Conceptual Models and Approaches to Understanding Long Term Performance of Cementitous Waste Forms

Presented by

David S. Kosson, Ph.D., Professor

Vanderbilt University

Consortium for Risk Evaluation with Stakeholder Participation (CRESP)

To

Advisory Committee on Nuclear Waste

Nuclear Regulatory Commission

July 18, 2006

Collaborations

Vanderbilt University

D. Kosson, A. Garrabrants, S. Mahadevan, F. Sanchez, J. Clarke, S. Lopez

Netherlands Energy Research Centre (ECN)

H. van der Sloot, R.Comans, J.C.L. Meeussen, A. van Zomeren, P. Seignette

DHI (Denmark)

O. Hjelmar

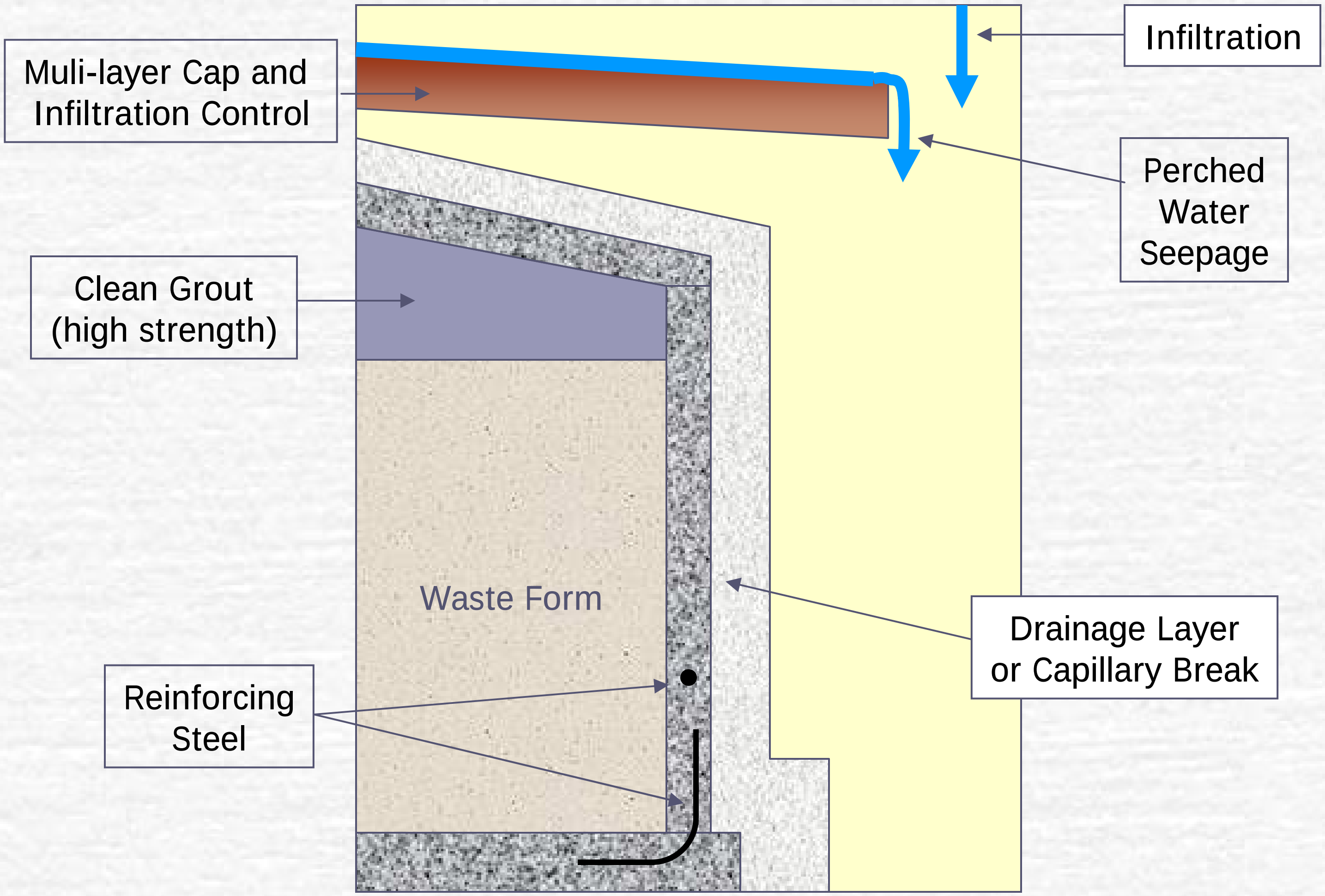
Savannah River National Lab

C. Langton, G. Flach

Pacific Northwest National Lab

J. Serne, T. Brouns

Generic Vault Disposal System



Motivation

Need for realistic (as practical) estimates of long-term constituent release for near-surface disposal of cementitious and other non-vitrified waste forms.

Applicability

- Performance Assessments and 3116 Determinations
  - HLW tank closure using grout
  - Disposal of saltstone & similar wastes at SRNL, INL, ORP
  - Primary and secondary waste streams from steam reforming
  - Secondary waste streams from vitrification
- Waste Treatment Acceptance Criteria
- Operational Controls
- Management of future wastes from reprocessing (GNEP)

Primary Constituents of Concern

- Long lived & Mobile: Tc-99, Np-237, Se-79, I-129, C-14, U,
- Mobile: Cs-137, Sr-90, Nitrate, tritium

Broader Questions

What basis should be used to

Define the appropriate type of waste form for specific wastes?

Estimate long-term waste form and disposal system performance?

Establish treatment (operational) criteria?

Define monitoring requirements that are pre-emptive to system failure?

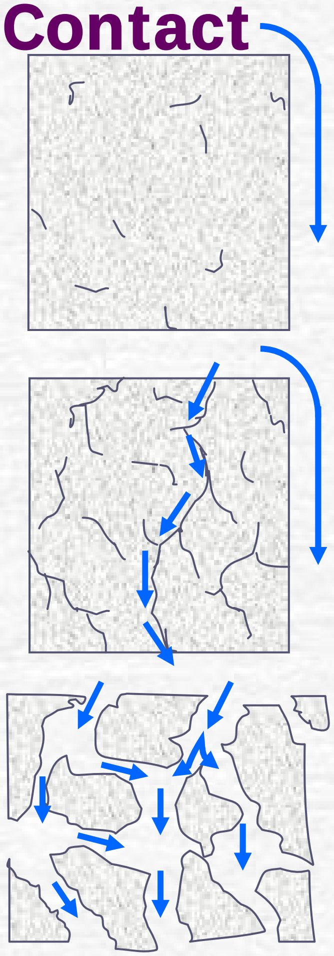
Constituent Release by Leaching

Primary Factors

- System Integrity
  - Engineered and Institutional Systems
- Waste Form Performance
  - Physical Integrity
  - Water Contact
  - Moisture Status
  - Oxidation Rates and Extent
  - Constituent Chemistry and Mass Transport

Processes and Impacts

Physical Integrity & Water Contact



Monolithic Matrix
- Flow-around
- Low interfacial area
- Diffusive release

Stressed Matrix
- Flow-around/through
- Higher interfacial area
- Diffusion-convection

