EVALUATING WASTEFORM LEACHING AND PERFORMANCE

DOE COMMUNITY OF PRACTICE (P&RA COP) ANNUAL TECHNICAL EXCHANGE MEETING

GERMANTOWN, MARYLAND
OCTOBER 19 AND 20, 2016

VANDERBILT UNIVERSITY

U.S. DEPARTMENT OF ENERGY

Hans van der Sloot Consultancy

ECN

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SUMMARY OF MAJOR ACTIVITIES

- Experimental – Evaluating impacts of oxidation and carbonation on cementitious waste form performance
- Experimental – Evaluating leaching chemistry, density, humidity-saturation relationships for Cast Stone screening materials
- Modeling – Software Quality Assurance – Calibration, Verification and Validation (V&V) of Important LeachXS/ORCHESTRA Models
  - 1-D and 3-D Saturated monolith leaching / diffusion (laboratory) models – (3-D parallelepiped and cylinder)
  - 1-D Unsaturated monolith leaching / diffusion (prediction) model under carbonation (and oxidation)
- Evaluation of Sulfate Attack model based on NRC Review
  - Support for parameterization and homogenization schemes used
  - We are evaluating as part of the V&V effort

OXIDATION/CARBONATION IMPACTS MOTIVATION/OBJECTIVES

- Cast stone investigated as low-activity (LAW) and secondary waste form for Hanford; analogous to saltstone at Savannah River
- Technetium-99 (Tc-99) is soluble when oxidized (as $Tc(VII)O_4^-$), which is a concern for potential groundwater contamination
- Material complexity coupled with component interactions and ingressing O_2/CO_2 can create significant characterization difficulties

Goal: Understand impact of oxidation/carbonation on performance

- Characterize rate of ingress and reaction of O_2/CO_2
- Determine impact of oxidation/carbonation on (i) solubility and leaching of Tc-99 and other constituents, and (ii) microstructure
- Understand impact of different fly ash types on redox behavior and progression of carbonation
- Improve <u>prediction</u> of redox behavior and carbonation under scenarios in support of long-term performance assessment

OXIDATION/CARBONATION IMPACTS EXPERIMENTAL OVERVIEW

1. Salt simulant prepared with Cr doping to serve as Tc-99 surrogate (i.e., redox sensitive contaminant)
   - Cr doping varied to achieve 0.1 or 1.0 wt. % in final cast stone
2. Cast stone materials prepared with screening LAW salt simulant
   - RCRA metals and radionuclides excluded
3. **Hydration**: 100% Relative Humidity and 100% N_2 for 100 days
4. **Aging**: 60 days in 100% N_2 (control); 100% air (oxidization) with CO_2 sink; 95% N_2 and 5% CO_2 (carbonation); or 95% air and 5% CO_2 (coupled)
5. Prepared samples to meet different physical requirements for different experimental techniques
   - EPA Methods 1313/1315, SEM-EDS, XRD, TGA, XRF, etc.

OXIDATION/CARBONATION IMPACTS VISUAL INSPECTION OF DEGRADATION

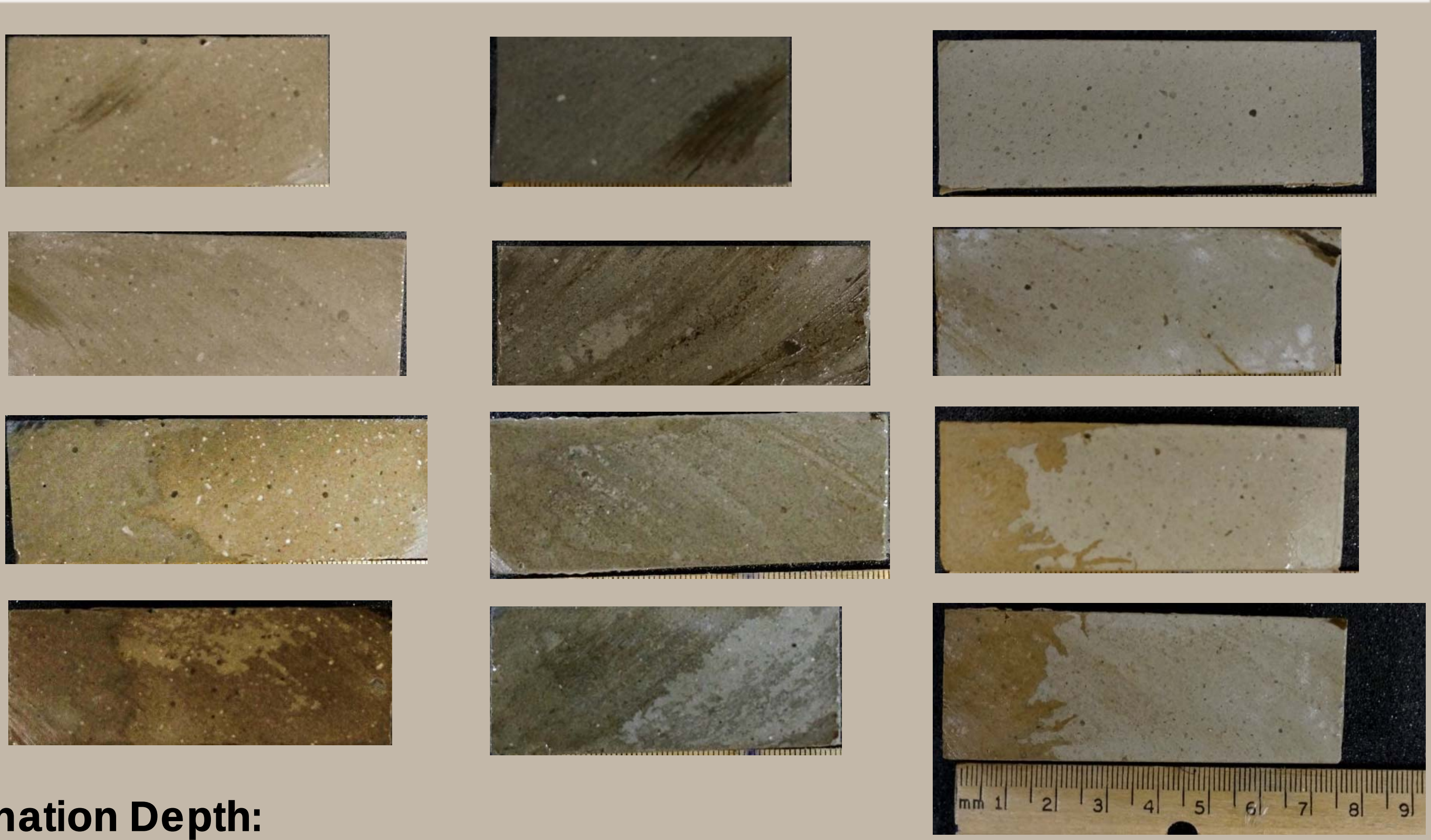
% 0.1 wt % Cr samples

N_2

O_2

CO_2

O_2 & CO_2



Carbonation Depth:

CS-FAF (24 mm) **CS-FA02 (10 mm)** **CS-FA18 (17 mm)**

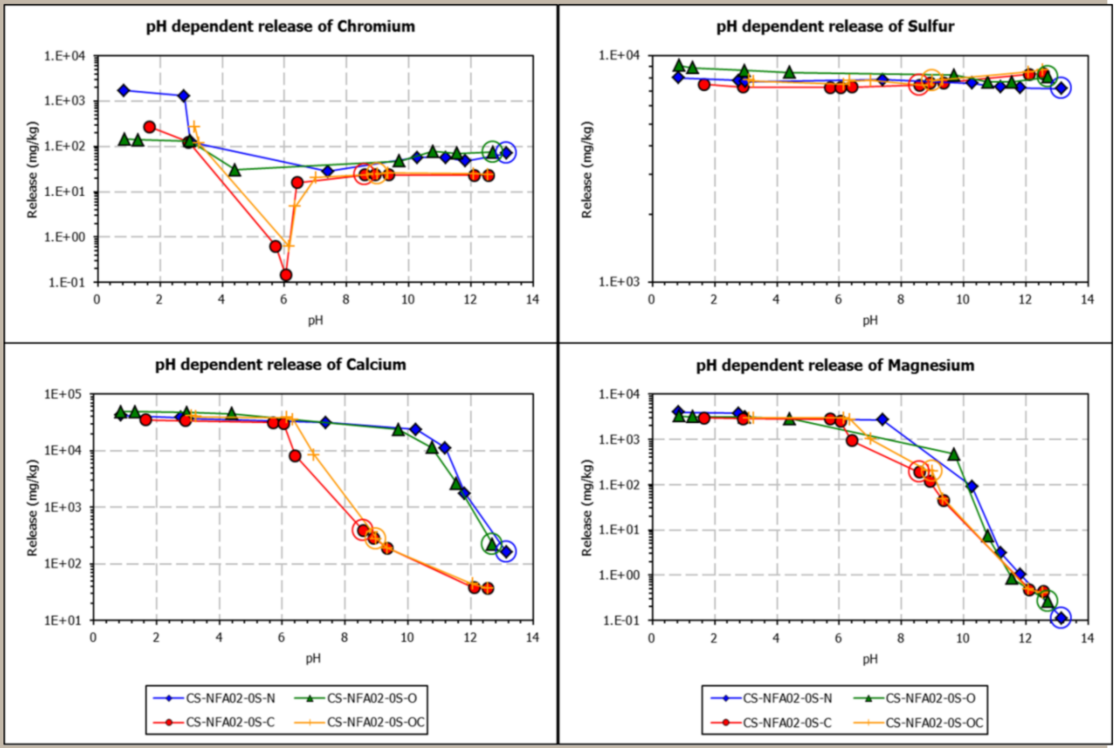
OXIDATION/CARBONATION IMPACTS
EPA METHOD 1313: SOLUBILITY

Key Takeaways at Natural pH:

1. Increased solubility of Cr, S, Ca, and Mg in oxidized material
2. Decreased solubility of Cr in carbonated materials
3. Increased solubility of S, Ca, and Mg in carbonated materials

Key Takeaways Over pH Range:

1. Greater changes in Ca and Mg solubility observed in carbonated materials
2. Relatively no changes in S solubility



*mg/kg

	Natural pH	Cr	S	Ca	Mg
CS-NFA02-0S-N	13.14	70.7	7170	162	0.111
CS-NFA02-0S-O	12.7	74.9	8060	221	0.267
CS-NFA02-0S-C	8.57	23.3	7430	392	187
CS-NFA02-0S-OC	8.99	24.6	7750	275	199

