Cementitious Barrier Partnership Program Update

Interagency Steering Committee on Performance and Risk Assessment

Community of Practice Annual Technical Exchange Meeting

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CBP Support of Tank Waste Challenges

- **Need:** Mechanistic modeling tools and supporting lab and field data *to build confidence* in the *prediction of long-term performance for unique DOE cementitious barriers and waste forms.*
- **CBP Response:**
  - *Developed software based on mechanisms* (phenomena) to predict long-term cementitious material behavior to sulfate/chloride attack, carbonation/oxidation, and leaching
  - *Conducted Integrated Experimental Programs* combining both modeling and experimental data for model parameterization and validation
- **CBP Priorities**
  - Support DOE Performance Assessments (Hanford and Savannah River Sites)
  - Support Software Quality Assurance for user to meet NQA-1/DOE O 414.1
  - Technetium-99 mobility
- **Technical Strategy / Approach**
  - Reference cases for unique DOE cementitious materials
  - Test bed exposure studies to study behavior of DOE cementitious materials
  - Extension/enhancement of existing tools – STADIUM, LeachXS/ ORCHESTRA, GoldSim Performance Assessment (PA) framework
  - Integrated experimental and modeling programs

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Example Key Question, Variables, & Processes

- Key Question
  - What is the rate of release for radionuclides and chemical contaminants from cementitious wasteforms (e.g., Cast Stone) under a range of PA scenarios?

- Material Variables
  - Composition (major contaminants, radionuclides, contaminant loadings)
  - Physical properties (porosity, strength, density)
  - Intrinsic leaching characteristics (liquid-solid partitioning, reducing capacity, liquid and gas phase effective diffusion coefficients/tortuosity)

- Scenario Variables
  - Physical configuration and initial/boundary conditions
  - Water – Saturation, infiltration rate and frequency
  - Cracking – Initial state, long-term

- Important Aging Processes
  - Initial hydration and material state (including cracking)
  - Sulfate attack (liquid phase) → cracking and release
  - Oxidation (predominantly through gas phase transport) → release
  - Carbonation (predominantly through gas phase) → pH effect/cracking/release
  - Leaching of wasteform primary constituents → pH effect
  - Microstructure changes (mineralogy, pore structure, etc.)

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What does the CBP Toolbox offer?

- Test methods and reference data
  - Leaching assessment (EPA 1313, 1314, 1315, 1316)*
  - Physical and chemical properties**

- Source-term Models
  - STADIUM (SIMCO Technologies, Inc.)
    - Ionic transport/reactions in saturated and unsaturated concrete
    - Focus on durability and structural performance
  - LeachXS/ORCHESTRA (Vanderbilt/ECN/NRG/HvdS)
    - Geochemical, speciation-based reactive mass transport
    - Focus on leaching and chemical performance

- CBP Generic Dynamic Link Library and GoldSim
  - Probabilistic analysis using Monte Carlo simulation
  - Integration with broader PA scenario modeling

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*   These EPA Methods are available in SW-846
     (http://www3.epa.gov/epawaste/hazard/testmethods/sw846/new_meth.htm)
** SIMCO, VU/ECN, & SRNL provide many ASTM and internal methods for material characterization

Why use CBP Tools?

- Robust consideration of material properties, scenarios, and aging/degradation processes
  - Physical scenarios – from intact monolith (limited cracking/water interface), to percolation with radial diffusion (extensive cracking), to dual regime (rubblized)
  - Multiple material layers (and variations within layers) and dimensions
  - Coupled processes (as needed) of chloride/sulfate attack, oxidation, carbonation, and leaching (and aging)

- Release estimation basis that reflects current state-of-the-science, rather than gross over-simplification that results in many orders-of-magnitude uncertainty and over-estimation of release
  - Conforms with "realistic case + uncertainty" assessments
  - Provides basis for evaluating potential system design enhancements and waste loading limits
  - Provides basis for performance monitoring

- Software Quality Assurance consistent with NQA-1 and DOE Order 414.1D

Experimental Program Highlights

- SRNL Experimental Results
  - Saltstone/ Cast Stone Tc Speciation / Mobility Studies
    (CBP-TR-2014-005 / SRNL-STI-2014-00399)
  - Unsaturated Hydraulic Conductivity in Fractured Materials
    (SRNL-STI-2014-00367 / WM2015 Paper)
  - Cementitious Materials Phase Characterization
    (CBP-TR-2014-004 / SRNL-STI-2014-00397, Rev.1)

- SIMCO Technologies Experimental Results
  - Exposure Studies of DOE Cementitious Barriers *(CBP-TR-2015-001)*
  - Transport Properties of Damaged CM *(CBP-TR-2015-002)*

- VU/CRESP Experimental Results
  - Cast Stone characterization & evaluation for Hanford *(Draft reports in review)*
  - Gas phase reactive species ingress (CO_2, O_2) *(PhD dissertation in progress and journal manuscript)*

