Conceptual Models and Approaches to Estimating Long-term Contaminant Release from Near Surface Disposal of Cementitious and Other Waste Forms

Presented by

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Collaborations

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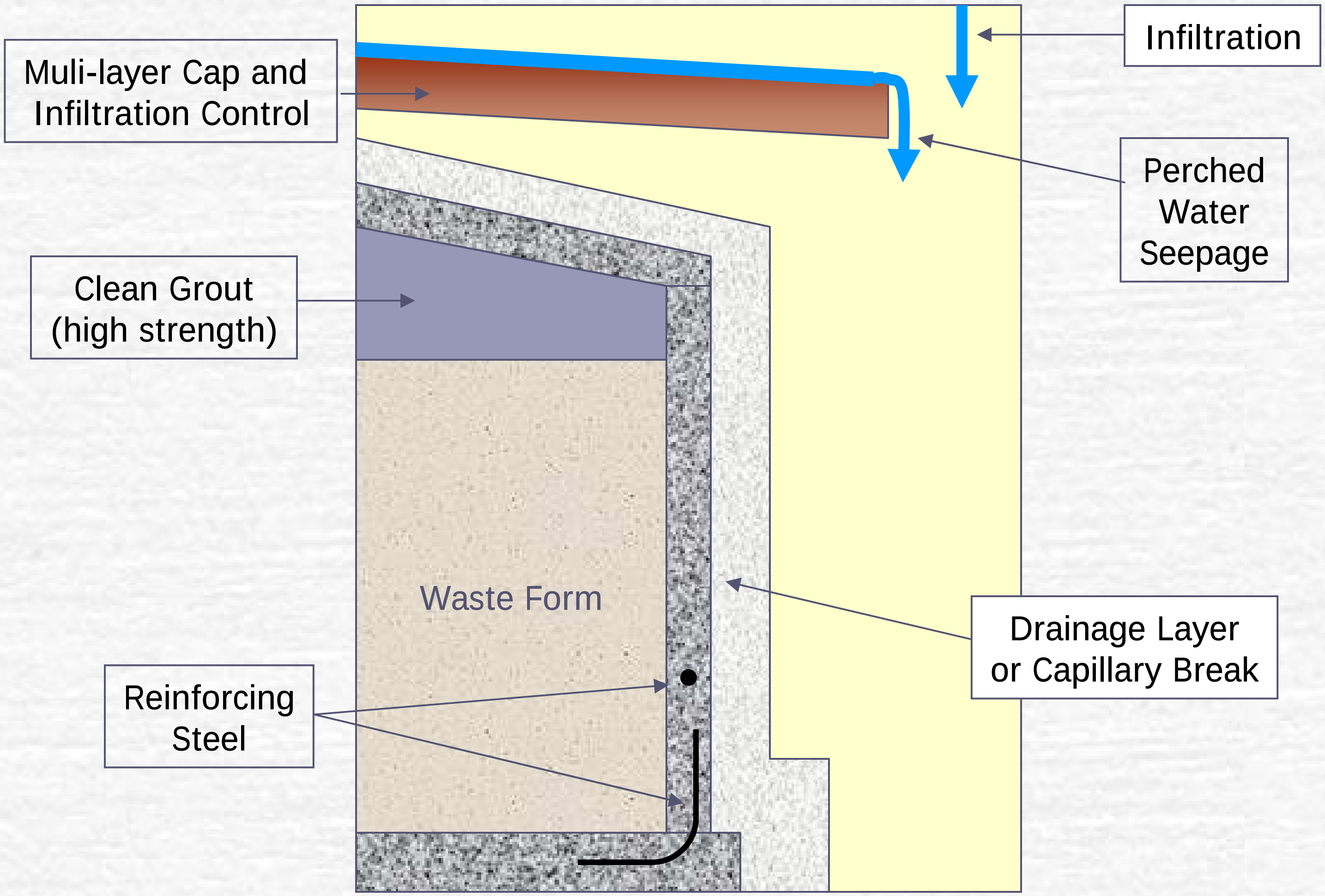
Generic Disposal System



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

Primary Constituents of Concern

- Tc-99, Np-237, Se-79, I-129, C-14, U, Cs-137, others

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?

Applicable to

- Waste forms for low activity wastes (SRNL, INL, ORP)
- Tank closures
- In-situ grouting
- Management of future wastes from reprocessing (GNEP)

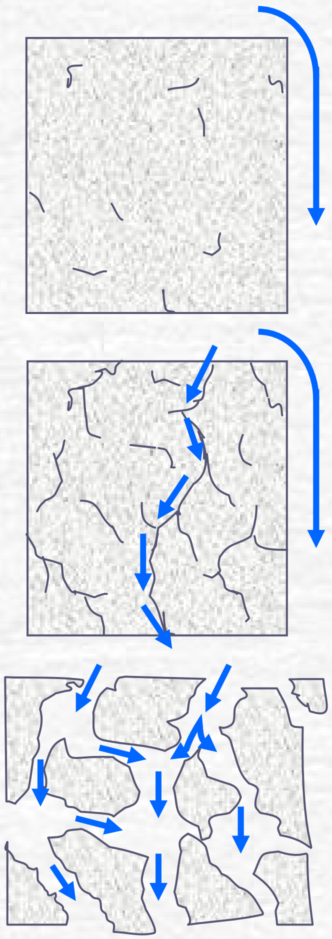
Constituent Release

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

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

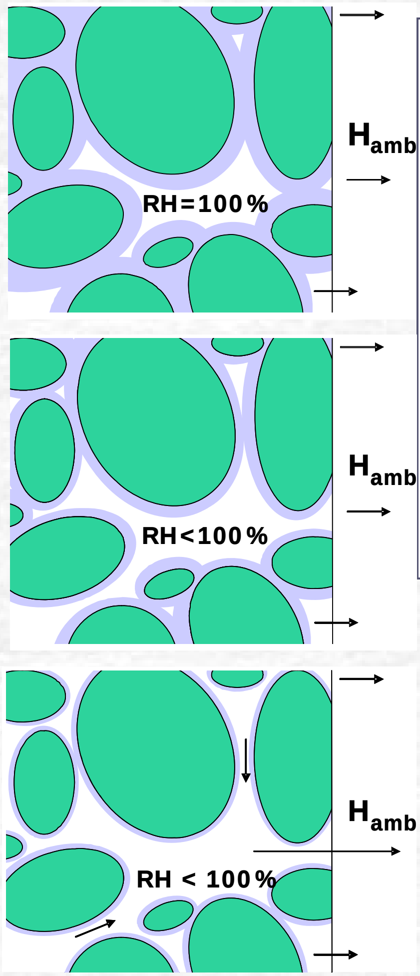
Impact
- Missing evolution of a crack network tied to water contact
- Both “intact” & “degraded” cases are not realistic