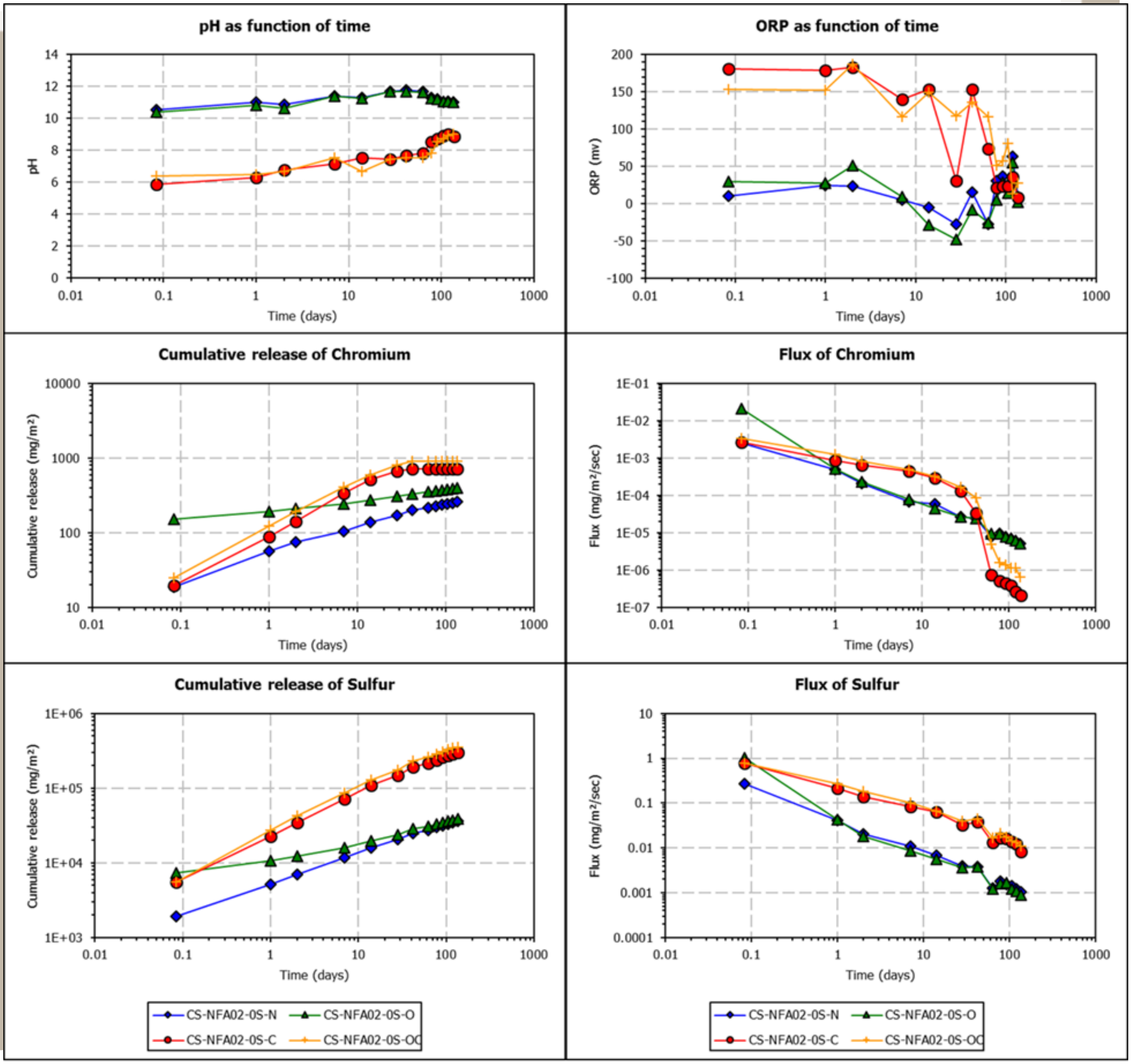
OXIDATION/CARBONATION IMPACTS METHOD 1315: MASS TRANSFER RATES

Key Takeaways:

1. Initial increase in Cr and S release in oxidized condition
2. Sustained increase in Cr and S release until day 63 (Cr) in carbonated materials

→ Slower moving leaching front through carbonated materials (pore structure) compared to oxidized materials

→ Larger carbonation depth compared to oxidation depth



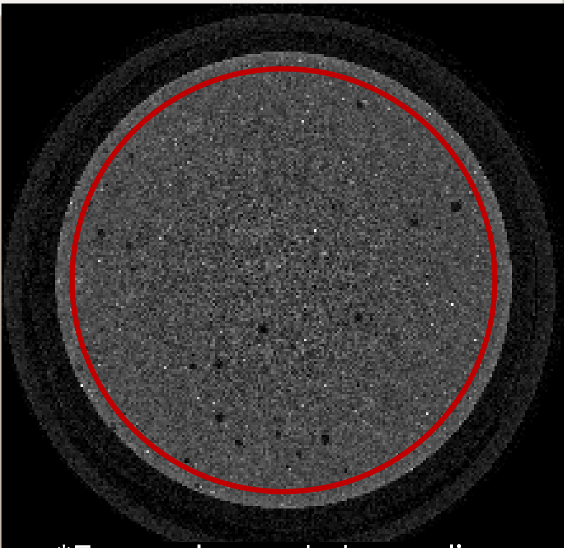
MICRO-CT: 3-D POROSITY

- Characterized top 1 cm of exposed surface
- Stacked slices for 3-D re-construction of material
- Determine porosity as a function of distance from exposed surface based on gray scale values

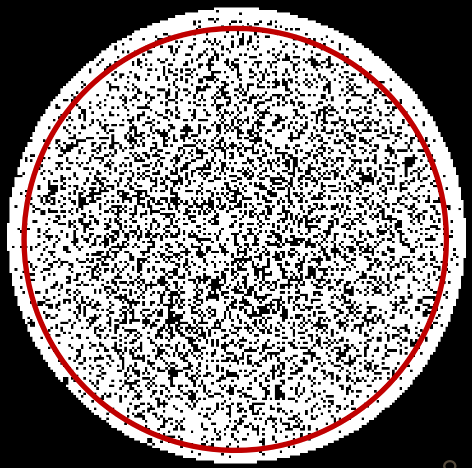
Key Takeaways:

1. Carbonation lowers porosity at exposed surface
2. Leaching increases porosity at exposed surface
3. Porosity ranges: 0.05 to 0.08 (SEM* measured porosity 0.30 to 0.50)

*Pore sizes > 4.3 μm



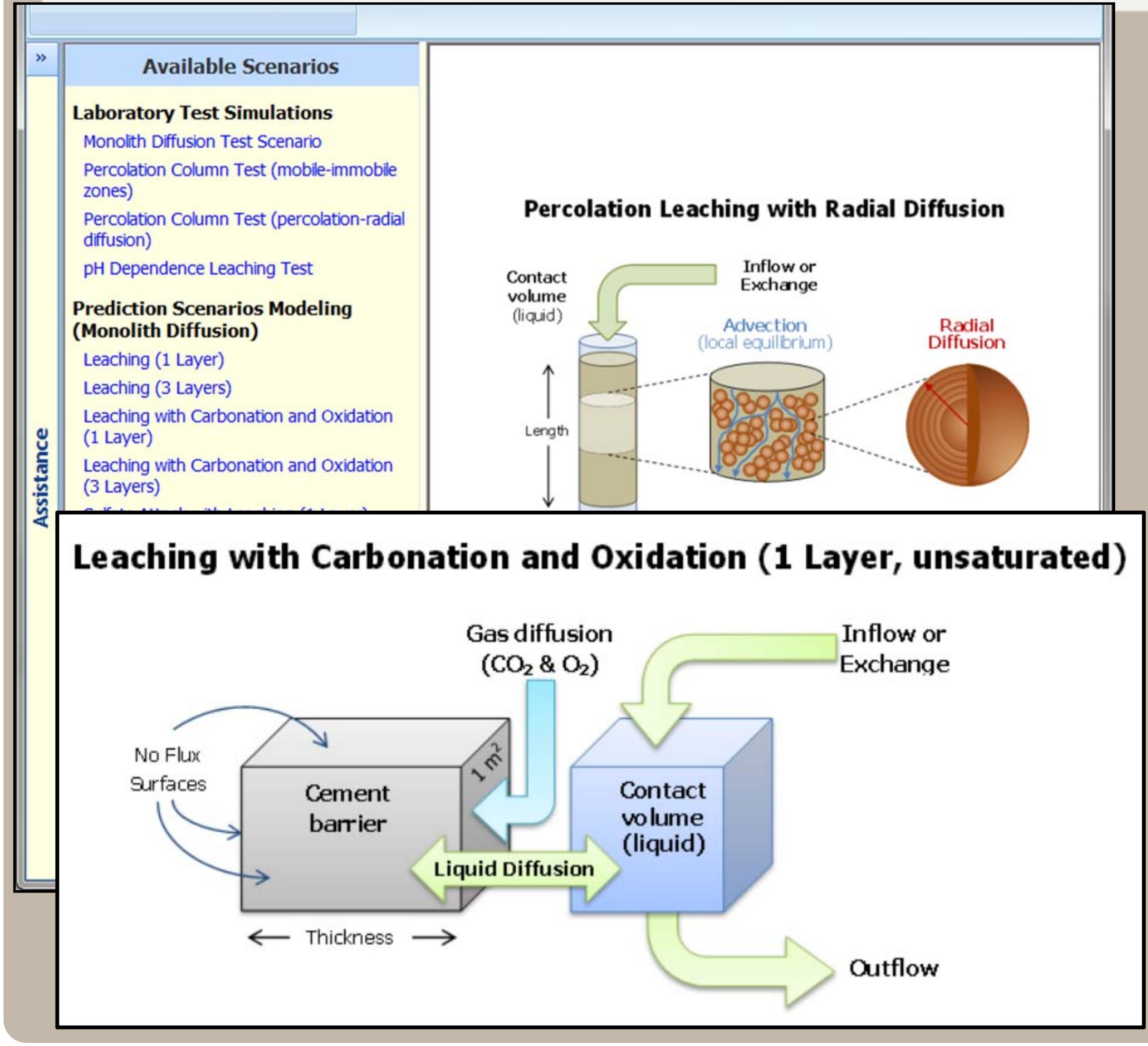
*Example cast stone slice



MODELING: CAST STONE PERFORMANCE SIMULATIONS

- EPA Methods 1313 and 1315 and preliminary modeling scenario-based results using LeachXS/ORCHESTRA (LXO)
- Preliminary sensitivity analysis to evaluate impacts of performance assessment assumptions
- Update sensitivity analysis based on improved calibrations using results from O_2 and CO_2 ingress experiments

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)

Percolation Leaching with Radial Diffusion

Leaching with Carbonation and Oxidation (1 Layer, unsaturated)

- Select general field or laboratory scenario
- Select from existing virtual materials or customize materials
- Select interface conditions (e.g., intermittent flow, $\mathbf{P_{CO_2}}$) & solutions
- Resulting model transferable to GoldSim for Monte Carlo simulations
- V&V described below

LEACHXS/ORCHESTRA (LXO) SIMULATION

1. Develop "chemical speciation" fingerprint (CSF) using EPA Method 1313 results (primary & trace constituents) for baseline material (*calibration*)
   - MINTEQ-V4 thermodynamic database, "cemdata07" (Lothenbach, et al. 2008), NEA Thermochemical Database (TDB) for radionuclides
2. Compare CSF with Method 1313 results using range of related materials (multiple formulations; *uncertainty assessment and validation*)
3. Include CSF in monolith model; compare with EPA Method 1315 results
   - Calibrate liquid phase tortuosity factor (unless independently measured)
   - Compare simulation results across primary constituents and multiple trace constituents for multiple formulations (*uncertainty assessment and validation*)
4. Use (calibrated) monolith model for scenario simulations
   - Use standard diffusion models; compare with data sets (e.g., field data)
   - Sensitivity evaluation of key scenarios and parameters

MINERAL PHASES: CAST STONE

- Base mineral set (“cemdata2007”) from Lothenbach, et al.* defined for Portland cements
  - Solid solutions included
  - Alternative ettringite solid solution model developed by ECN
- Additional mineral phases may be identified by XRD
  - E.g., akermanite, vaterite, rustamite
- Trace species identified through experimental data and expert knowledge
- Incorporate calibration from van der Sloot, et al.