SRNL Experimental Programs

Mixed Oxidation States / Oxidation Front (130 days)
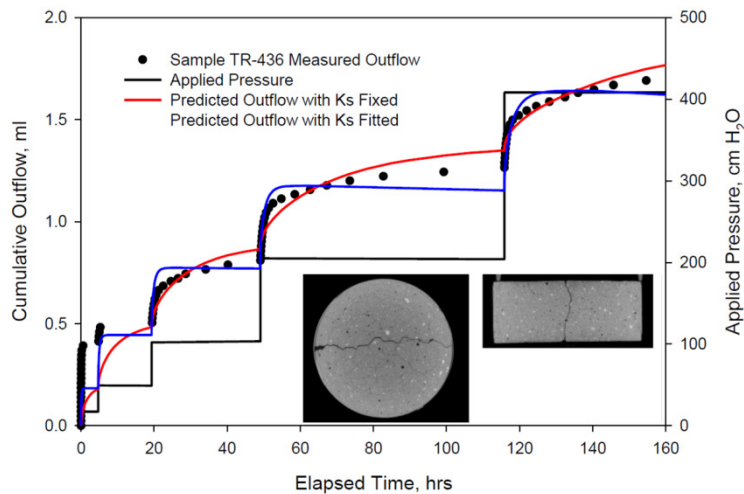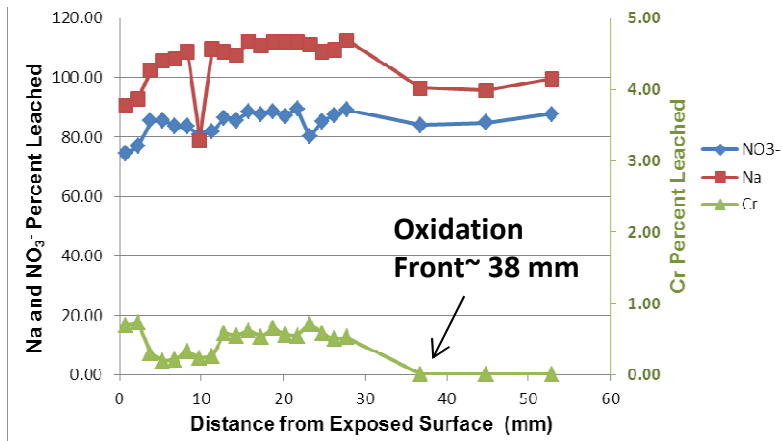
Redox Sensitive (Tc/Cr) Oxidation Studies
- Contaminant specific oxidation fronts identified by depth-discrete sampling
- Leachable and non-leachable Tc-99 fractions coexist
- Leaching in water without prior aging may not be conservative

Mineralogy Studies
- XRD studies enables more accurate long-term phase evolution

Hydraulic Property Characterization
- Method development for *unsaturated* and *fractured* cementitious materials

SIMCO Experimental & Model Development
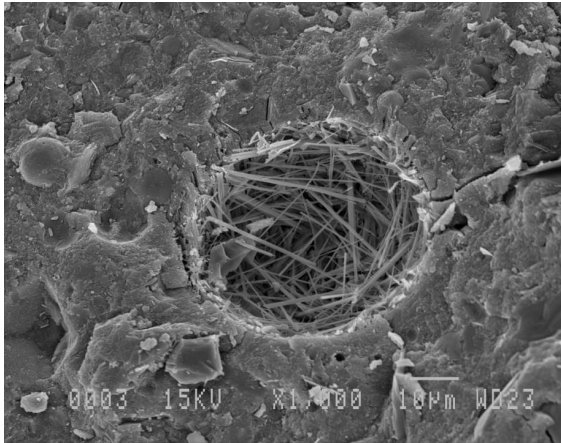
Experimental work:

- Concrete mixtures characterization

- Monitoring of samples in aggressive environments

- Physical damage characterization on concrete
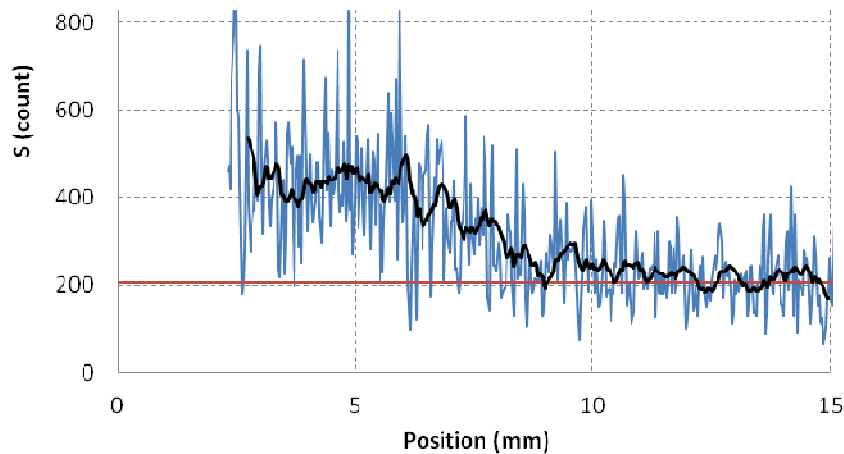
Model development:

