Impact of Moisture Transport on the Release of Constituents from Cement-Stabilized Materials Stored in Intermittently Saturated Environments

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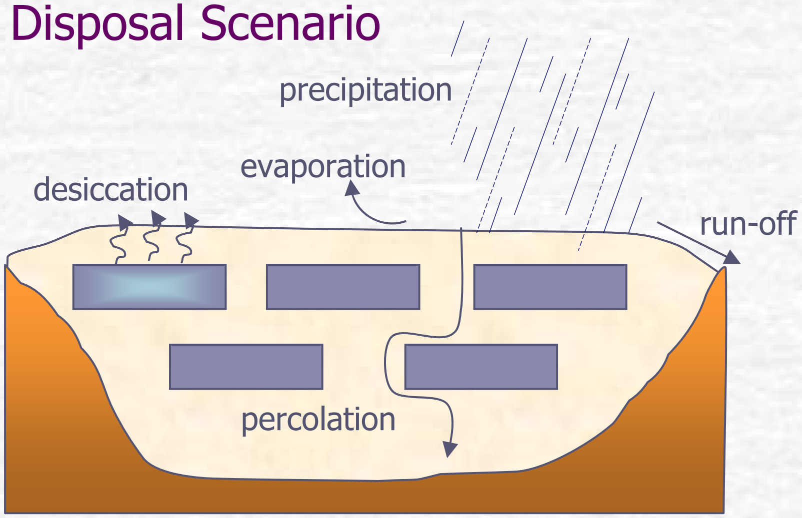
Cementitious Materials for Waste Treatment, Disposal, Remediation and Decommissioning
Savannah River National Labs, Aiken, SC
11-14 December 2006

Consortium for
Risk Evaluation with
Stakeholder Participation

Motivation

Disposal Scenario



Complex transport models

- Pore water chemistry coupled with mass transfer

$$\frac{\partial C_k}{\partial t} = \nabla\left(D_k^{eff} \nabla C_k\right) + F_k \left\langle S_p, C_1, \ldots, C_N \right\rangle$$

Semi-infinite diffusion model

- Constant Source
- Zero concentration boundary

$$M_t = 2\left(\frac{S}{V}\right) C_o \left(\frac{D^{obs} \cdot t}{\pi}\right)^{1/2}$$

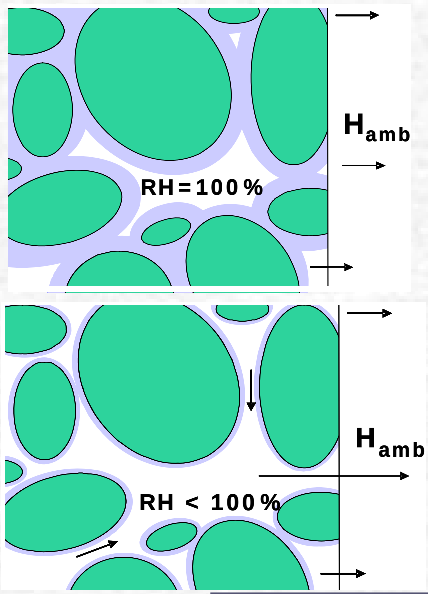
- Intermittent wetting adjustment
  - Time correction assumes simple "shut off" of leaching

$$M_t = 2\left(\frac{S}{V}\right) C_o \left(\frac{D^{obs}}{\pi}\right)^{1/2} (F_w)^{1/2}$$

  - Wetting frequency (F_w)

$$F_w = \left(\frac{t_w}{t}\right)$$

Moisture Transport



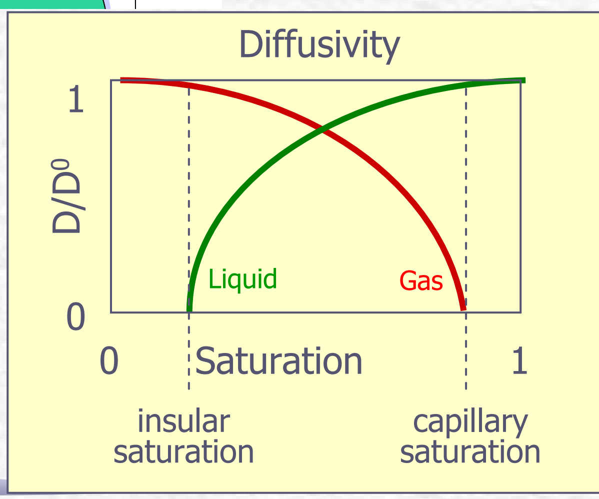
Full Saturation

Capillary Saturation
- Continuous Liquid
- Discontinuous Gas

Transition Zone
- Continuous Liquid
- Continuous Gas

Insular Saturation
- Discontinuous Liquid
- Continuous Gas

Completely Dry



Conceptual Model

- Moisture exchange w/environment
  - Evaporation/condensation
  - Capillary suction
  - Intermittent wetting (precipitation)
- Water content determines
  - Gaseous degradation processes (oxidation, carbonation)
  - Constituent diffusion pathways

Current Approach Limitations

- Moisture status undefined or unknown
- Wasteform assumed saturated
  - Gas phase reactions limited to external surfaces

Objectives

Develop a mathematical representation of moisture transport for a cementitious matrix

Integrate moisture transport into mass transport models
- Coupled Dissolution Diffusion model
- Intermittent Mass Transport (IMT) model

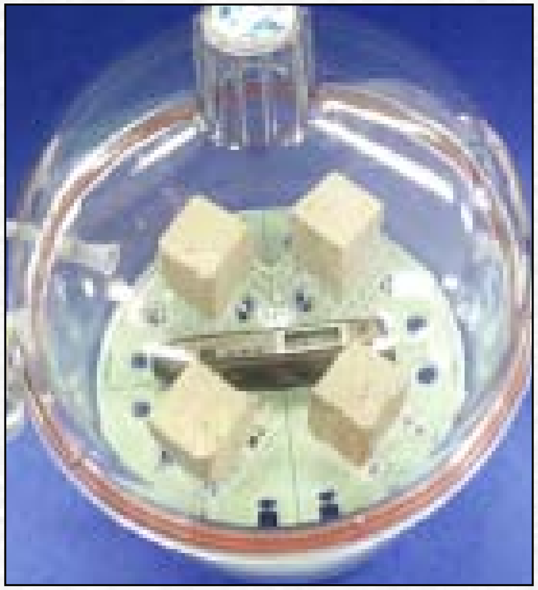
Validate IMT mass release
- Independent data set
- Cycles of wetting and storage (with/without drying)

Compare IMT model results:
- Among several wetting/drying scenarios
- To current saturated modeling approaches
- To simple wetting frequency adjustments