Akermanite C_2MS_2	(Al-) Ettringite $C_6A\bar{S}_3H_{32}$	Alumina Al_2O_3	Amorphous Gibbsite $Al(OH)_3$ (am)
Amorphous Silica SiO_2 (am)	Anhydrite $CaSO_4$	Brucite $Mg(OH)_2$	Calcite $CaCO_3$
CO_3^{2-} hydrotalcite $M_4A\bar{C}H_9$	Dicalcium Silicate C_2S	Fe-ettringite $C_6Fs_3H_{32}$	Fe-hemicarbonate $C_4F\bar{C}_{0.5}H_{12}$
Fe-hydrogarnet C_3FH_6	Fe-hydrotalcite M_4FH_{10}	Fe-hydroxy Afm C_4FH_{13}	Fe-monocarbonate $C_4F\bar{C}H_{12}$
Fe-monosulfate $C_4F\bar{S}H_{12}$	Ferric Oxide Fe_2O_3	Fe-strätlingite C_2ASH_8	Gypsum $CaSO_4*2H_2O$
Hemicarbonate $C_4A\bar{C}_{0.5}H_{12}$	Hydrocalumite $C_4AH_5(\bar{C}H)_2 \cdot 4H$	Hydrogarnet C_3AH_6	Hydrotalcite M_4AH_{10}
Hydroxy Afm C_4AH_{13}	Jennite $C_{1.67}SH_{2.1}$	Microcrystalline Iron Hydroxide $Fe(OH)_3$ (mcr)	Monocarbonate $C_4A\bar{C}H_{11}$
Monosulfate $C_4A\bar{S}H_{12}$	Mullite $3A_2S$	Nitrate $(AFm)_N$ $C_3A \cdot (Ca(NO_3)_2) \cdot H_{10}$	Nitratine $NaNO_3$
Portlandite CH	Quartz SiO_2	Rustumite $C_9S_5H \cdot CaCl_2$	Siliceous Hydrogarnet $C_3AS_{0.8}H_{4.4}$
Strätlingite C_2ASH_8	Tetracalcium Aluminoferrite C_4AF	Tricalcium Aluminate C_3A	Tricalcium Silicate C_3S
Tobermorite $C_{0.83}SH_{1.3}$	Tricarboaluminate $C_6A\bar{C}_3H_{32}$	Unstable metastable phase C_2AH_8	Unnamed metastable phase C_2FH_8
Vaterite $CaCO_3$			

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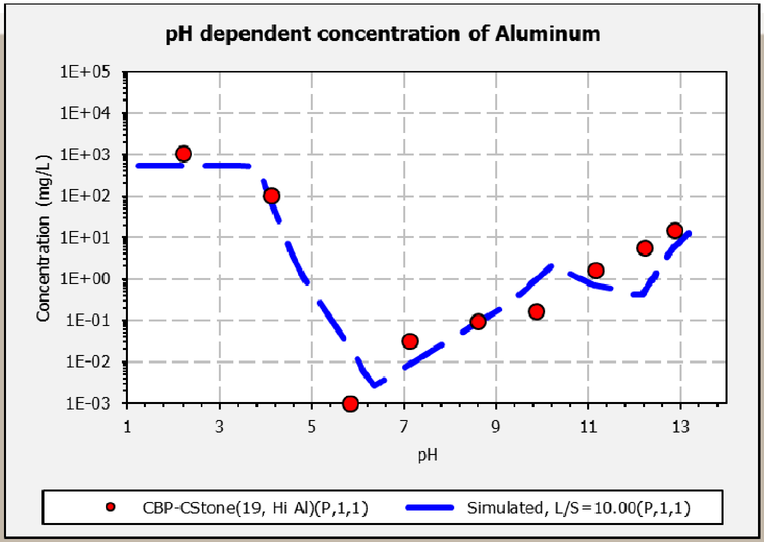
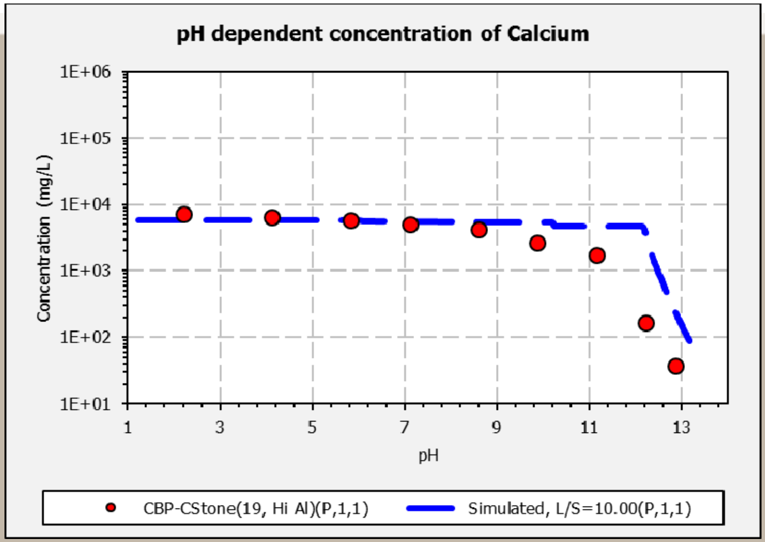
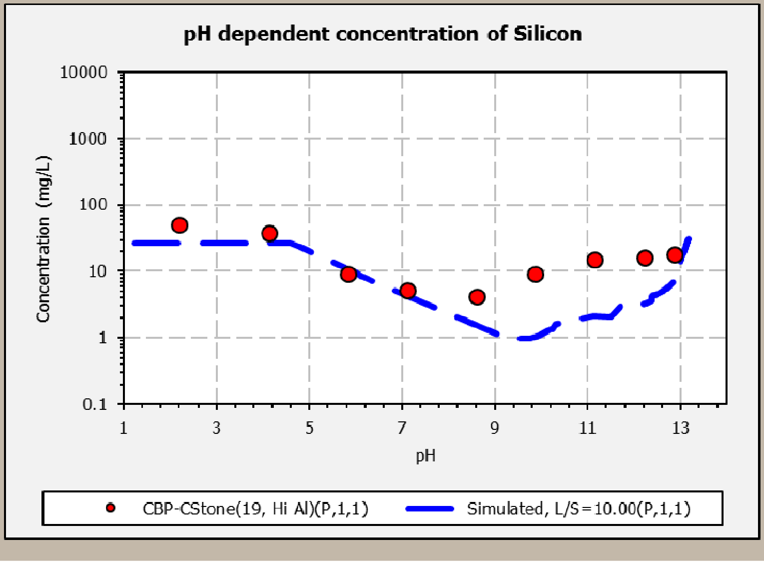
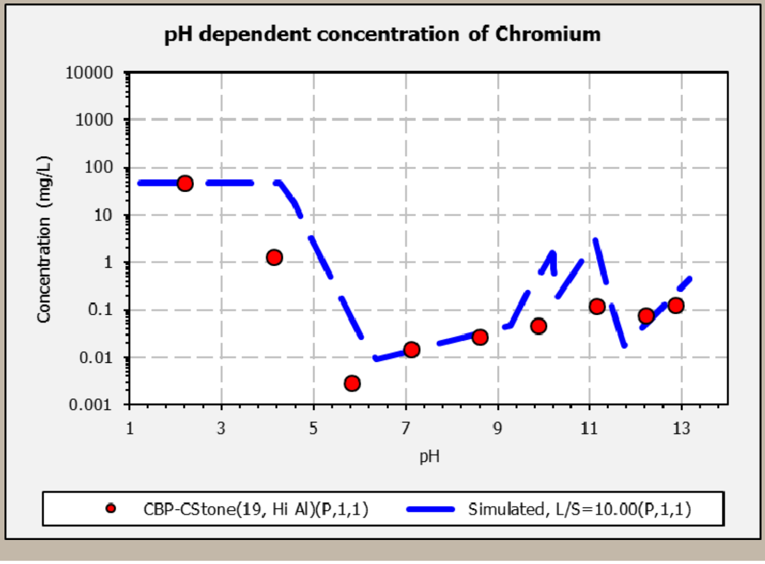
*B. Lothenbach, T. Matschei, G. Möschner, F.P. Glasser, Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement, Cement and Concrete Research, 38 (2008) 1-18.