- Sulfate attack

- Carbonation

- Relationship between damage level and concrete properties

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FY14 Vanderbilt Experimental / Model Development

Exposed Surface

0 mm

0.4 mm

0.6 mm

1.8 mm

2 mm

Increasing Ca content

Carbonation Depth Comparison

Mean Carbonation Depth (mm) vs Ca (wt%)
- w/ Low Ca FA
- w/ High Ca FA
- Control (no FA)

Low Ca fly ash replacement (M45-02)

Calcium (mg/L) vs pH

Ca solubility lower in carbonated material

ML
MDL

M-45-02
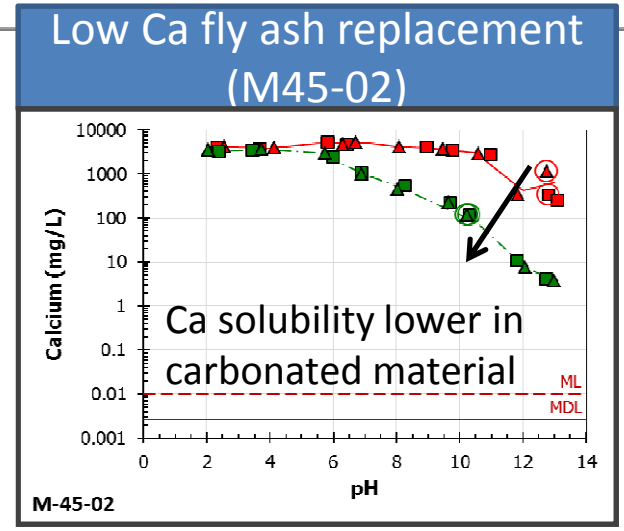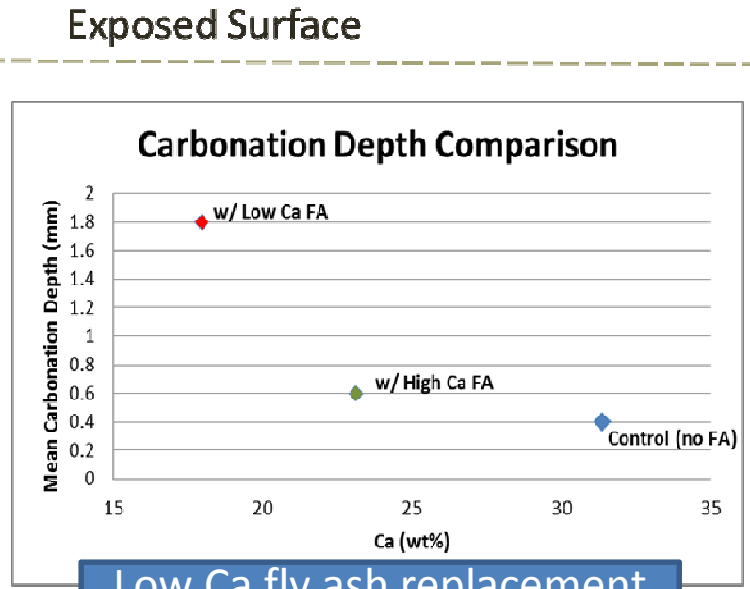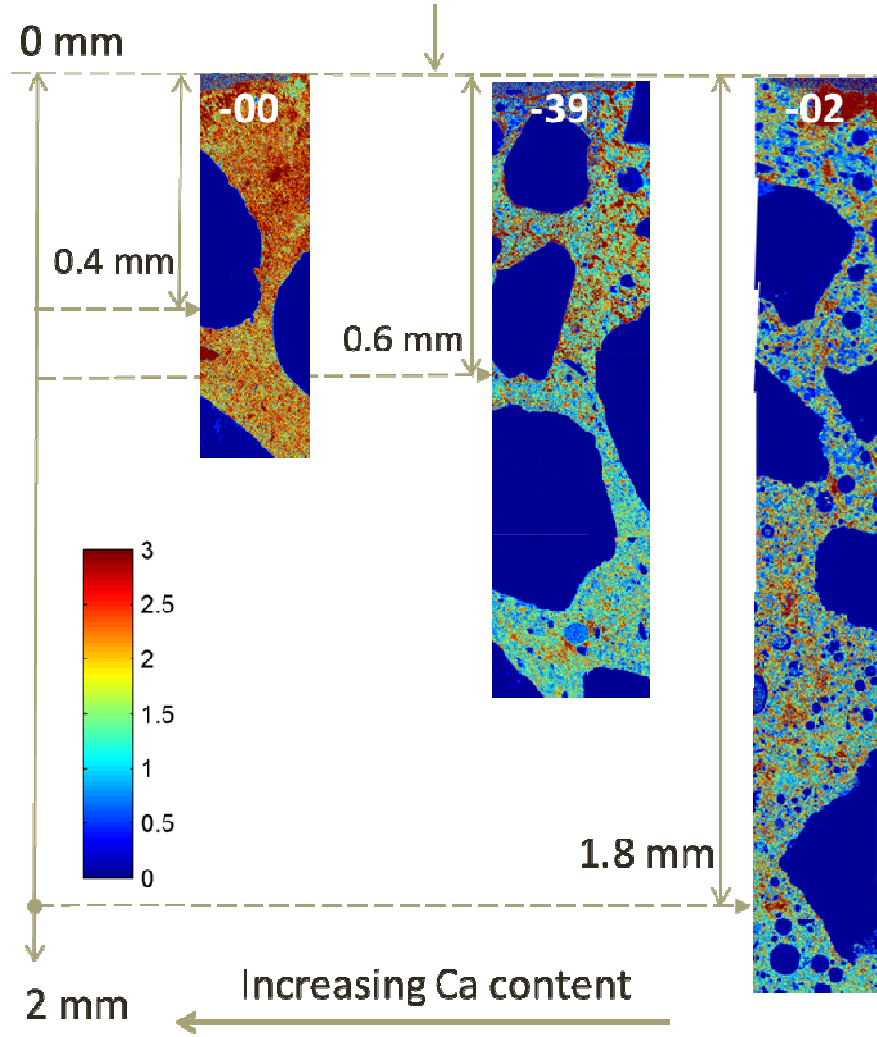
Leaching Environmental Assessment Framework

