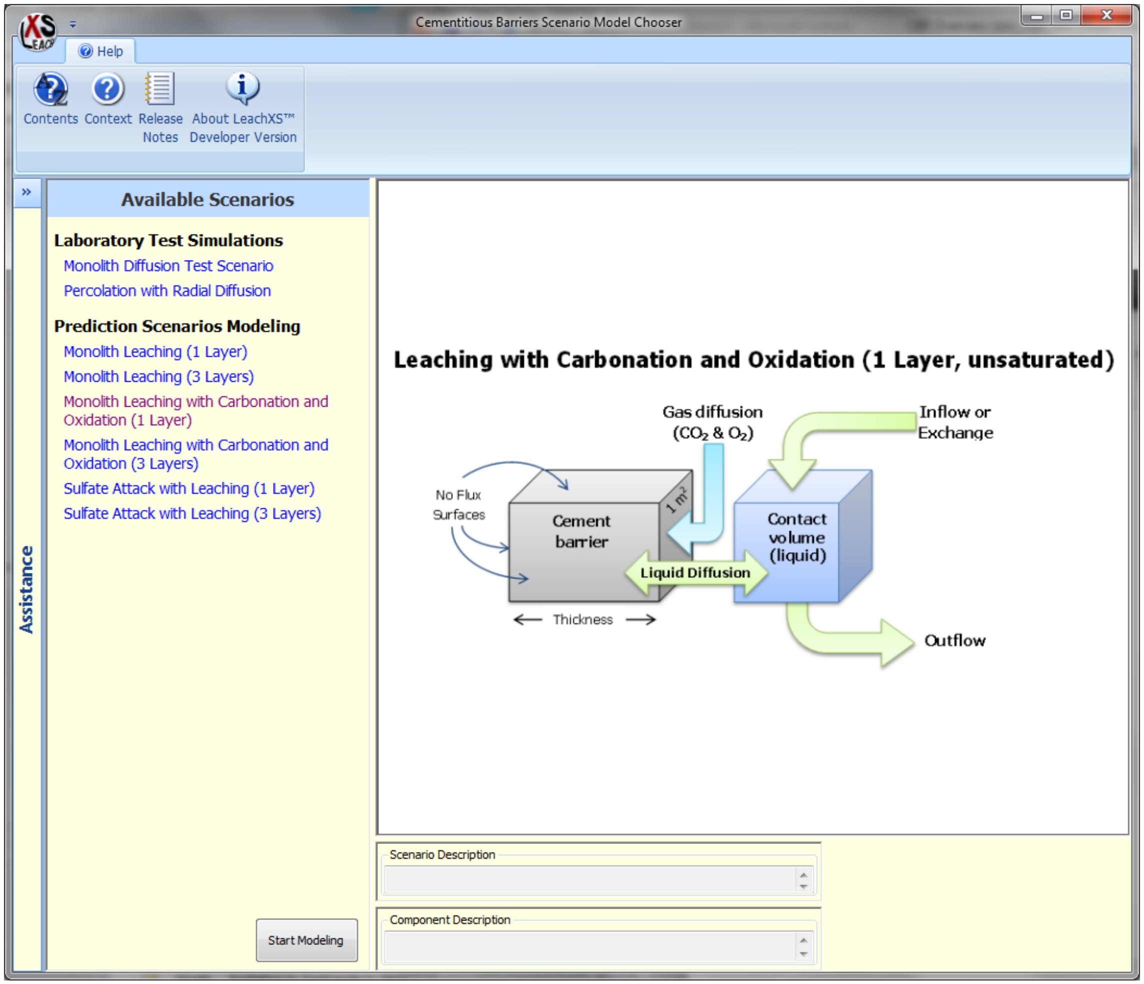
CBP
Cementitious Barriers Partnership

LeachXS/ORCHESTRA

- LeachXS
  - Database expert/decision support system that includes leaching test results for 600+ materials, scenarios and regulations
  - Platform for assessing short- and long-term release of constituents of potential concern
  - Assists in source term evaluation through reactive transport and damage progression modeling
- ORCHESTRA
  - Numerical reactive transport simulation framework embedded in LeachXS
  - Models geochemical speciation and mass transport
  - Flexible and allows users to add/modify existing equations
  - Automatic usage of multiple processors/parallelization

Multiple, Flexible Base Models Available in LeachXS/ORCHESTRA



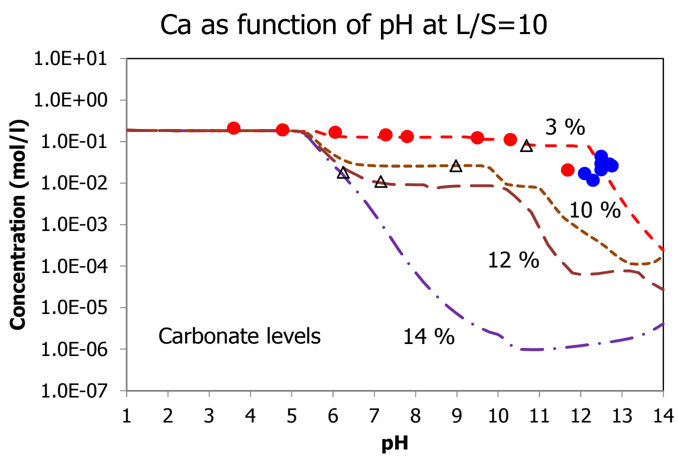
- Select general field or laboratory scenario to model
- Select from existing CBP reference materials or customize materials
- Select interface conditions (e.g., fixed volume, continuous flow or intermittent flow/ exchange & solutions (e.g., “Hanford infiltration” or “saltstone pore water”)
- Resulting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

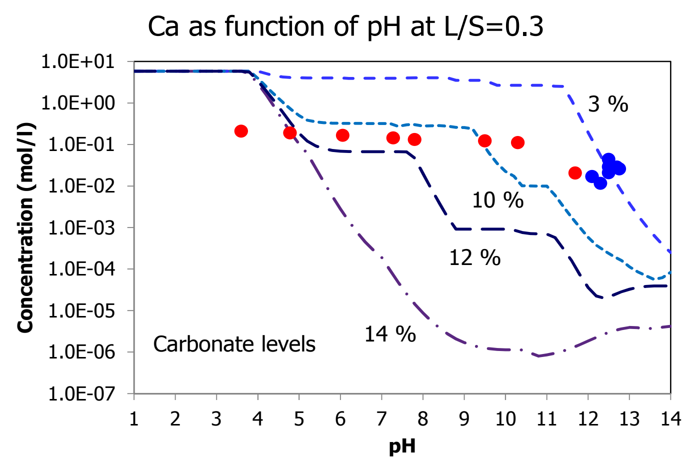
Cementitious Barriers Modeling Scenarios

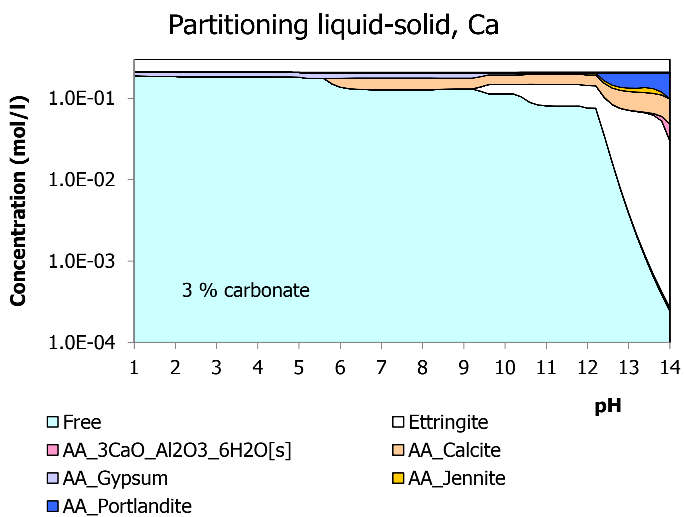
- Currently available:
  - pH dependent equilibrium
    - Test (M1313) and prediction cases
  - Monolith leaching scenario
    - Test (M1315) and prediction cases
  - Monolith leaching with carbonation and oxidation scenario
    - Prediction cases
  - Leaching with sulfate attack scenario
    - Prediction cases
  - Percolation scenario
    - Test (M1314) and prediction cases (local equilibrium & multiple mixed regime models)

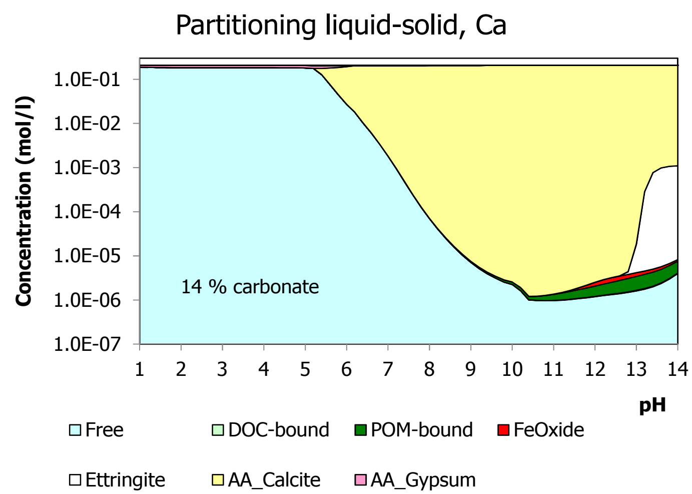
Geochemical Speciation Modeling

Progressive Carbonation of Stabilized Waste





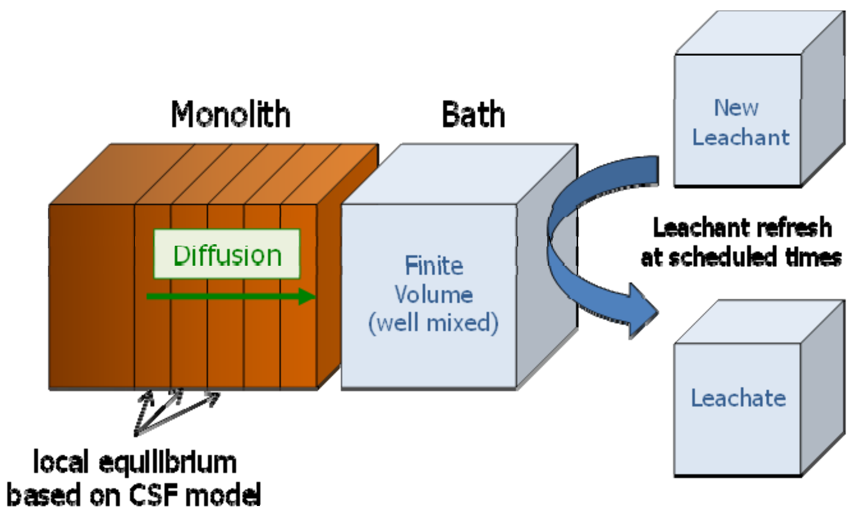




Allows evaluation of conditions not readily reproduced in the Lab (e.g., redox changes, aging processes)

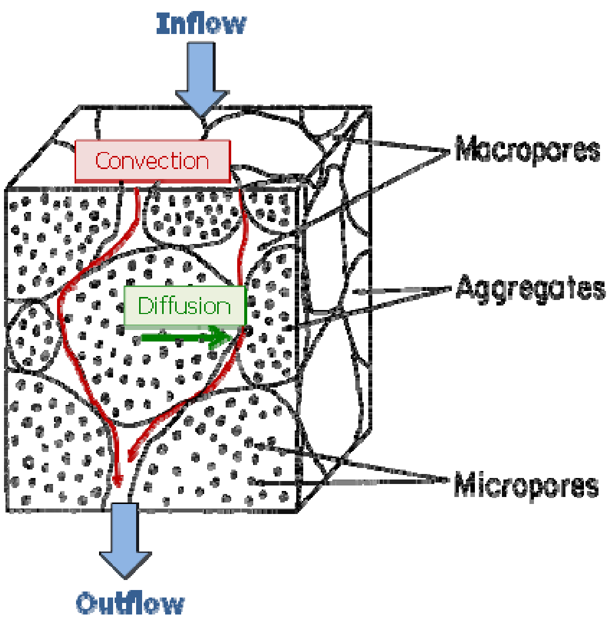
Chemical Speciation Fingerprint (CSF) developed based on Method 1313 and other information sources

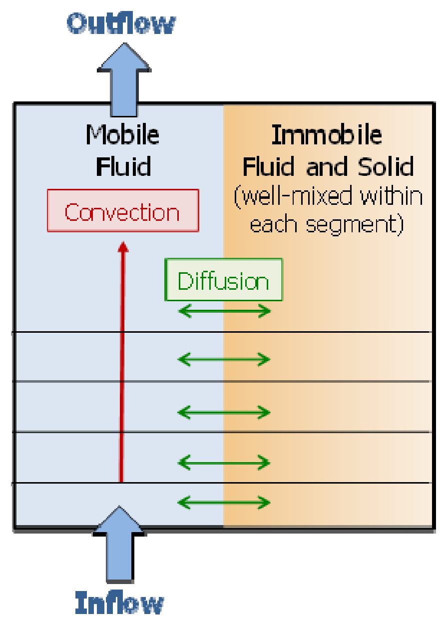
Monolith Diffusion



- Laboratory and field simulations
- Variable water contacting sequence, chemistry
- Saturated or unsaturated
- Carbonation, oxidation ingress
- Sulfate attack with leaching

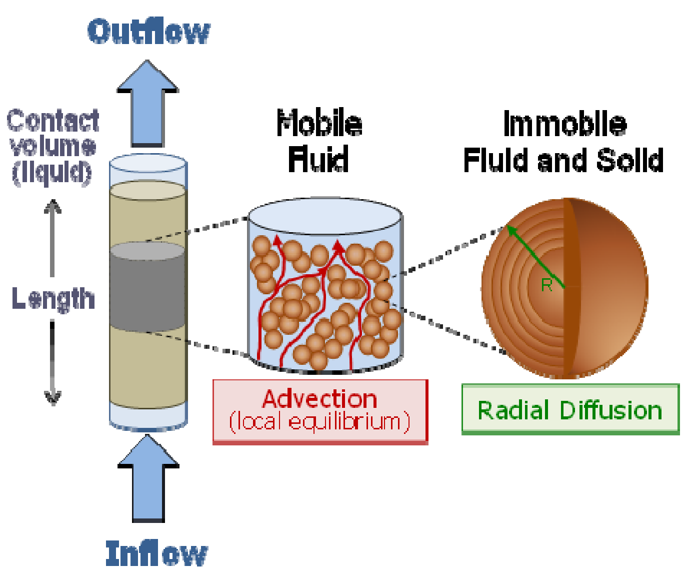
Percolation with Mobile-Immobile Zones

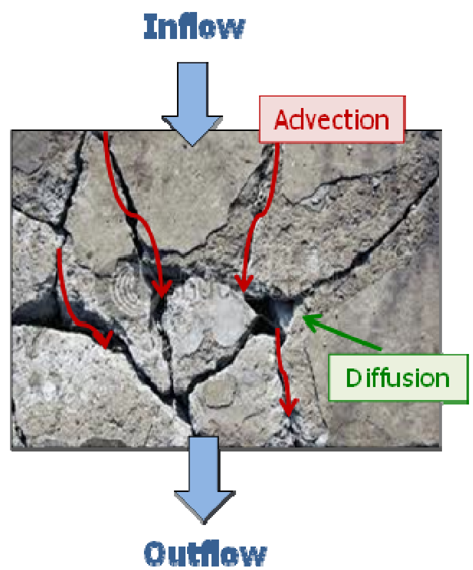




- Laboratory and field simulations
- Variable water flow rate, chemistry
- Effects of preferential flow (e.g., grouted materials, contaminated soils)