Model System

Cement-based mortar containing powders of metal oxides

Portland cement	36 wt%
Normal sand	49 wt%
Water	13 wt%
NaCl	1 wt%
PbO	3000 mg Pb/kg
CdO	3000 mg Cd/kg
As_2O_5	3000 mg As/kg



Cured at high RH for >28 days

Experiments

- Controlled drying (vapor-liquid isotherm)
- Atmosphere comparison
- Intermittent wetting and mass transport

Water Vapor Transport Experiments

Controlled Drying

- 2-cm cubes
- Dried to constant mass
- RH controlled – sat'd salts
  - 23% LiCl
  - 33% $MgCl_2$
  - 52% KNO_2
  - 88% K_2CrO_4
  - 97% KNO_3

Isotherm at end-state

Kinetic drying data

- 23% RH - parameterized drying model (h_c, α, n)
- Model validated at other RH values

Atmosphere Comparison

- 4-cm cubes
- Dried for 3 months
- RH controlled
  - 23% over silica oxide
  - 48%
  - 98% bubbled in water column
- CO_2 controlled
  - 100% carbon dioxide
  - 0% nitrogen

Carbonation depth using 1% phenolphthalein in ethanol

Kinetic drying data

- Model validation for larger geometry

Moisture Transport Model

(Garrabrants and Kosson, Drying Technology, 21, 775-805, 2003)

Two-Regime Drying Model

- Parameters: θ = saturation [-], H = relative humidity [-]
- Liquid-vapor isotherm (θ as a function of H)

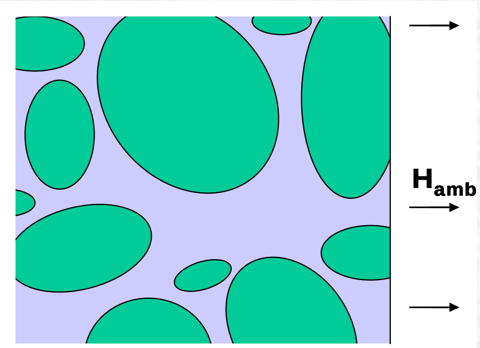
#1 - Funicular Regime ($\theta \geq \theta_{cap}$)

- Surface evaporation controls transport rate
- Movement of bulk liquid by capillary pressure
- Saturation spatially uniform
- Relative humidity constant w/ time, space

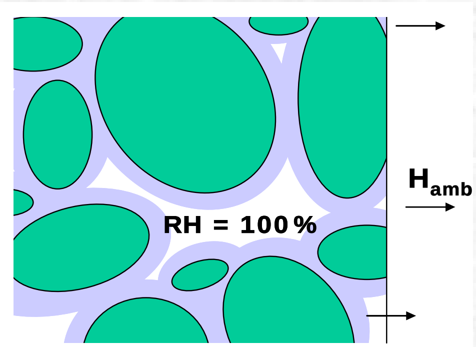
$$\frac{\partial \theta}{\partial t} = \frac{\eta(H_{surf} - H_{amb})}{\rho_{liq} \cdot \varepsilon \cdot \theta_0}\left[\frac{A}{V}\right]$$

$$H_x = 1$$

η = film mass transfer coefficient [kg/m^2 s]
H_{surf} = relative humidity at surface [-]
H_{amb} = ambient relative humidity [-]
ρ_{liq} = liquid phase density [kg/m^3]
ε = porosity [-]
θ= saturation [-]
A = matrix surface area [m^2]
V = matrix volume [m^3]



Full Saturation



Capillary Saturation θ_{cap}

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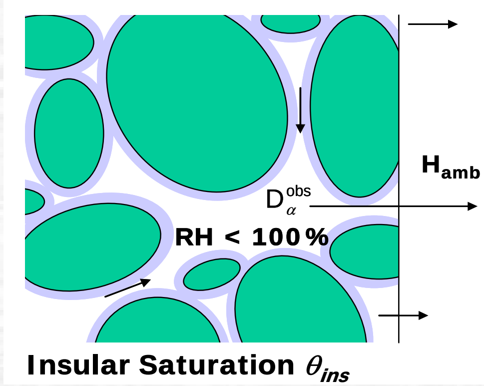
Moisture Transport Modeling

#2 - Isothermal Regime ($\theta_{ins} \geq \theta$)

- Pore vapor diffusion controls transport rate
- Saturation in equilibrium w/ relative humidity

$$\frac{\partial H}{\partial t} = D_{\alpha}^{obs} \frac{\partial^2 H}{\partial x^2} \qquad \theta = \theta \langle H_x \rangle$$



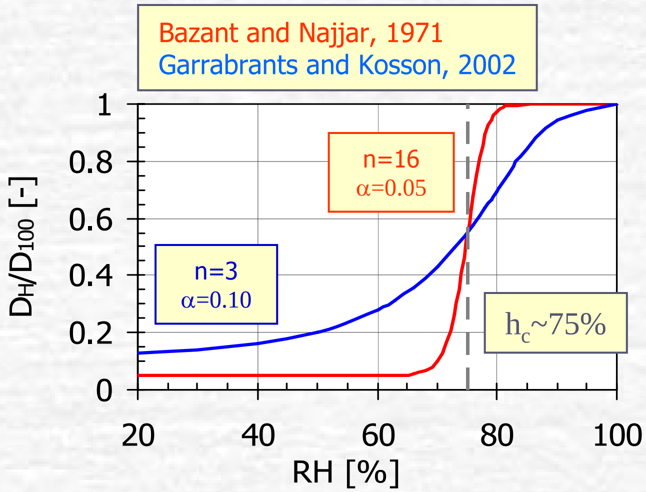
Transition Zone ($\theta_{cap} \geq \theta \geq \theta_{ins}$)

- Observed diffusivity is a function of humidity
- Saturation is provided by a liquid-vapor isotherm

$$\frac{\partial H}{\partial t} = D_{H}^{obs} \frac{\partial^2 H}{\partial x^2} \qquad \theta = \theta \langle H_x \rangle$$

where $D_H^{obs} = D_{100}^{obs} \left[\alpha + \frac{1-\alpha}{1+\left(\frac{1-H}{1-h_c}\right)^n} \right]$