- Key foundation for new EPA regulations and guidance on: disposal of coal combustion residues; use of coal fly ash in concrete; waste treatment and disposal; site remediation; beneficial use of secondary materials – *EPA guidance planned to be issued in 2016*

- Provides basis for international use of LEAF (European Union, Australia, China, Israel)

- EPA 600/R-14/061
  - Leaching Assessment Fundamentals
  - 10 Cases of Large-scale Field Analysis Coupled with Laboratory Testing For 7 Materials – *field validation*
  - Recommendations for Use of LEAF
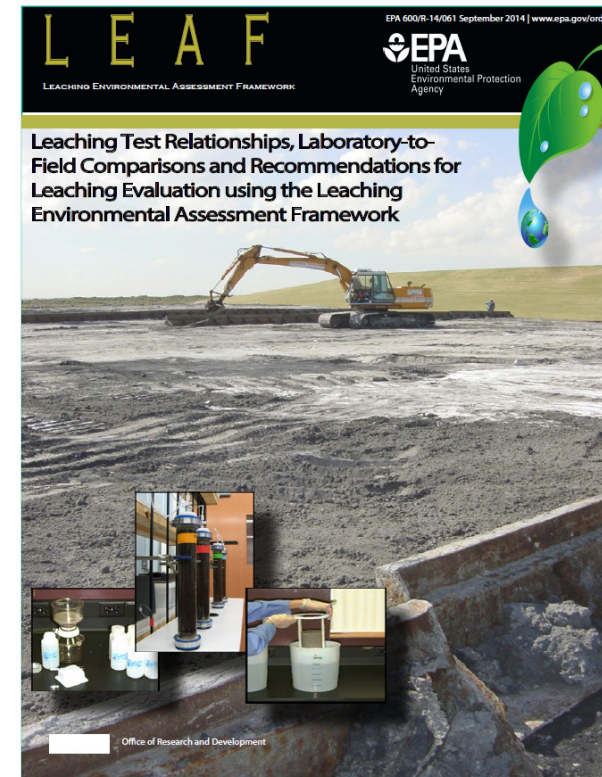
EPA 600/R-14/061

LEAF Leaching Methods*

Method 1313 – Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure

Method 1314 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio (L/S) using an Up-flow Percolation Column Procedure

Method 1315 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure

Method 1316 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

*Posted to SW-846 as "New Methods" August 2013

Example Data Sets Available

- CBP/CRESP -- EPA 1313 & 1314 -- 3 Cast Stone compositions (Blends 6, 19, 21; not including Tc) and component materials (e.g., blast furnace slag, fly ash)

- PNNL – EPA 1315 -- Range of Cast Stone compositions
  - Long-term leaching w/DI water & synthetic Hanford groundwater

- CBP/CRESP – Saturation-Relative Humidity relationships

- SRNL & SIMCO – Leaching data and oxidation information available on analogous materials (e.g., surrogate wasteforms and Saltstone)

- CBP/CRESP, PNNL, SIMCO & SRNL – Wasteform, concrete, and SCM characterization data

- CBP/CRESP – XRD/SEM analysis of microconcretes (with fly ash) and Cast Stone under carbonation and oxidation