Percolation with Radial Diffusion



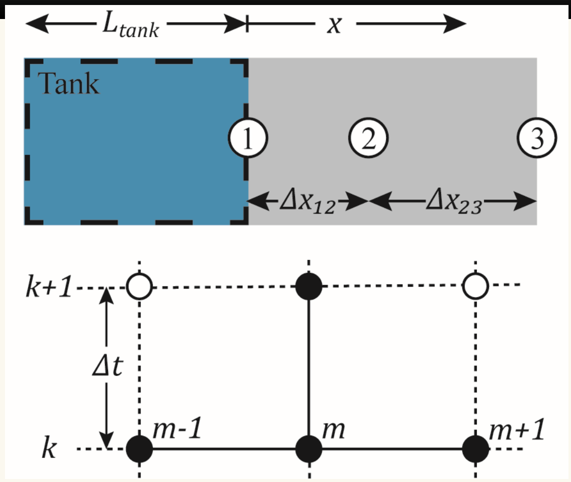


- Laboratory and field simulations
- Cracked materials or packed beds (e.g., wasteforms, tank closure)
- Effects of preferential flow
- Variable water flow rate, chemistry

Applications of Cementitious Barriers Models

Models	Applications
pH dependent equilibrium	Assessment of waste, waste form, grout and concrete leaching chemistry
Monolith leaching	Waste form leaching; grout and concrete durability
Leaching with oxidation and carbonation	Waste form leaching; grout and concrete durability; HLW tank integrity
Leaching with sulfate attack	Concrete durability and interfacial processes
Column percolation Homogeneous Dual porosity w/radial and orthogonal diffusion	Leaching from contaminated soils; leaching and pH evolution from tank grouting (cracking scenarios)

Finite difference method



Linear approximation of

$$\frac{\partial C_i}{\partial t} = \frac{D_i}{\tau}\frac{\partial^2 C_i}{\partial x^2}$$

Three commonly employed schemes

- $FTCS$ – forward in time, centered in space; "fully explicit"; "forward Euler"
- $BTCS$ – backward in time, centered in space; "fully implicit"; "backward Euler"
- CN – Crank Nicolson; "semi-implicit"; average of FTCS and BTCS solutions

$FTCS$ requires least computational expense but is only stable for $\frac{D_i}{\tau}\frac{\Delta t}{\Delta x^2} < \frac{1}{2}$

$BTCS$ and CN are unconditionally stable

For $\Delta x = 0.5$ mm and $D_i/\tau = 1.5(10^{-9})$ m^2/s:

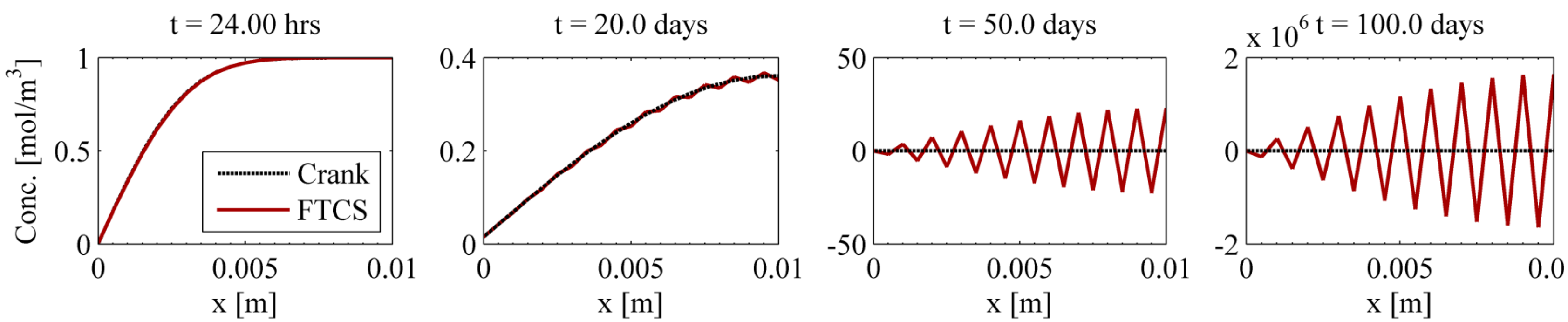
- $\tau = 50 \rightarrow \Delta t_{\max} < 69.44$ min
- $\tau = 5 \rightarrow \Delta t_{\max} < 6.94$ min

For $\Delta x = 0.5$ mm and $D_i = 1.5(10^{-5})$ m^2/s (*gas diffusion*):

- $\tau = 50 \rightarrow \Delta t_{\max} < 0.4167$ s
- $\tau = 5 \rightarrow \Delta t_{\max} < 0.0417$ s ($7.6(10^{11})$ timesteps for a 1000 year simulation)

Case Study: Oscillating solution example

- Model parameters
  - External (Matlab) transport model utilizing FTCS method
  - 1D model, $L_{medium} = 10\text{mm}$, LS = 10
  - $\Delta x = 0.5$ mm, $D_i = 1.5(10^{-9})$ m²/s, $\Delta t = 70$ min, $\phi = 0.2$, $\tau = 50$



- FTCS approximates the solution at early times, but ultimately diverges from the analytical solution
- Similar results obtained in Orchestra for $\Delta t = 71$ min
- For porosity opening (decreasing τ), $\Delta t_{\max}$ may become prohibitively small
- For gas diffusion case, time steps will be prohibitively small

Understanding Carbonation at Interfaces

Microconcrete Preparation

Microconcrete sample types:

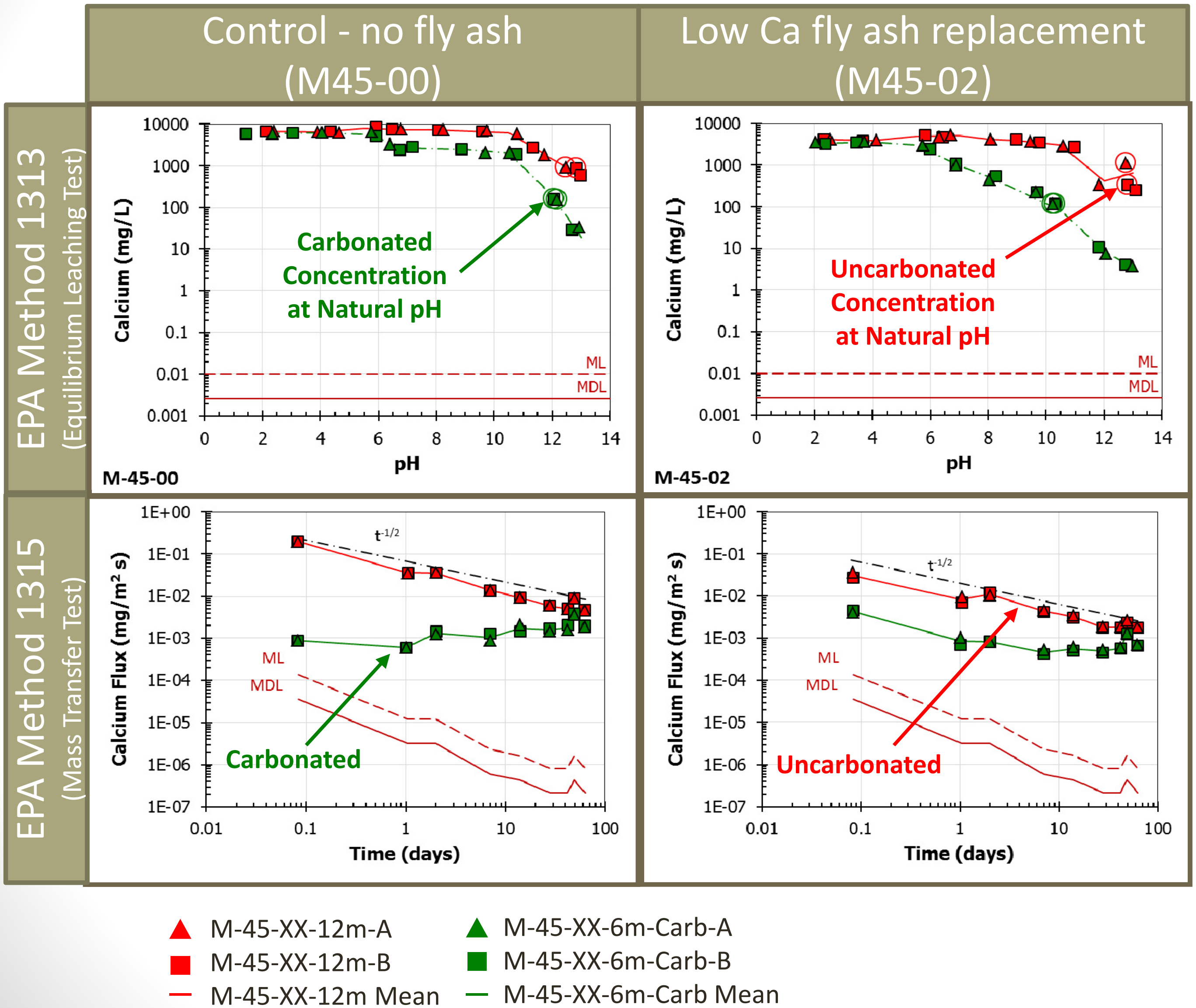
- Microconcrete with no fly ash (Control)
- Microconcretes with 45% fly ash replacement using either
  FA02 (bituminous coal, low calcium fly ash, ~4 wt% Ca) or
  FA39 (sub-bituminous coal, high calcium fly ash, ~23 wt% Ca)

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

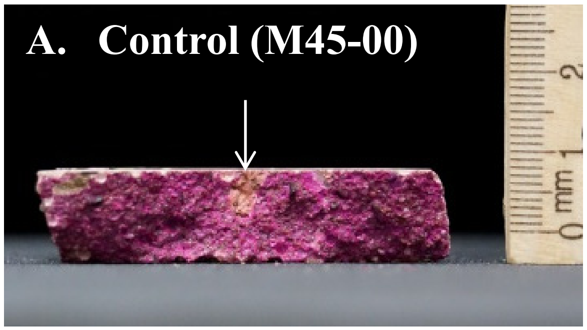


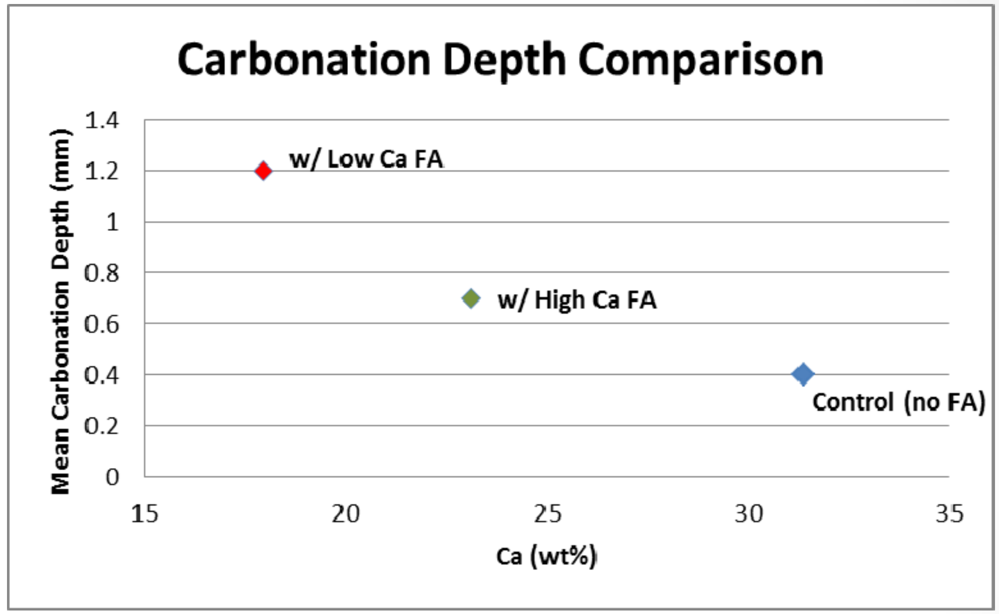
1. Solubility of Ca is lowered in carbonated materials compared to non-carbonated materials at their respective natural pH