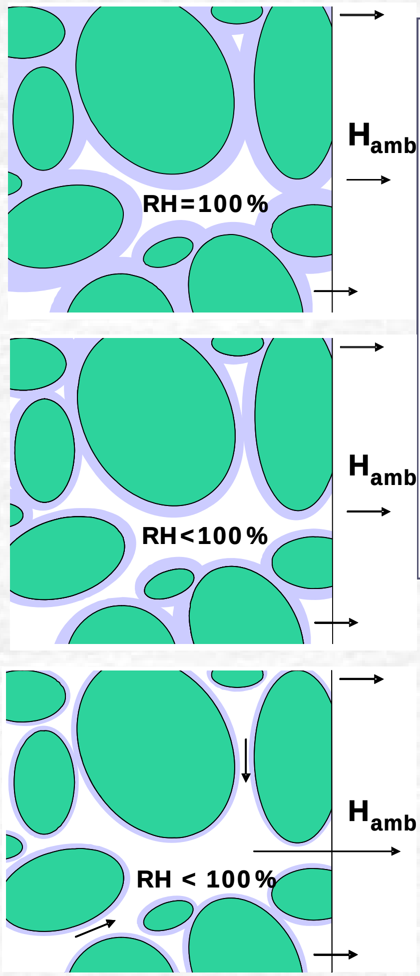
Spalled Matrix
- High permeability
- Very high interfacial area
- Equilibrium-based release

Conceptual Model
- Micro-cracks develop, increasing solid-liquid surface area
- Bridging of micro-cracks create macro-cracks
- Through-cracks develop over time, leading to convective flow
- Ultimate end state may be permeable matrix – equilibrium release

Impact
- Need to account for the sequence of physical states and rate of changes
- Influences chemical reactions and constituent release
- Both “intact” & “degraded” cases are not realistic

Processes and Impacts

Moisture Transport



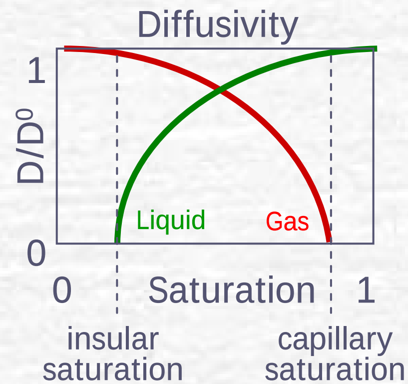
Full Saturation

Capillary Saturation
- Continuous Liquid
- Discontinuous Gas

Transition Zone
- Continuous Liquid
- Continuous Gas

Insular Saturation
- Discontinuous Liquid
- Continuous Gas

Completely Dry



Conceptual Model

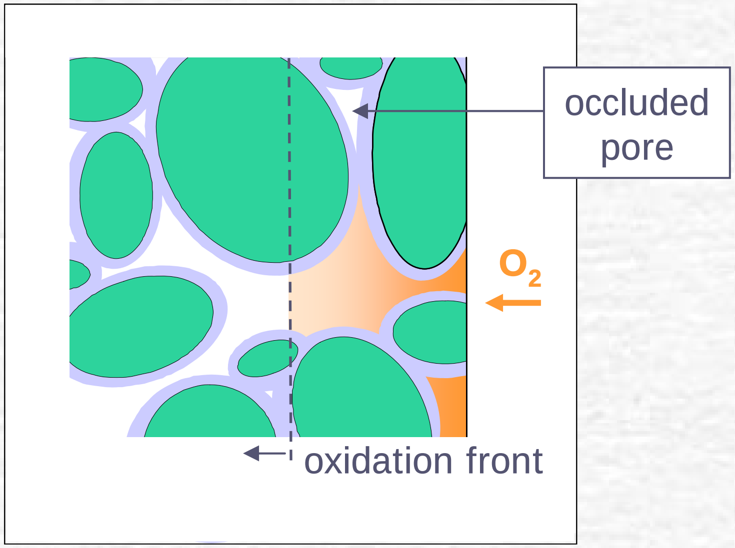
- Waste form consumes water via hydration reactions
- Moisture exchange w/environment
  - Evaporation/condensation
  - Capillary suction
  - Intermittent wetting (precipitation)
- Water content determines
  - Gaseous degradation processes (oxidation, carbonation)
  - Constituent diffusion pathways

Impact

- Diffusivities are not constant over moisture regime
- Fractional saturation
  - Increases the importance of gas phase transport & reactions
  - Decreases rate of liquid phase transport

Processes and Impacts

Oxidation
Rates and Extent



	Air	Water	Ratio (A/W)
D_{O2} [cm²/s]	0.21	0.000019	1.1E+04
Conc of O_2 [mole/L]	8.9E-03	2.6E-04	1.4E+01

(1) Wilke and Chang, 1955
(2) www.swbic.org/education/ env-engr/gastransfer/gastransf.html

Conceptual Model

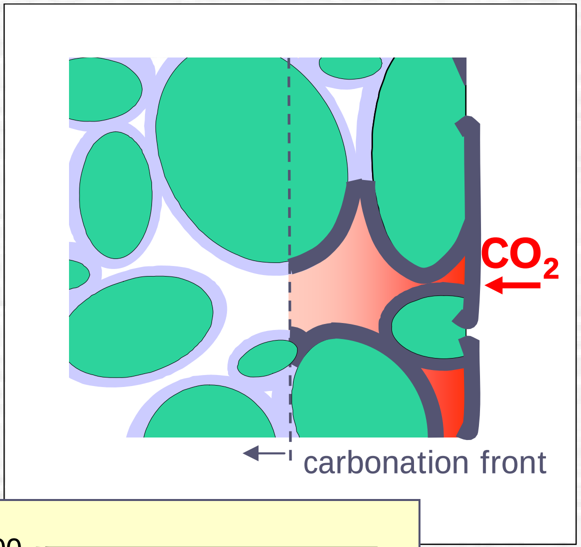
- Waste form pores – two phase system of gas and liquid; depends on moisture content (saturation)
- O_2 transport via gaseous diffusion may be important depending on saturation.
- Oxidation may lead to change in leaching behavior
  - Increased Tc-99 release; other constituents

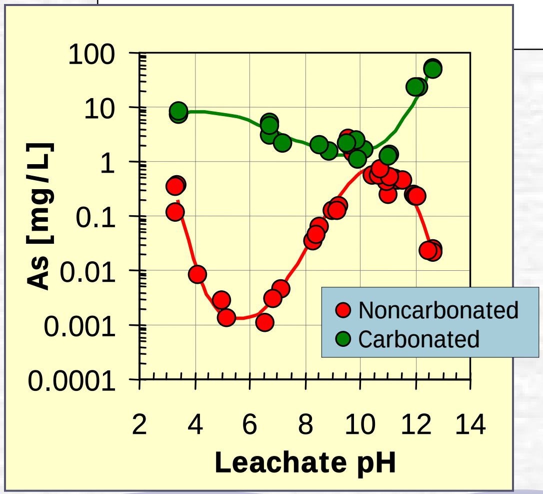
Impact

- Gas phase transport not considered
  - Flux of O_2 (gas) ~10^5 > liquid phase flux
- Impact to Tc-99 oxidation minimized

Processes and Impacts

Carbonation





Conceptual Model

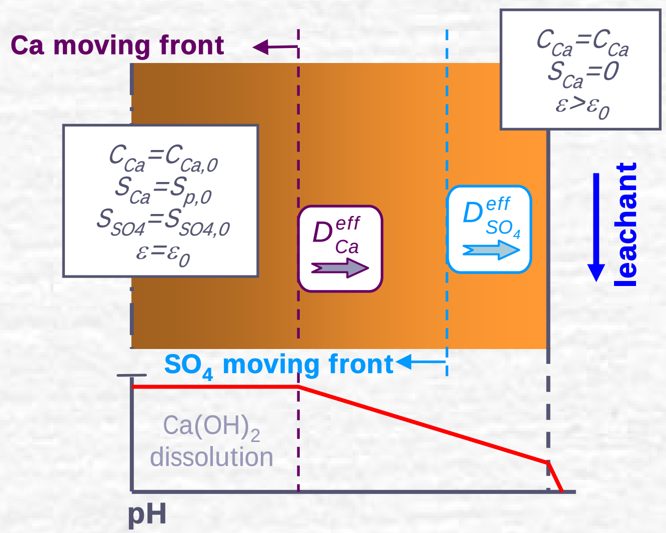
- $CO_3^{-2} + Ca^{+2} \rightarrow CaCO_3$ (s)
  - Gas phase diffusion of CO_2
  - Liquid phase diffusion of HCO_3^-
- Pore water pH decreased
  - Alters solubility of constituents (increase or decrease depending on species).
- Carbonation
  - Expansive precipitate – internal stress (cracking)
  - Pore blocking – increases diffusional resistance (decreases oxidation, release rates).
  - Extent and pore effects depend on waste form alkalinity and saturation