CBP Software Toolbox Components
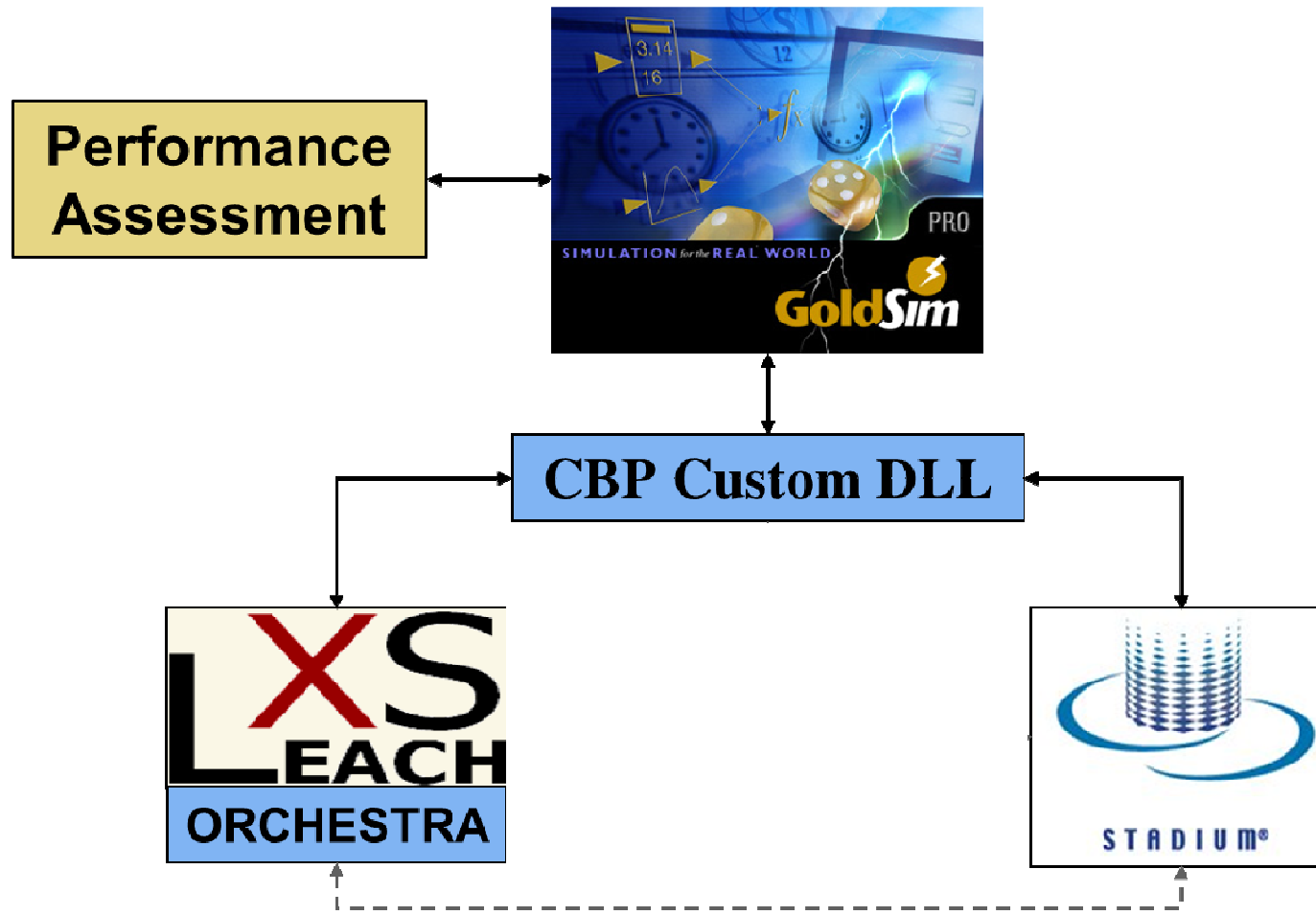
CBP Software Toolbox Capabilities

