L E A F

Leaching Environmental Assessment Framework

Laboratory-to-Field Relationships and Recommendations for Leaching Assessment Using the Leaching Environmental Assessment Framework (LEAF)

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Leaching Environmental Assessment Framework

A Decision Support System for Beneficial Use and Disposal Decisions in the United States and Internationally…

- Four leaching test methods
- Data management tools
- Geochemical speciation and mass transfer modeling
- Quality assurance/quality control for materials production
- Integrated leaching assessment approaches

… designed to identify characteristic leaching behaviors for a wide range of materials and scenarios &

… provide a material & scenario-specific “source-term”.

More information at http://www.vanderbilt.edu/leaching

Objectives for Laboratory-to-Field Evaluation

(EPA-600/R-14/061, 2014)

- Evaluate applicability and limitations of using LEAF laboratory leaching tests for estimating leaching of COPCs from a broad range of materials under field disposal and beneficial use scenarios.
  - Compare testing "as produced" and "field aged" materials using LEAF methods, and results from field leaching studies.
  - Interpret LEAF leaching data within the context of a defined conceptual model for leaching
  - Use chemical speciation modeling as a tool to facilitate evaluation of scenarios beyond the conditions of common laboratory testing
- Provide recommendations on the selection and use of LEAF testing for different types of materials or wastes when evaluating disposal or use scenarios.

Materials and Cases Evaluated

- Coal Fly Ash
  - Multiple Landfills (US)
  - Large-scale Lysimeters (DK)
  - Roadbase & Embankments (NL)
- Fixated Scrubber Sludge
  - coal fly ash + FGD scrubber sludge + lime
  - Landfill (US)
- Municipal Solid Waste Incinerator (MSWI) Bottom Ash
  - Landfill (DK)
  - Roadbase (SE)

Materials and Cases Evaluated

- Predominantly Inorganic Waste Mixture
  - Lysimeters and Landfill (NL)
- Municipal Solid Waste
  - Bioreactor Landfill (leachate recirculation, NL)
  - Multiple Landfills (multiple countries)
- Cement-Stabilized MSWI Fly Ash
  - Pilot Test Cells & Landfill (NL)
- Portland Cement Mortars and Concrete
  - Recycled Concrete Used in Roadway (NO)
  - Field Samples (multiple countries)

LEAF Leaching Methods*

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

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

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

Method 1316 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure (L/S dependence)

**Posting to USEPA SW-846 as "New Methods" completed August 2013*

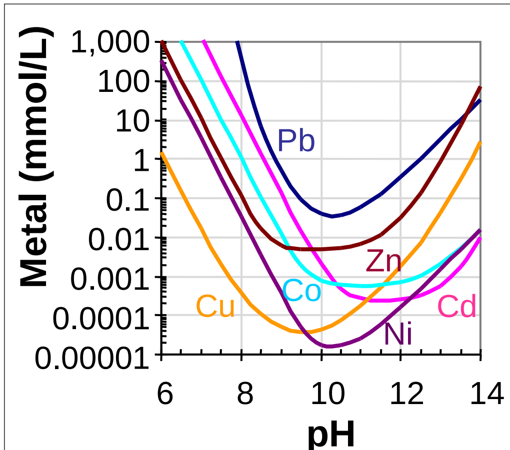
LEAF and EU Methods

Parameter	LEAF	EU Method	EU Applications
pH-dependence	Method 1313	PrEN 14429 PrEN 14997 ISO/TS 21268-4	Waste, mining waste, construction Waste, mining waste Soil, sediments, compost, sludge
Percolation	Method 1314	PrEN 14405 FprCENTS 16637-3 NEN 7373 (NL) ISO/TS 21268-3	Waste, mining waste Construction products Waste, construction products Soil, sediments, compost, sludge
Mass Transport	Method 1315	PrEN 15863 FprCENTS 16637-2 NEN 7375 (NL) NEN 7347 (NL)	Monolithic waste Monolithic & granular construction Monolithic waste Granular waste and construction
L/S dependence	Method 1316	EN12457-2	Waste