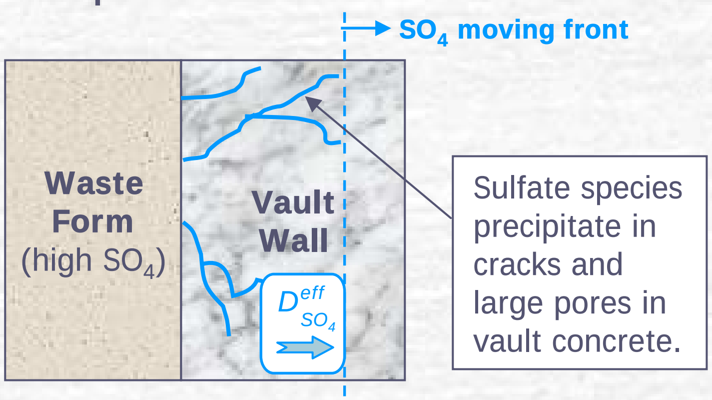
Impact

- Potential for speciation changes (e.g., As)
- Pore structure changes
- May have either positive (e.g., pore capping) or detrimental (i.e., increased solubility) impacts

Processes and Impacts

Leaching of Major Constituents





Conceptual Model

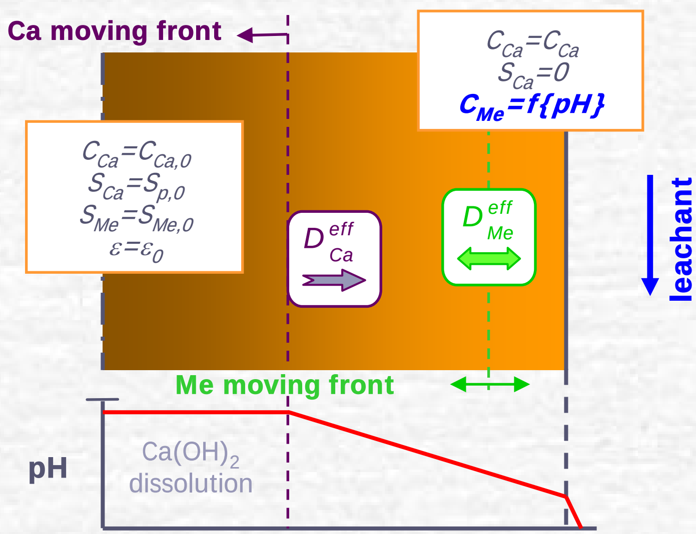
- Transport described by moving dissolution fronts
- Precipitation/reaction processes near external boundaries may significantly impact release (+ or -)
- Dissolution/diffusion of $Ca(OH)_2$ and CSH control pore water pH
  - pH gradients alter trace species release
- SO_4 leaching from waste into vault attacking concrete physical structure.
- Source of SO_4 may be waste or external environment

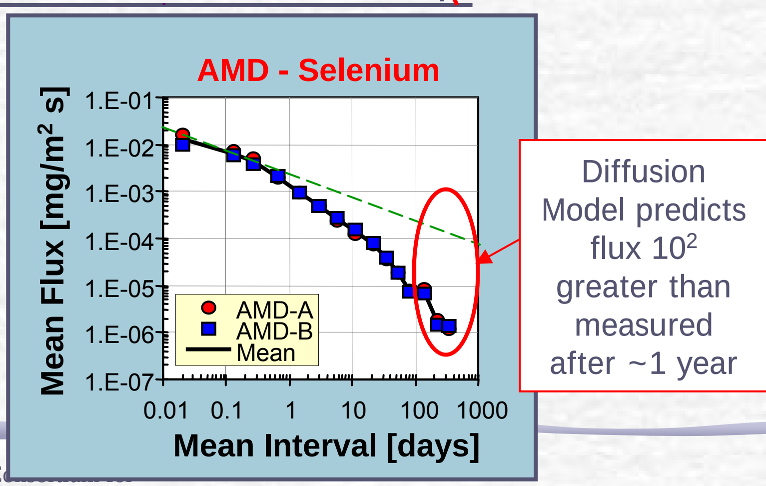
Impact

- Mass transport estimates do not reflect the dynamic chemistry and mineralogy of the waste form.
- Release rates and extents mechanistically different from simplified assumptions, limiting predictability.

Processes and Impacts

Leaching of Trace Constituents





Conceptual Model

- Release based on coupled chemistry and mass transport.
- Release dependent on:
  - Moisture conditions
  - pH gradients
  - Redox chemistry
  - Boundary layer formation

Impact

- Performance assessments may grossly over- or under-predict release

Integrated Long-Term Degradation

Chemical degradation and physical stress effects are coupled and integrated.

Physical stress

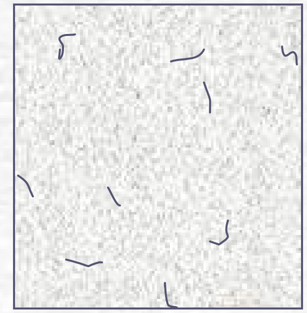
- Cyclic loading
- Flexural bending
- Drying shrinkage
- Seismic events
- Settlement

Chemical degradation

- Oxidation
- Leaching
- Expansive reactions
  - Carbonation
  - Sulfate attack
  - Rebar corrosion

Microcracks

- Increase porosity
- Increase interaction pore water/surface



Through-cracks

- Preferential flow path
- Diffusive and convective release
- Loss of strength

Spalling

- Loss of cohesiveness
- Two body problem
- Eventual release from "granular" material

Current Studies on Secondary Waste from ORP

Motivation

- Tc-99, I-129 in secondary wastes from vitrification

Objective

- Leaching assessment of reducing grout for secondary waste treatment.
- Comparison with "ANS16.1-type" testing in synthetic ground water.