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

Current Assumptions and Limitations (DOE)
- Case 1: Waste form is intact for all time
- Case 2: Waste form has evenly-spaced through-cracks at beginning of assessment

Processes and Impacts

Moisture Transport



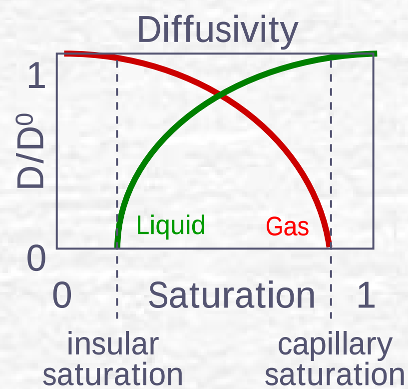
Full Saturation

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

Current Assumptions and Limitations (DOE)

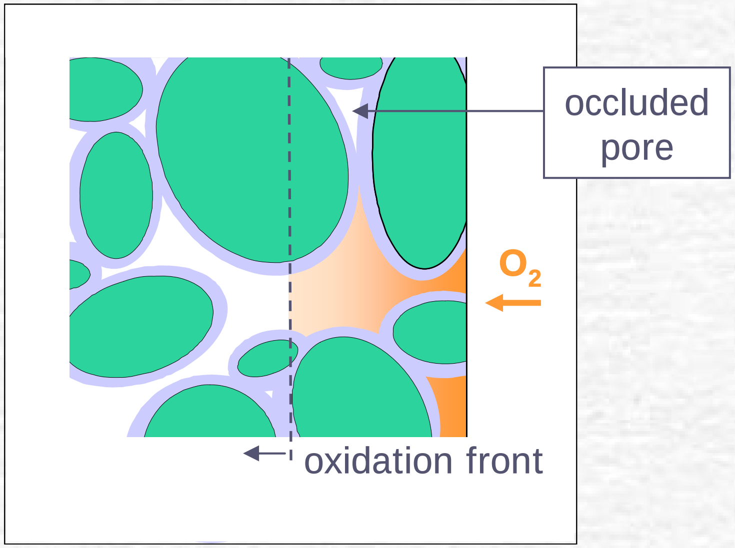
- Waste form remains saturated
  - Gas phase reactions limited to external surfaces

Impact

- Diffusivities are not constant over moisture regime

Processes and Impacts

Oxidation
Rates and Extent



	Air	Water	Ratio (A/W)
D_{O2} [cm²/s] (1)	0.21	0.000019	1.1E+04
Conc of O_2 [%] (2)	21	0.00052	4.0.E+04

(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
- O_2 transport via gas is dominant.
- Oxidation may lead to change in leaching behavior
  - Increased Tc-99 release

Current Assumptions and Limitations (DOE)

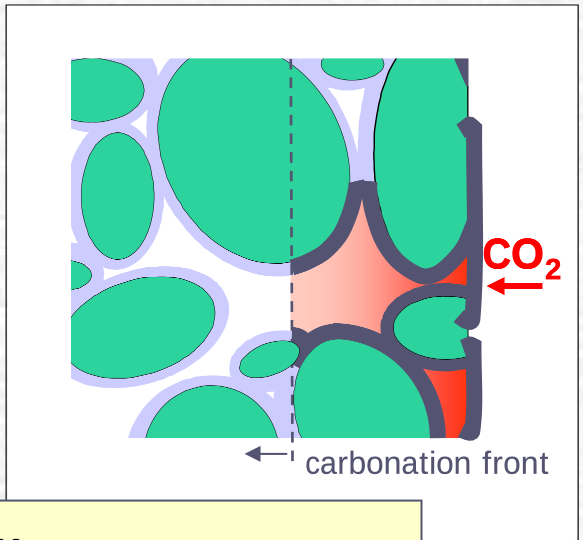
- O_2 transport via liquid only
- Instantaneous reaction with O_2 leading to release

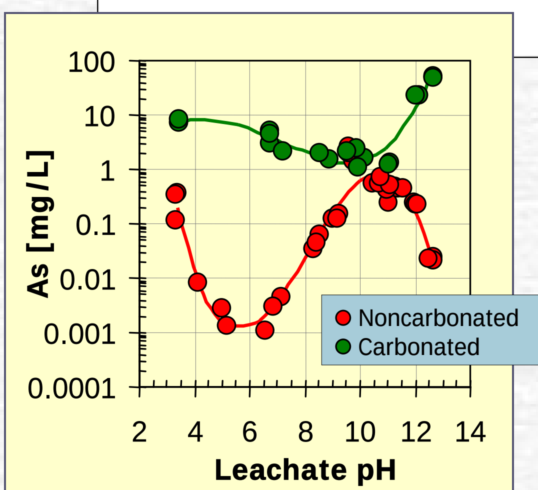
Impact

- Gas phase transport not considered
  - Flux of O_2 (gas) ~10^8 > 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.
- Carbonation
  - Increases mineral dissolution
  - Expansive precipitate – internal stress (cracking)
  - Pore blocking – increases diffusional resistance (decreases oxidation, release rates).

Impact

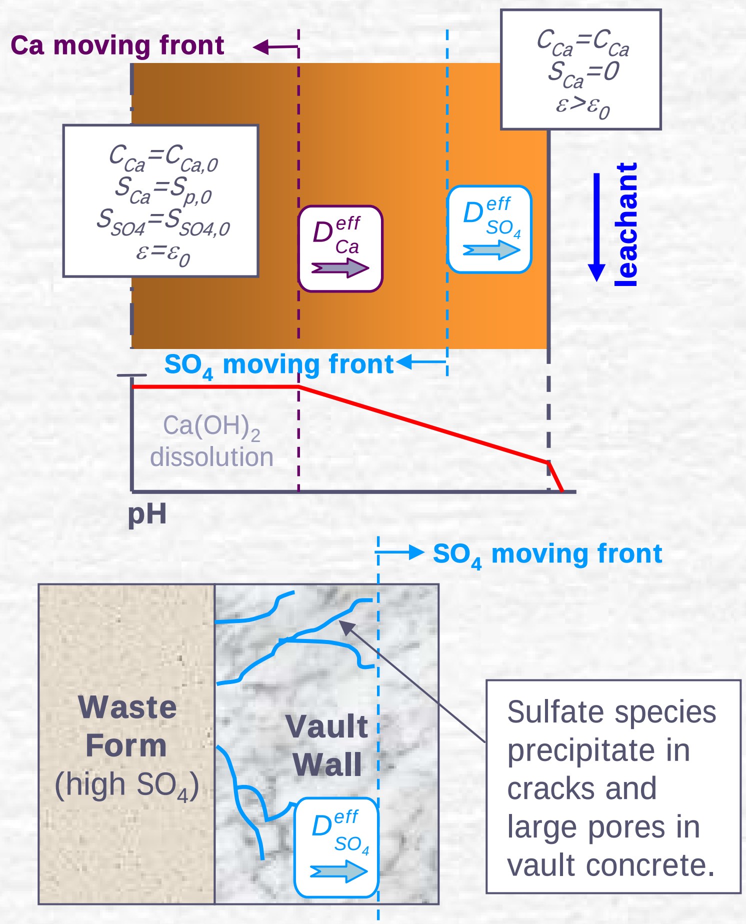
- Rate calculation does not account for CO_2 transport
- Potential for speciation changes (e.g., As)
- Pore structure changes