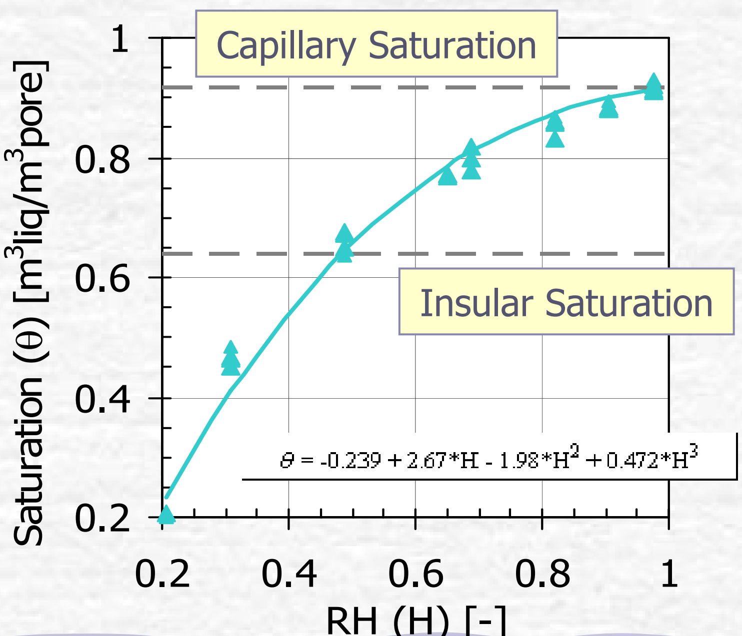
α = ratio of D_{min}/D_{max} [-]
h_c = critical relative humidity [-]
n = spread of drop in curve



Controlled Drying Results

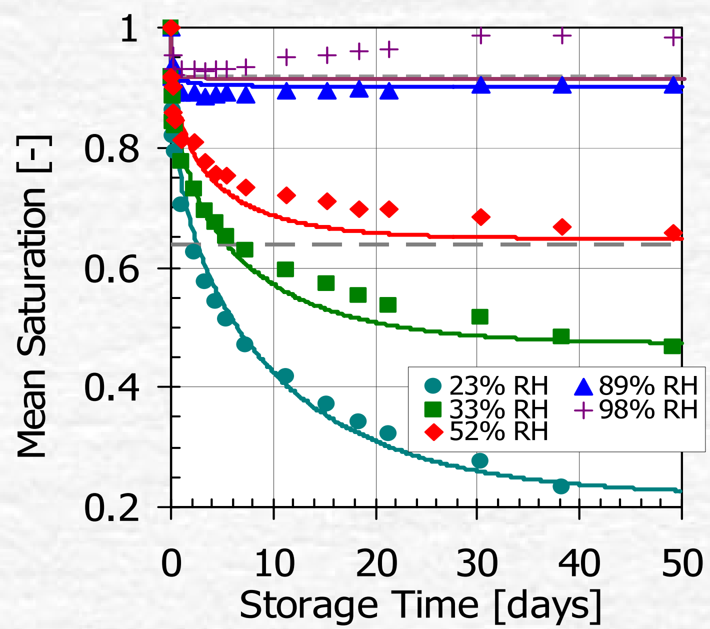
Water-Vapor Isotherm

- Capillary Saturation
  continuous liquid phase, capillary forces
- Insular Saturation
  discontinuous liquid phase, vapor transport



Drying Model Validation

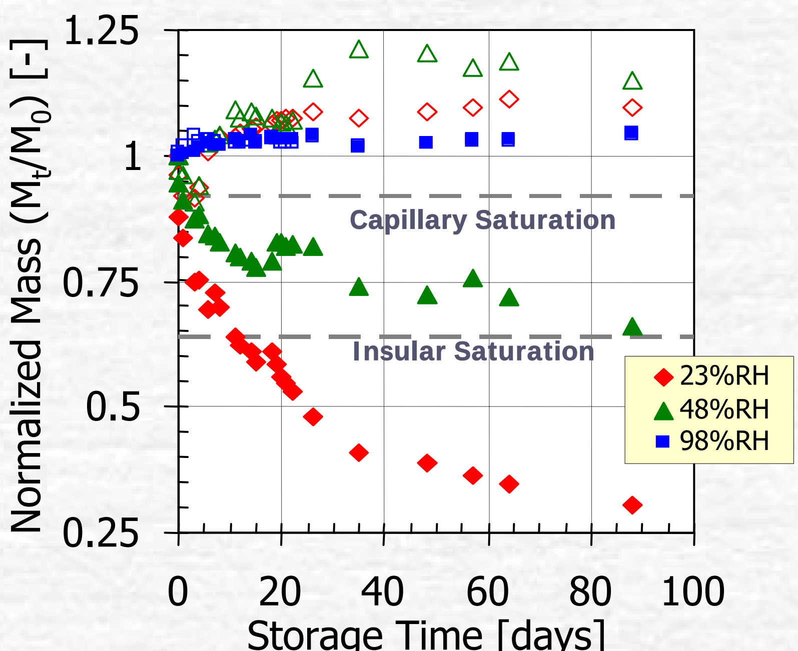
- Parameters set using 23% RH
- Acceptable estimate at all RH



Drying Atmosphere Comparison

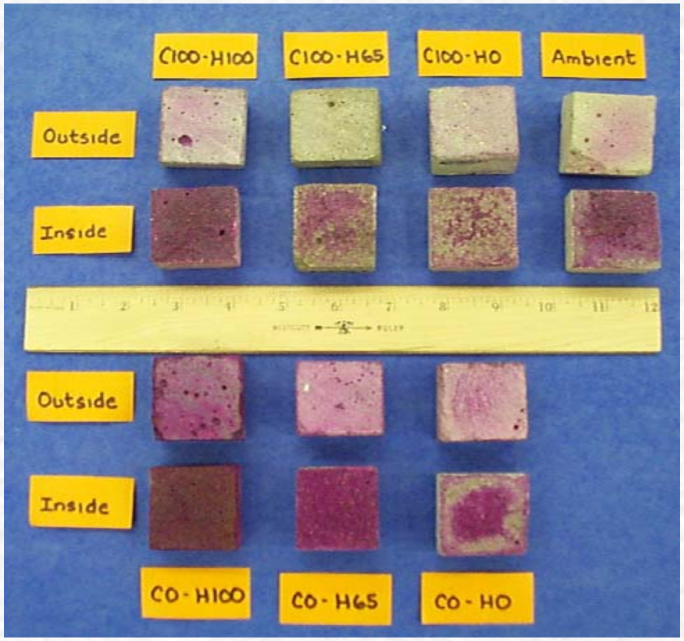
Kinetic Drying Data

- Inert atmosphere (closed symbols)
- Reactive atmosphere (open symbols)
  - Increased mass - $CaCO_3$
  - Max mass effect at 48% RH



Carbonation Depth

- Phenolphthalein indicator (1%)
  - Noncarbonated (red)
  - Carbonated (clear)



Note: apparent "carbonation" of C0-H0 sample due to spill of KCO_3 solution

Intermittent Wetting and Release

Intermittent Wetting

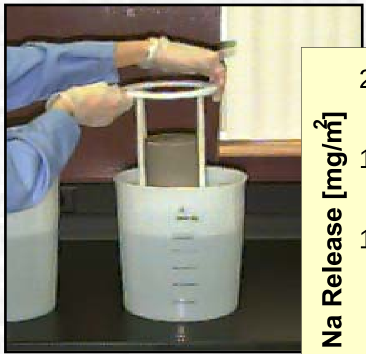
- Tank leaching interspersed w/ atmospheric storage