Reducing Grout

- Ground Steel Slag 43 wt%
- Class F Fly Ash 42
- OPC 7
- DI Water 7

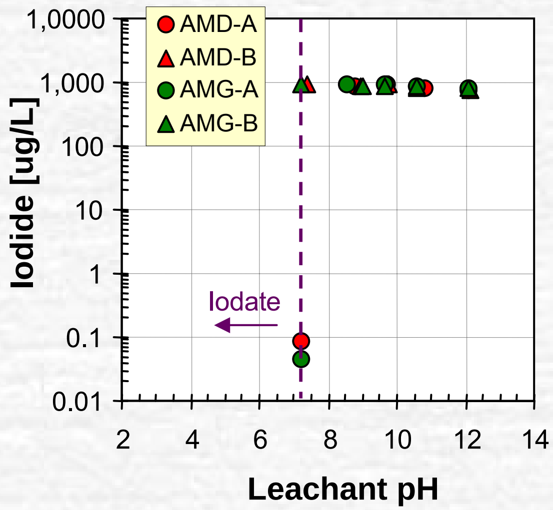
Synthetic Hanford Groundwater

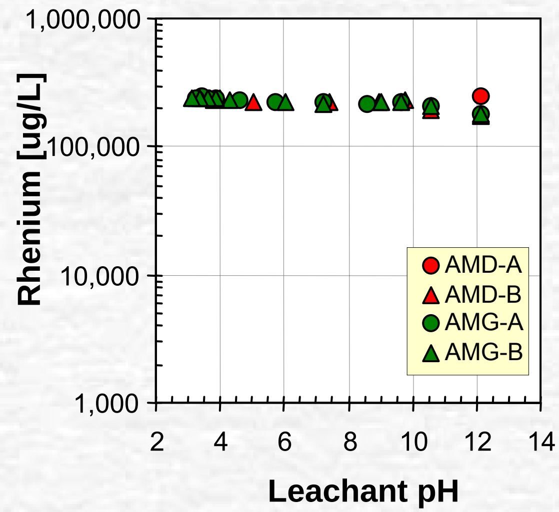
- $CaSO_4$ 1.20 mmol/L
- $NaHCO_3$ 1.04
- $Mg(HCO_3)_2$ 0.62
- $CaCl_2$ 0.34
- $KHCO_3$ 0.19
- $Ca(HCO_3)_2$ 0.18

Contaminants in Reducing Grout

	mg/kg	Added As
Ag	243	$AgNO_3$
As(V)	1000	$Na_2HAsO_4 \cdot 7H_2O$
Ba	500	$Ba(NO_3)_2$
Cd	1000	$Cd(NO_3)_2 \cdot 4H_2O$
Cu	1000	$Cu(NO_3)_2 \cdot 2.5H_2O$
Cs	1000	CsCl
I	1214	NaI
Pb	1000	$Pb(NO_3)_2$
Re	971	$KReO_4$
Sb	952	Sb_2O_3
Se	751	$KSeO_4$
Zn	1000	$Zn(NO_3)_2$