Current Assumptions and Limitations (DOE)

- CO_3 transport via liquid only
- Carbonation causes cracking which increases permeability

Processes and Impacts

Leaching of Major Constituents



Conceptual Model

- Transport described by moving dissolution fronts
- 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.

Current Assumptions and Limitations (DOE)

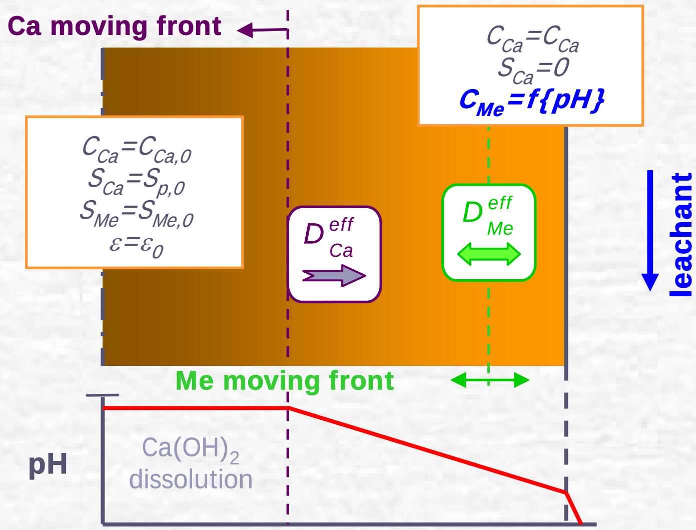
- Simple mass transport models
- Nature of and potential for sulfate attack from waste is not considered

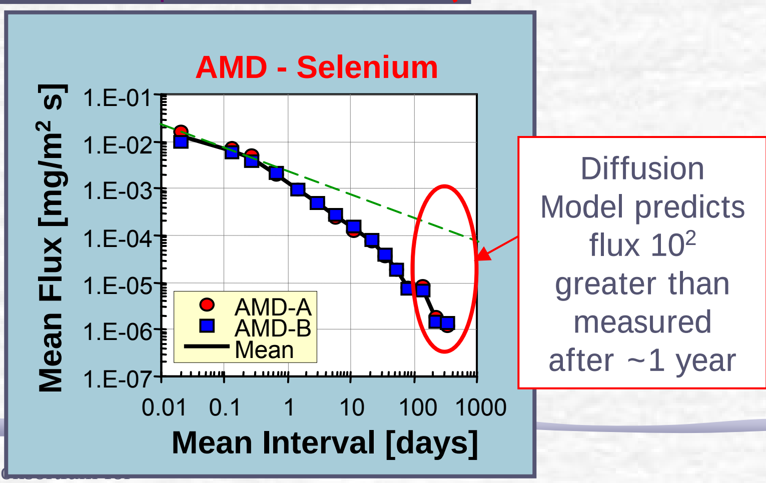
Impact

- Mass transport estimates do not reflect the dynamic chemistry and mineralogy of the waste form

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

Current Assumptions and Limitations (DOE)

- Simplified mass transport models
- WACs and projections based on TCLP and ANS-16.1
  - Constant D_{eff} (space and time)
  - Unrealistic release environment

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

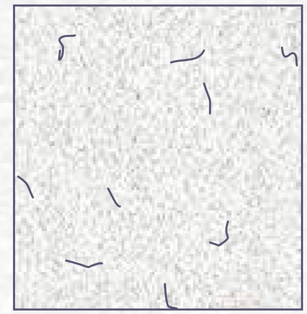
- Cyclic loading
- Flexural bending
- Drying shrinkage
- Seismic events
- Settlement