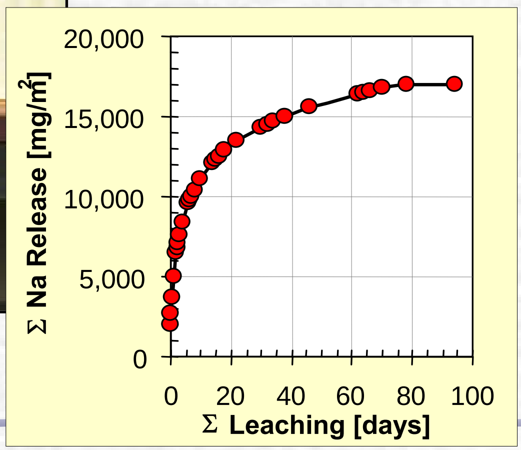
MT001.1 Mass Transfer in Monolithic Materials

- Tank Leaching in DI Water
- Liquid-to-Surface = 10 mL/cm^2
- Leachate exchange

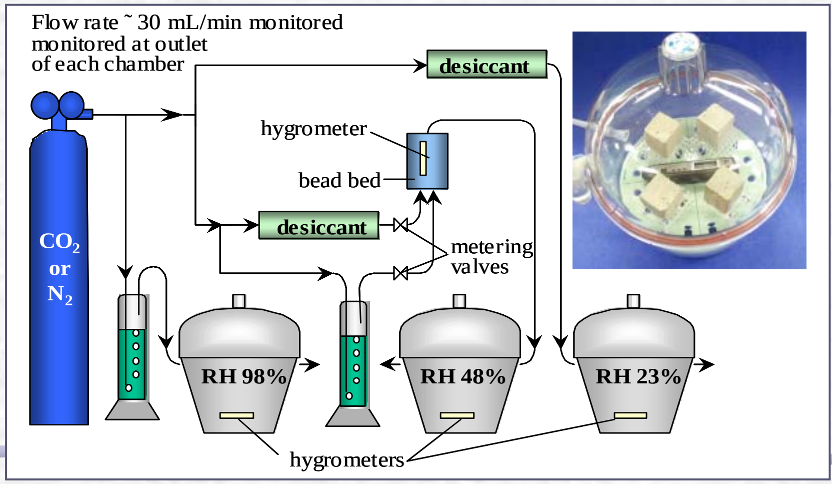
Storage Atmospheres

- Carbon dioxide
  - 0%, 100%
- Relative Humidity
  - 98%, 48%, 23%





Intermittent Wetting Apparatus

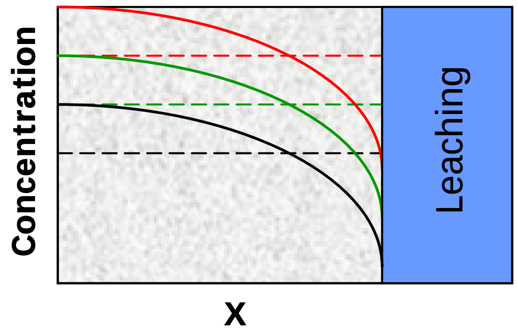


Drying and Constituent Release

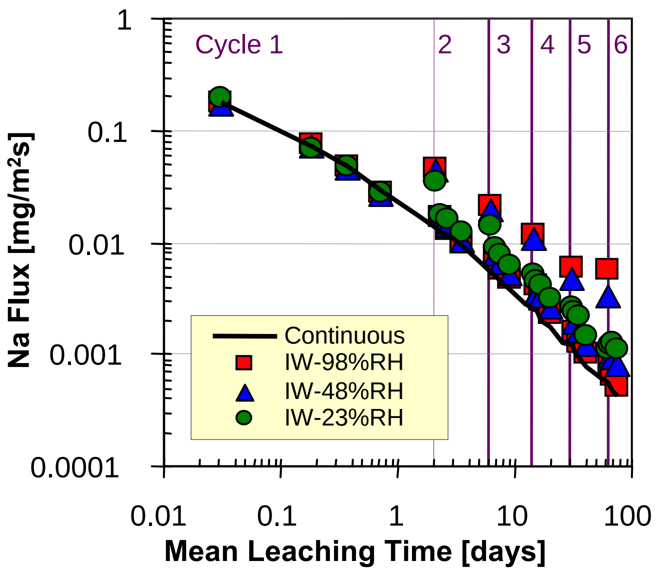
OPC Mortar

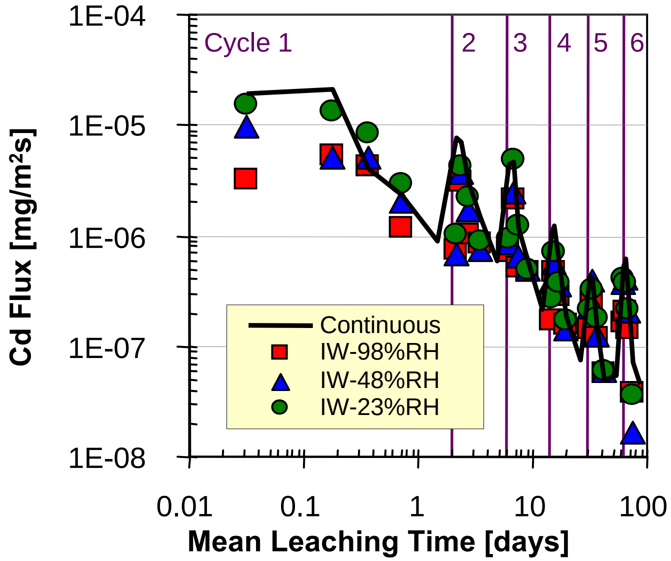
Intermittent Wetting/Release
- Tank Leaching Cycles
  - 1, 2, 4, 8, 16, 16 days
- Storage Cycles
  - 1, 2, 4, 8, 16, 16 days
  - no carbonation (100% nitrogen)