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

Phenolphthalein Indicator Test

Decreasing Ca composition

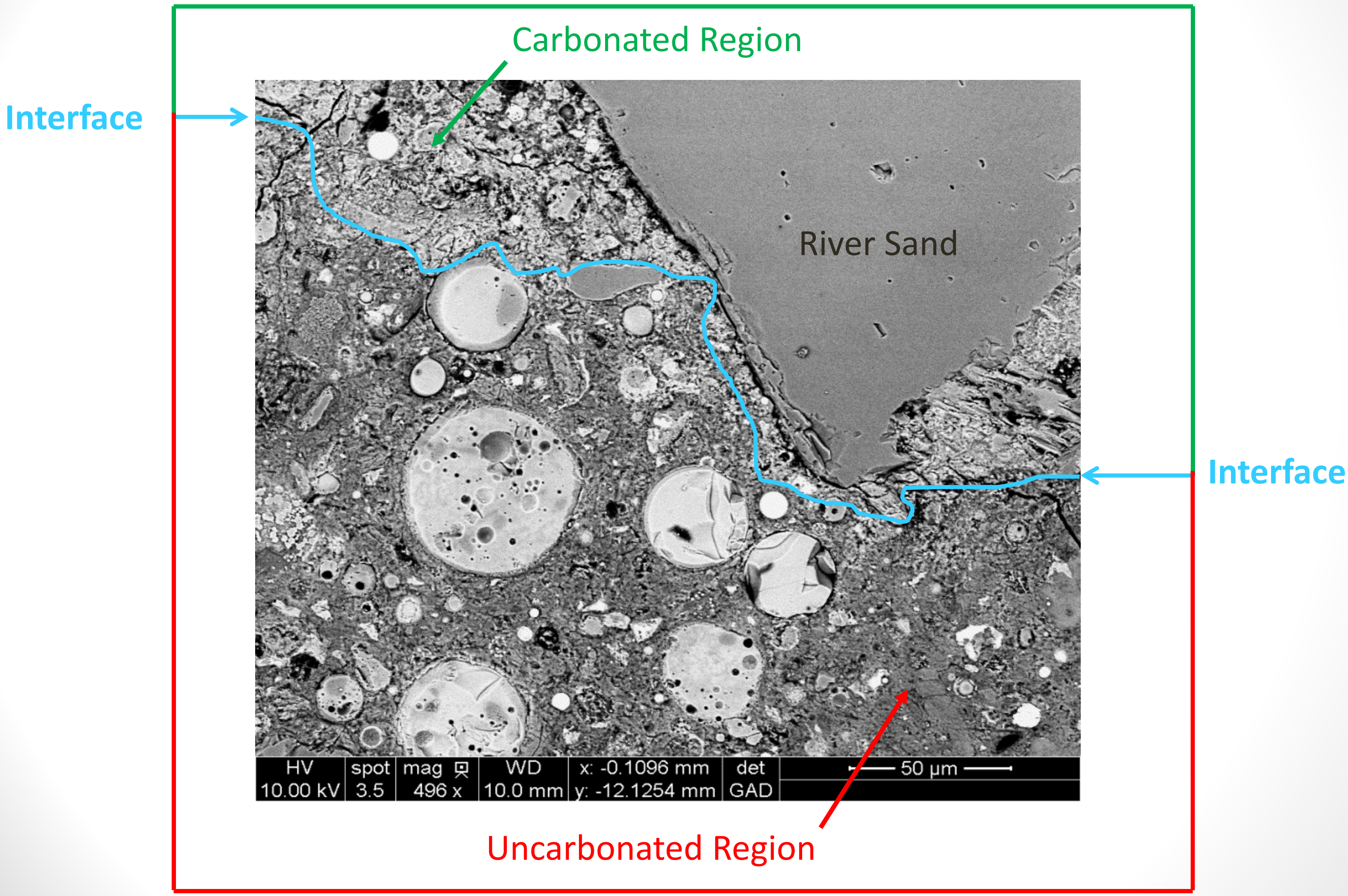




Type	Mean Depth (mm)
Control (no FA)	0.4
w/ High Ca FA	0.7
w/ Low Ca FA	1.2

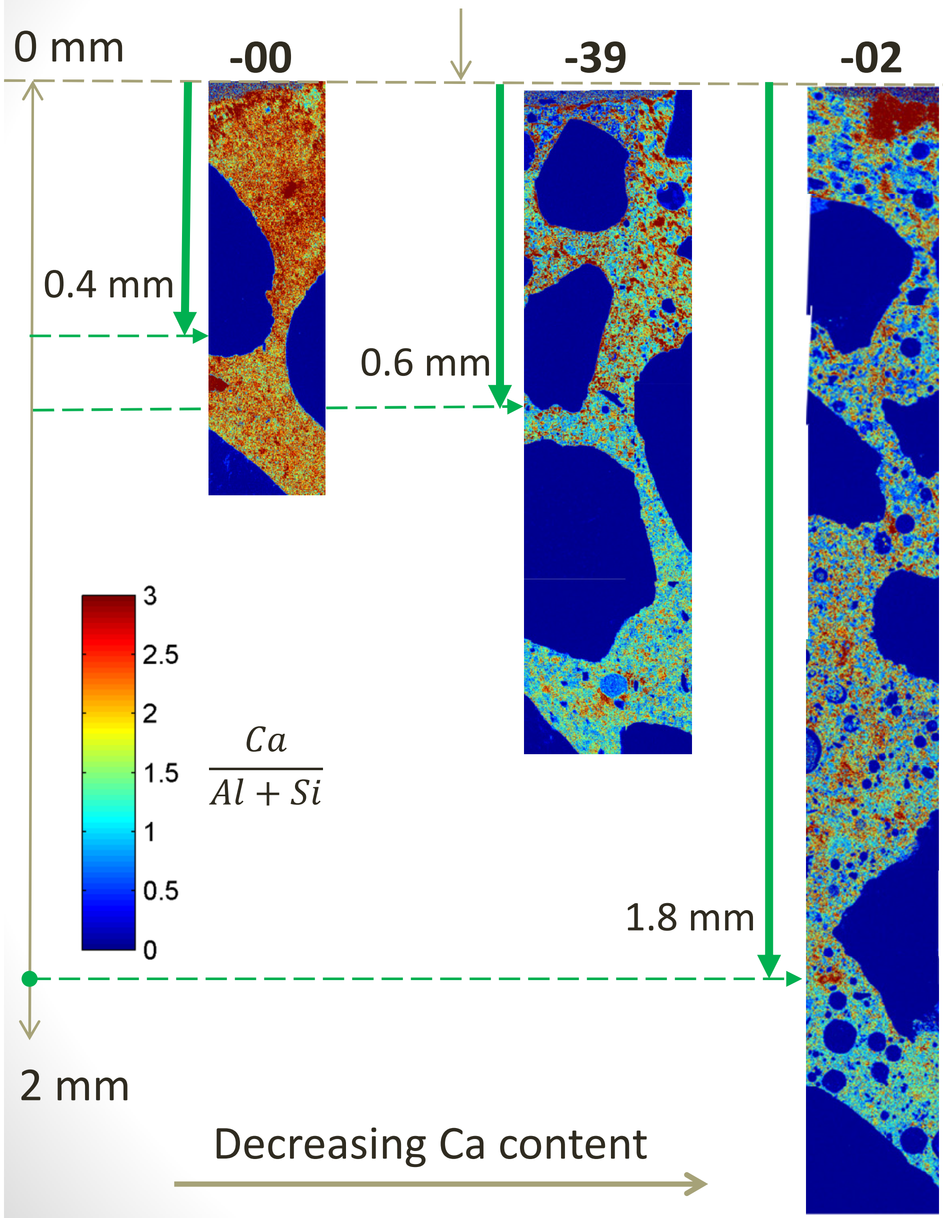
- Ca wt% is of the unhydrated Portland cement and fly ash (excluding fine aggregates)
- Ca wt % estimated by Method 3052B, excludes C and B

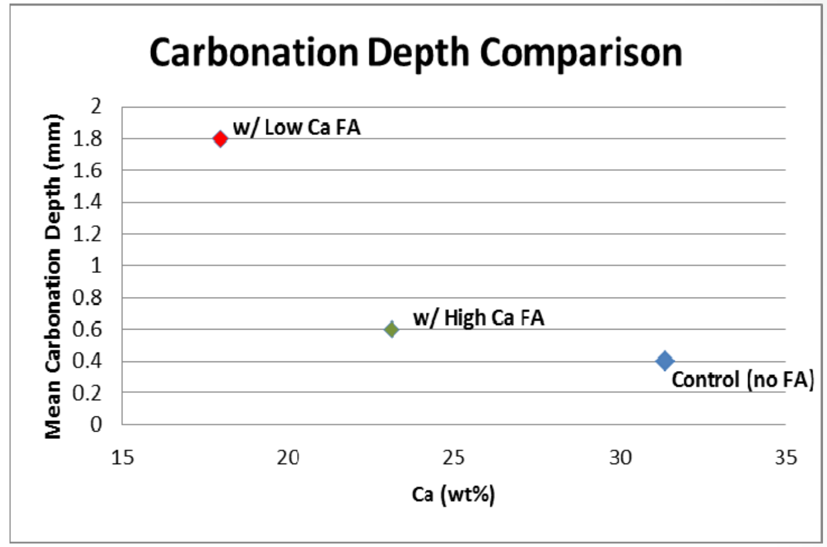
Carbonation Microstructure



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

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

Flexible Models in LeachXS™/ORCHESTRA

- Select general field or laboratory scenario
- Select from existing CBP reference materials or add materials
- Select interface conditions (e.g., fixed volume, continuous flow or intermittent flow / exchange & solutions)
- Leaching data management integrated with chemical speciation – reactive transport modeling

Mineral Set

Thermodynamic model

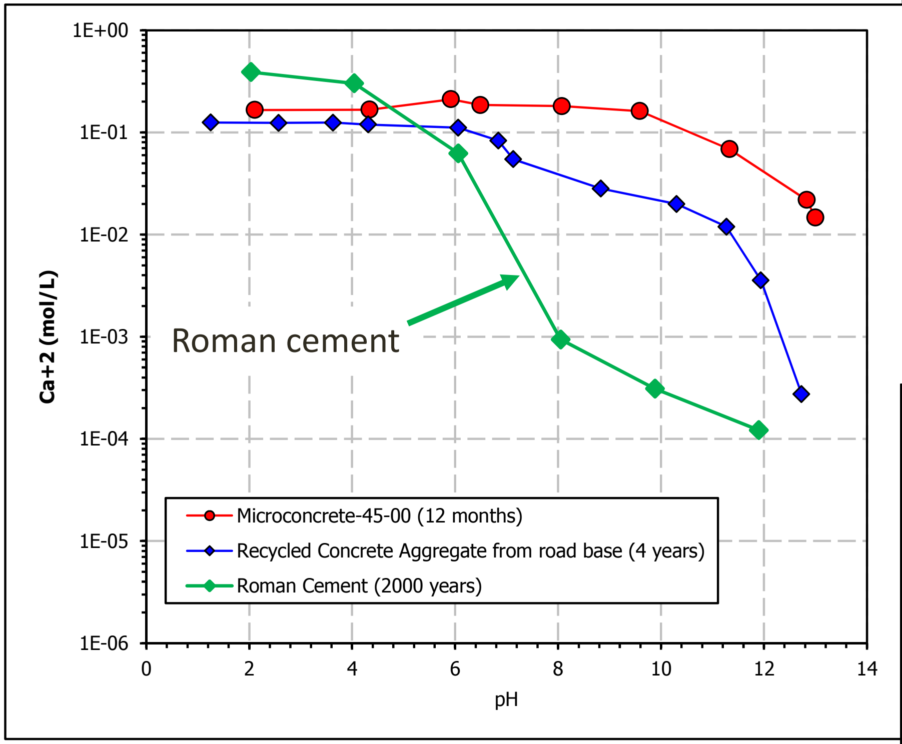
- LeachXS/ORCHESTRA
  - Solves system of equations:
    - Conservation of mass
    - Laws of mass action
  - Yields solid, aqueous, and gaseous speciation
- C-S-H
  - Ideal solid solution with Tobermorite- and Jennite-like end-members (Lothenbach et al., 2008)
- Adsorption models
- Additional minerals included in the model for trace species
  - As, B, Ba, Cd, Cr, Cu, Sb, Se, Sr, Th, U, V, Zn

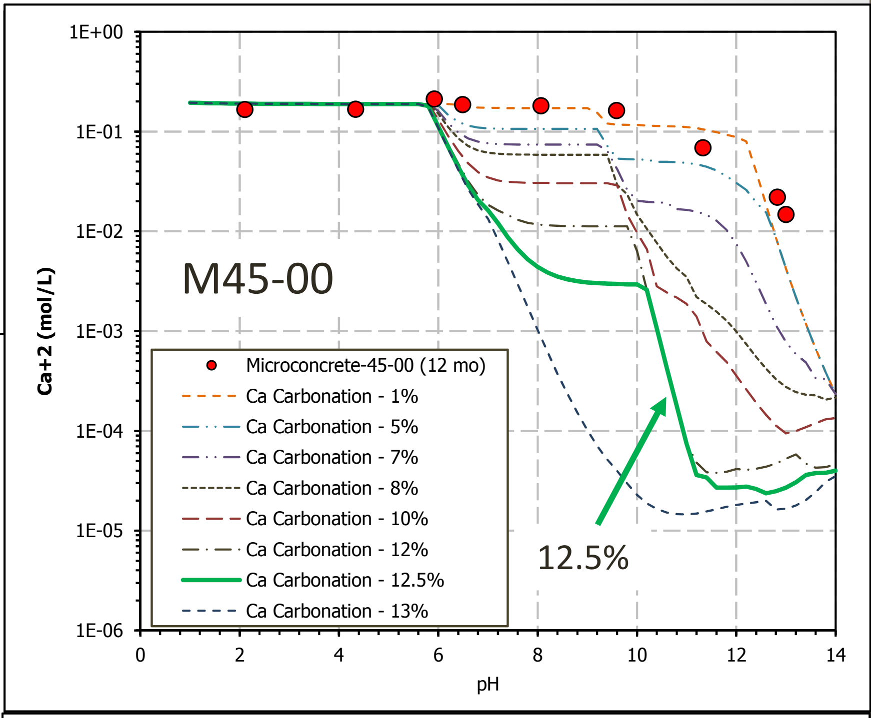
Major Mineral Phases

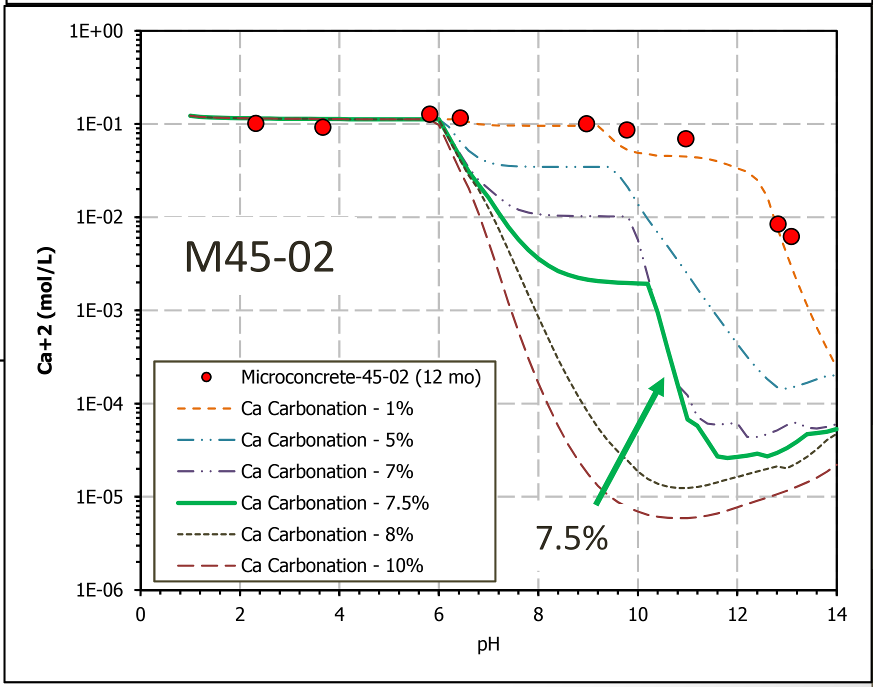
$Mg(OH)_2$ *Brucite*	$Ca(OH)_2$ *Portlandite*	CAH_{10}* *Unnamed meta-stable phase*
$CaSO_4 \cdot 2H_2O$ *Gypsum*	$CaCO_3$ *Calcite*	C_3AH_6* *Hydrogarnet*
SiO_2 (am) *Amorphous Silica*	C_2ASH_8* *Strätlingite*	C_3FH_6* *Fe-hydrogarnet*
$Al(OH)_3$ (am) *Amorphous Aluminum hydroxide*	C_2FSH_8* *Fe-Strätlingite*	C_4AH_{13}* *Hydroxy AFm*
Al_2O_3 *Alumina*	C_2AH_8* *Unnamed meta-stable phase*	C_4FH_{13}* *Fe-hydroxy AFm*
$Fe(OH)_3$ (am) *Amorphous Iron hydroxide*	C_2FH_8* *Unnamed meta-stable phase*	***Solid Solution:*** $C_{1.67}SH_{2.1}$* *Jennite* $C_{0.83}SH_{1.3}$* *Tobermorite*
$K_2Ca(SO_4)_2 \bullet H_2O$ *Syngenite*	$CaSO_4$ *Anhydrite*	