STADIUM

- Transport of chemical species
- Formation of deleterious minerals
- Alteration to concrete microstructure
- Capillary flow
- Temperature effects
- Multi-layer capabilities
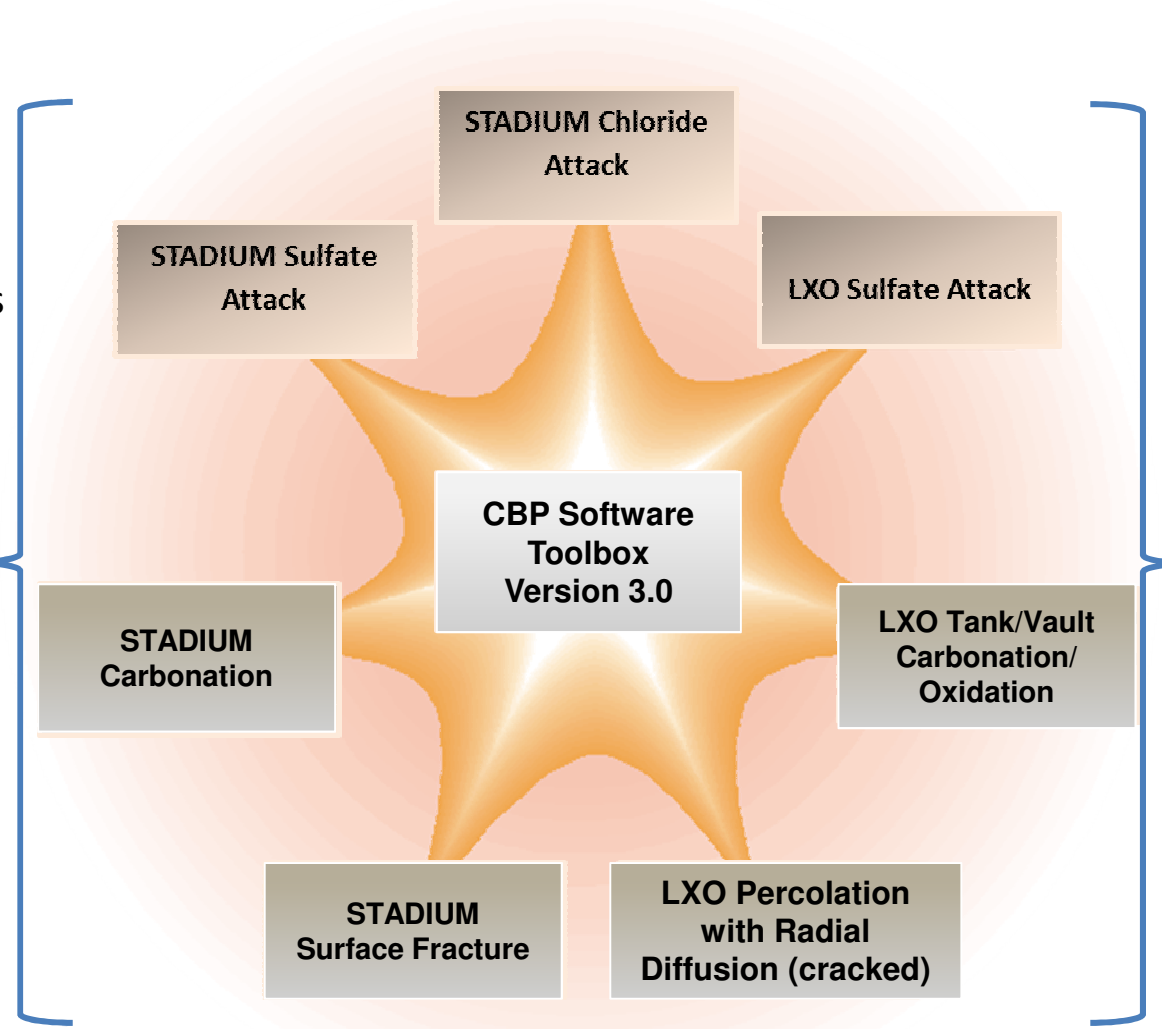
LeachXS/ORCHESTRA

- Leaching of major, trace & radionuclide constituents
- Chemical evolution (pH, redox, etc.)
- Transport (diffusion and advection), changes in pore structure
- Initial and evolving cracks and impact on transport

STADIUM Chloride Attack

STADIUM Sulfate Attack

LXO Sulfate Attack

CBP Software Toolbox Version 3.0

STADIUM Carbonation

LXO Tank/Vault Carbonation/ Oxidation

STADIUM Surface Fracture

LXO Percolation with Radial Diffusion (cracked)

LXO = LeachXS/ORCHESTRA

LeachXS Monolith Diffusion
Intact Material with Limited Cracking
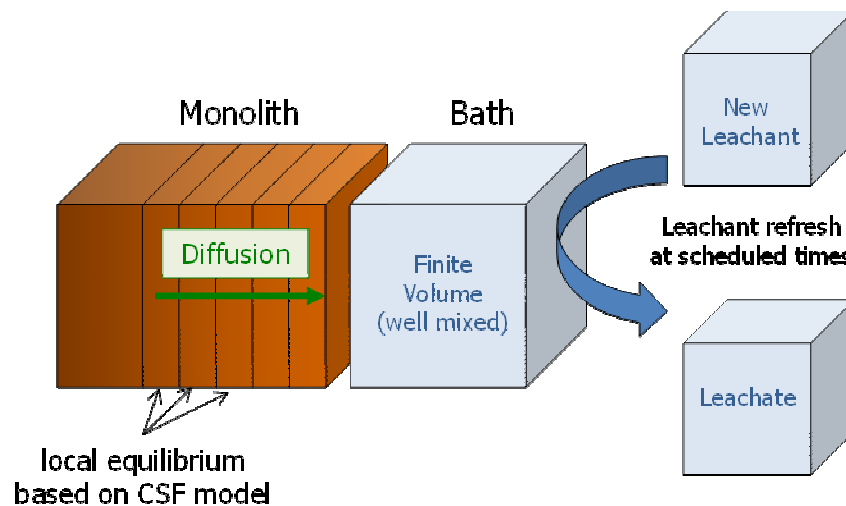
- Laboratory and field simulations
- Variable water contacting sequence, chemistry
- Saturated or unsaturated
- Carbonation and oxidation ingress (gas & liquid)
- Sulfate attack with leaching