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

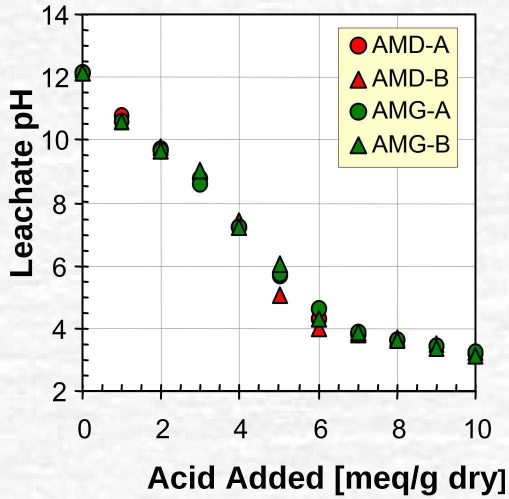
Synthetic Hanford Groundwater

$CaSO_4$	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 – Major Species

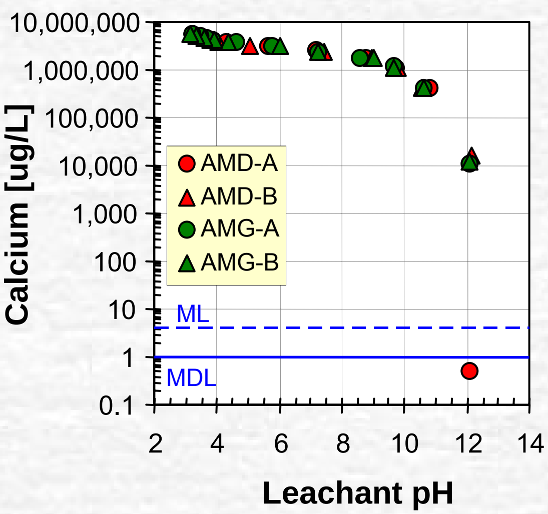


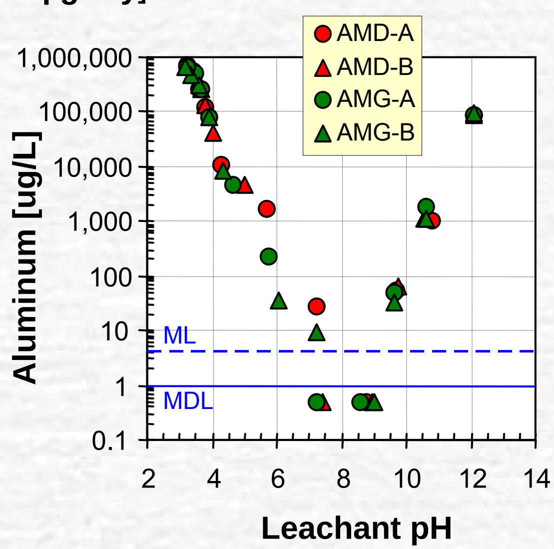
SR002 Test

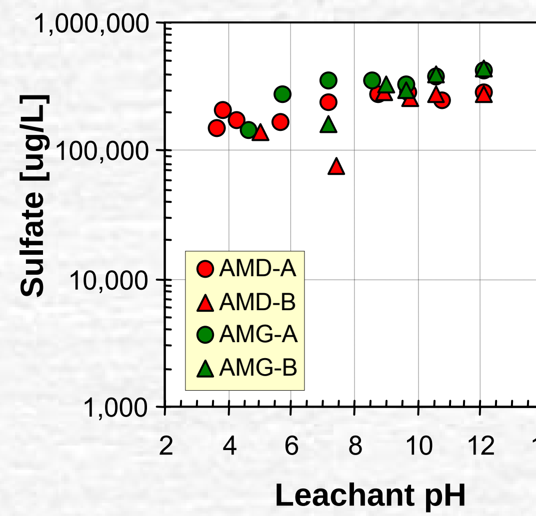
- Titration curve of material
- Solid-liquid partitioning (solubility & release)
- pH-dependence of species

Comparison

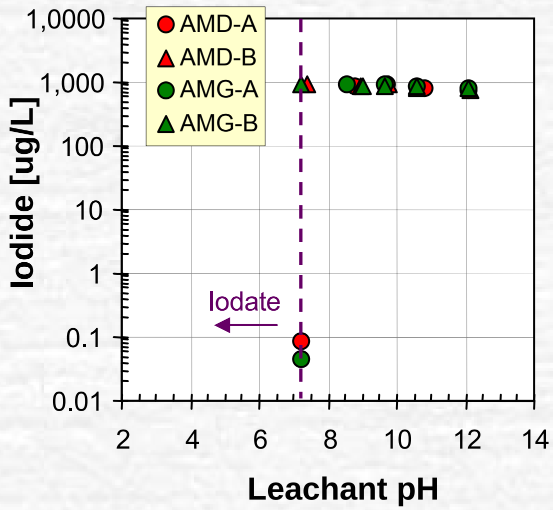
- AMD – DI Water
- AMG – Synthetic Hanford Ground Water