* Notation: C = CaO, A = Al_2O_3, F = Fe_2O_3, S = SiO_2, H = H_2O

Carbonation of Cement Materials







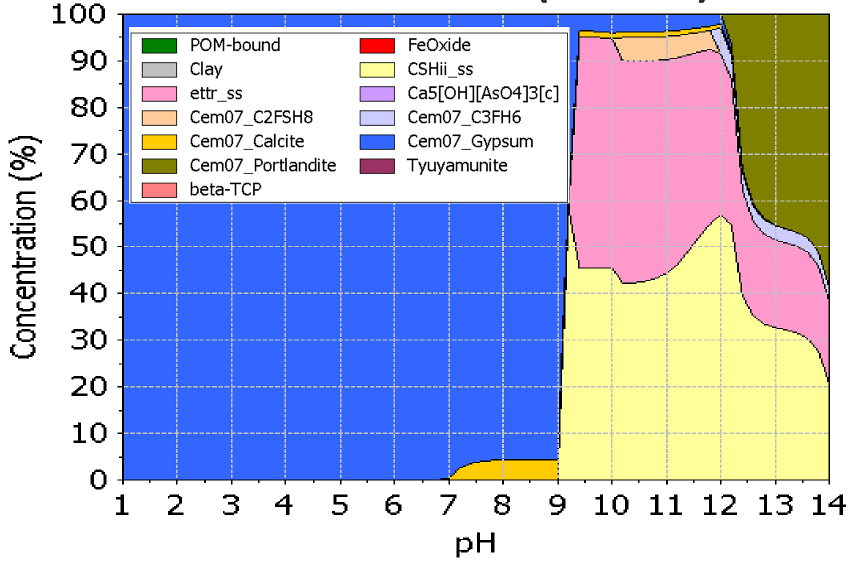
Degree of Carbonation

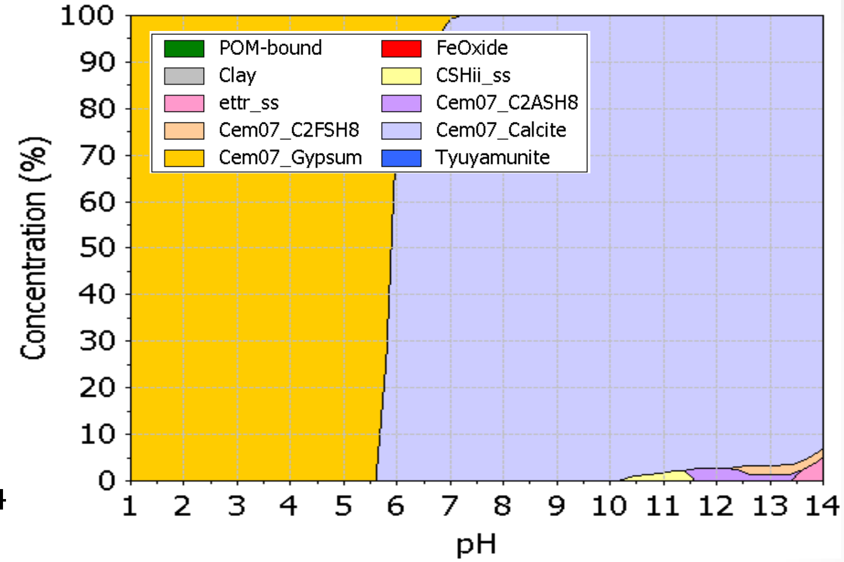
- Modeled by input CO_3 content
- 2000-yr-old Roman Cement (green diamonds) – completely carbonated

Speciation of Cement Materials

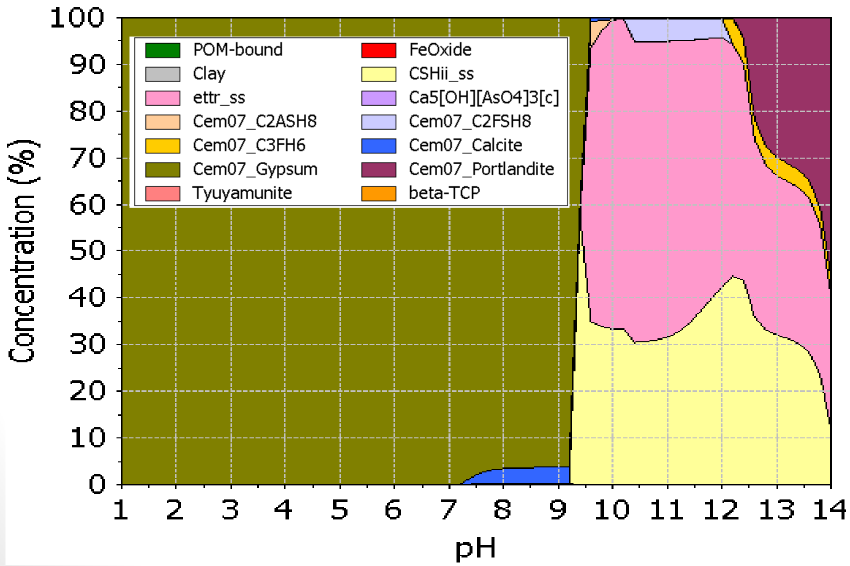
Uncarbonated (Control) | **Carbonated**

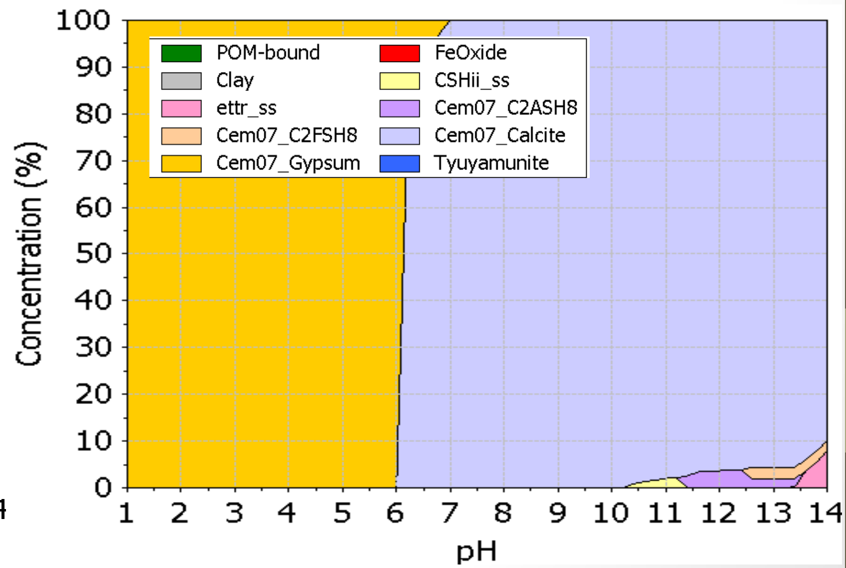
M45-00 (no FA)



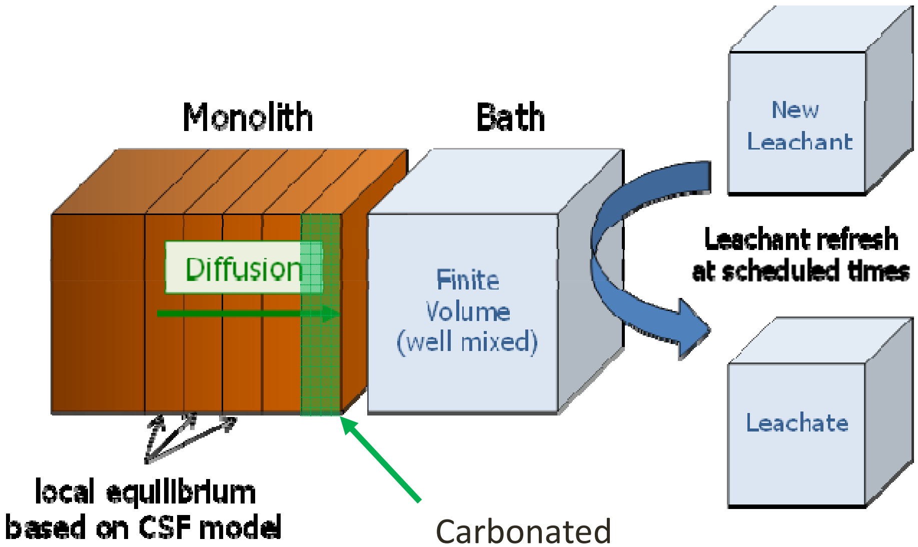


M45-02 (low Ca FA)





Monolith Diffusion Modeling



Modeling Options

- Laboratory and field simulations
- Variable water contacting sequence, chemistry
- Saturated or unsaturated
- Carbonation, oxidation ingress
- Sulfate attack with leaching

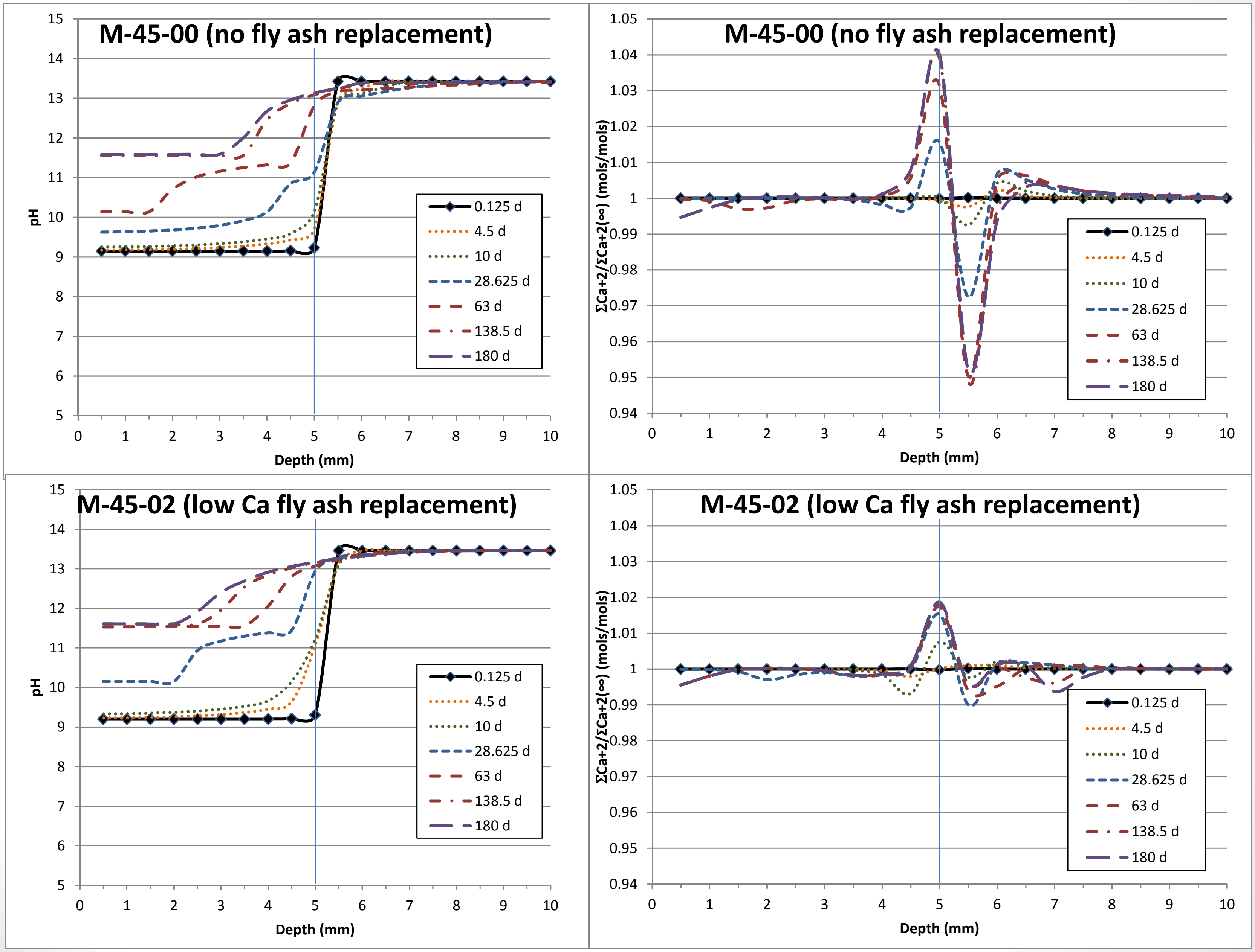
For this study

- 180 days simulated to represent experimental results
- Saturated conditions with tortuosity and porosity at upper ends of reasonable ranges
- No fluxes at boundaries – diffusion only
- Five (5) millimeters “pre-carbonated” based on field results

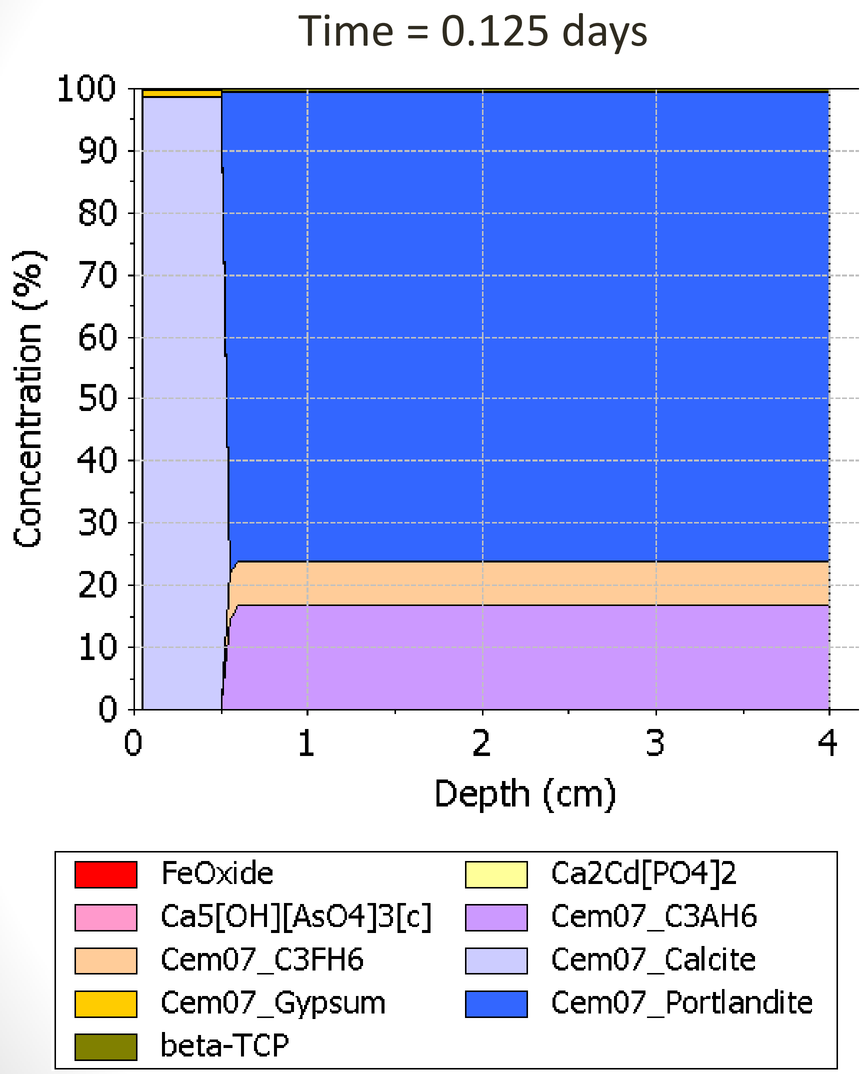
Monolith Diffusion Results

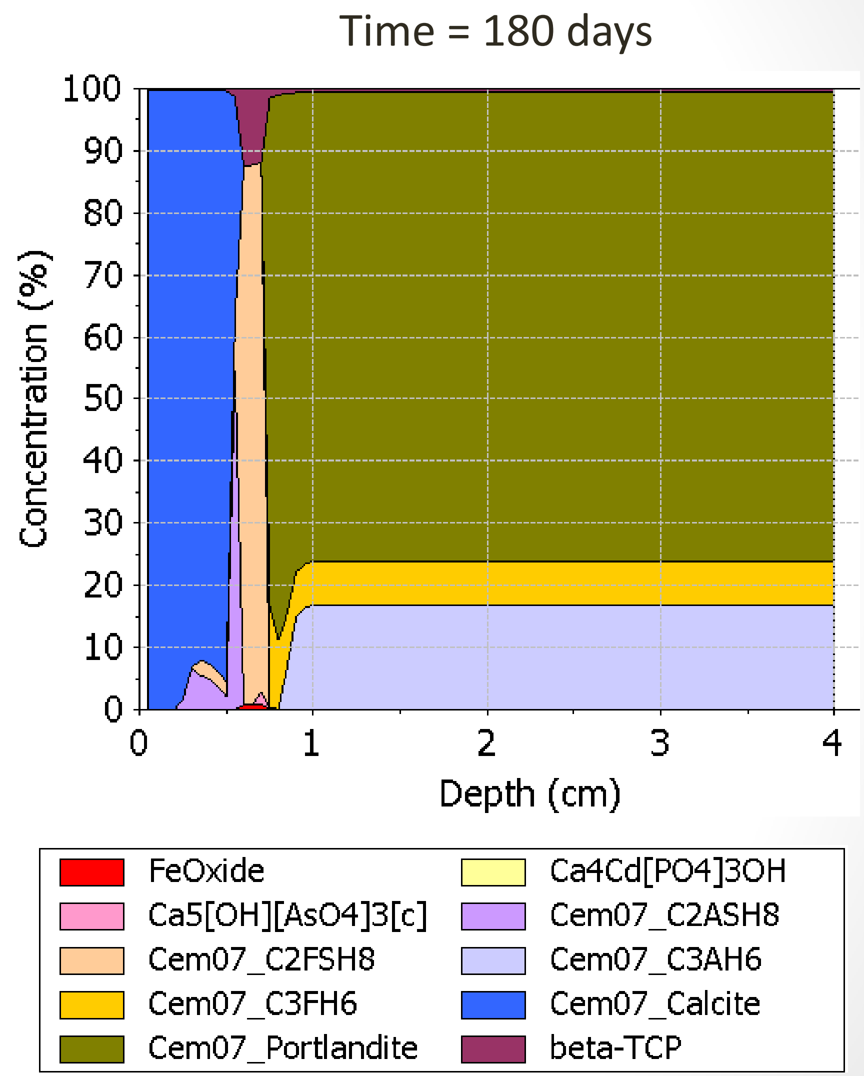
M45-00 (no FA)