Gradient Relaxation



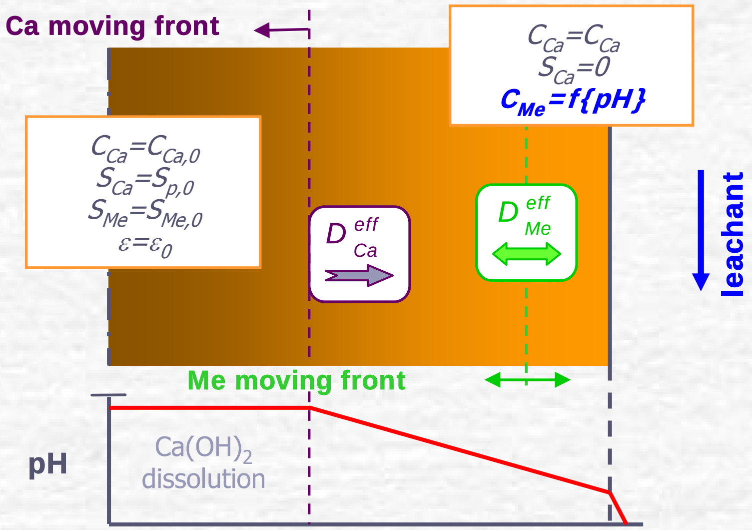
Click on graph
to display animation





Coupled Dissolution-Diffusion (CDD) Model

Sanchez *et al.*, Chem. Engr. Sci., 55, 115-128, 2000



$$\frac{\partial C_k}{\partial t} = \nabla\left(D_k^{eff}\nabla C_k\right) + F_k\left\langle S_p, C_1, \ldots, C_N\right\rangle$$

Conceptual Model

- Moving dissolution fronts
- Dissolution/diffusion of $Ca(OH)_2$ and decalcification of CSH control pore water pH
- pH gradients alter trace species release
- Boundary layer formation may significantly impact release (+ or -)

Impact

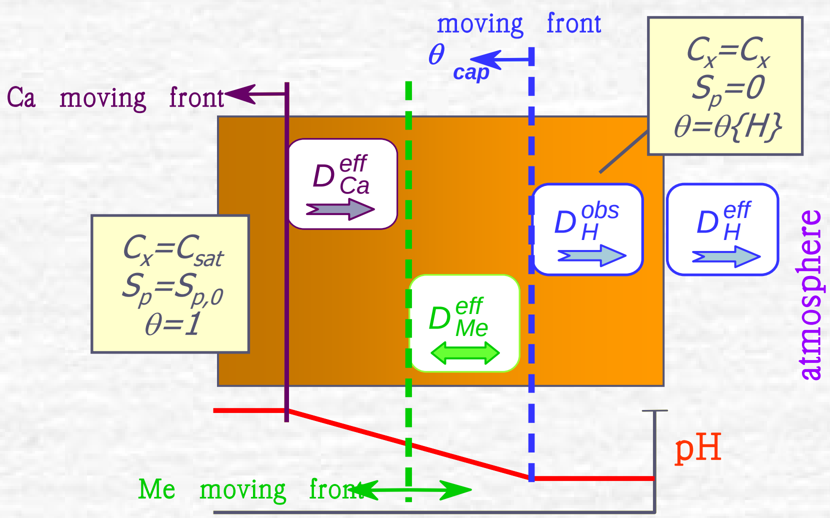
- Mass transport estimates reflect the dynamic chemistry and mineralogy.
- Mechanistically different than simplified models ($T^{1/2}$ models may limit predictability)

Intermittent Mass Transport (IMT) Model

Garrabrants *et al.*, AIChE Journal, 49, 1317-1333, 2003

Incorporates drying and CDD mass transport models to simulate IW scenarios for cementitious matrices

- Saturated Leaching
  - CDD mass transport model
- Storage at Constant RH
  - Moisture transport model for RH < 100%
  - Gradient relaxation by CDD model



Two-regime moisture transport (θ - saturation, H - humidity)

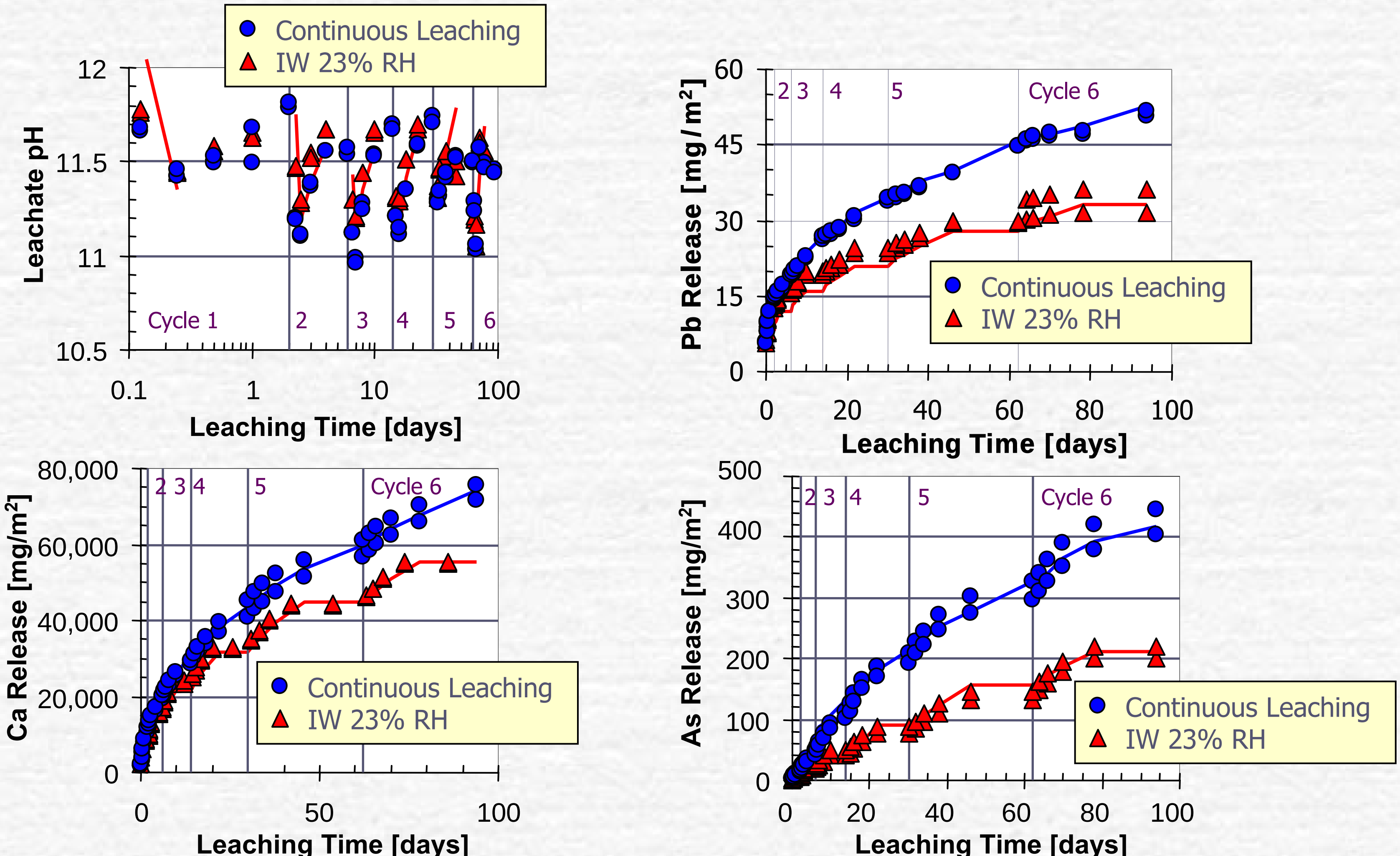
$\frac{\partial \theta}{\partial t} = \frac{\eta(H_{surf} - H_{amb})}{\rho_{liq} \cdot \varepsilon \cdot \theta_0}\left[\frac{A}{V}\right]$	$H_x = 1$	$\frac{\partial H}{\partial t} = D_H^{obs}\frac{\partial^2 H}{\partial x^2}$	$\theta = \theta\langle H_x \rangle$