Conceptual Model for Leaching

- Primary factors that effect leaching
- Relationships between results from multiple leaching tests
- Definition of field scenarios
  - Range of applicable field conditions (pH, pE)
  - Useful simplified source-term models & chemical speciation models
- Relationships between leaching test results & field conditions
  - Screening assessments
  - Sensitivity analysis
  - Site-specific evaluations
  - Regional probabilistic evaluations

Factors Influencing Material Leaching



Moisture Transport

Leachant Composition

Water, Acids, Chelants, DOC

Leaching Factors

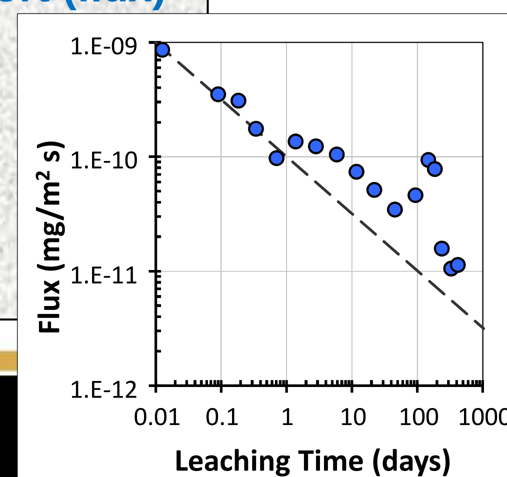
- **Equilibrium or Mass Transport**
- **pH**
- **Liquid-to-solid ratio**
- **Redox conditions**
- **Rates of mass transport (flux)**

Chemical Reactions
(Sulfate, Oxygen, Carbon Dioxide)

Physical Factors

- **Hydraulic conductivity (water contact mode)**

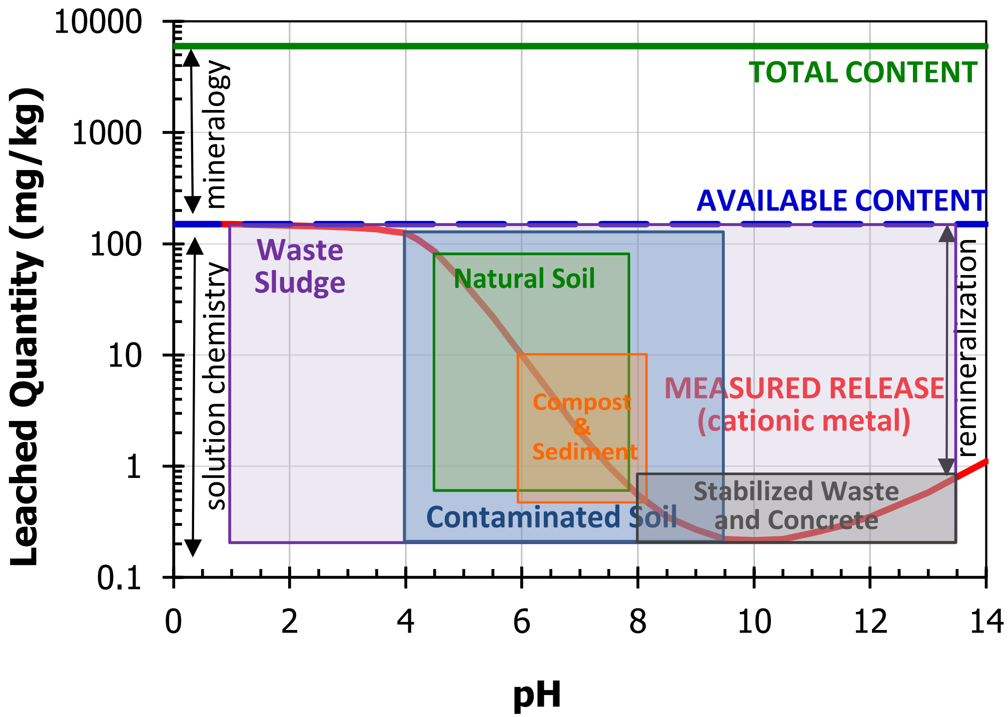
Physical Degradation
(Erosion, Cracking)