Equilibrium – Trace Species

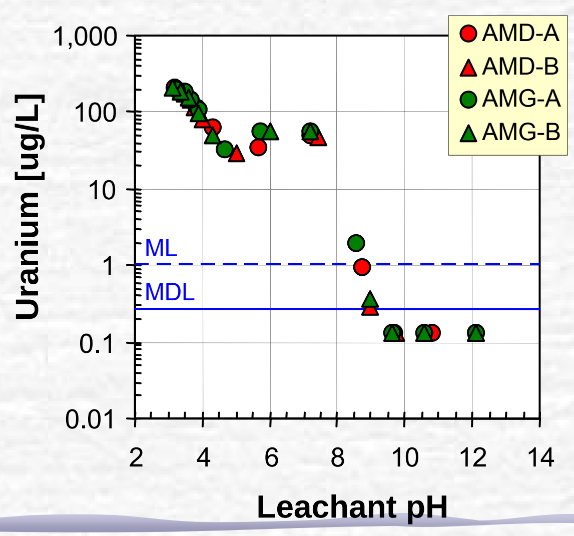


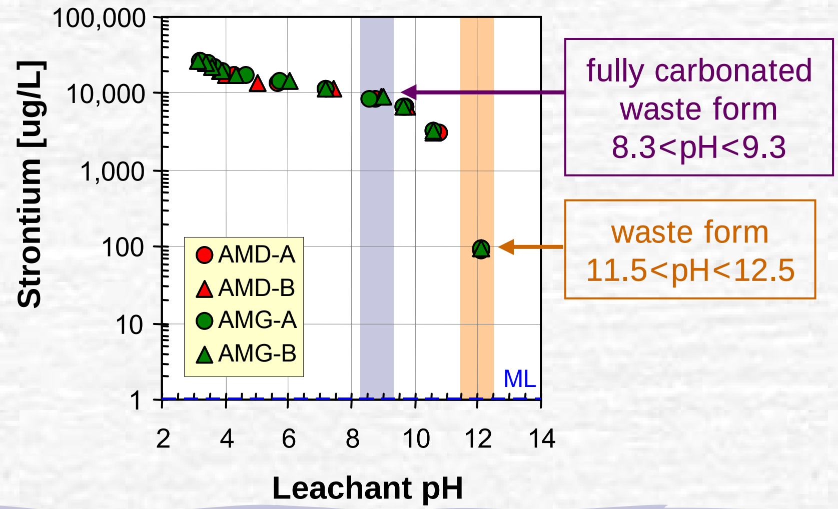


Solid-Liquid Partitioning

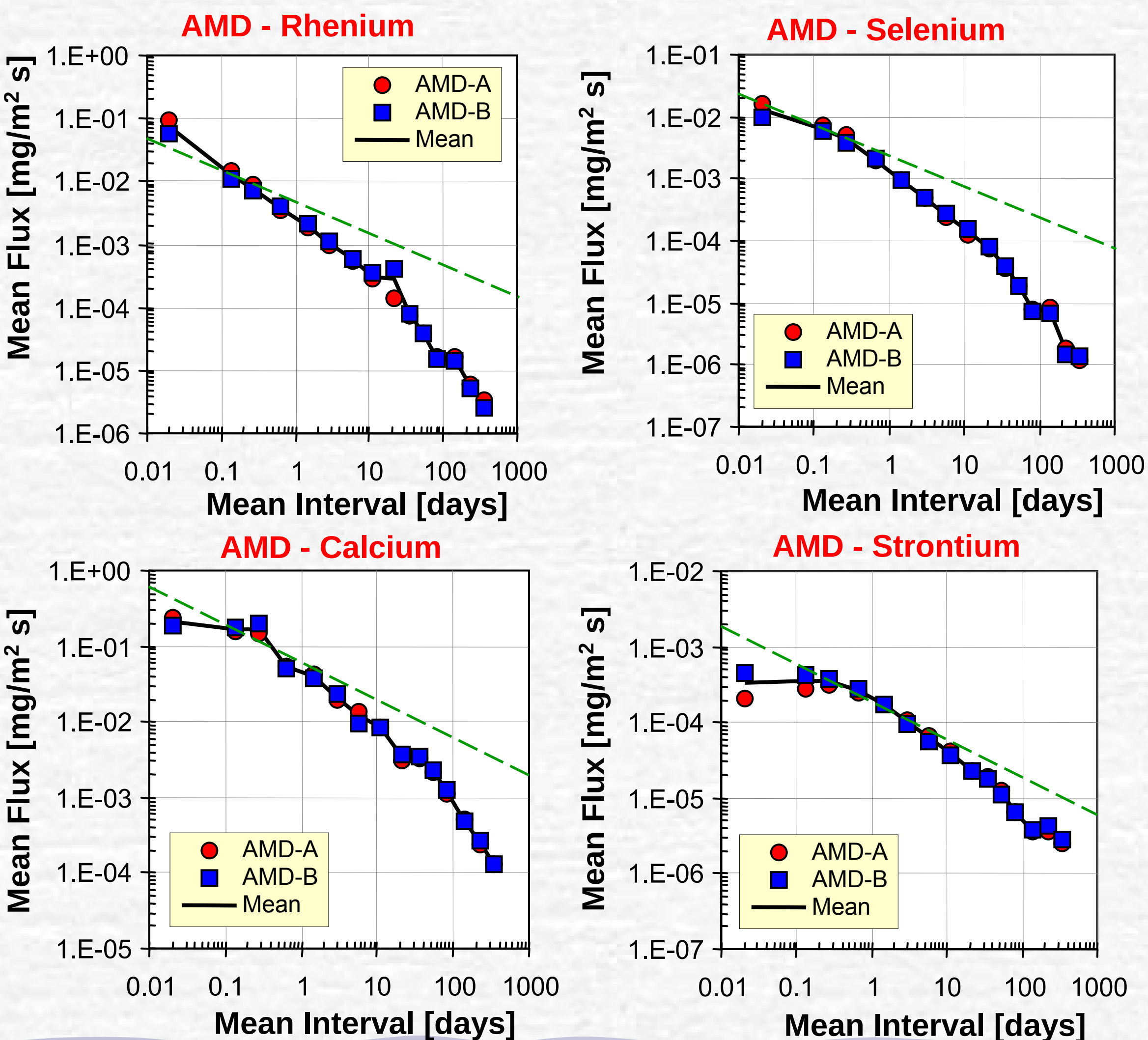
Comparison

- AMD – DI Water
- AMG – Synthetic Hanford Ground Water





Mass Transport Tests



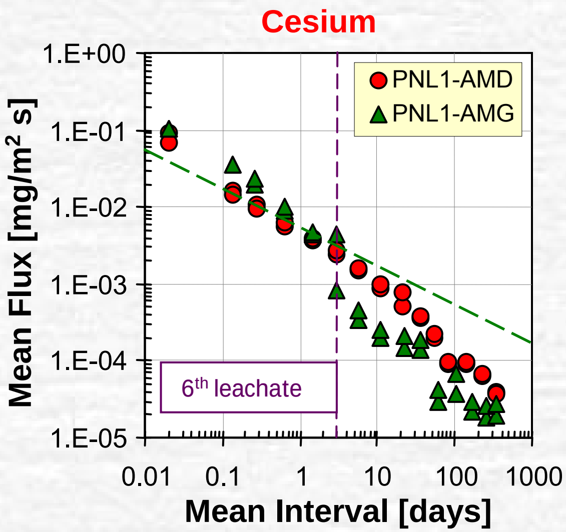
MT001 Test

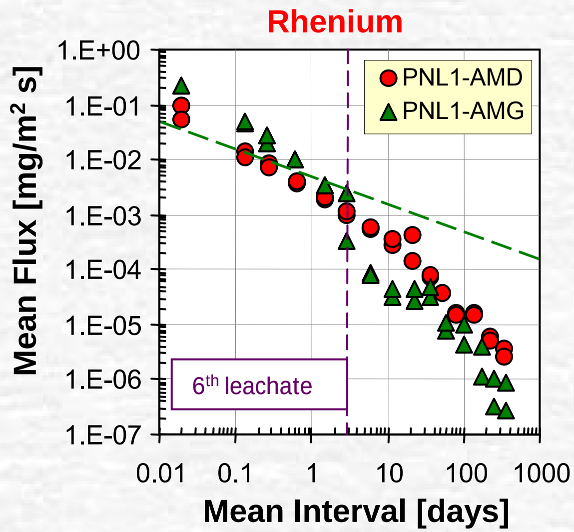
- Tank Leaching in DI Water
- Constituent Flux
- Constituent Release

Comparison

- AMD – DI Water
- Flux @ constant diffusivity (green dash)