Funicular regime ($\theta \geq \theta_{cap}$)

Isothermal regime ($\theta < \theta_{cap}$)

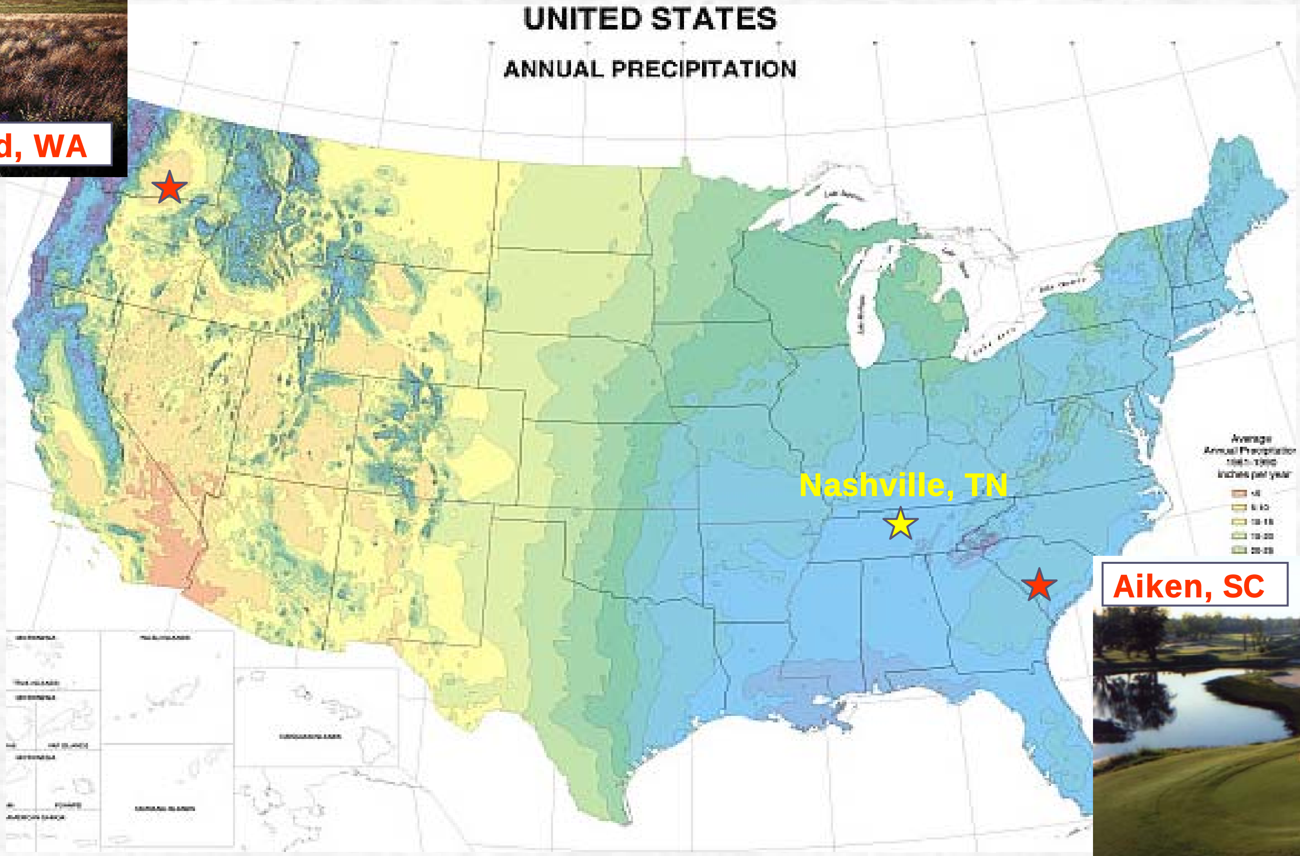
IMT Model Results

Garrabrants *et al.*, J. Haz. Mat., 91, 159-185, 2002

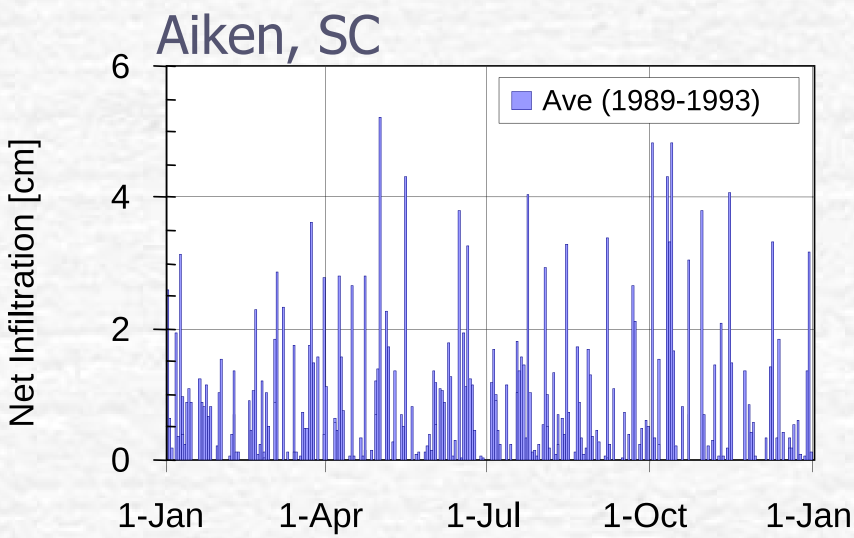


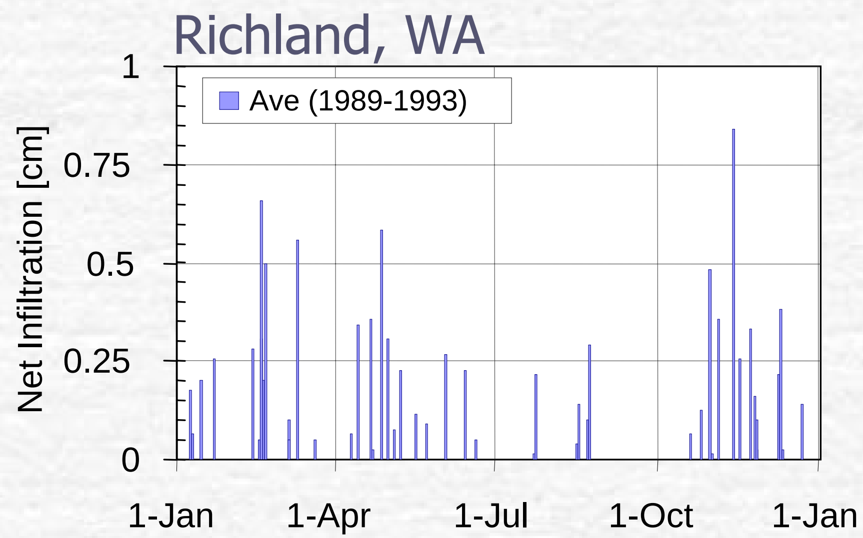
Site-Specific Comparison

Richland, WA vs. Aiken, SC



Precipitation and Simulation Data





Period	Data Set	IW Cycles/ Data Set	# Data Set Loops	Wet Days/ Data Set	F_w	RH [%]
Default Wet	7 days	1	5200	2.1	0.30	100