M45-02 (low Ca FA)



Diffusion Modeling – Phases





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

Modeling Carbonation and Leaching through Cracked Concrete for HLW Tank Integrity and Closure

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J.C.L. Meeussen[2], H. van der Sloot[3], G. Flach[4]

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[2]NRG, Energy Research Centre of The Netherlands
[3]Hans van der Sloot Consultancy

[4]Savannah River National Laboratory

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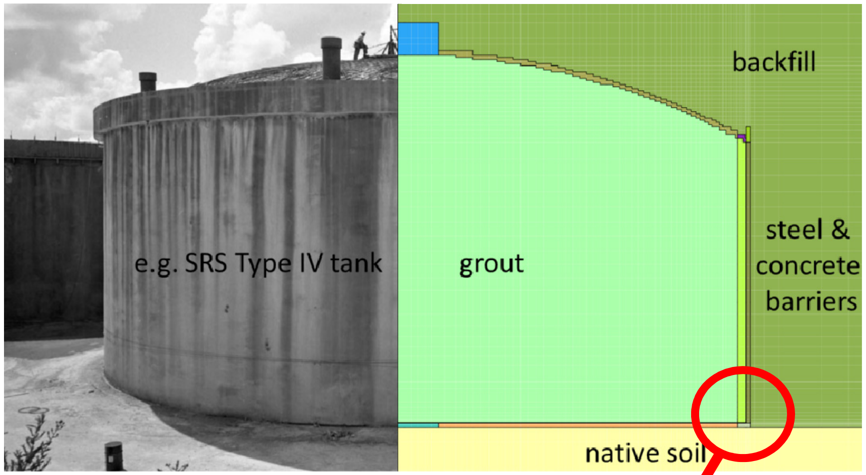
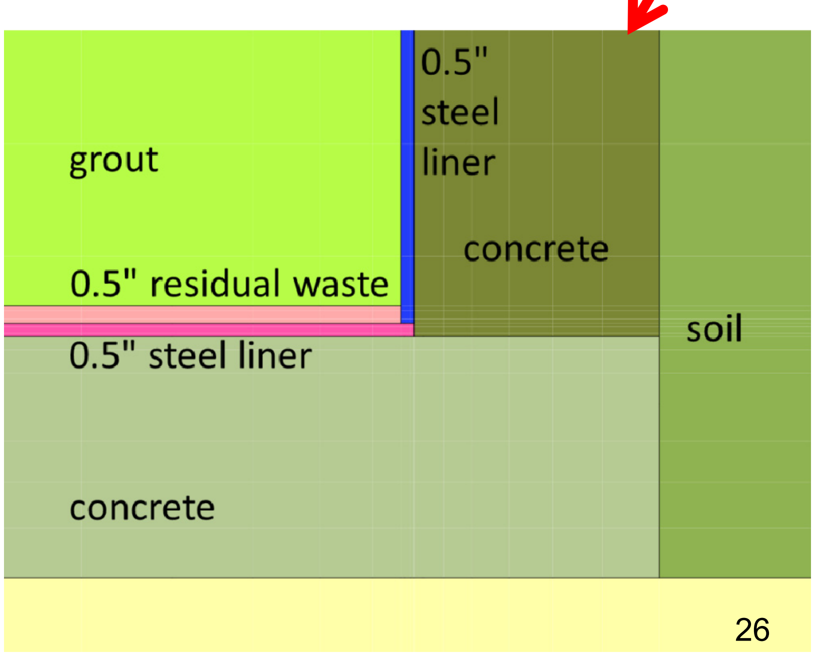
Motivation: Stabilize Residual High-Level Waste

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

- Tanks in service:
  - Capacity of 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

Primary Degradation Mechanisms

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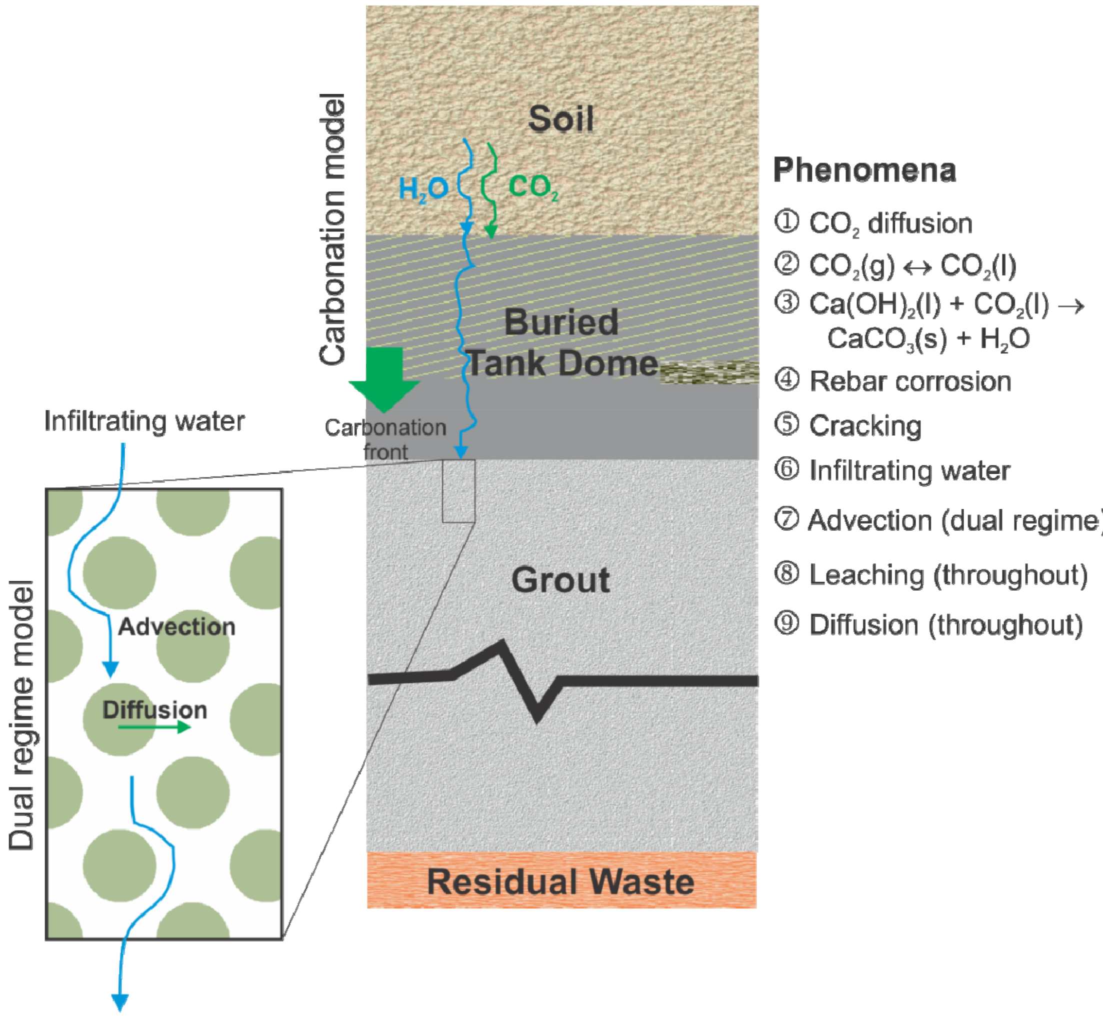
Important degradation phenomena that can lead to radionuclide release:

- Dome:
  - CO_2 ingress (carbonation) and major constituent leaching
  - Depassivation of embedded steel (pH<9) and cracking leading to water infiltration
- Grout:
  - Cracking allowing water percolation, constituent leaching, and release to environment
  - Grout: CO_2/O_2 ingress resulting in pH change and respeciation of grout and waste constituents (future)

- LeachXS/ORCHESTRA used to model phenomena



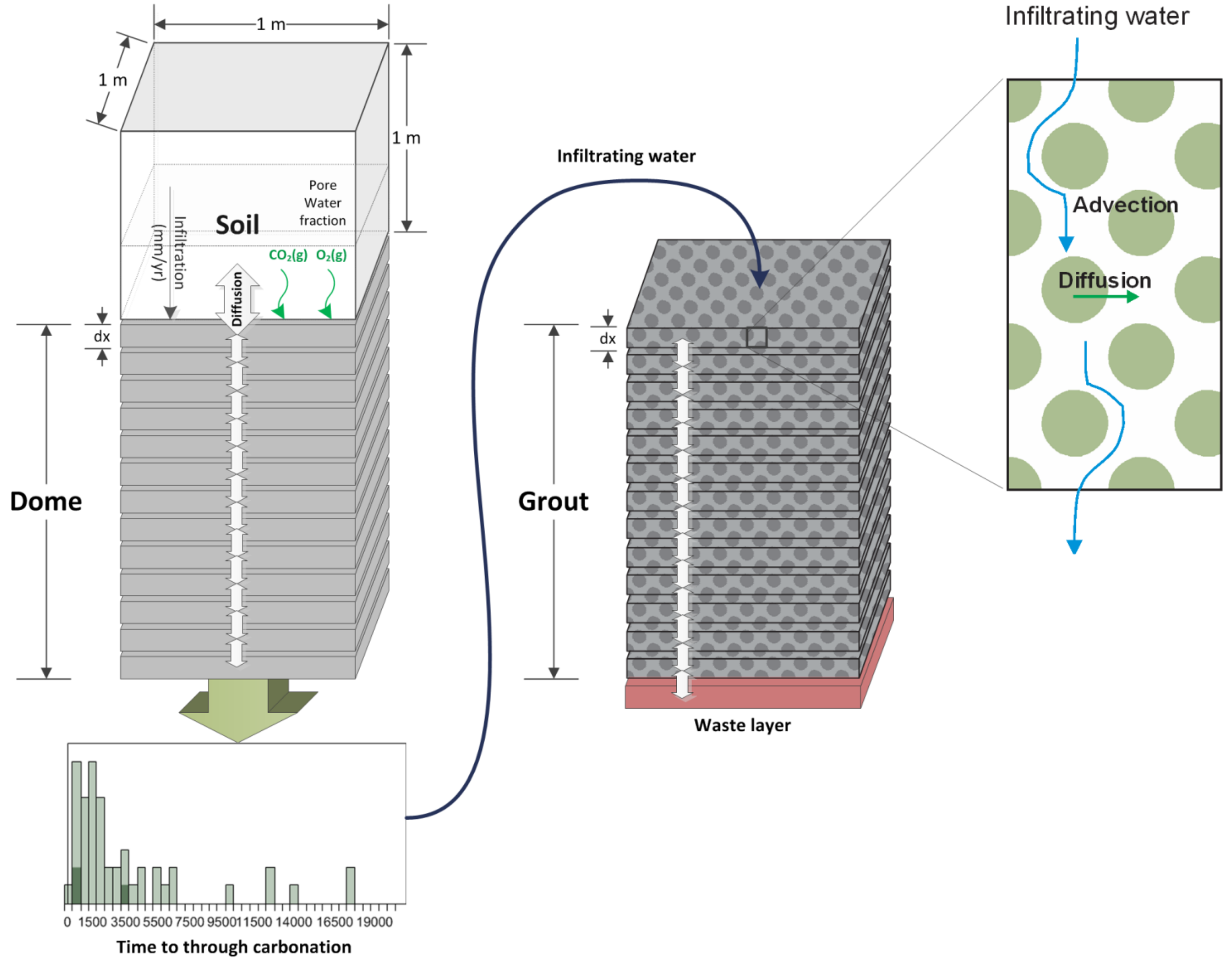
CBP Cementitious Barriers Partnership

Modeling Approach

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)
- Thus, 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

jra1



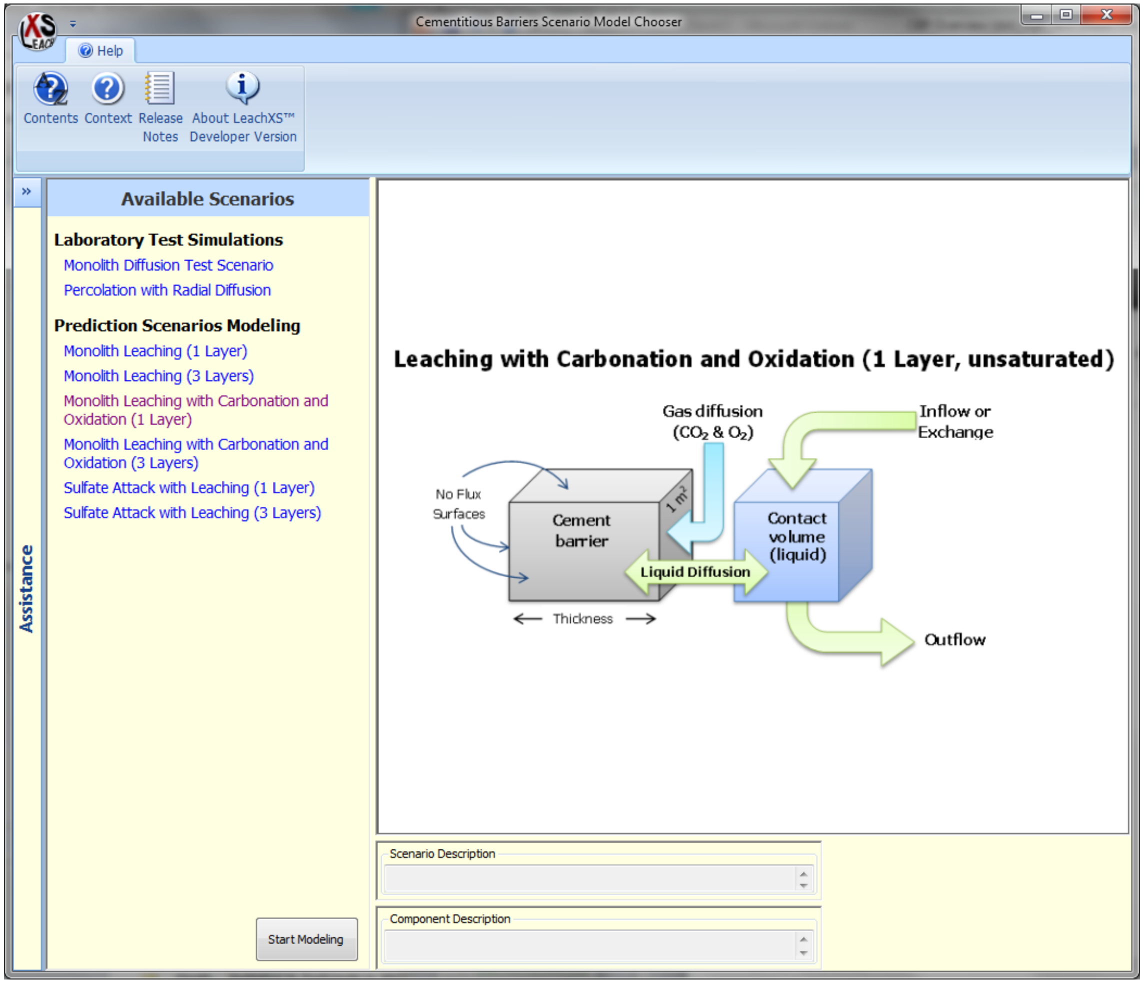
Slide 28

jra1 "Assume that transport through the grout is negligible until the dome is carbonated and cracked (allowing infiltration"
Arnold, Joshua Robert, 5/3/2013