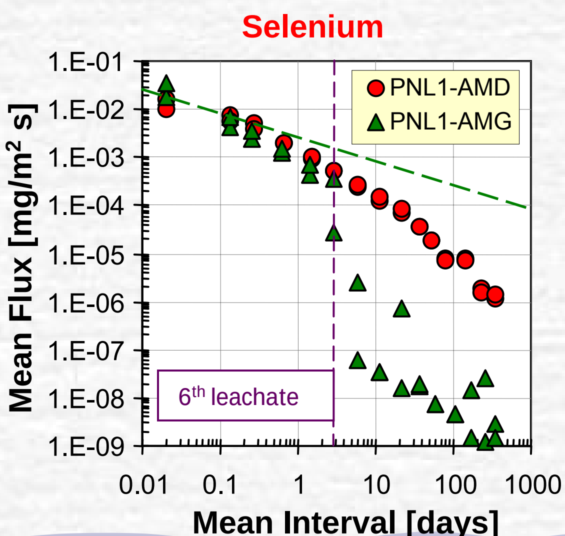
Synthetic Groundwater

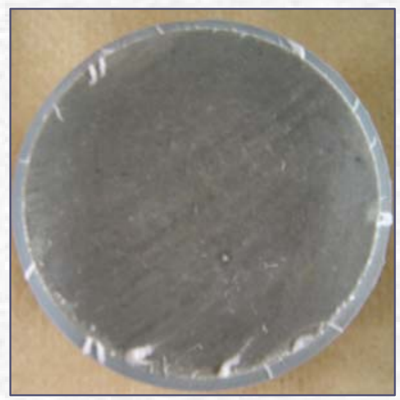




MT001 Test Comparison

- AMD – DI Water
- AMG – Synthetic Hanford Groundwater



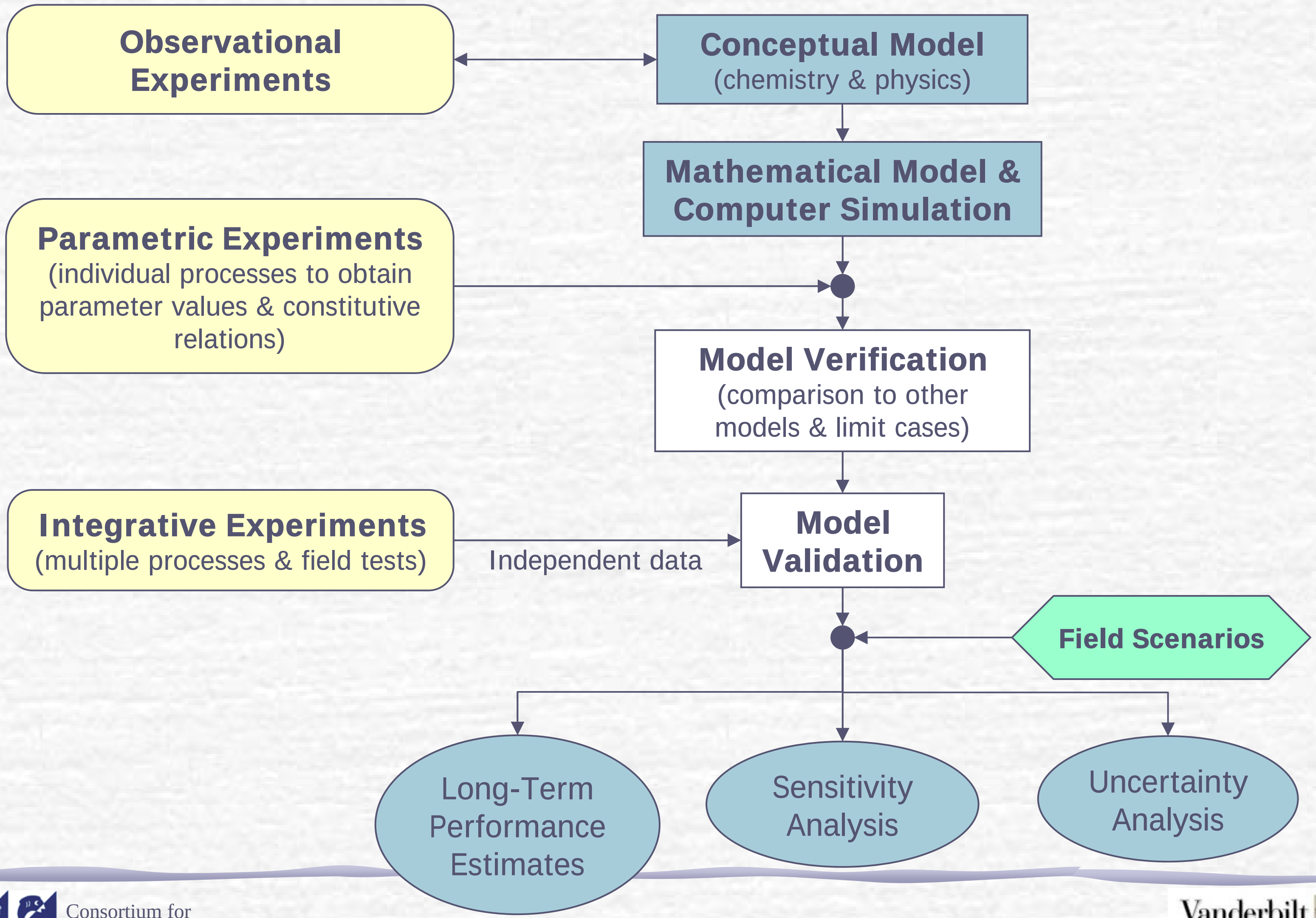


Precipitate on sample AMG-B after 6th leaching interval

Hanford Groundwater

- $CaSO_4$ 1.20 mmol/L
- $NaHCO_3$ 1.04
- $Mg(HCO_3)_2$ 0.62
- $CaCl_2$ 0.34
- $KHCO_3$ 0.19
- $Ca(HCO_3)_2$ 0.18

Process- and Mechanism-Based Experimentation & Modeling



Overarching Framework

(Kosson, van der Sloot, Sanchez & Garrabrants, 2002, Environ. Engr. Sci., 19, 159-203)

Measure intrinsic leaching characteristics of material (aqueous-solid partitioning (pH and LS); release kinetics)

- Batch extractions & tank leaching (monoliths)
- Constituent fraction readily leached
- Controlling mechanism for release (mineral dissolution and solubility, solid phase adsorption, aqueous phase complexation)
- Release kinetics for mass transfer parameters

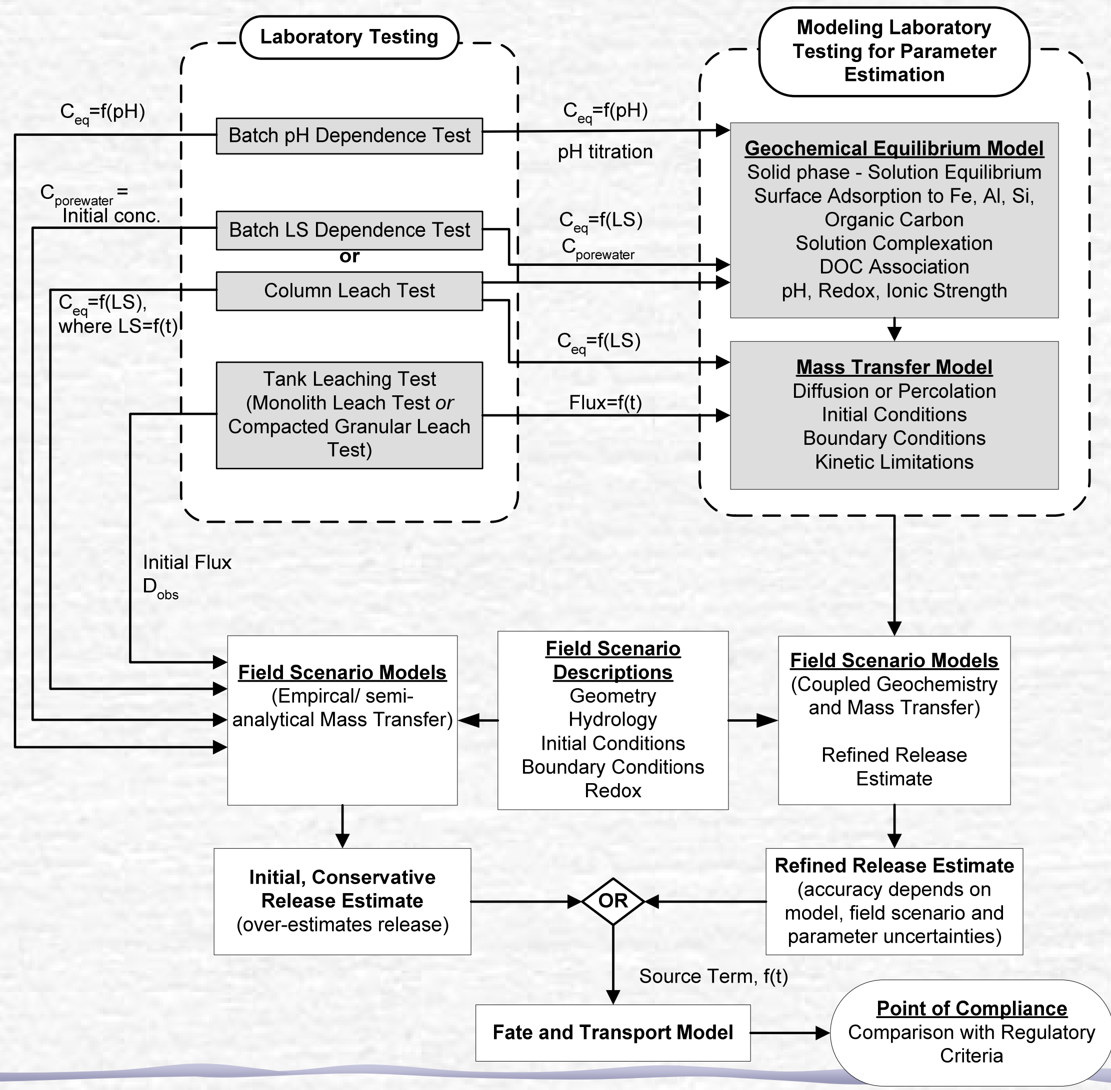
Evaluate release in the context of field scenario

- External influencing factors such as carbonation, oxidation
- Hydrology
- Mineralogical changes

Use geochemical speciation and mass transfer models to estimate release for alternative scenarios

- Model complexity to match information needs
- Many scenarios can be evaluated from single data set

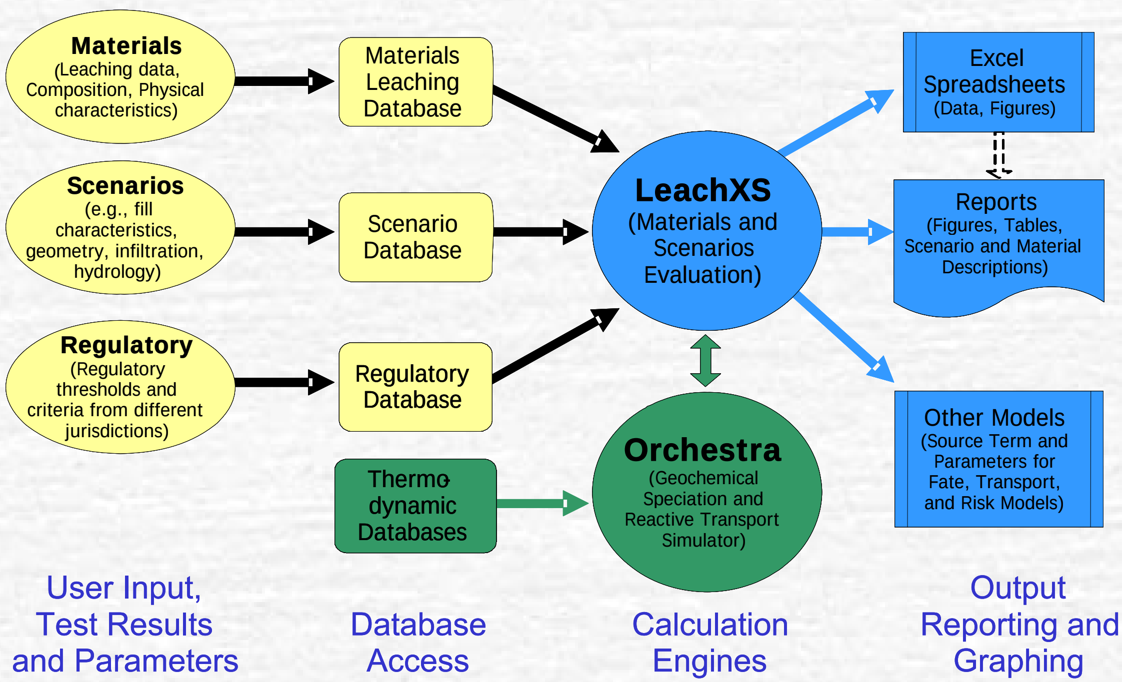
Integrated Use of Testing and Simulation