Default Dry	30 days	1	1200	3	0.10	100
Aiken, SC	5 years	218	20	314	0.17	100
Richland, WA	5 years	48	20	52	0.03	100, 65

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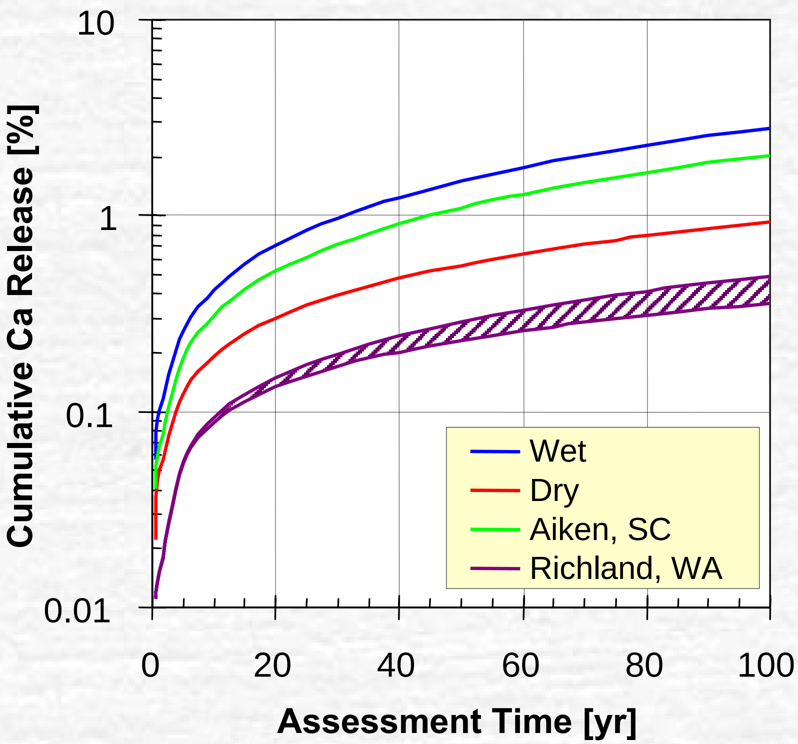
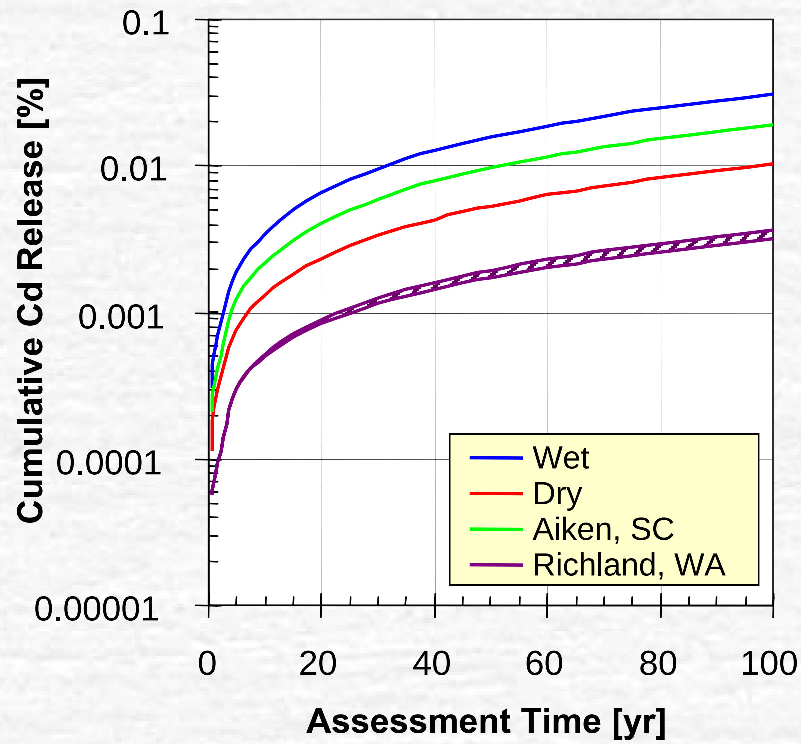
Intermittent Mass Transport Model Results

Comparison of scenario cases



Calcium



Cadmium

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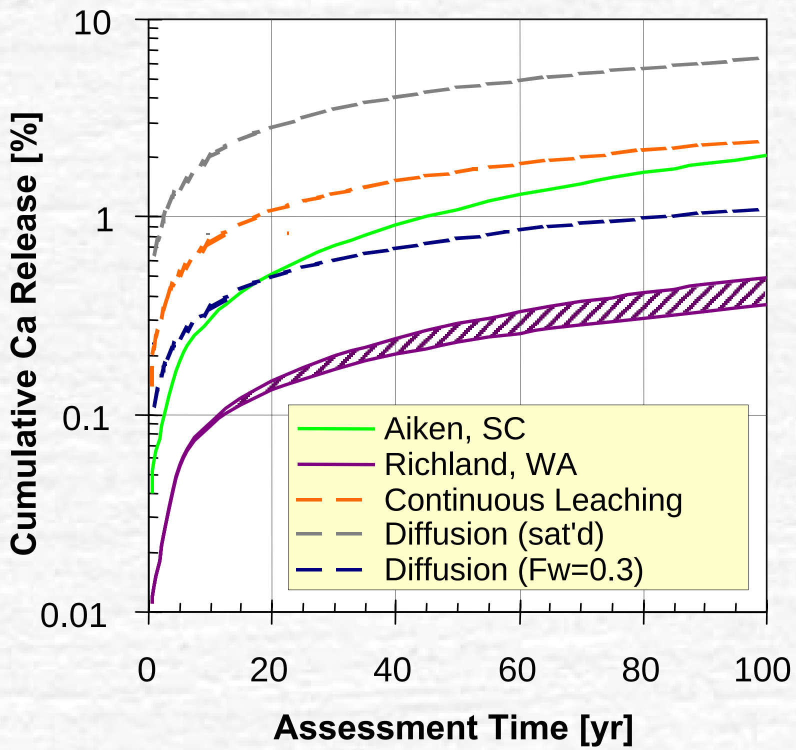
100-year Release Estimates