Modeling Approach: LeachXS/ORCHESTRA

Multiple, flexible base models are available in LeachXS/ORCHESTRA

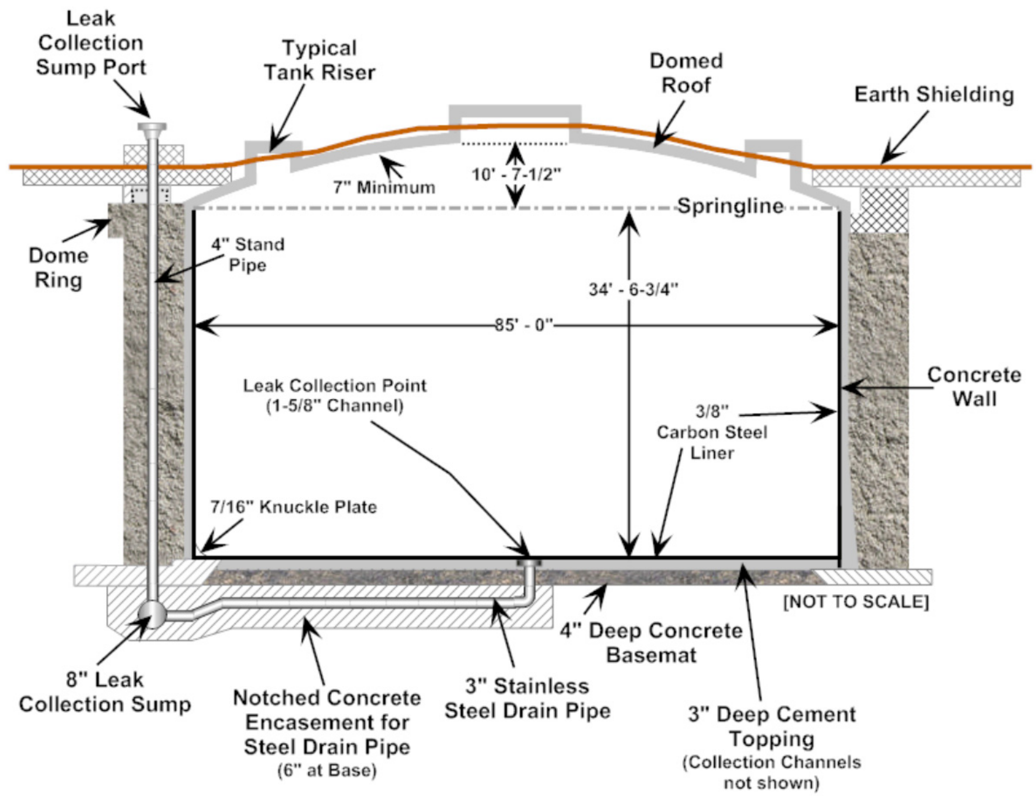
- Select general field or laboratory scenario to model
- Select from existing CBP reference materials or customize materials
- Select interface conditions (e.g., fixed volume, continuous flow or intermittent flow / exchange & solutions
- Resulting model transferable to GoldSim probabilistic framework (CBP Software ToolBox)



Representative High Level Waste Tank

Representative HLW Tank

- Roof constructed of reinforced concretjra2ssuming minimum 0.040 m concrete cover (to rebar) – no steel liner under roof
- Selected thinnest dome concrete (0.18 m) where SRS tank domes range up to 1.22 m
- Selected vertical (grouted) span of 9 m that is the shortest path for SRS HLW tanks
- Material of construction assumed to be Ordinary Portland Cement (where tanks built in late 1950s)
- Closed HLW tank will be buried in at least 3 m of backfill material (properties assumed similar to SRS clayey vadose zone soil)



Source: SRS-REG-2007-00002, Rev. 1

Slide 30

jra2 Conical as opposed to hemispherical?
Arnold, Joshua Robert, 5/3/2013

Dome Model Description

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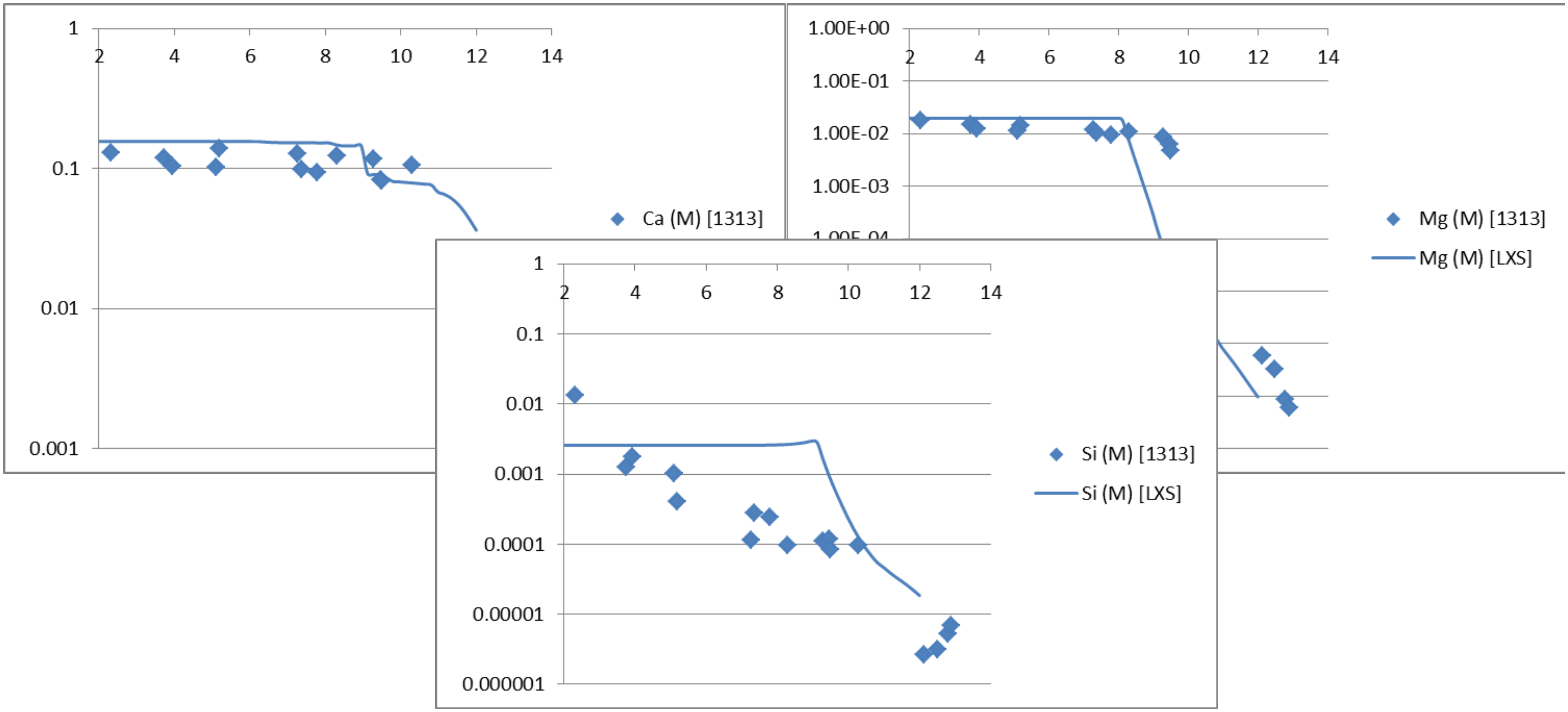
Thermodynamic model

- LeachXS/ORCHESTRA:
  - Solves system of equations:
    - Conservation of mass
    - Laws of mass action
  - Yields solid, aqueous, and gaseous speciation
- C-S-H:
  - Ideal solid solution with Tobermorite- and Jennite-like end-members (from Lothenbach et al., 2008)
- No adsorption and (some) additional minerals in the model
- Dome construction material assumed to be Ordinary Portland Cement

Mineral phases

$Mg(OH)_2$ *Brucite*	$Ca(OH)_2$ *Portlandite*	C_3AH_6 *Hydrogarnet*	$C_4Ac_{0.5}H_{12}$ *Hemi-carbonate*	$C_6As_3H_{32}$ *Ettringite*
$CaSO_4 \cdot 2H_2O$ *Gypsum*	$CaCO_3$ *Calcite*	C_3FH_6 *Fe-hydrogarnet*	$C_4Fc_{0.5}H_{12}$ *Fe-hemi-carbonate*	$C_6Fs_3H_{32}$ *Fe-ettringite*
SiO_2 (am) *Amorphous Silica*	C_2ASH_8 *Strätlingite*	$C_3AS_{0.8}H_{4.4}$ *Siliceous Hydrogarnet*	C_4AcH_{11} *Mono-carbonate*	$C_6Ac_3H_{32}$ *Tricarbo-aluminate*
$Al(OH)_3$ (am) *Amorphous Aluminum hydroxide*	C_2FSH_8 *Fe-Strätlingite*	C_4AH_{13} *Hydroxy AFm*	C_4FcH_{12} *Fe-mono-carbonate*	M_4AH_{10} *Hydrotalcite*
Al_2O_3 *Alumina*	C_2AH_8 *Unnamed meta-stable phase*	C_4FH_{13} *Fe-hydroxy AFm*	C_4AsH_{12} *Monosulfate*	M_4FH_{10} *Fe-hydrotalcite*
$Fe(OH)_3$ (mic) *Microcrystalline Iron hydroxide*	C_2FH_8 *Unnamed meta-stable phase*	***Solid Solution:*** $C_{1.67}SH_{2.1}$ *Jennite*	C_4FsH_{12} *Fe-monosulfate*	M_4AcH_9 *CO_3-Hydrotalcite*
Fe_2O_3 *Ferric oxide*	$CaSO_4$ *Anhydrite*	$C_{0.83}SH_{1.3}$ *Tobermorite*		

Comparison of Data [USEPA 1313] and Thermodynamic Model Predictions [LXS]



Experimental data from
USEPA Method 1313 (SW-846)

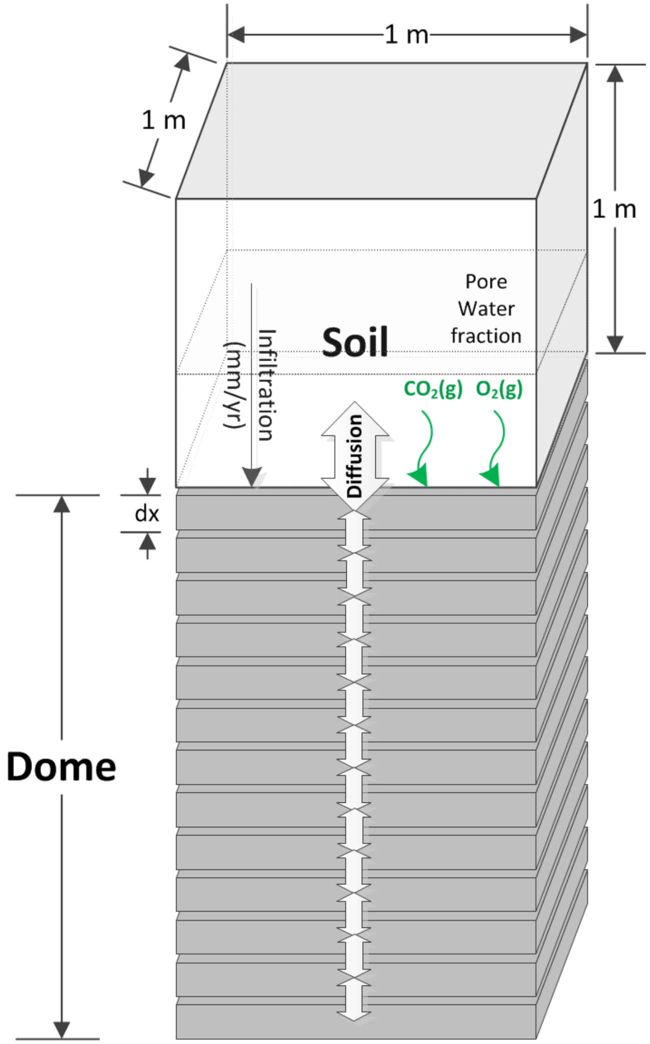
Probabilistic Dome Analysis

Non-Stochastic Parameters

- Dome thickness 0.18 m (7 in)
  - Varies between 0.18 and 1.22 m (SRS-REG-2007-00002)
- Burial depth 3 m (10 ft) (SRR-CWDA-2010-00128)
- Temperature 20°C at 3 m (WSRC-STI-2007-00184, Rev. 2)

Stochastic Parameters

- CO_2 and O_2 Diffusivities – U(D_m at 20°C, ±5%) m^2/s
  - Based on data from Marrero and Mason (1972)
- Infiltration Rate – N(0.18, 0.051) m/yr
  - Distribution of 1,000-yr rates (WSRC-STI-2007-00184)
- Soil: ϕ – N(0.37, 0.011), τ – Δ(0.202, 0.331, 0.557), and S – Δ(0.843, 0.858, 0.873)
  Concrete: ϕ – N(0.221, 0.013), τ – Δ(0.011, 0.05, 0.217)
  - Information from WSRC-STI-2006-00198
- Concrete Saturation S – U(0.74, 0.90)
  - Rubble min (WSRC-TR-2005-00054); max to allow CO_2 ingress
- Soil-Gas CO_2 – Δ(0.01, 0.015, 0.032)
  - Distribution of well data (SRNL-L3200-2012-00017)