PRELIMINARY CSF FOR CAST STONE


pH dependent concentration of Aluminum


pH dependent concentration of Calcium

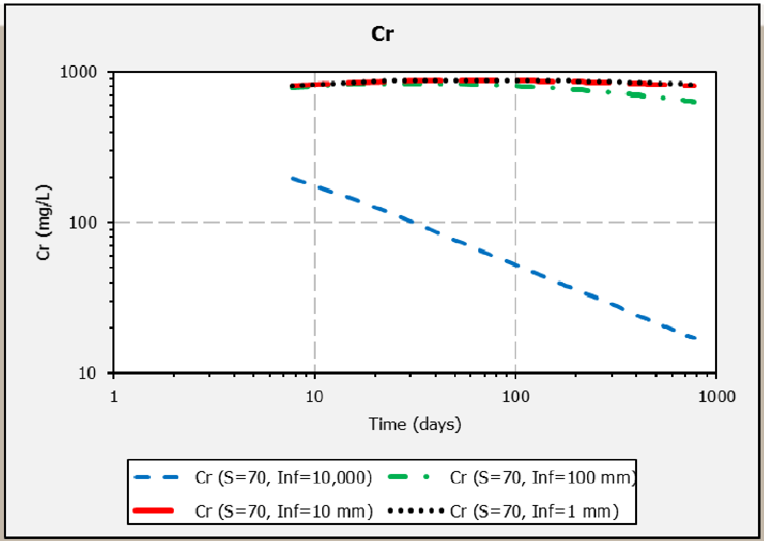

pH dependent concentration of Silicon

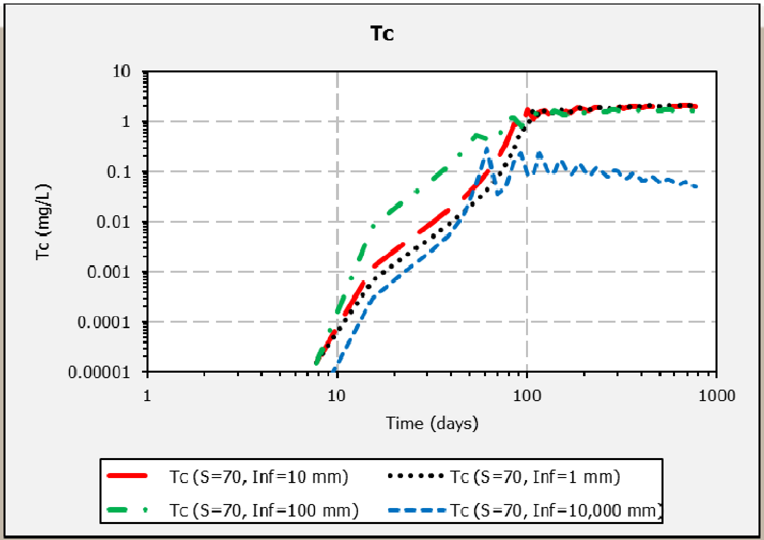

pH dependent concentration of Chromium

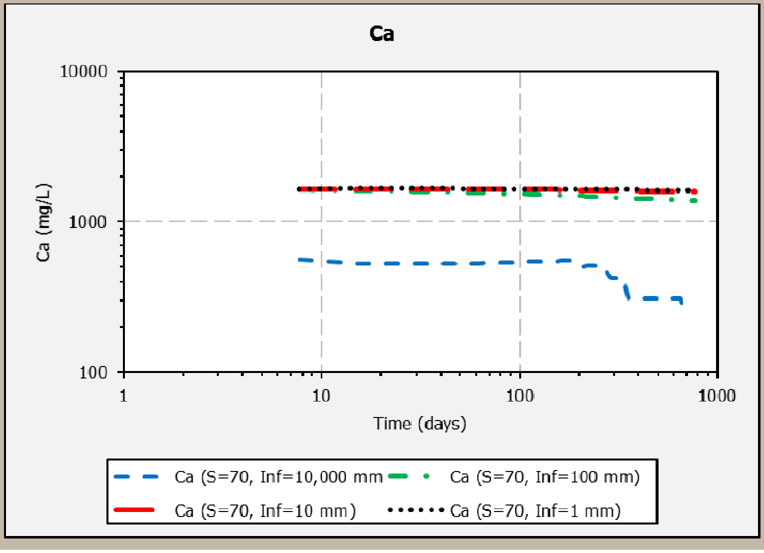
EXAMPLE MONOLITH DIFFUSION CASES

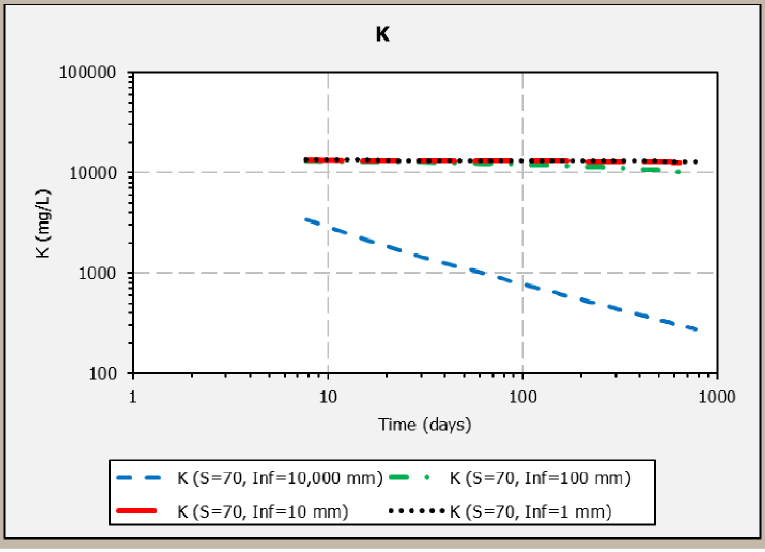
- Boundary Conditions: O_2=20%; CO_2= 400 ppm
- Material Conditions
  - Material – Cast Stone Blend 19 (high Al)
  - Base Case: S=70%, Inf.=10mm/y @ 1x/wk, η=0.58
  - Sensitivity Cases:
    - Saturation (S) = 90, 99%
    - Infiltration (Inf.) = 1, 100, 10,000 mm/y (infinite bath case)
    - Inf. @ 1x/5 wks
    - 1 y "no inf" followed by 1 y "inf"
    - 20 cm clean top layer (vapor diffusion resistance)

MONOLITH LEACHING WITH O_2 & CO_2 – EFFECT OF INFILTRATION

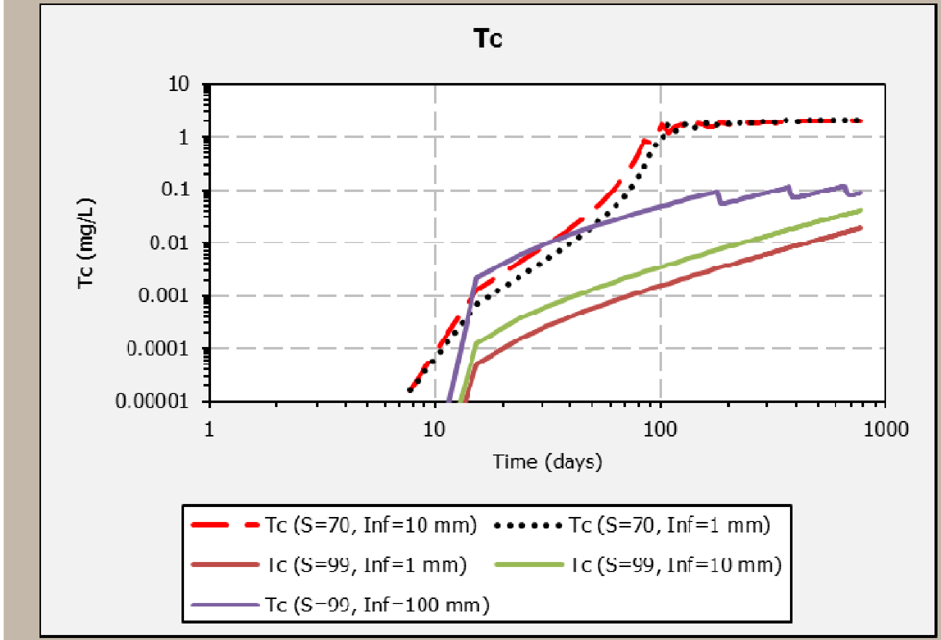




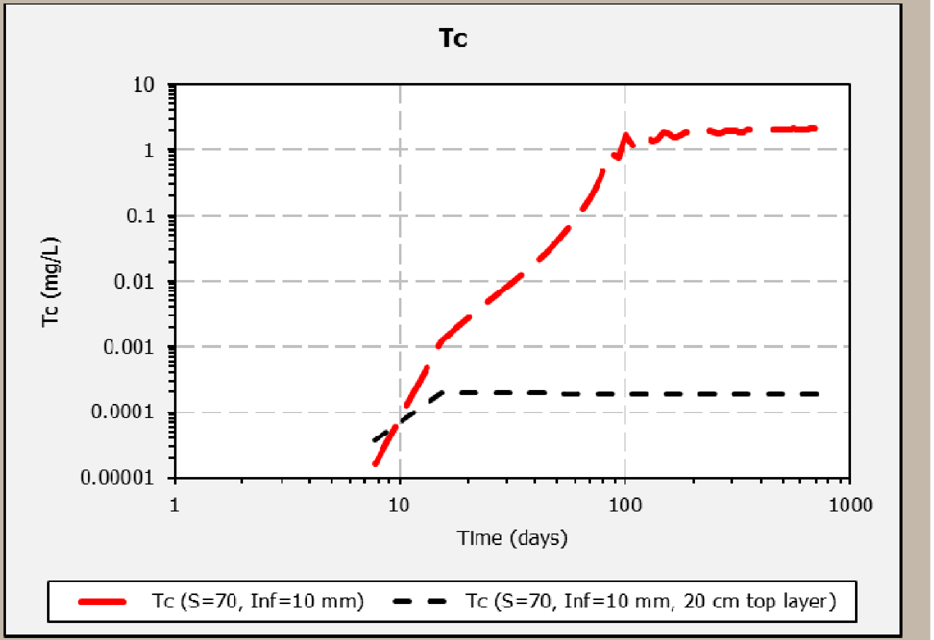




MONOLITH LEACHING WITH O_2 & CO_2 – EFFECTS OF SATURATION, INFILTRATION, AND CLEAN COVER



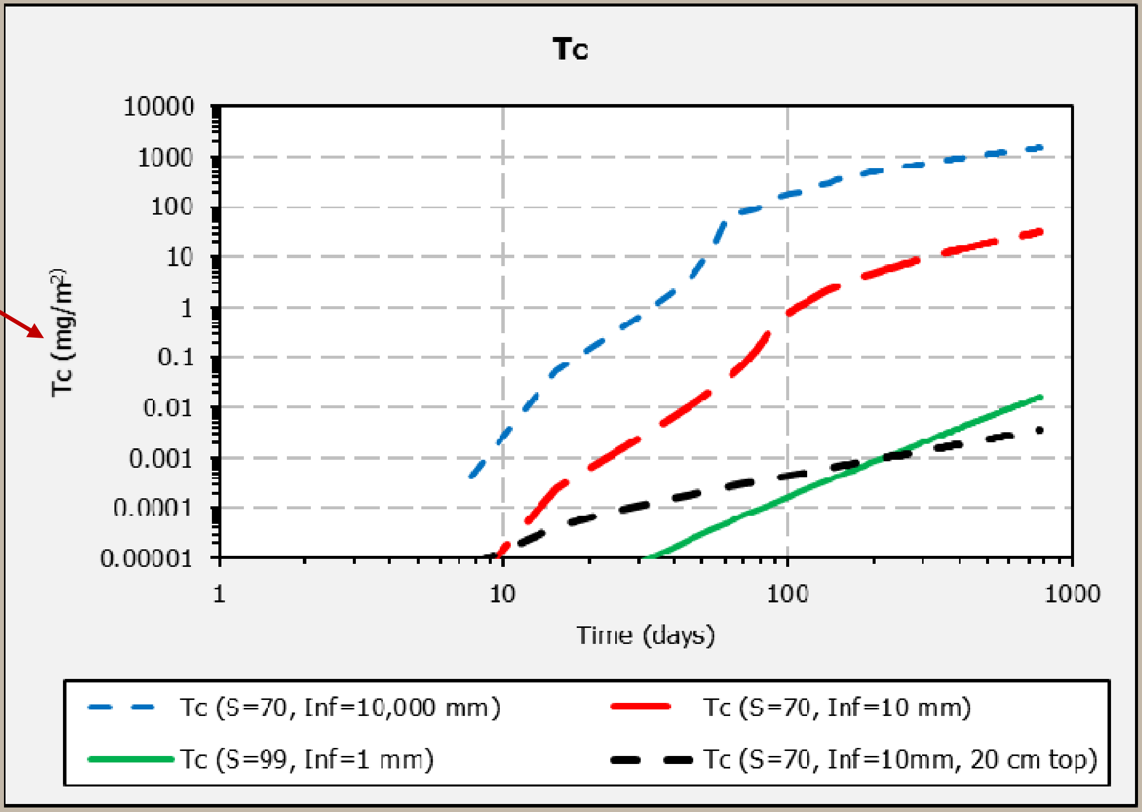
Effects of Saturation and Infiltration



Effect of 20 cm Clean Top Layer

MONOLITH LEACHING WITH O_2 & CO_2 – CUMULATIVE EFFECTS OF ASSUMPTIONS

Cumulative Flux, (mg/m^2)