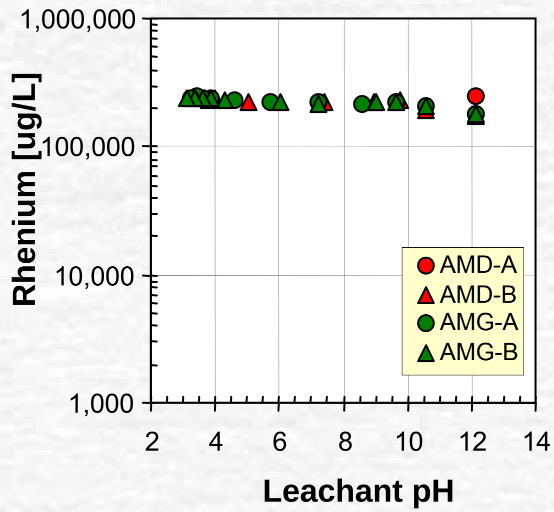


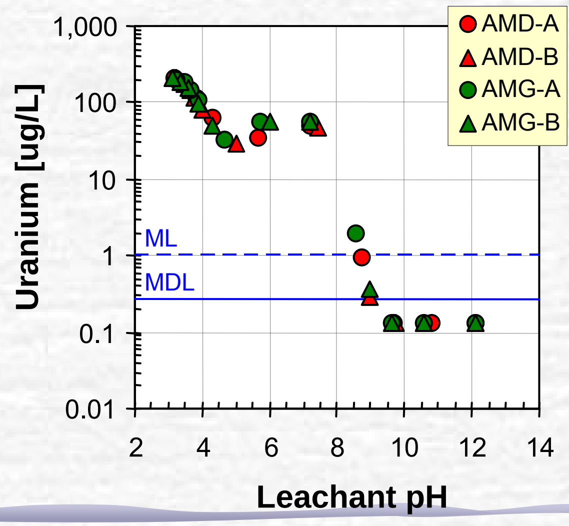


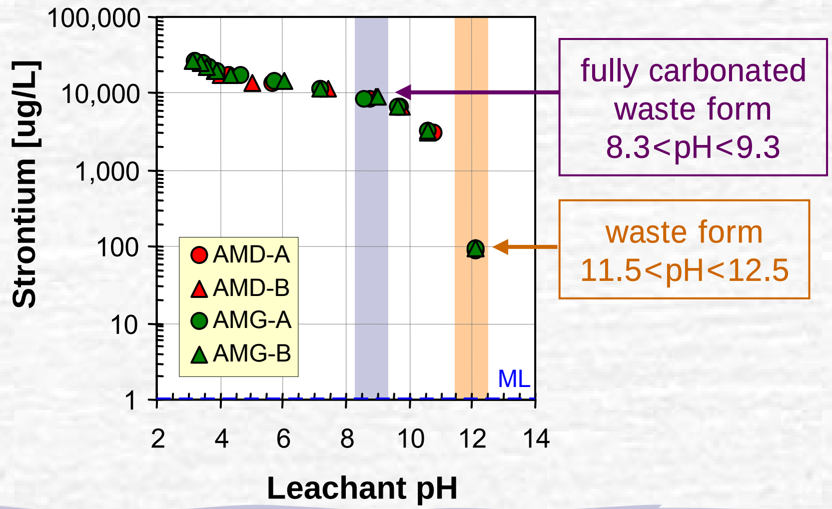


Equilibrium – Trace Species







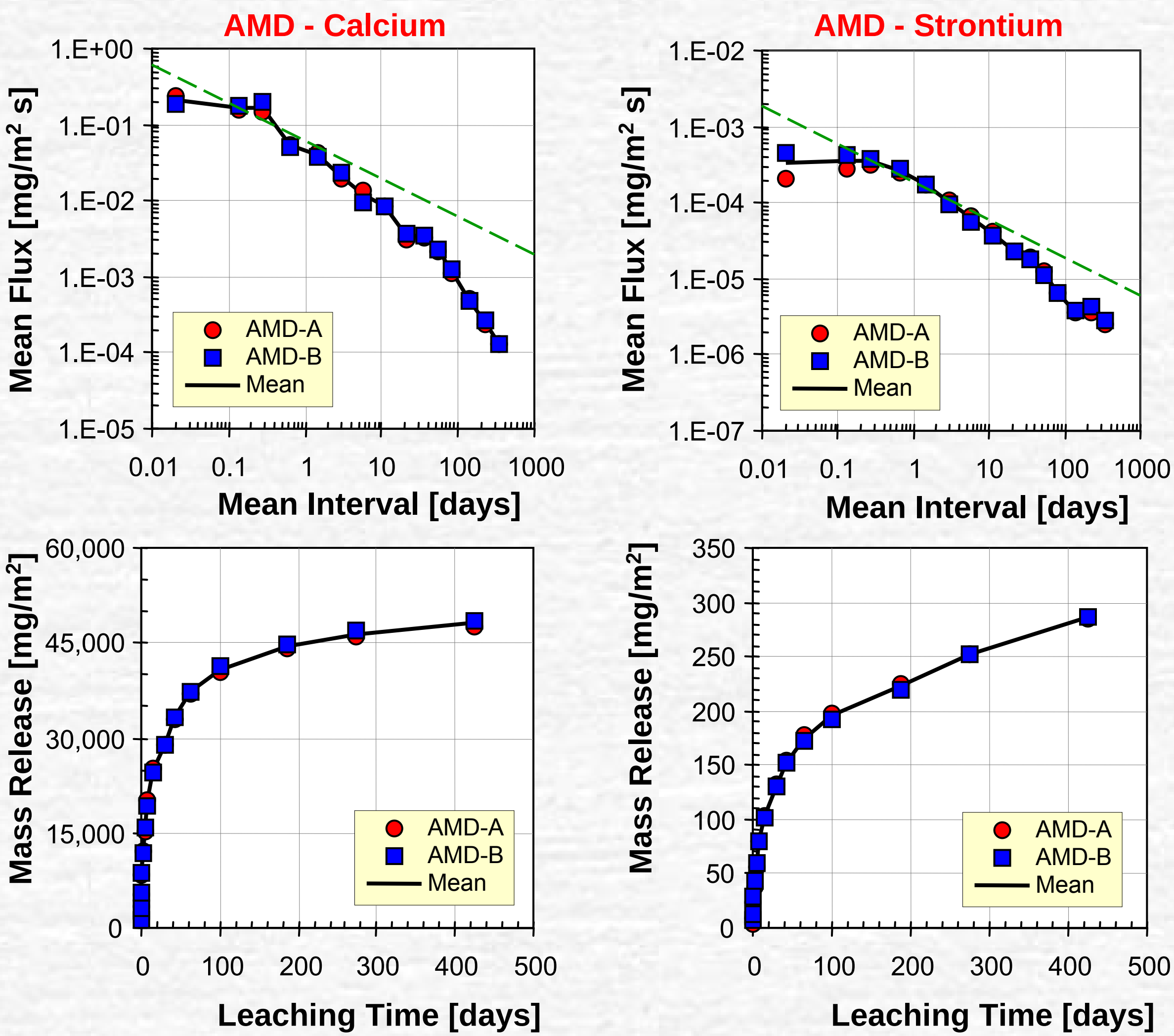


Solid-Liquid Partitioning

Comparison

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

Mass Transport Tests



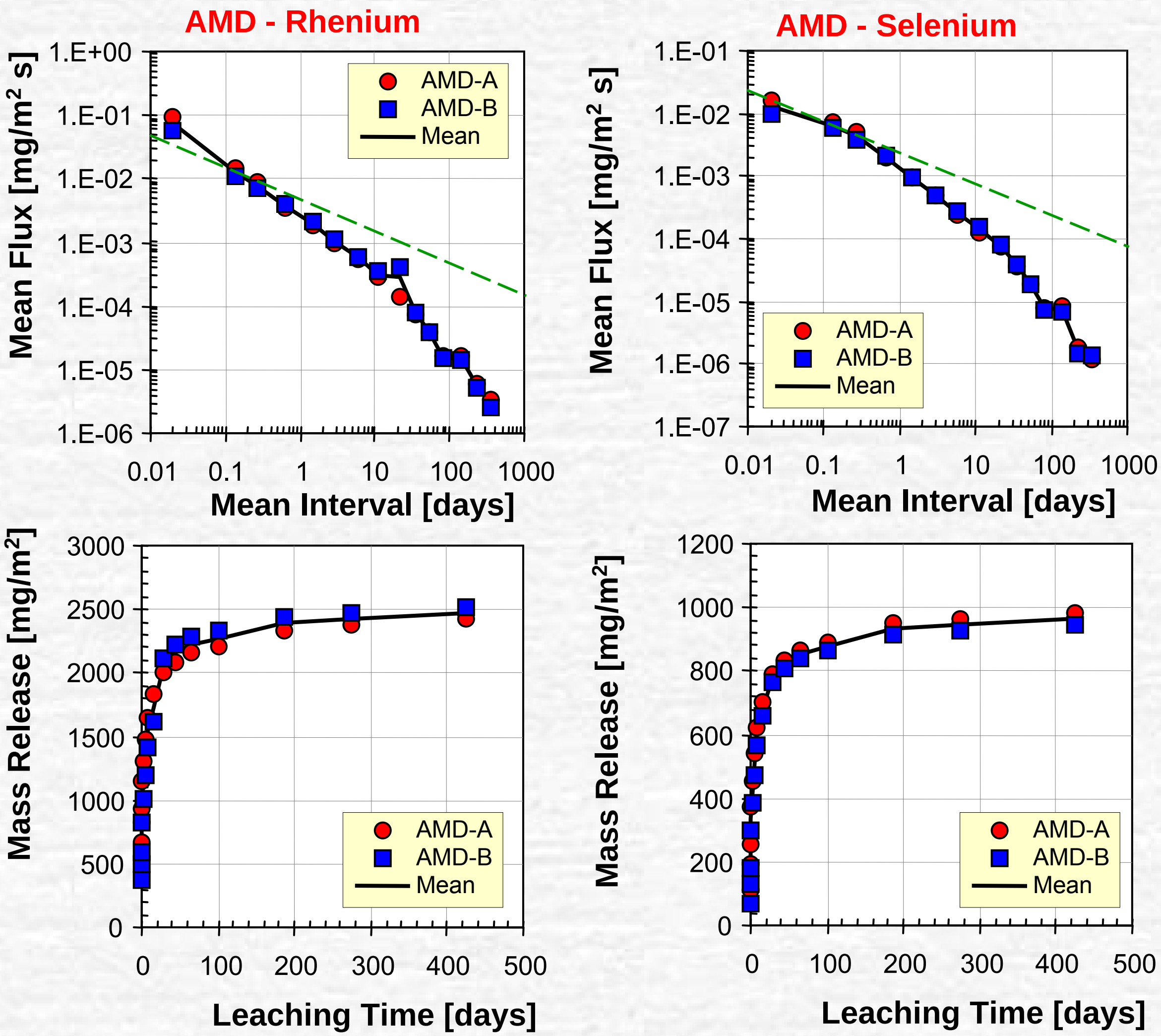
MT001 Test

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

Comparison

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

Mass Transport Tests



MT001 Test

- Tank Leaching in DI Water
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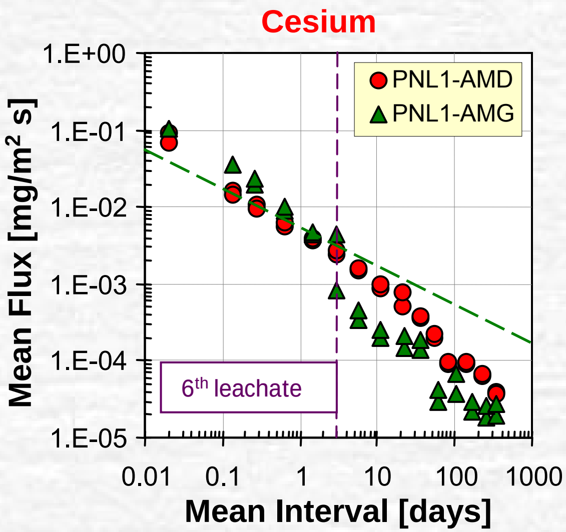