Dome Analysis Results

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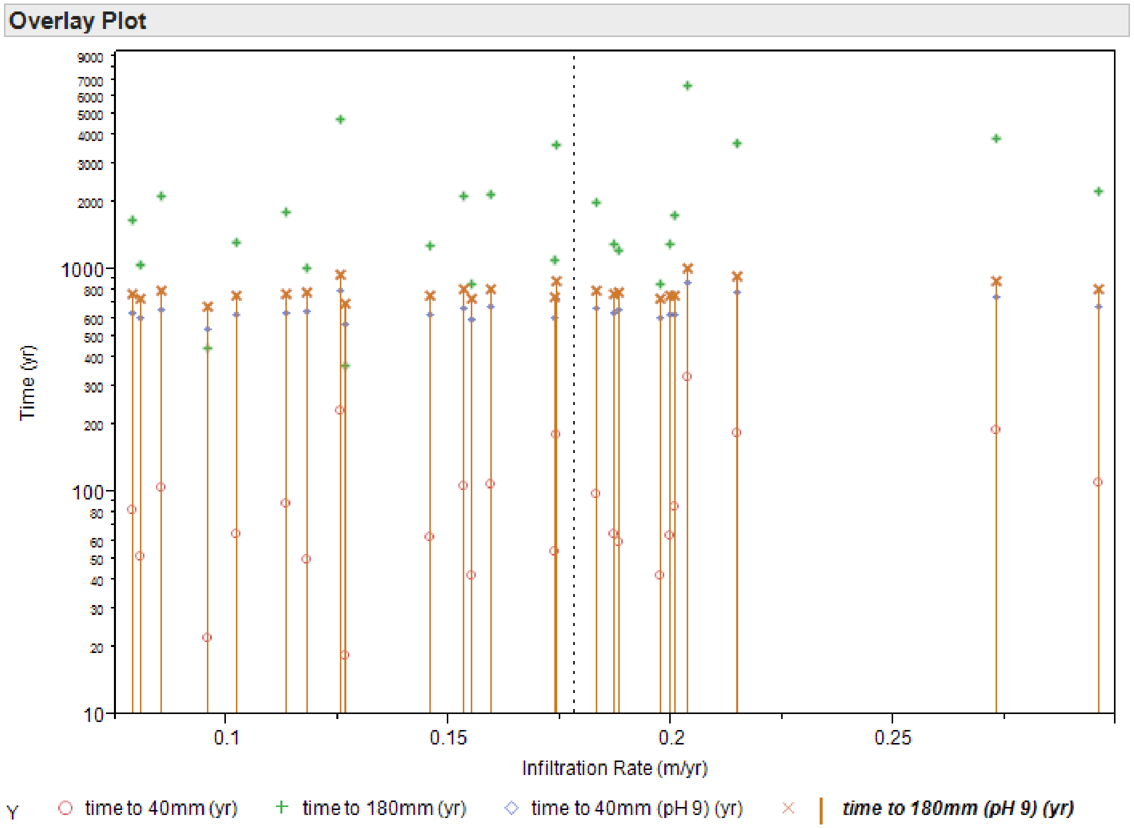
- Simulation times to estimate when pH<9 were prohibitive
- Simulated when carbonation front reached 0.04 m (cover to rebar) and 0.18 m (dome)
- Used previous results to estimate time after front reaches 0.04 m that pH < 9
  - Time to pH < 9 -- N(570, 20) years
- Assumed that concrete (0.14 m with rebar) cracking would proceed at 0.001 m/yr
  - Maximum carbonation rate (ASM Handbook Volume 13B, Nov. 2005)
- Assumptions result in much shorter estimates than times to carbonate through dome



Note log scale ordinate

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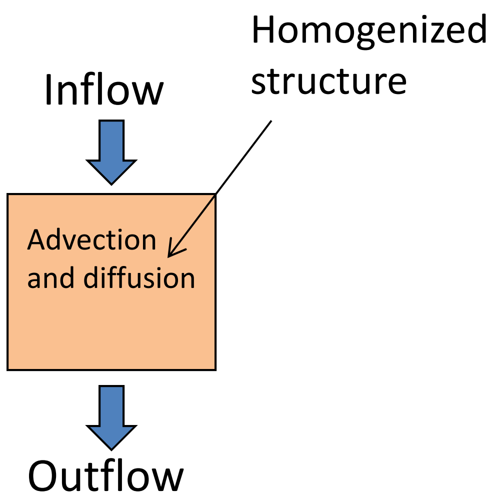
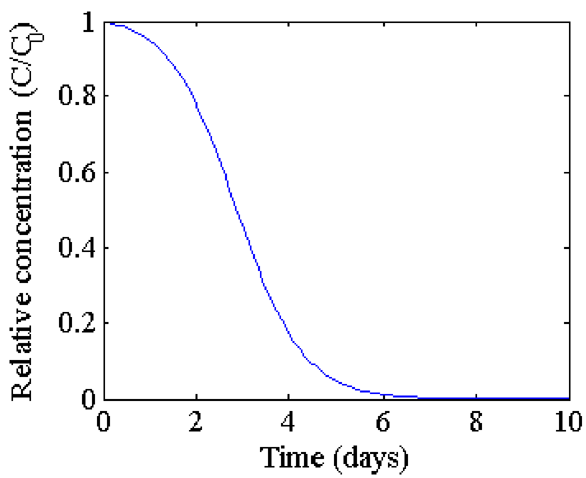
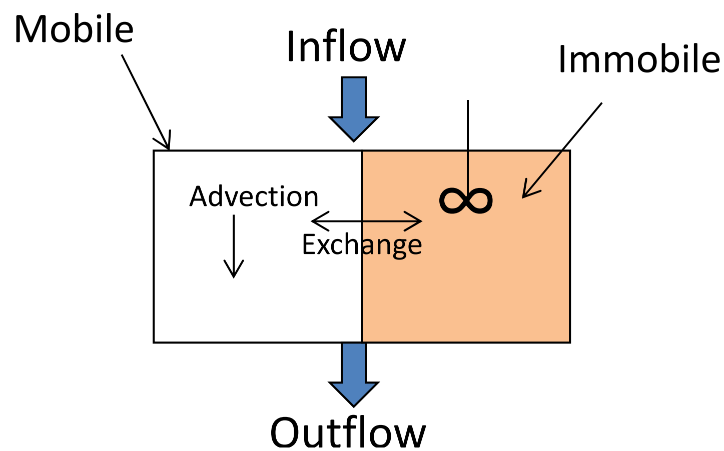
Transport in Heterogeneous Media

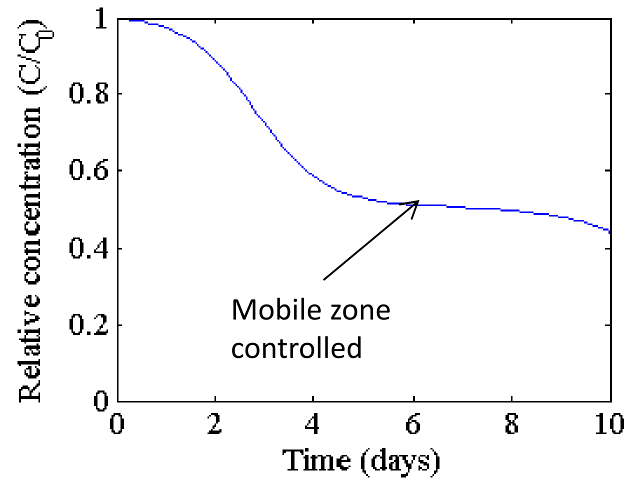
Equilibrium approach





Mobile-immobile zone





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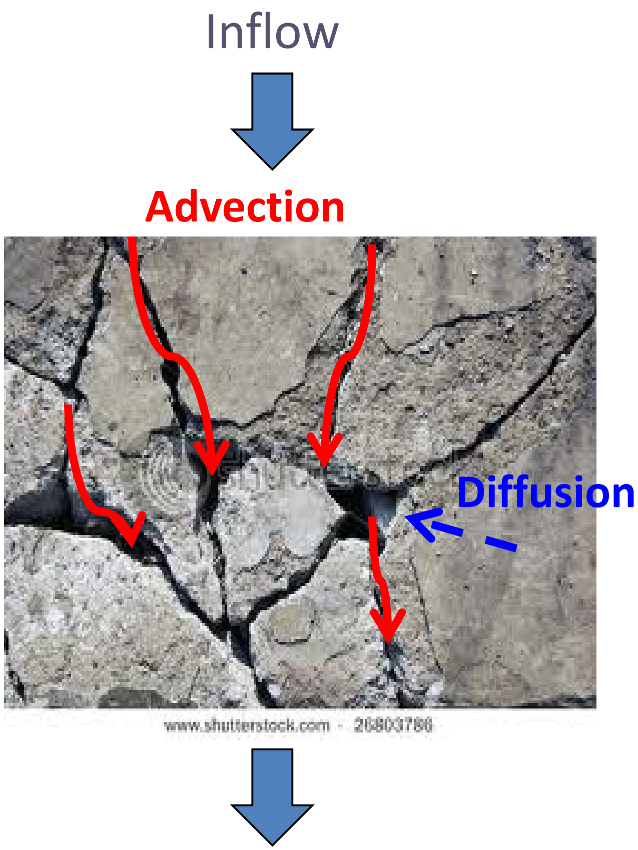
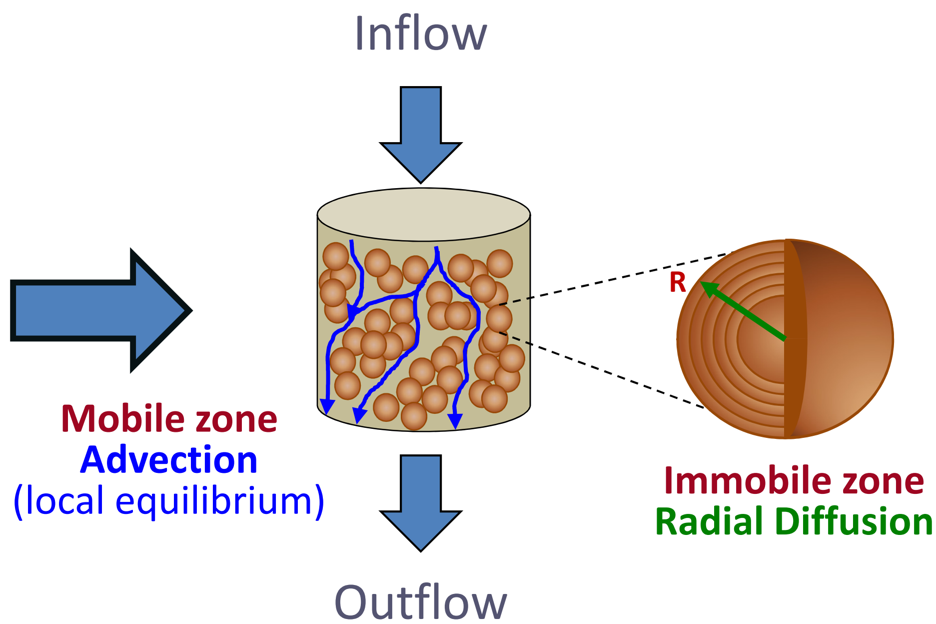
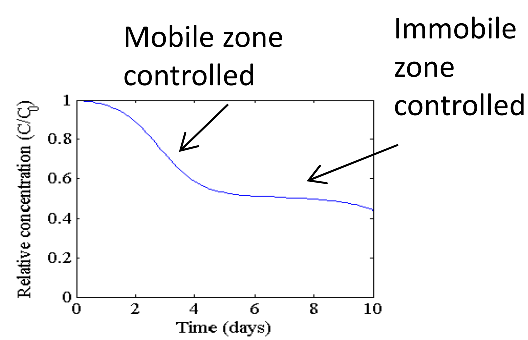
Flow through Heterogeneous Media



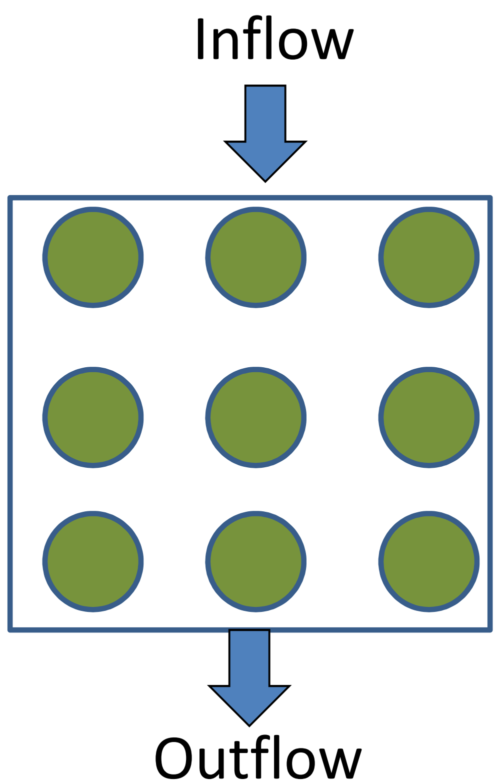
Advection – radial diffusion approach

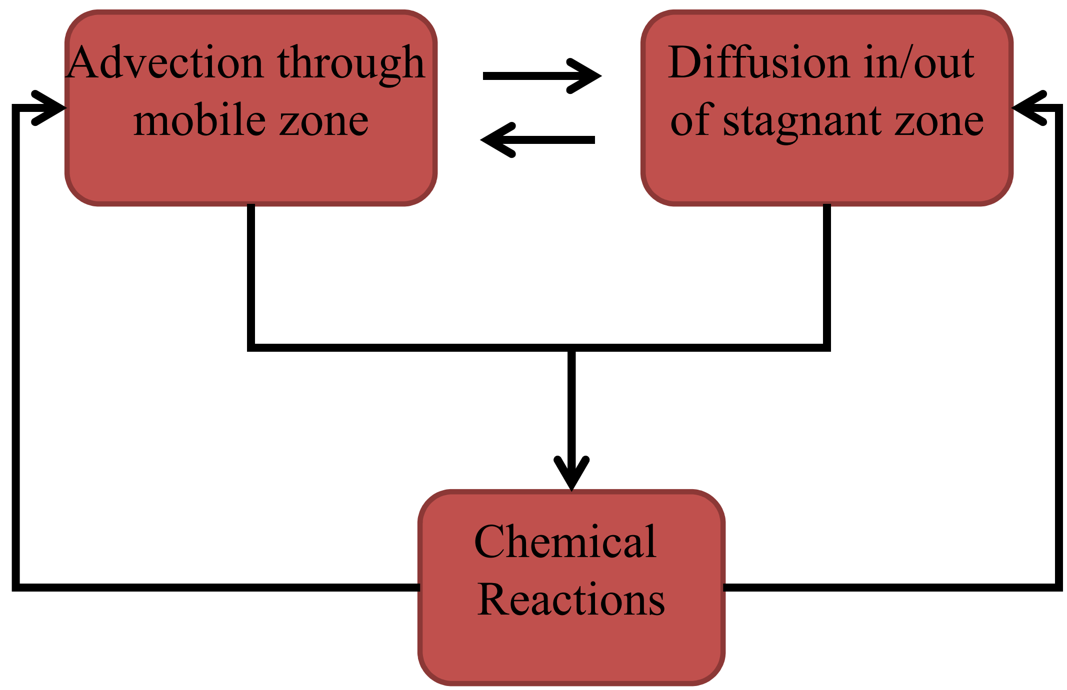




- Refined mobile-immobile approach
- Can capture micro-macro pore and particle size distributions

Conceptual Simulation Scenario





Source: van Beinum *et al*., 2000

- Solids with cracks and macropores: Mobile zone
- Solid matrix with micropores: Immobile zone