Current assumptions can overestimate leaching of Tc-99 by up to 6 orders of magnitude

OXIDATION/CARBONATION IMPACTS SIMULATION CONCLUSIONS

- Carbonation and oxidation fronts move at different rates – both impact leaching
- "Infinite bath" assumption alone can result in about 3 orders of magnitude overestimation of Tc-99 leaching
- Saturation strongly effects oxidation rate and thus Tc-99 leaching
- A limited thickness top grout barrier can significantly reduce leaching by providing vapor diffusion resistance
- The impacts of intermittent infiltration are less significant than the net amount of infiltration
- Ideal case would maintain saturation with minimal net water flux

2013 LAW Cast Stone Screening Study

- PNNL and SRNL Program (Westsik et al., 2013)
  - Acceptable formulations of LAW cast stone
  - Contaminant release data for PA and risk assessment
- 26 Cast Stone Materials (CSMs) studied
  - Components
    - Ordinary Portland Cement (OPC) (8% in dry blend)
    - Fly ash (45% in dry blend)
    - Slag cement (47% in dry blend)
  - Waste Simulants
    - Single-shell tank, average LAW feed (HTWOS), high-Al, high-SO4
    - 5.0 M sodium and 7.8 M sodium
- Material Properties (strength, density, porosity, etc.)
- Leaching Characterization using EPA Method 1315

Westsik J.H. Jr., G.F. Piepel, M.J. Lindberg, P.G. Heasler, T.M. Mercier, R.L. Russell, A.D. Cozzi, W.E. Daniel, R.E. Eibling, E.K. Hansen, M.M. Reigel and D.J. Swanberg. *Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests.* RPP-RPT-55960 Rev 0, U.S. Department of Energy, Office of River Protection, Richland, Washington, September 2013.

Supplemental Studies

- Leaching and Material Parameterization Studies
  - Supports improved understanding of CSMs
  - Establishes a basis for geochemical speciation models
  - Facilitates validation, verification and uncertainty assessments
- Three CSMs (-6 control, -19 Hi Al, and -21 Hi SO_4) selected from 2013 Screening Evaluation
  - 7.8 M Na, OPC:FA:SC of 8:45:47, W/DB of 0.4 (-6,-19) | 0.6 (-21)
- Liquid-solid Partitioning (LSP) as function of pH (Method 1313, Method 1314) – critical performance parameter
  - Inorganics and organics (through DOC-complexation)
  - Indicative of speciation – geochemical speciation modeling
- Porosity approaches and analysis
- Moisture-Saturation Relationships

Porosity of Cast Stone

- Critical Parameter
  - Leaching, saturation, permeability, microstructure, degradation
- 51% to 62% reported in 2013 Screening Report
- Complicating Factors
  - Hygroscopic nature of high-salt wastes
  - Solubility of salts precipitated in pores
- Different Approaches
  - Drying of Fluid-saturated Materials (water, 2-propanol, ethanol)
  - Scanning Electron Microscopy (images at 3-mm x 3-mm)

Material ID	Reported	Water	2-Propanol	Ethanol	SEM
CSM-6 (control)	51.0	47.5	30.9	35.2	43.4
CSM-19 (Hi Al)	53.0	46.9	28.1	35.4	30.4
CSM-21 (Hi SO$_4$)	62.2	57.3*	41.5	49.7	--

Humidity-Saturation Relationships

- Relative Saturation (Θ) at Controlled Relative Humidity (RH)
  - 82% RH (KBr)
  - 68% RH ($NaNO_3$)
  - 33% RH ($MgCl_2$)
- Critical Parameter
  - Moisture Transport
  - Gaseous Transport
    - Oxidation
    - Carbonation
- Gravimetric Determination of Relative Saturation

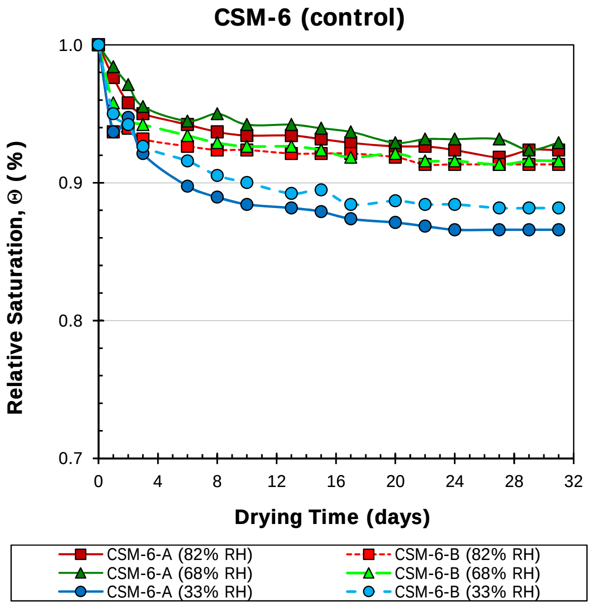
$$\theta_t = \frac{(M_{sat} - M_t)}{(M_{sat} - M_{dry})}$$

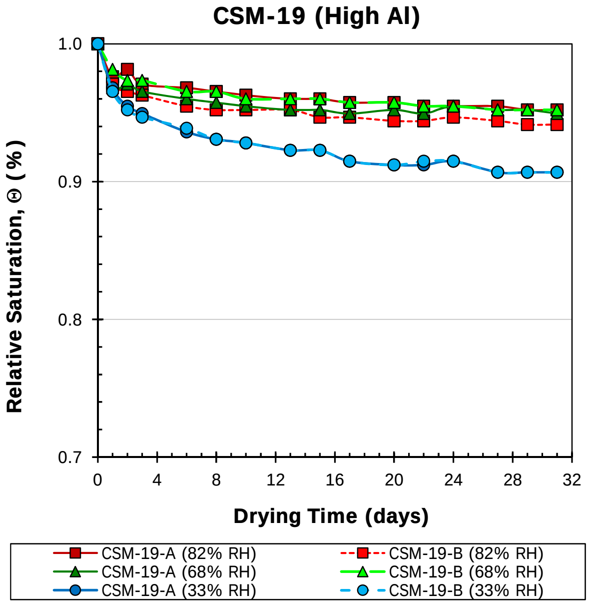
M_{sat} is the mass of a saturated sample (g)

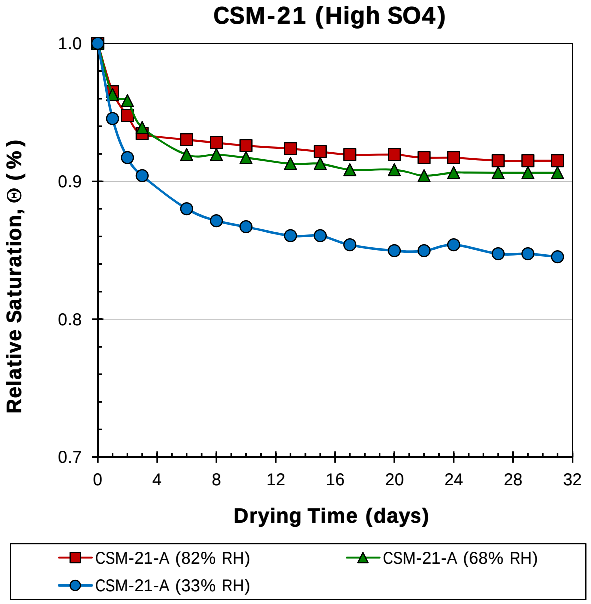
M_t is the measured mass of the sample as a function of storage time (g)

M_{dry} is the dried mass of the sample (g)

Saturation During Drying at Controlled RH





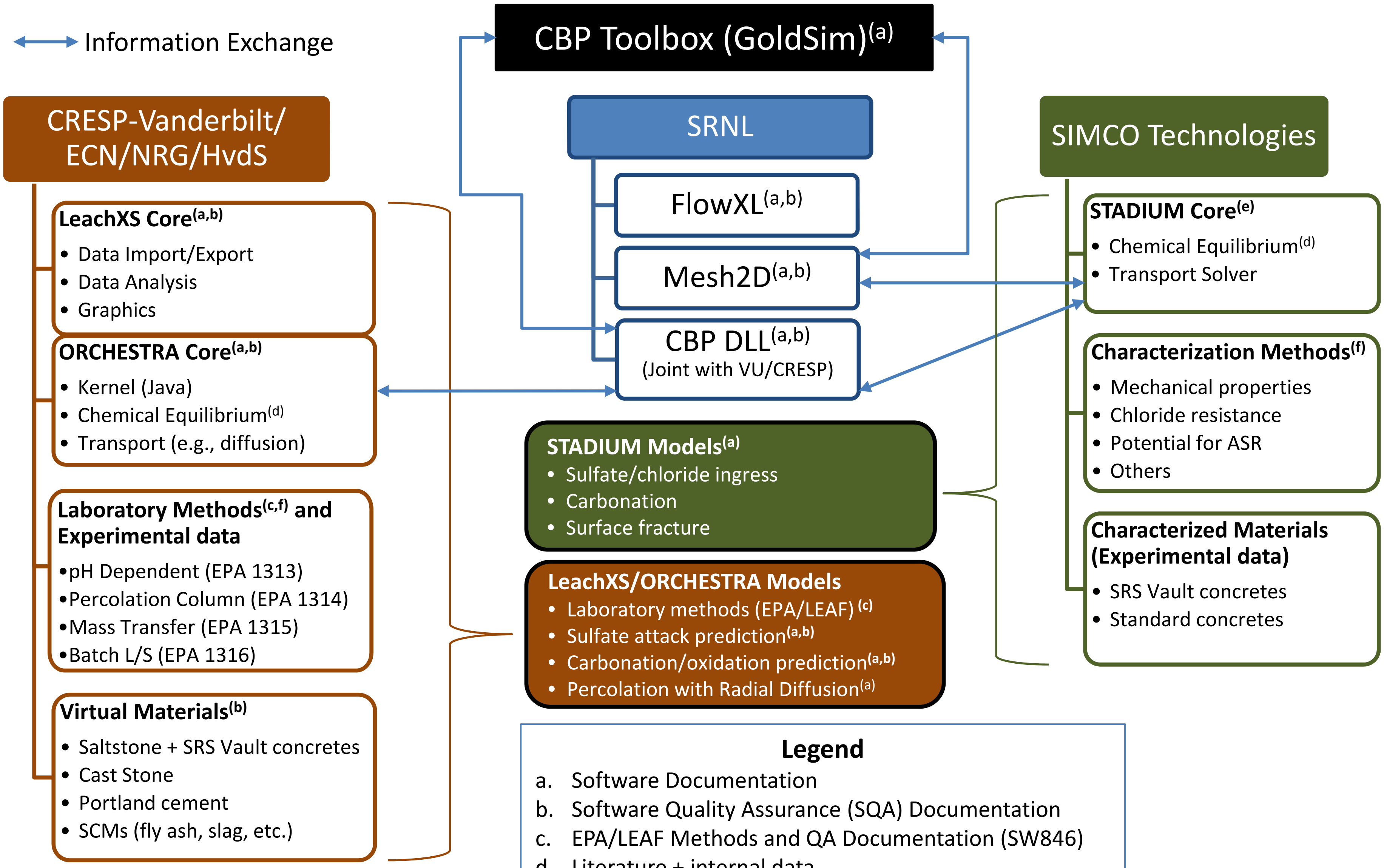


- CSM lose moisture when stored at RH less than 100%
- CSMs absorb water (hygroscopic) – similar Θ at 82% RH and 68% RH
- Sensitivity to strong RH changes