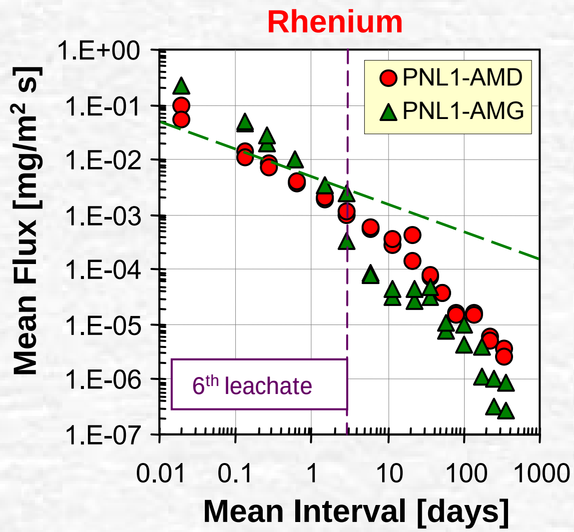
Comparison

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

Synthetic Groundwater





MT001 Test Comparison

- AMD – DI Water
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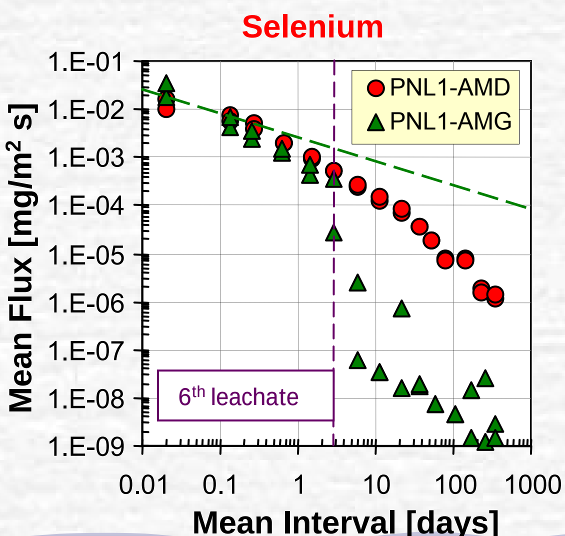
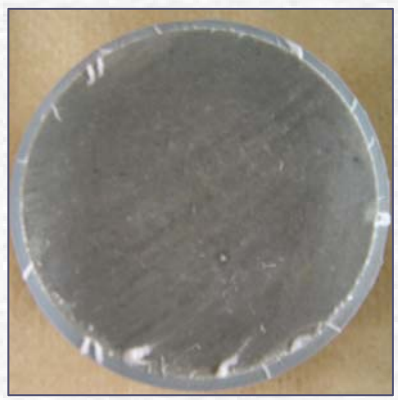




Precipitate on sample AMG-B after 6th leaching interval

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

Summary of Key Gaps in Current Performance Evaluations

Gas Phase Processes and Transport
- Oxidation
- Carbonation

Geochemistry-based Release Modeling
- Pore water chemistry (e.g., pH, redox, composition)
- Boundary layer and gradient effects