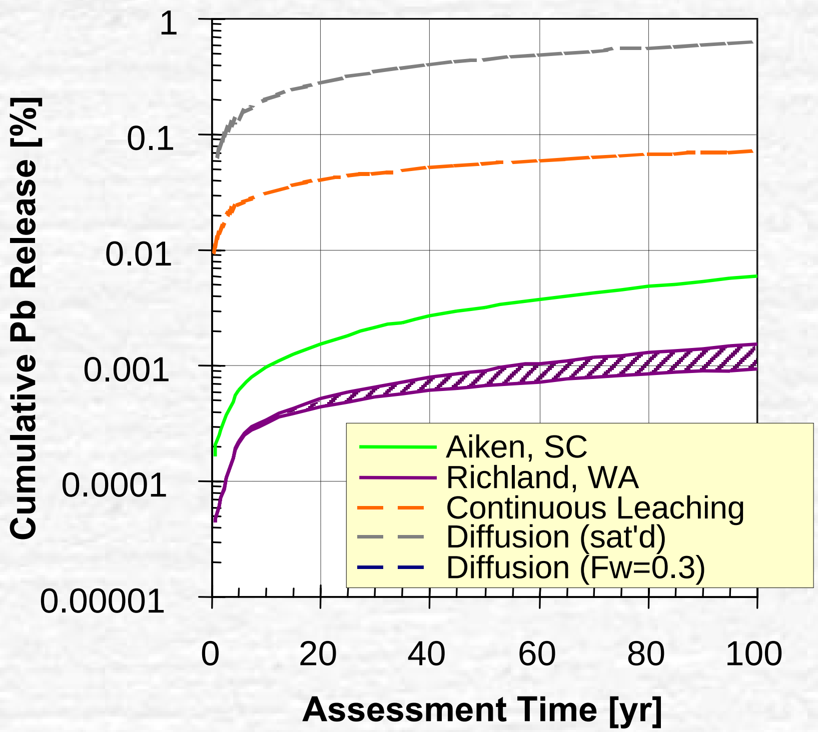
Comparison of model results

- IMT model w/ precipitation data
  - Aiken, SC
  - Richland, WA
- Continuous Leaching
  - Saturated release under CDD
- Simple diffusion model
  - Saturated (Fw = 1)
  - 30% wetted (Fw = 0.3)

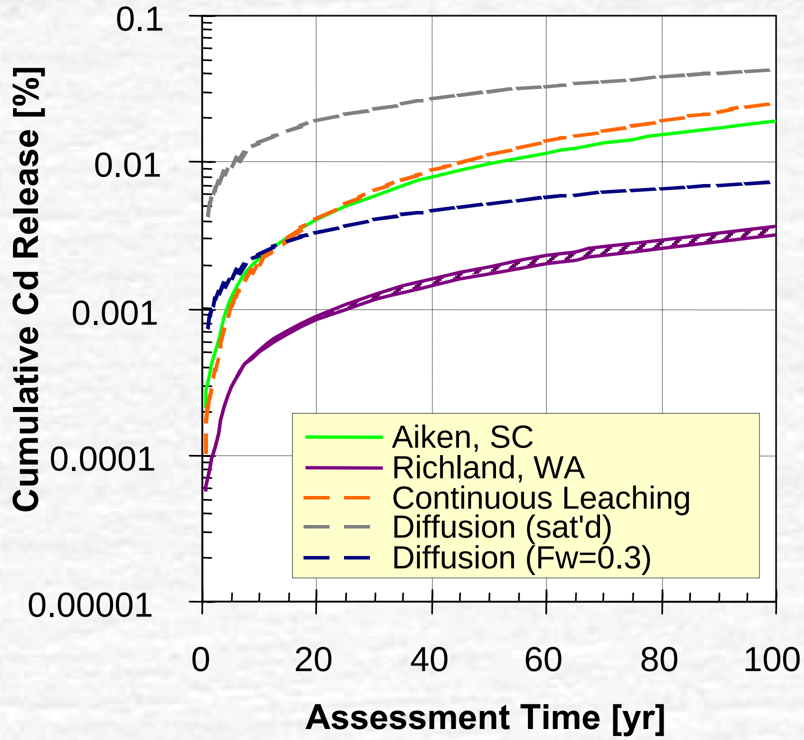


Calcium

100-Year Release Estimates



Lead



Cadmium

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Conclusions

Long-term release estimates from cementitious matrices influenced by

- Model formulation (percolation, diffusion, CDD, IMT)
- Scenario conditions (LS_{site}, Field pH)
- External stresses (carbonation, intermittent wetting)

IMT model approach is useful to describe constituent release for cementitious materials exposed to intermittent wetting conditions.

- Combines pore chemistry with mass transport
- Drying as function of isotherm and external relative humidity
- Release is function of wetting frequency

Constituent release incorporating intermittent wetting

- Refines saturated scenario estimates
- Can be based on:
  - Default scenario
  - Site-specific precipitation data

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Remaining Issues

Gas Phase Phenomena

- Cracking related to expansive pressure (e.g., carbonation, rebar corrosion)
- Mechanistic interpretation of carbonation, oxidation
- Coupling of moisture and degradation models

Transport Models

- Validation of predicted moisture transport and profiles
- Numerical simulations based on measurable parameters
- Integration of durability, degradation, and leaching

Standardization Needs

- Degradation testing procedures
- Long-term predictions to include degradation evaluation
- Regulatory interpretation of leaching
  - Intermittent wetting conditions
  - Long-term degradation approaches

Acknowledgements

Collaborators

- VU – Vanderbilt University, Civil and Environmental Engineering
- ECN – Netherlands Energy Research Foundation

Research Support

- CRESP III – Consortium for Risk Evaluation with Stakeholder Participation
- USDOE – US Department of Energy
- USEPA-OSW – US Environmental Protection Agency/Office of Solid Waste

Questions?