  CSM-21 (High SO_4) > CSM-6 (control) > CSM-19 (High Al)
- Also evaluated saturation during pore condensation

CBP
Cementitious Barriers Partnership

CBP Software QA Summary



Information Exchange

CBP Toolbox (GoldSim)$^{(a)}$

CRESP-Vanderbilt/ ECN/NRG/HvdS

LeachXS Core$^{(a,b)}$
- Data Import/Export
- Data Analysis
- Graphics

ORCHESTRA Core$^{(a,b)}$
- Kernel (Java)
- Chemical Equilibrium$^{(d)}$
- Transport (e.g., diffusion)

Laboratory Methods$^{(c,f)}$ and Experimental data
- pH Dependent (EPA 1313)
- Percolation Column (EPA 1314)
- Mass Transfer (EPA 1315)
- Batch L/S (EPA 1316)

Virtual Materials$^{(b)}$
- Saltstone + SRS Vault concretes
- Cast Stone
- Portland cement
- SCMs (fly ash, slag, etc.)

SRNL

FlowXL$^{(a,b)}$

Mesh2D$^{(a,b)}$

CBP DLL$^{(a,b)}$
(Joint with VU/CRESP)

STADIUM Models$^{(a)}$
- Sulfate/chloride ingress
- Carbonation
- Surface fracture

LeachXS/ORCHESTRA Models
- Laboratory methods (EPA/LEAF)$^{(c)}$
- Sulfate attack prediction$^{(a,b)}$
- Carbonation/oxidation prediction$^{(a,b)}$
- Percolation with Radial Diffusion$^{(a)}$

SIMCO Technologies

STADIUM Core$^{(e)}$
- Chemical Equilibrium$^{(d)}$
- Transport Solver

Characterization Methods$^{(f)}$
- Mechanical properties
- Chloride resistance
- Potential for ASR
- Others

Characterized Materials (Experimental data)
- SRS Vault concretes
- Standard concretes

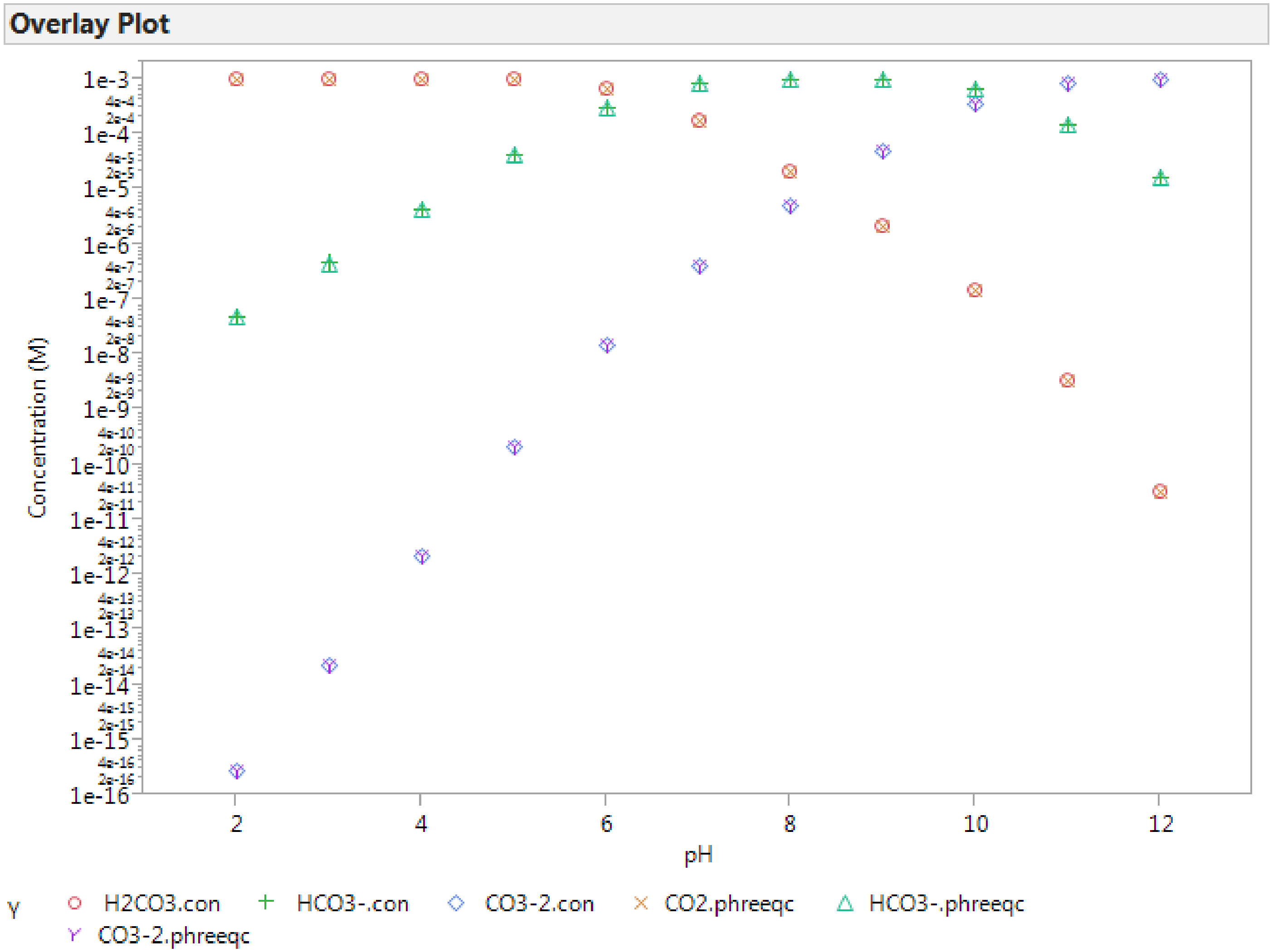
Legend

a. Software Documentation
b. Software Quality Assurance (SQA) Documentation
c. EPA/LEAF Methods and QA Documentation (SW846)
d. Literature + internal data
e. Patented
f. Published methods (e.g., ASTM, SW-846)

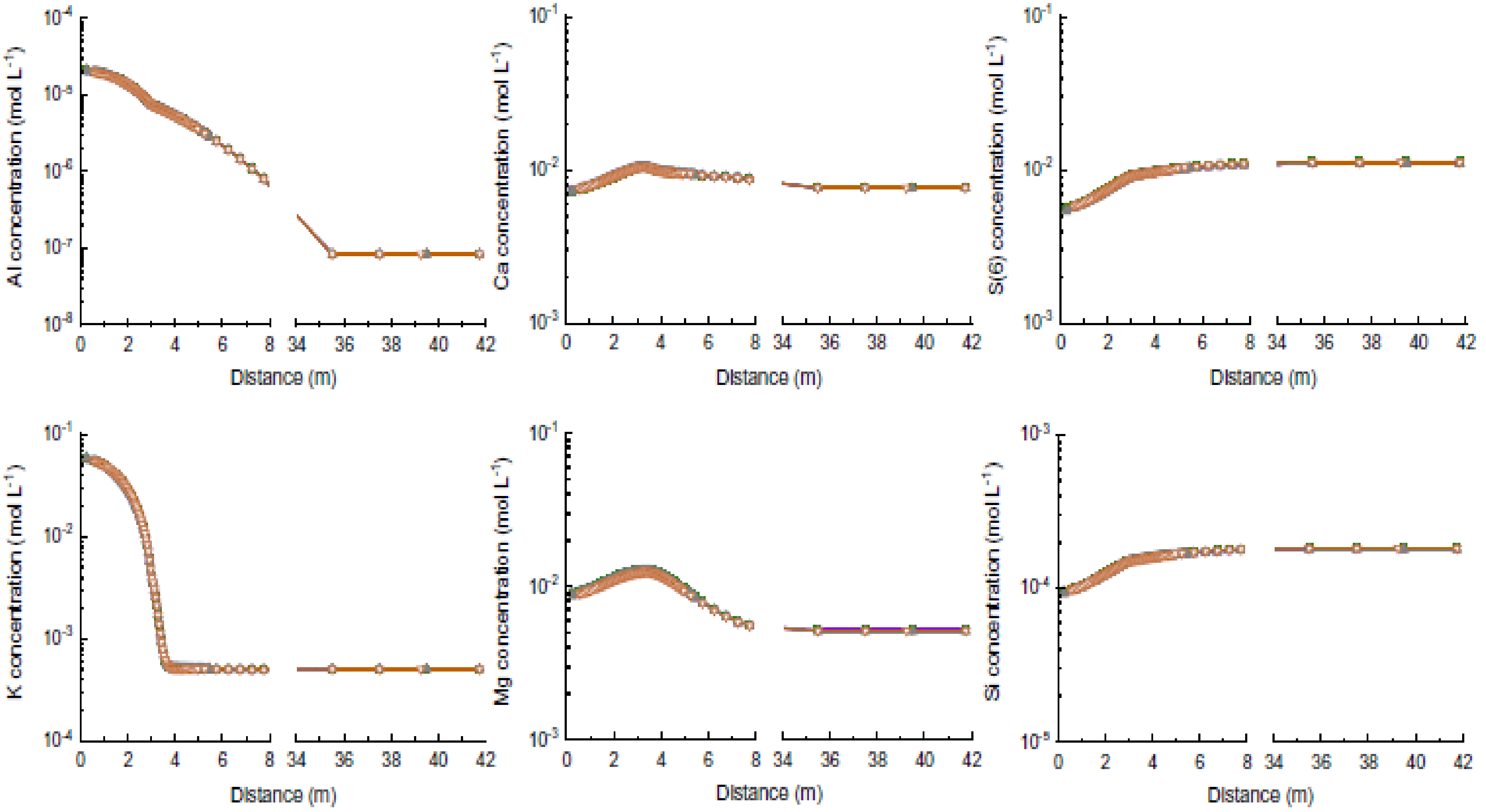
Software Quality Assurance – Verification & Validation

- Verification: Progressing from simpler calculations with analytical solutions to more complex models using code-to-code evaluations
  - ORCHESTRA chemical equilibrium versus PHREEQC
  - Reactive transport system for diffusion of a non-reactive constituent undergoing first-order (radioactive) decay versus analytical solution
  - International benchmarking studies – code-to-code
- Validation: Compare to laboratory and/or field results
  - Sulfate Attack in SRS vault concrete exposed to a high-sulfate waste form compared to microprobe data
- Verification & Validation:
  - Unsaturated carbonation monolith model verified using analytical solution from Crank and validated using
  - Saturated laboratory monolith model verified using analytical solution from Crank and validation in progress