LeachXS

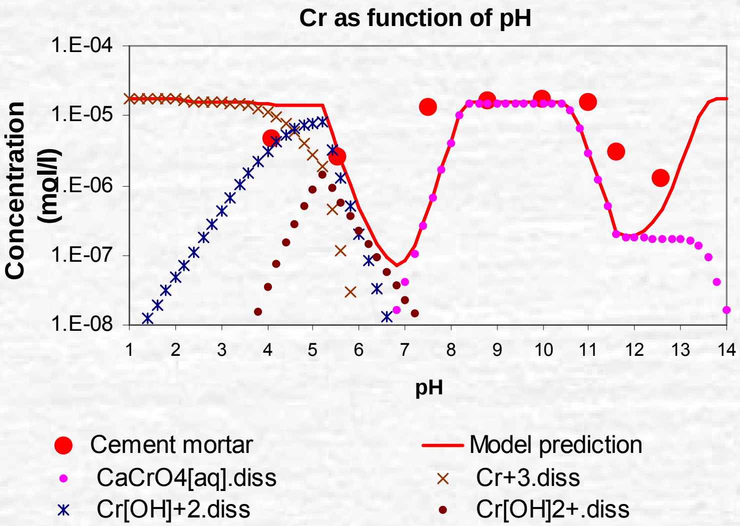
Software-based system for evaluating leaching

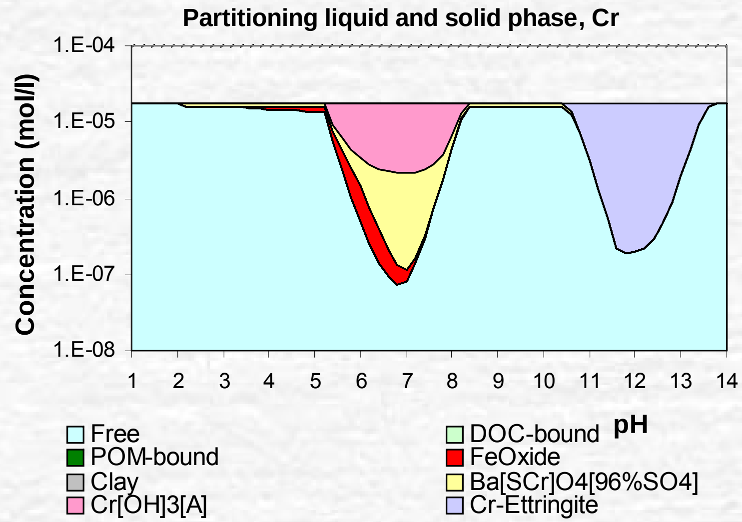
- Incorporates multiple processes and system configurations
- Data management/interpretation
- Geochemical analysis via ORCHESTRA (Meeussen, 2003)
- Database of material leaching information