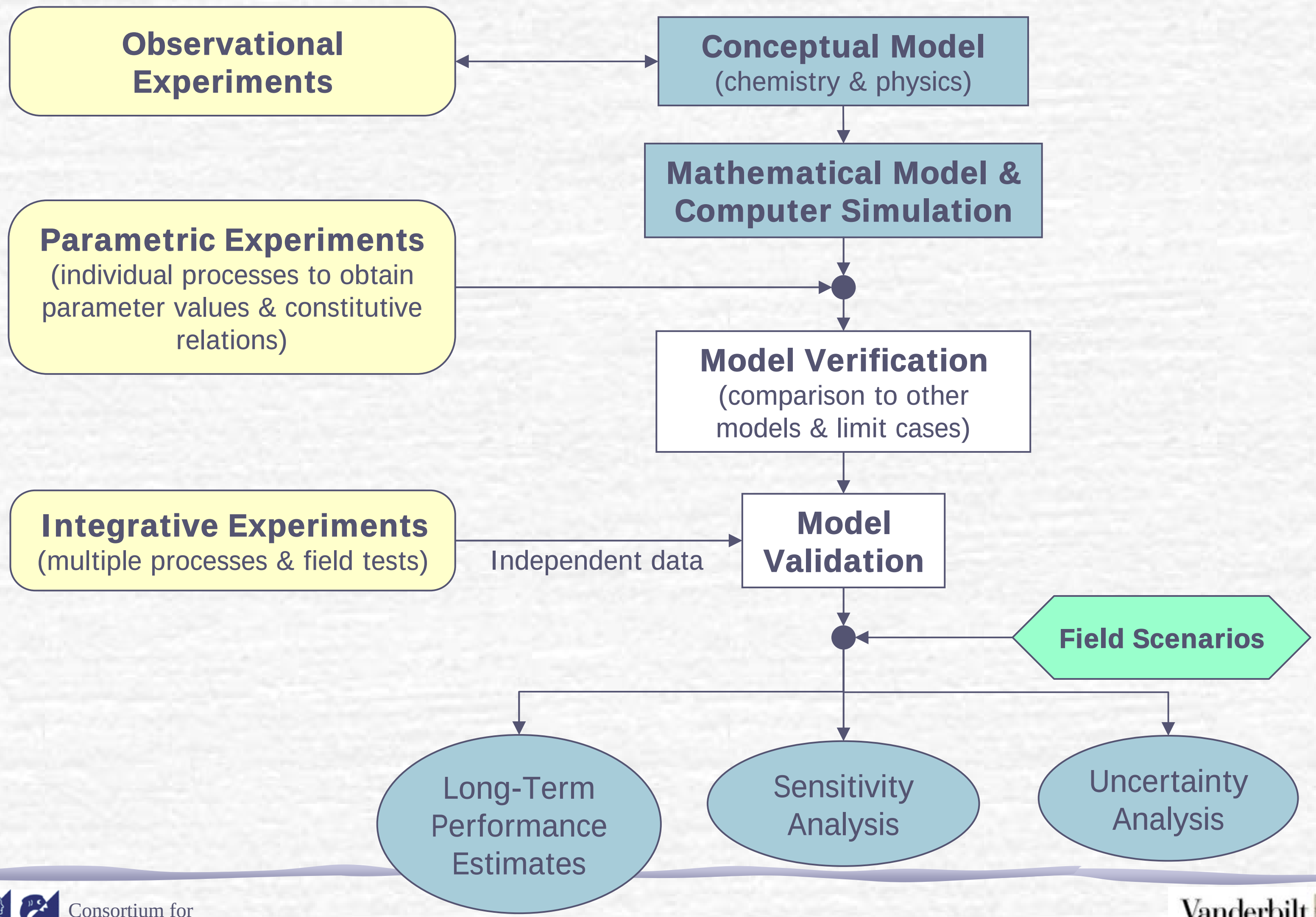
Moisture Transport and Water Content
- Gas phase attack
- Transport under unsaturated conditions (pore connectivity)

"Degradation" and Aging Mechanisms
- Physical deterioration (crack formation at multiple scales)
- Chemical aspects of carbonation
- Oxidation of waste form increasing release of Tc, Se
- Physical changes from Precipitation and Expansive Reactions (e.g., SO_4) at external surfaces (e.g., pore sealing) and in pores

Integration of Models Coupling Degradation Mechanisms

Validation of Assumptions/Simulations

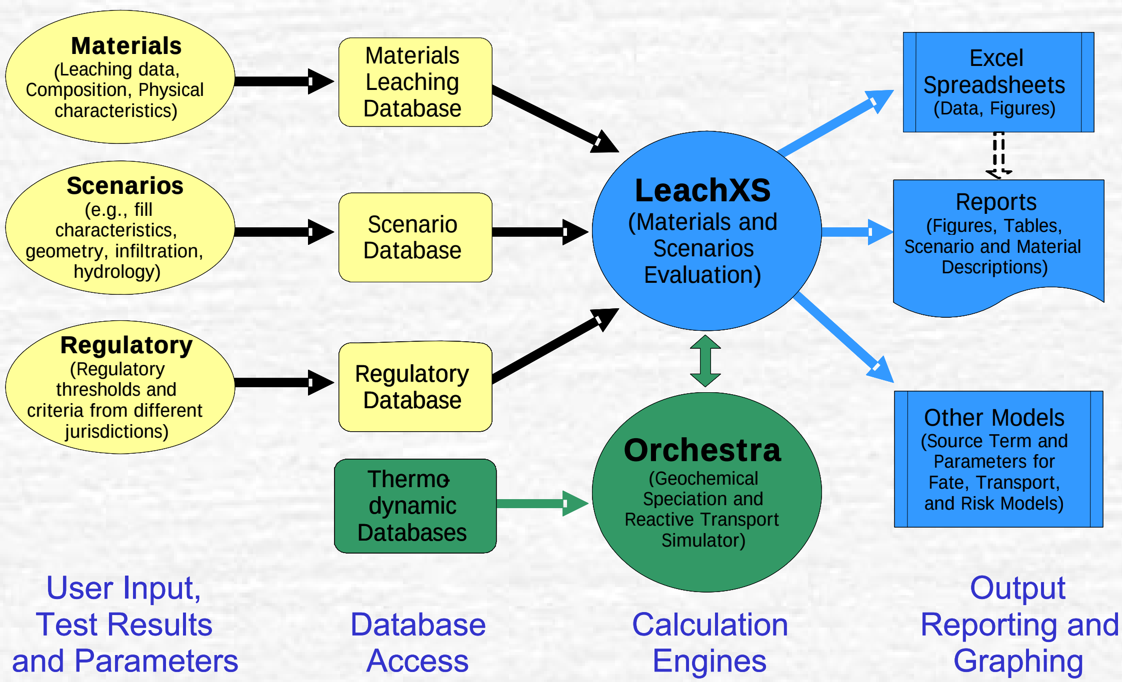
Process- and Mechanism-Based Experimentation & Modeling



LeachXS

Software-based system for evaluating leaching

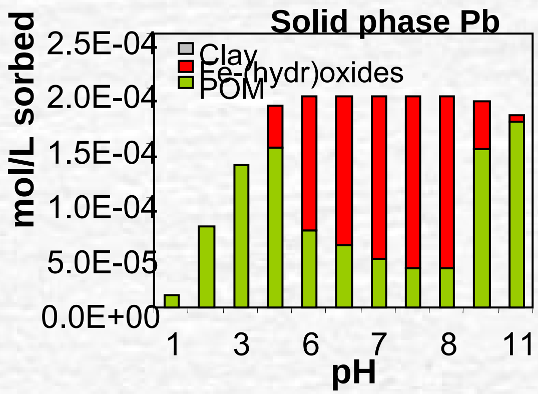
- Incorporates multiple processes and system configurations
- Data management/interpretation
- Geochemical analysis via ORCHESTRA (Meeussen, 2003)
- Database of material leaching information