Comparison of ORCHESTRA and PHREEQC Results for Verification Test Problem 2 (Simple Carbonate System)

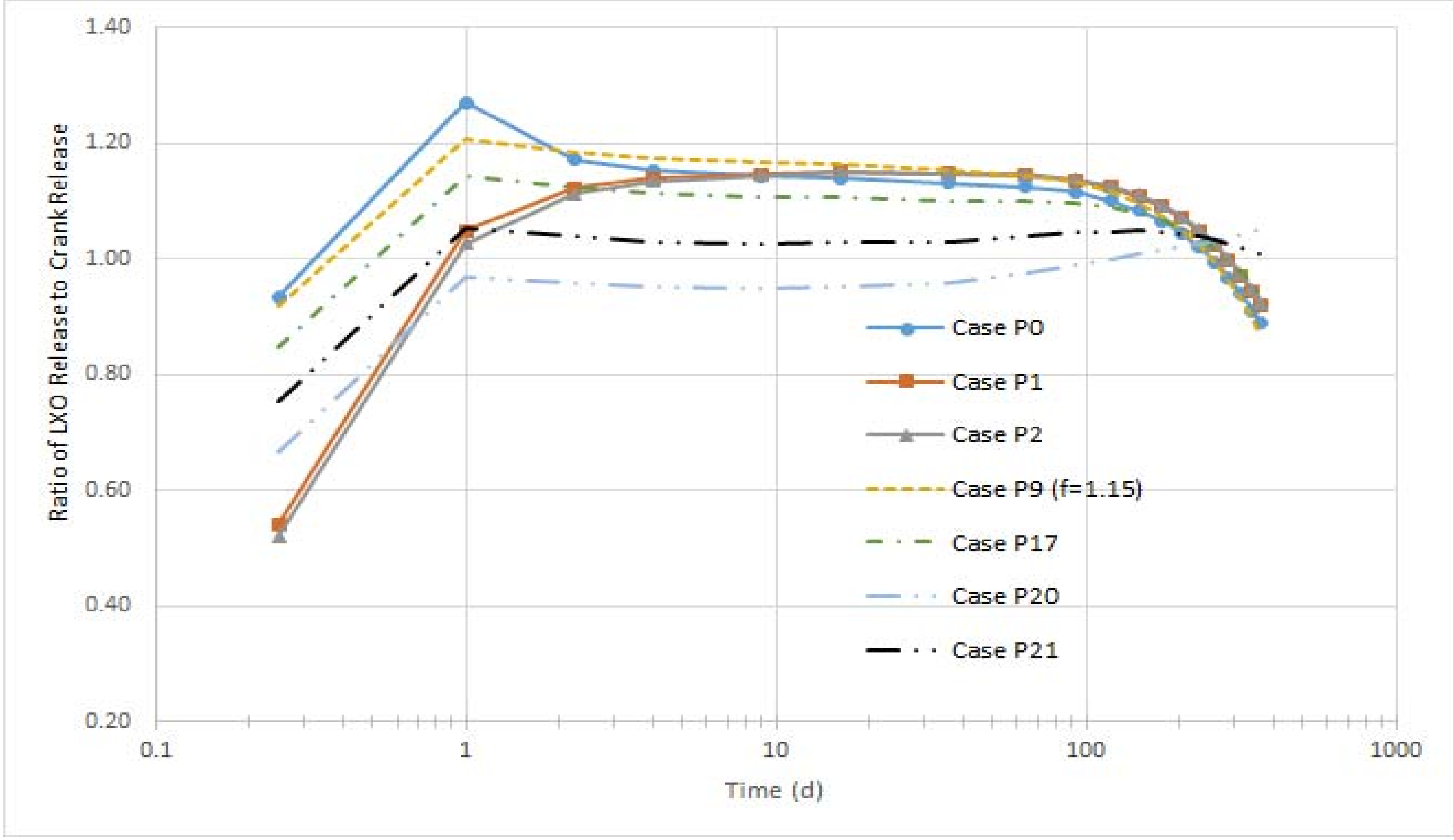


International Benchmark Studies

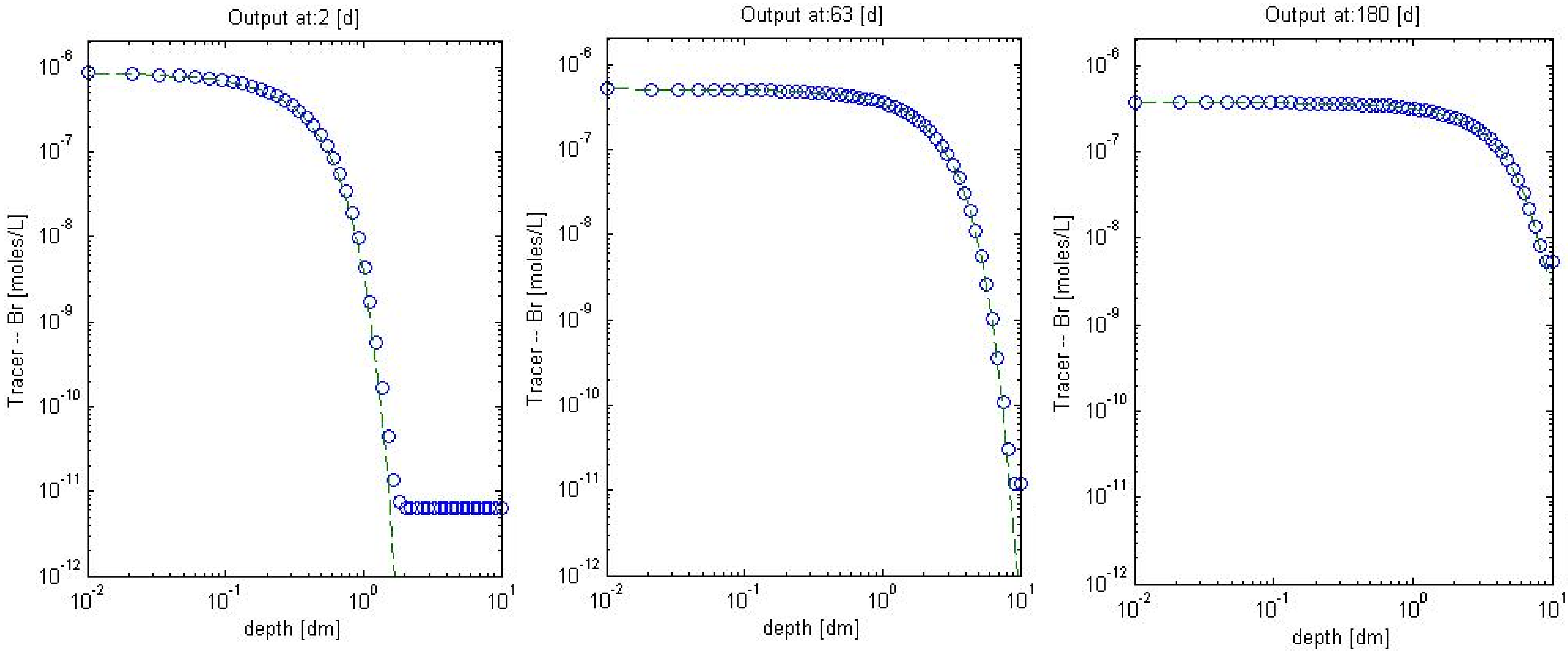


Marty, NCM, Bildstein, O, Blanc, P, Claret, F, Cochepin, B, Gaucher, EC, Jacques, D, Lartigue, J-E, Liu, S, Mayer, KU, Meeussen, JCL, Munier, I, Pointeau, I, Su, D & Steefel, CI 2015, 'Benchmarks for multicomponent reactive transport across a cement/clay interface,' Computational Geosciences, vol. 19, Issue 3, pp 635-653.

4x4x16 cm Monolith Parallelepiped Solution Comparisons (fully explicit finite difference)



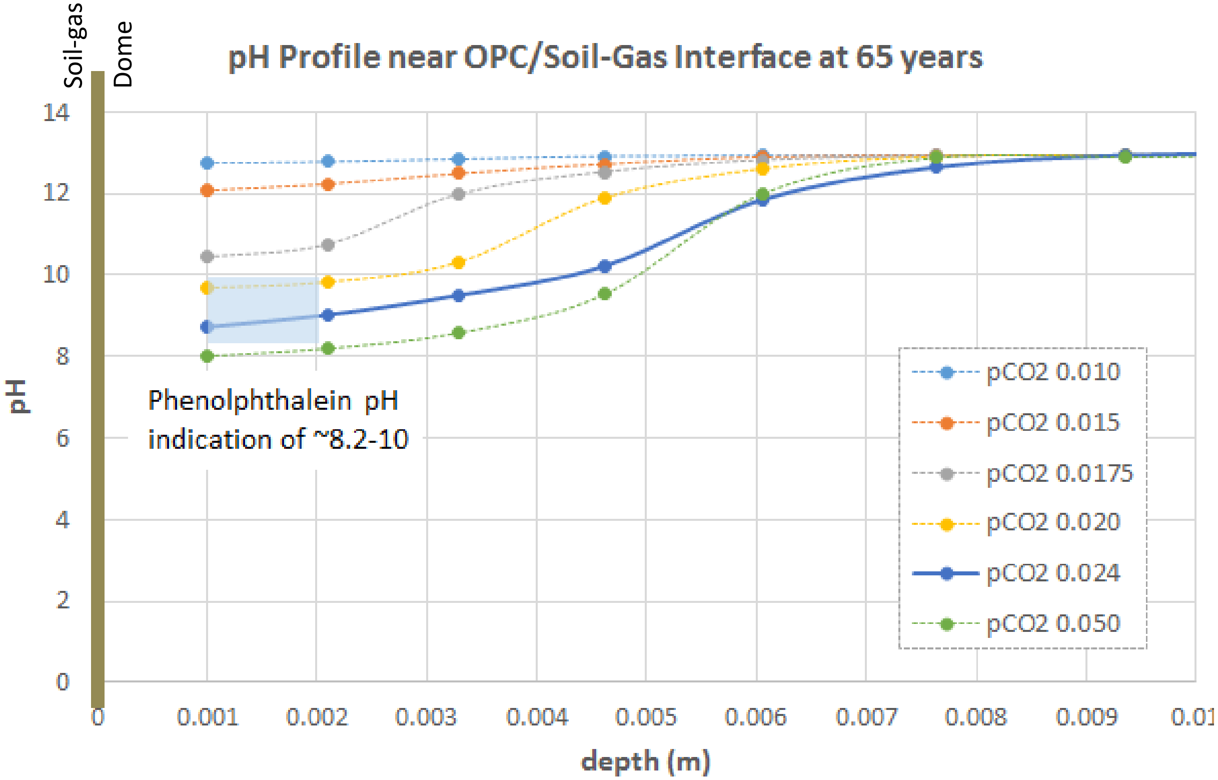
ORCHESTRA (o) versus analytical (--) monolith diffusion predictions (Crank-Nicholson finite difference) for a non-reactive tracer