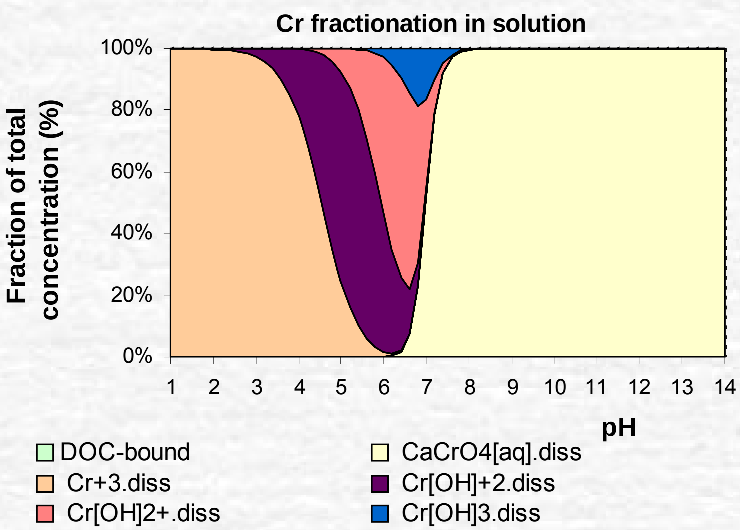


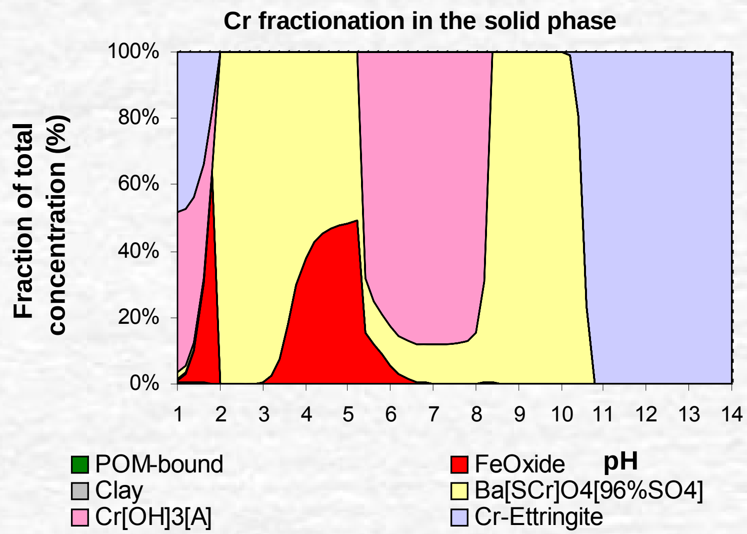
LEACH XS

CHROMIUM SPECIATION IN MORTAR AND WATER



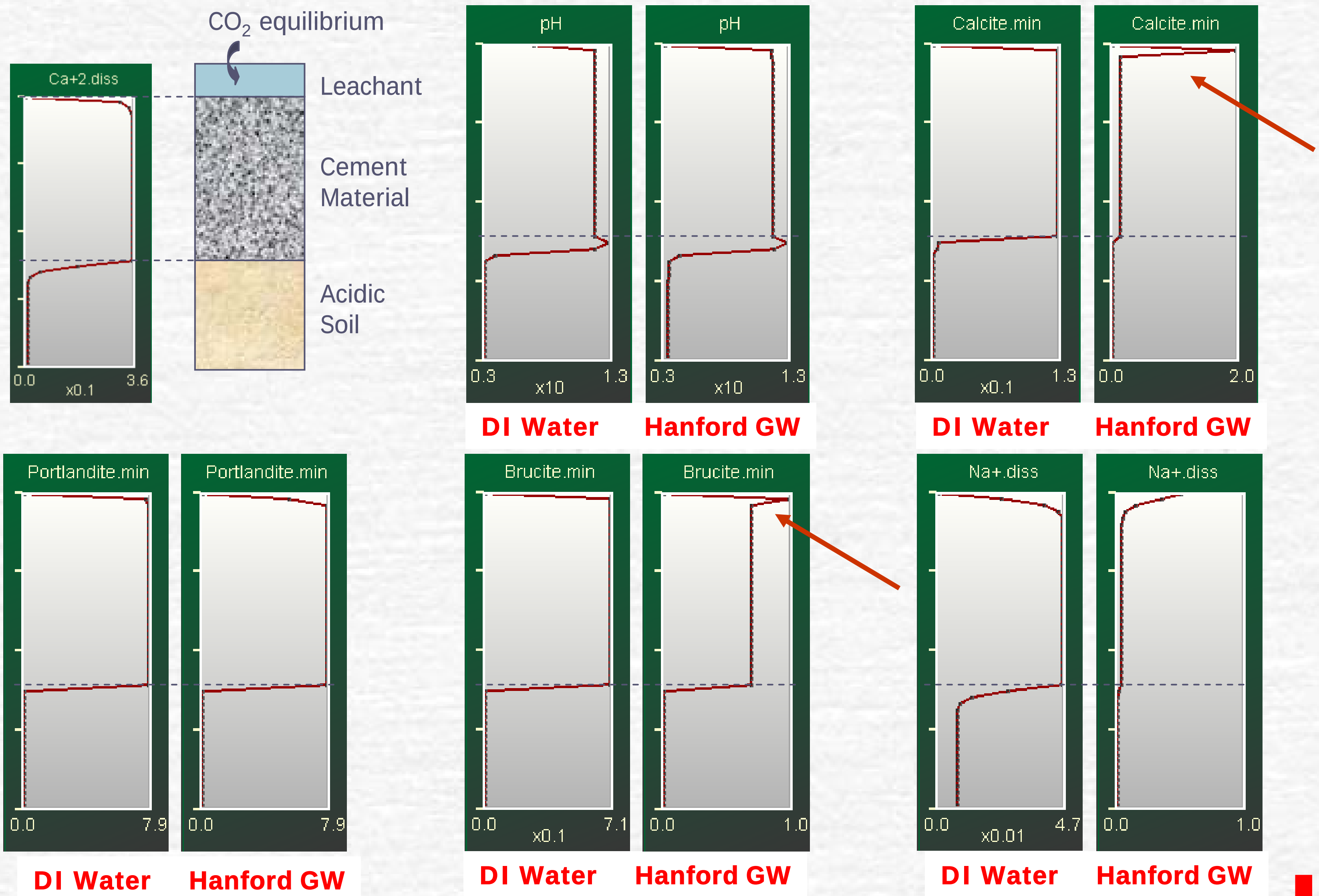




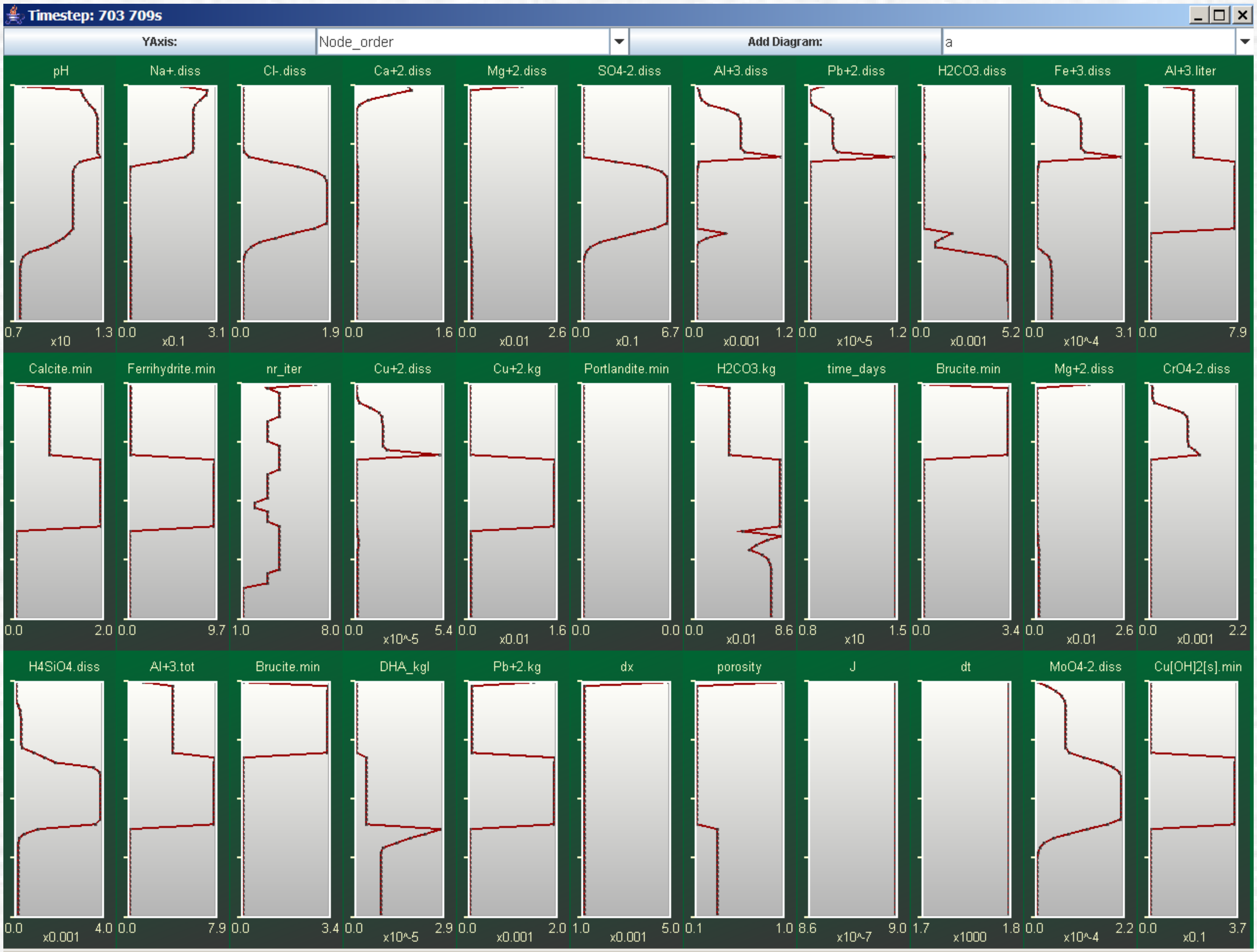


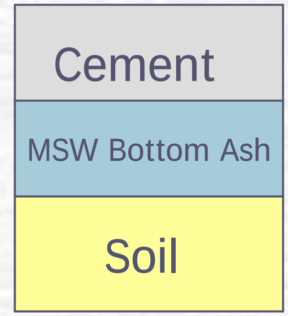
LXS EACH

Leachant Simulation – Boundary Effects



MODELLING OF 3 LAYER SYSTEM WITH FULL CHEMICAL SPECIATION AND TRANSPORT





Suggested Path Forward

Process of continuous improvement, such that assessments incorporate "state of the art" understanding to extent practical

- Important for current assessments and future nuclear waste management (legacy and future wastes)
- Need to define short-term and long-term needs

Experimental studies coupled with model development and validation

- Formation/effect of boundary layers (e.g., $CaCO_3$, oxidized layer)
- Moisture transport and status
- Oxidation rates
- Full geochemical model (equilibrium & mass transfer) for key systems
- Physical changes considering key geochemistry and mass transfer

Conclusions

Significant processes are not included in current DOE performance evaluations that can have major impacts constituent release.

It is important to have a more robust system understanding and model for near-term and longer-term DOE waste management decisions.

CRESP and SRNL, along with others, are currently working together to provide the needed evaluation system components.