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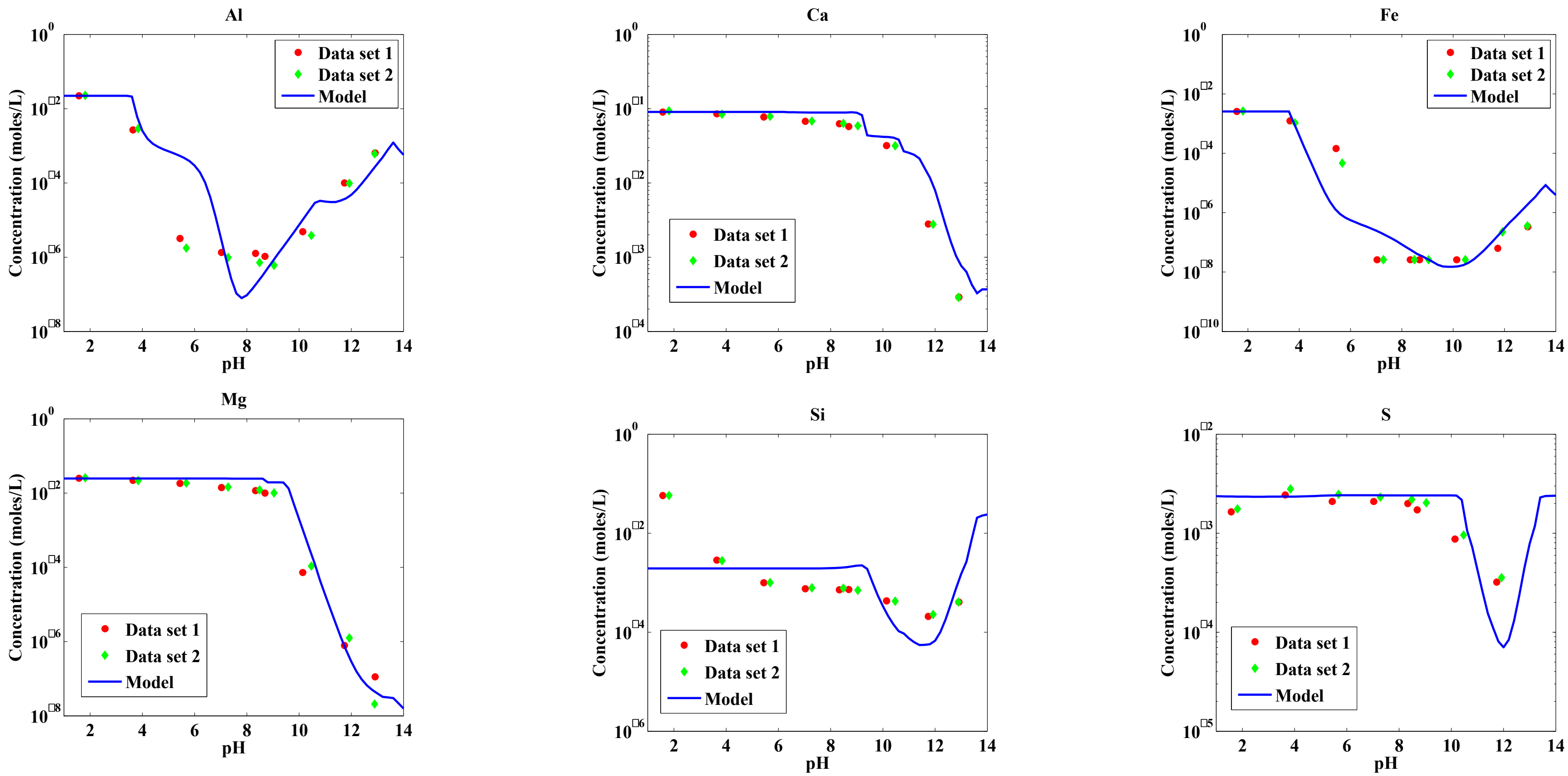
Geochemical Speciation Analysis



- Mineral set selected to achieve best agreement with pH dependence test data (USEPA method 1313) for major species
- Databases used: MINTEQA2 (Allison et al., 1992) and CEMDATA07 (Lothenbach et al., 2006 and 2008)

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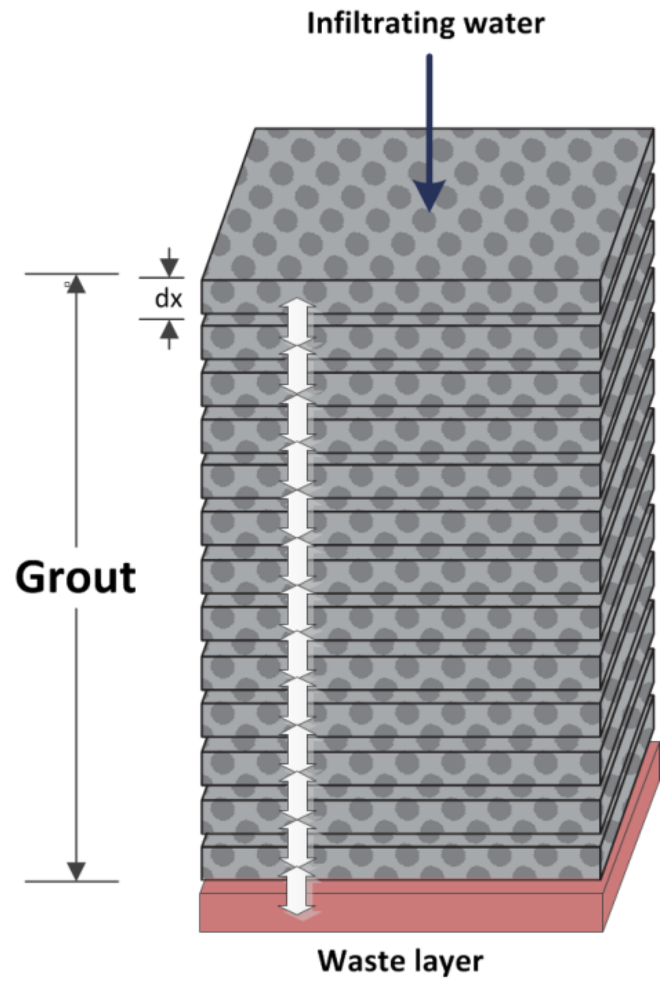
Probabilistic Grout Analysis

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

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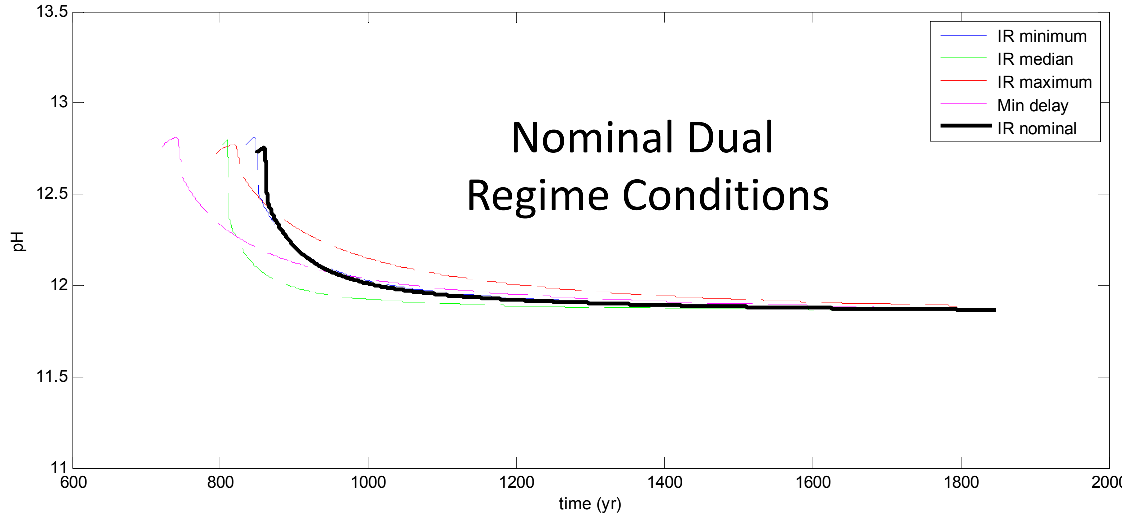
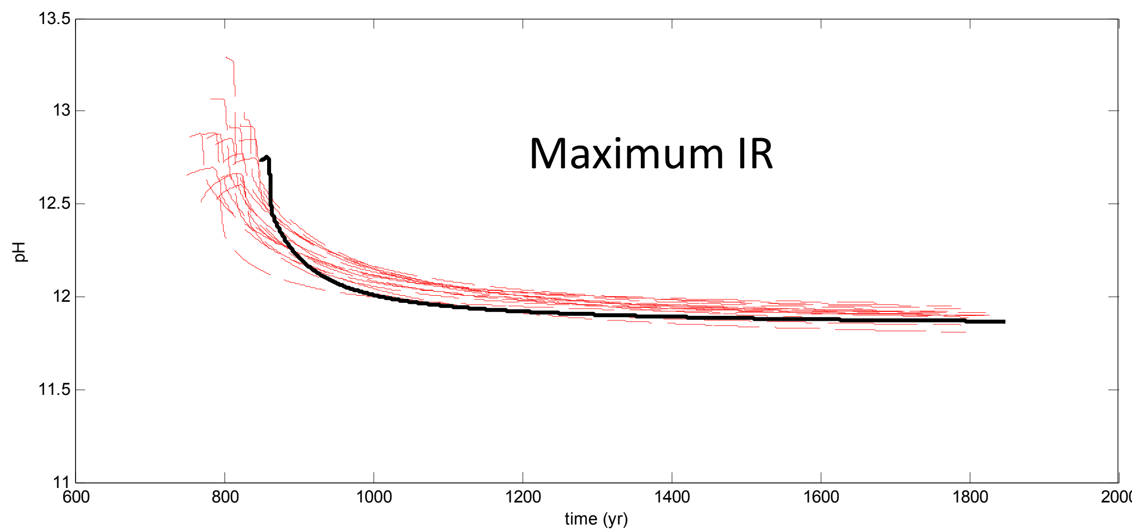
- Simulated pH response at grout – waste layer interface
- Upper graph indicates fairly insensitive pH response to infiltration rate *for nominal grout parameters*
  - Especially at longer times where responses converge
- Lower graph (red) indicates some initial variability in pH response *at maximum infiltration rate* but pH responses tend to approach nominal values at long times





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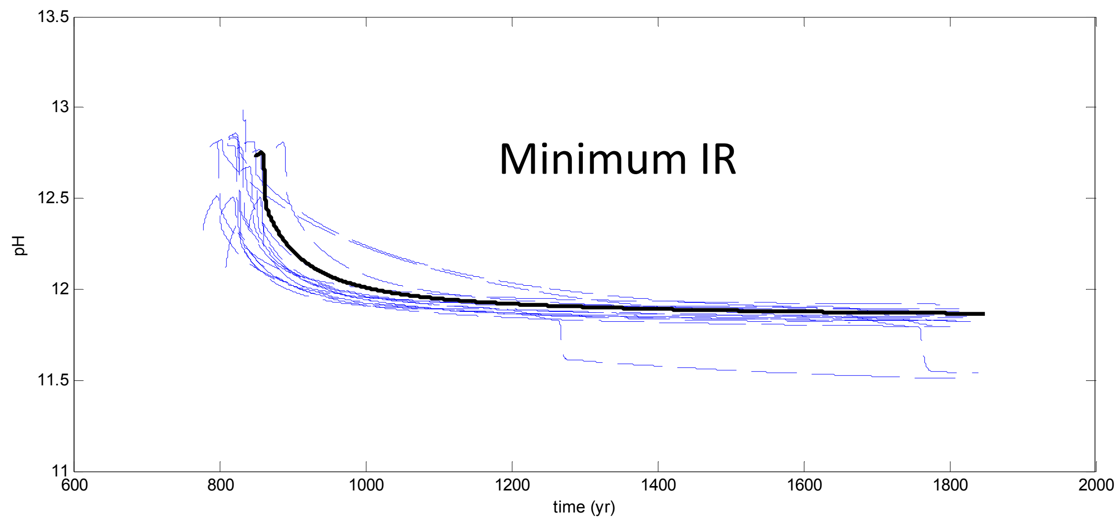
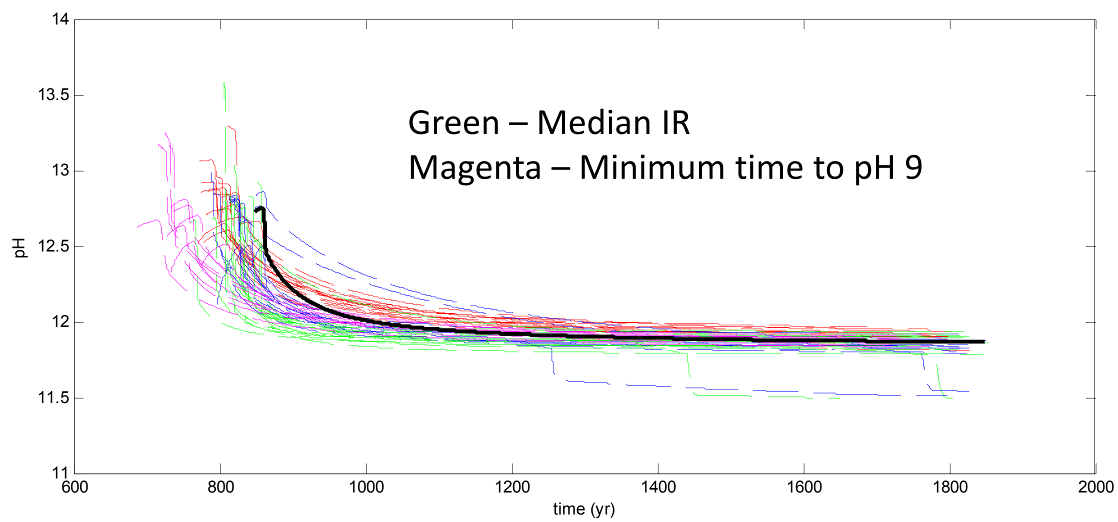
Coupled Analysis Results (2)

- 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 required to better evaluate





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Summary

- Implemented both a 1) concrete carbonation model and 2) dual regime reactive transport model for simulating percolation through cracked grout
  - Carbonation model results previously compared to Hanford HLW tank dome core measurement
  - Dual regime model calibrated and validated using up-flow column percolation test data
- Probabilistic analyses were carried out for both models
  - Carbonation to pH 9 (depassivation of embedded steel) requires at least on the order of 700 years (and likely 10X this estimate)
  - Significant pH effects at the grout – waste layer interface over the first two millenia tend to be observed as the infiltration rate is lower
- An efficient method for assessing effectiveness of current closure grouts and designing of future grouts
  - Longer simulation times and coupling of nominal cases would provide useful additional information
  - Consider gas phase exchange reactions (e.g., CO_2 and O_2) for future models

Significance of CBP Modeling Scenarios

- Applicability:
  - Evaluation of waste forms and treatment process effectiveness
  - Concrete vault durability and radionuclide release
  - Source term for contaminated soils/vadose zone and waste disposal scenarios
  - HLW tank integrity analysis and closure
- Flexible framework that can be easily modified to reflect various testing and field conditions
- Can be compared with available test results from the database of a large selection of materials
- Useful framework for designing future structures and maintenance scheduling for existing structures