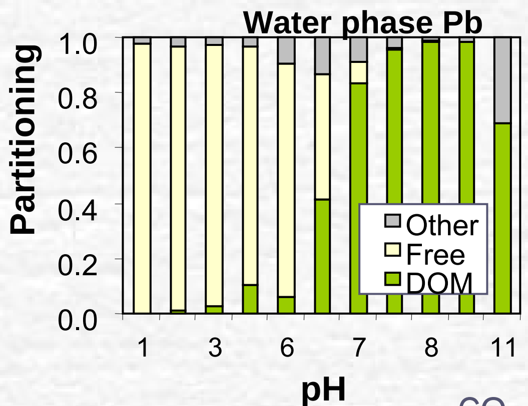


LeachXS Simulations

Solid-liquid partitioning

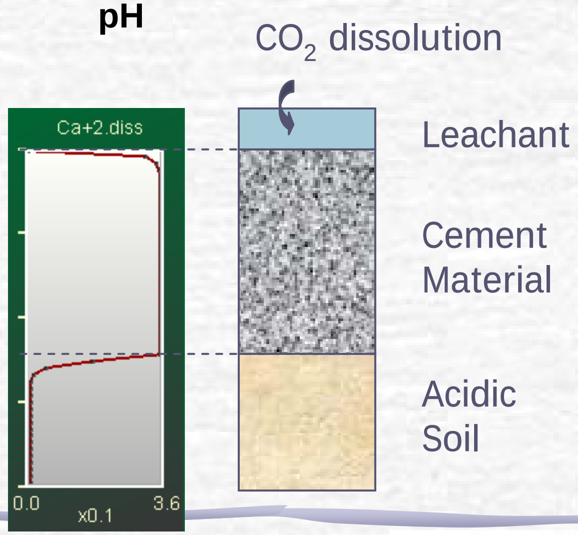
- Adorption to DOM, FeOH



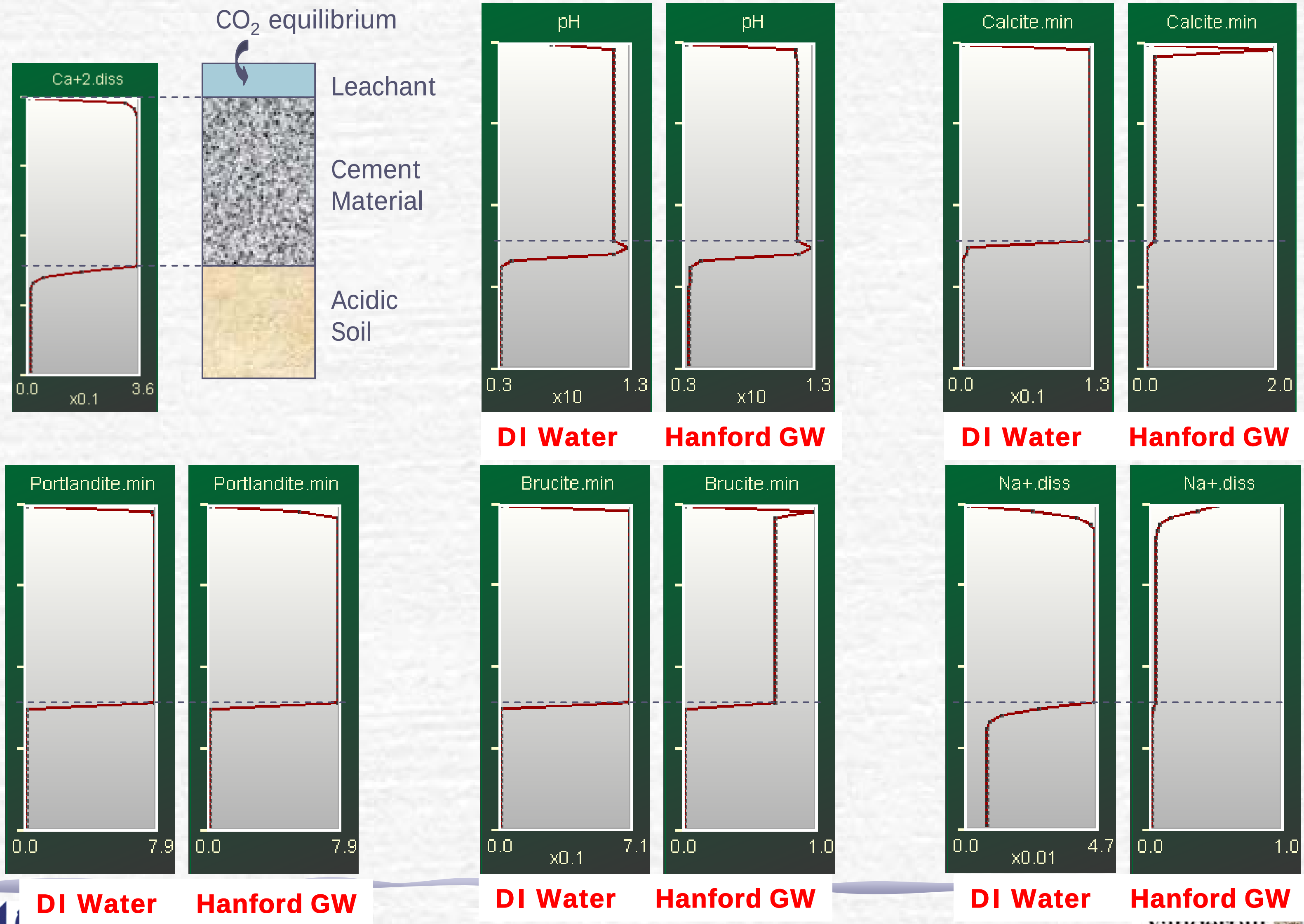


Mass Transfer

- Diffusion coupled with geochemistry
- Example: Cement Material
  - Leachant (open to air) at upper surface
  - Acidic soil at lower surface



Leachant Simulation - LeachXS



Suggested Path Forward

Continue on-going CRESP work with SRNL personnel and others on development of long-term release framework.

- Cement/concrete degradation “State-of-the-Art”
- Developing approaches for short-term (< 1 year) improvement of assessments
- Developing experimental and modeling plan (ca. 3-5 year) on waste form degradation to account for major processes

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
- 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.

Backup slides

Integrated Use of Testing and Simulation