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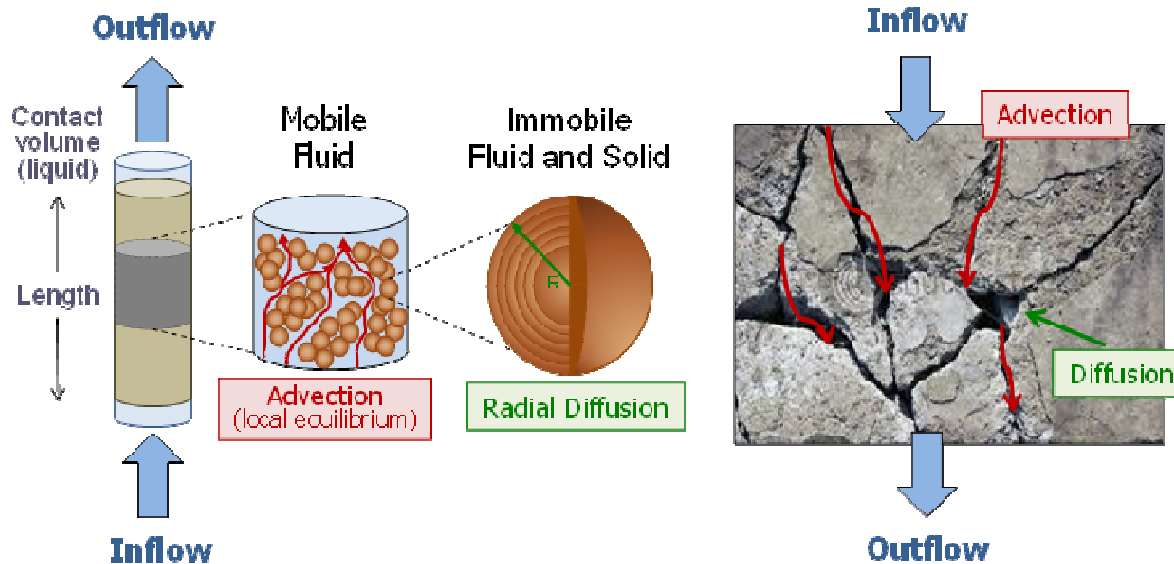
- Laboratory and field simulations
- Cracked materials or packed beds (e.g., wasteforms, tank closure)
- Effects of preferential flow
- Variable water flow rate, chemistry

Percolation with Mobile-Immobile Zones
Percolation through Rubblized Material
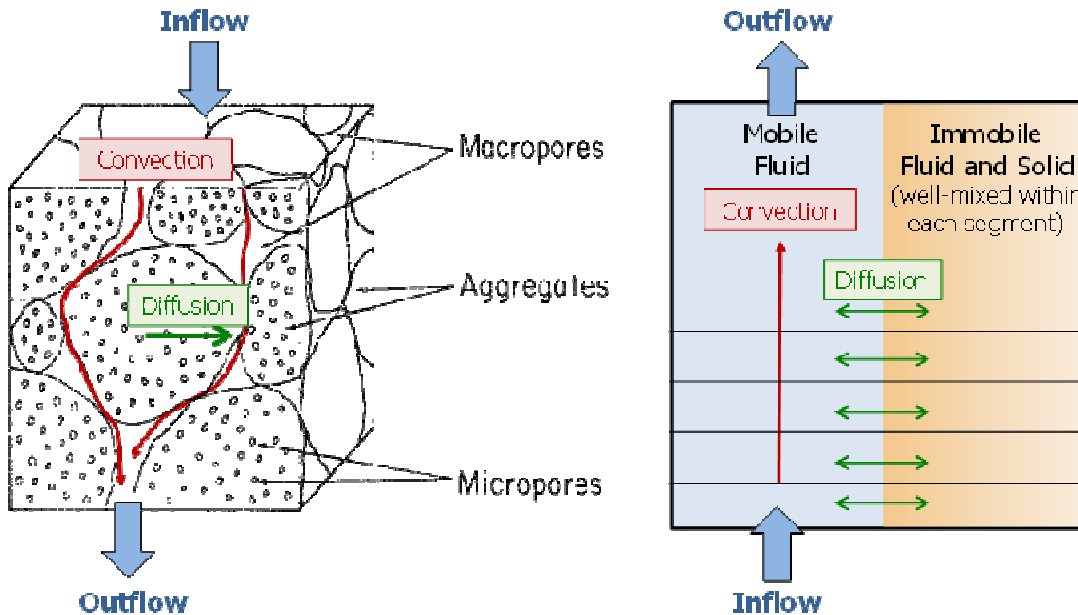
- Laboratory and field simulations