LXO Carbonation Model Validation


SST 241-C-107 Dome Plug

- 55-in section removed from Tank 241-C-107 dome in December 2010
- Concrete in good condition, with no noticeable cracks or voids
- Depth of carbonation was shallow, ~0.04 to 0.08 in. (1 to 2 mm) from top surface

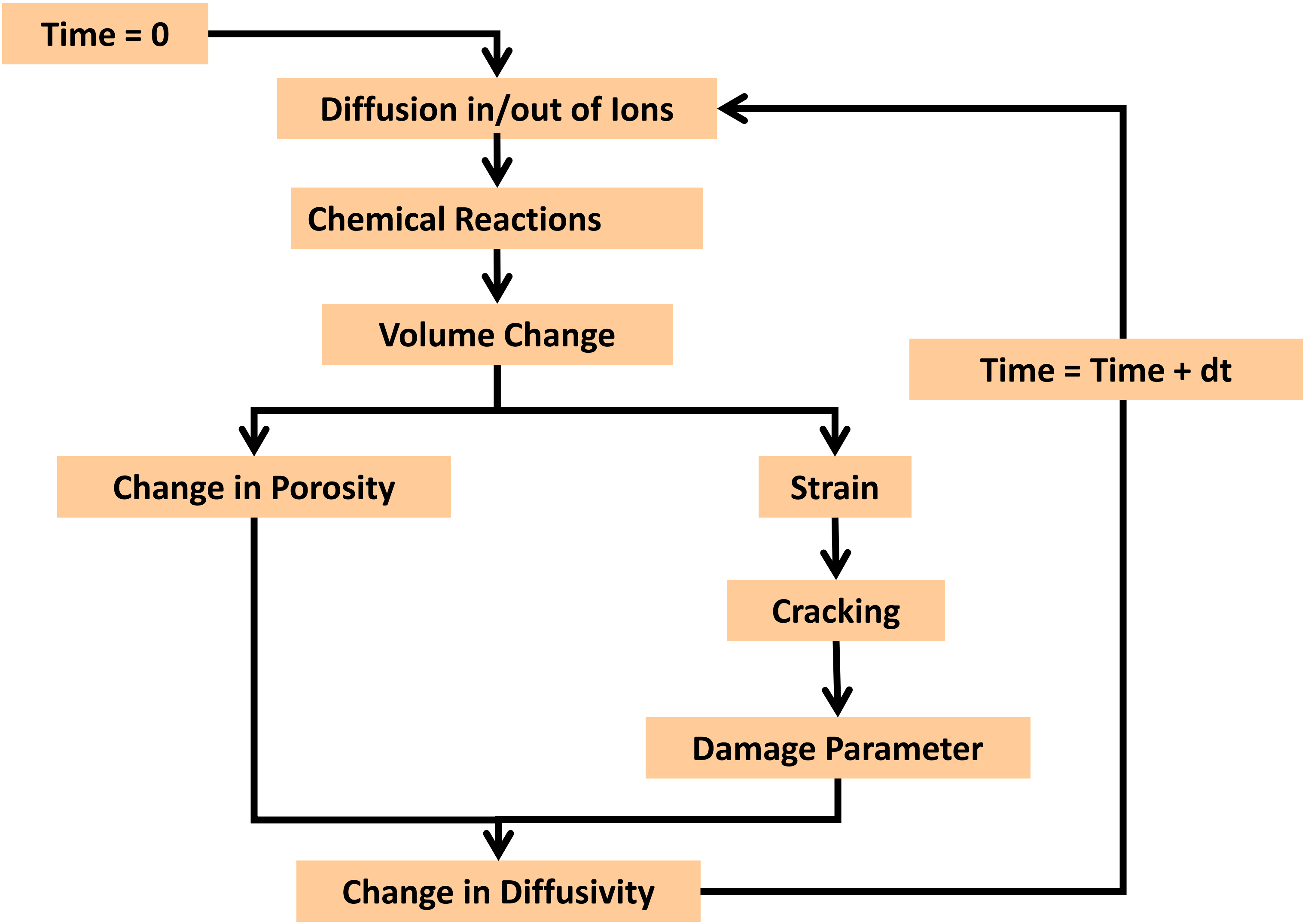


- OPC -- tank constructed in mid-1940s assumed 79% saturation (low)
- LeachXS/ORCHESTRA (LXO) predicted speciation and pH as a function of time and depth where maximum CO_2 is ~2.4% in soil-gas
- Predicted pH ranges corresponding to phenolphthalein is < ~4 mm at 65 years for pCO_2 at 2.4% versus 1-2 mm observed in dome core
- Based on LXO predictions, a CO_2 of 1.75-2.0% would correspond to the observed carbonation depth – reasonable value from literature

On-going Work

- Complete Software Quality Assurance (SQA) including V&V
  - LeachXS including Virtual Materials
  - ORCHESTRA including monolith models (Method 1315 laboratory, carbonation/oxidation prediction, sulfate attack) followed by column and radial diffusion models
  - Thermodynamic database update (e.g., “cemdata14”)
  - Field data modeling and verification
- Examine relative effects of different extents of initial cracking
- Revise scenarios to reflect IDF PA sensitivity cases and revise long-term release simulations
- Uncertainty assessment (parameter and model uncertainty)
  - Improved mineral selection basis and capture as model uncertainty
  - Bayesian calibration of CSH and ettringite solid (trace) solution models
- Evaluating additional coupling of phenomena, when warranted

Sulfate Attack Modeling Framework



Time = 0

Diffusion in/out of Ions

Chemical Reactions

Volume Change

Change in Porosity

Strain

Cracking

Damage Parameter

Change in Diffusivity

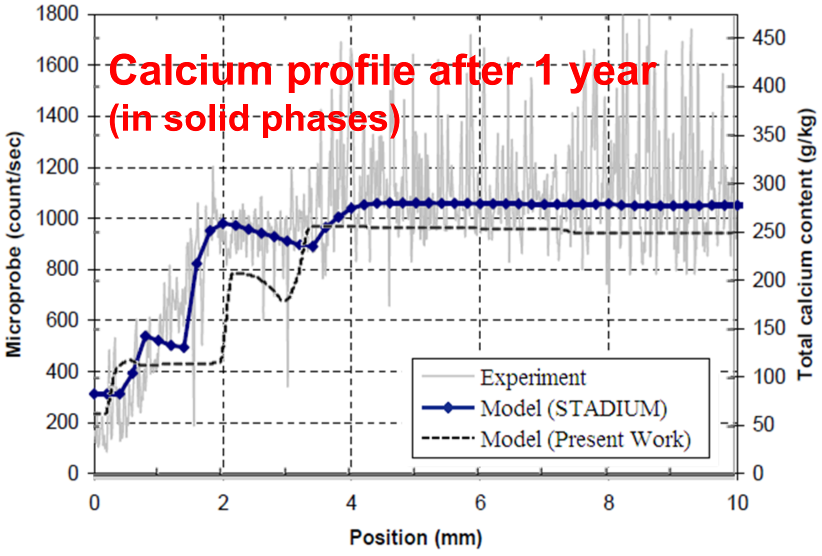
Time = Time + dt

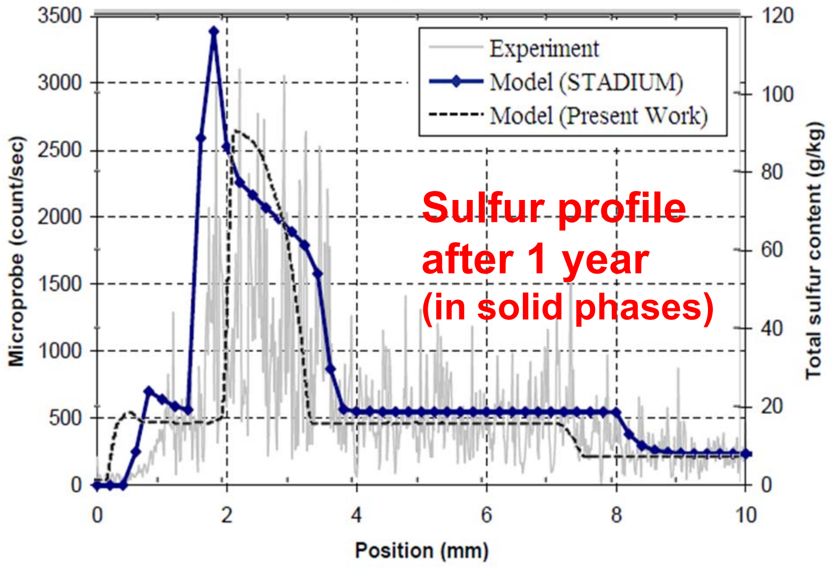
Model Calibration and Validation

- 7 cm x 20 mm CSA type 10 cement paste, porosity = 0.52, one face exposed
- 50 mmol/L of Na_2SO_4 solution at pH 10.3 in 30 L tank renewed every 7 days

- Porosity : 0.52
- Calibration parameter: tortuosity (= 35) and b (= 0.3)

Model calibrated with experimental results after 3 months and validated against experimental results after 1 year (experimental data from Samson and Marchand, 2007)





NRC -- SULFATE ATTACK COMMENTS AND CONCERNS

- *NRC – "… not clear …. if …. volume change associated with sulfate ingress can be predicted by thermodynamic calculations and the formation of expansive phases in the pore space of cementitious materials"*
- *Sulfate attack [approach] may be considered "state-of-the-art," but significant uncertainties remain*
  - *Additional experiments needed to better understand behavior, refine uncertain parameters, and validate underlying conceptual models.*

We are evaluating existing sample and experimental results as well as other decalcification and sulfate exposure studies and stored materials to see what additional testing is needed.

We are planning to use additional measurement techniques (e.g., SEM) to better support model assumptions.

SULFATE ATTACK--PARAMETERIZATION

1. *Applicability of [calibrated/material-specific] results from Tixier & Mobasher to other cementitious systems must be better supported.*

We are mining data supporting the original sulfate attack model development and other, pertinent decalcification and sulfate exposure studies, results, and materials to determine what additional testing and analysis may be needed to support model applicability.

2. *Use of the [available fraction of porosity] as an independent parameter is not adequately supported.*
3. *Range of fractional porosity values used in ORCHESTRA does not appear to be adequately supported.*

As part of the current V&V effort, we are investigating the relationships among available porosity, diffusivity, tensile strength, modulus of elasticity, and cement type; how these were parameterized in the existing model; and what changes may be needed to better support the model and better describe how the model handles these parameters.

SULFATE ATTACK -- HOMOGENIZATION

4. Original model (Sarkar 2010) used assumption (for computational homogenization) that “hydration products are homogeneously distributed throughout the structure.” … filling of pores may occur as a moving front... not clear how this simplifying assumption … could impact long-term concrete degradation calculations.

The very detailed discussion of the homogenization schemes used (as well as the others that were considered for use) and how model discretization mimics a moving front are being evaluated as part of the V&V effort.