- Variable water flow rate, chemistry

- Effects of preferential flow (e.g., grouted materials, contaminated soils)

Software Program Highlights

- CBP Software Toolbox Version 3.0 with new and enhanced modules
  - Added Carbonation/Oxidation (LXO) – replaced Carbonation (LXO)
  - Enhanced Sulfate Attack (LXO & STADIUM)
  - Added Carbonation (STADIUM)
  - Added Surface Fracture (STADIUM)
  - Transport Properties (SRNL)
- Three CBP User Workshops Version 2.0 (~65 Attendees)
  - Hanford Site
  - NIST/NRC
  - Savannah River Site
- Emerging DOE issues identified at workshops and meetings incorporated into CBP Programs
  - ASR, dual mechanisms, acidic soil, mercury management

CBP Benefits: DOE Mission Direct Support

- DOE – Savannah River Field Office
  - Direct Saltstone PA Support *(SRNL-STI-2013-00118)*
  - CBP Software Toolbox Release and Training
  - Consulting on Saltstone Waste forms and Future Disposal Designs
    - Higher sulfate concentrations
    - Interior protective coatings
    - Experimental plans
  - Saltstone Oxidation Studies & Characterization
- DOE – Hanford Office of River Protection
  - CBP Software Toolbox Release and Training
  - Program review and consulting on Integrated Disposal Facility
  - Cast Stone Oxidation Studies & Characterization and Modeling

Release – late 2015

- SQA documentation consistent with NQA-1 and DOE Order 414.1D

- LXO Monolith w/carbonation, oxidation, leaching

- Enhancements for other LXO models

- STADIUM enhanced sulfate attack, carbonation, and surface fracture models

- Verification & validation for multiple models

CBP Software Toolbox Versions 3.0

CBP Software QA Summary

SRNL

FlowXL[a,b]

CBP Toolbox (GoldSim)[a]

CRESP-Vanderbilt/ ECN/NRG/HvdS

SIMCO Technologies

Mesh2D[a,b]

CBP DLL[a,b]
(Joint with VU)

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]
- 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.)

STADIUM Core[e]
- Chemical Equilibrium[d]
- Transport Solver

Characterization Methods[f]
- Mechanical properties
- Chloride resistance
- Potential for ASR
- Others

Characterized Materials
- SRS Vault concretes
- Standard concretes

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]

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)

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CBP Timeline FY12-18
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FY12 ACCOMPLISHMENTS
CBP Toolbox V-1.0/ Workshops
- STADIUM Sulfate Attack (SA)
- LXO Sulfate Attack

FY14 ACCOMPLISHMENTS 1
CBP Toolbox V-2.0/ Workshops
- LXO Carbonation
- LXO Dual Regime
- STADIUM Chloride
- CBP/ASCEM Integrated Demo Development

FY15 MILESTONE 1
CBP Toolbox V-3.0/ Workshops
- STADIUM Carbonation
- STADIUM SA Surf. Frac.
- LXO Oxidation& Gap Flow
- SRNL Transport Prop.
- Uncertainty Framework

FY15 MILESTONE 2
CBP/ASCEM
Demo – Phase 1

FY17 MILESTONE 1
CBP Toolbox V-5.0
- NIST CM Additions (SA & Carbonation)
- SRNL Tc Oxidation
- Alkali Silica Reaction (ASR)

FY17 MILESTONE 3
Exp. Studies
ASR Cont'd

FY17 MILESTONE 2
CBP/ASCEM
Demo – Phase 3

Timeline: 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018

FY14 ACCOMPLISHMENTS 2
Experimental Studies
- Tc Oxidation Leaching
- CM Phase Characterization

FY15 MILESTONE 3
Experimental Studies
- Tc Oxidation Rate
- Carbonation Rate
- Method Dev. for Hydraulic Cond. in Fractured Materials

FY16 MILESTONE 1
CBP Toolbox V-4.0
- NIST Cement. Microprobe (CM)
- STADIUM SA Variations
- SRNL Trans. Prop. & Flow
- LXO GAP Flow

FY16 MILESTONE 2
CBP/ASCEM
Demo – Phase 2

FY16 MILESTONE 3
Experimental Studies
- ASR
- Oxidation/carbonation

FY18 MILESTONE 1
CBP Toolbox V-6.0
- Dual Mechanisms
- NIST CM Enhancements
- Acidic Soil Exposure
- Uncertainty Framework

FY18 MILESTONE 2
CBP/ASCEM
Demo – Phase 4

FY18 MILESTONE 3
Experimental Studies
Acidic Soil Exposure Cont'd

Next Steps

- Complete Software Quality Assurance including V&V
  - LeachXS including Virtual Materials
  - ORCHESTRA including carbonation/oxidation model
  - STADIUM including carbonation and surface fracture models
- Examine relative effects of different extents of initial cracking
- Revise scenarios to reflect IDF PA sensitivity cases
- Carry out longer-term release simulations
- Uncertainty assessment (parameter and model uncertainty)