Relevant pH Range

pH-dependent Leaching

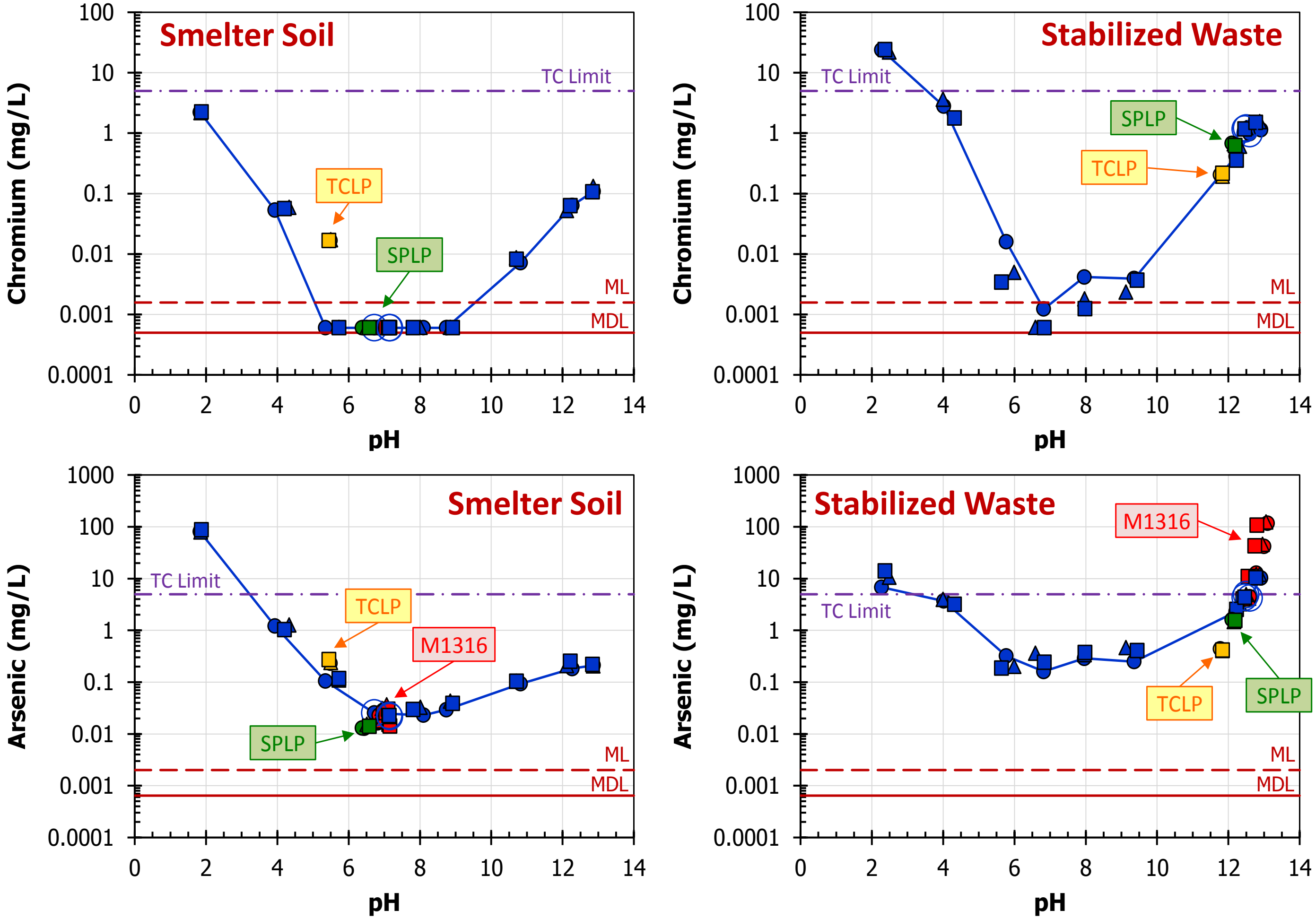
- Liquid-solid partitioning ≈ chemical equilibrium
- Interpreted with respect to relevant pH range for a material
- Available Content = Maximum leaching (mg/kg) over 2 ≤ pH ≤ 13



Relevant pH Range Should Consider

- Natural pH of the material (no acid or base addition)
- Life cycle pH (fresh to end-of-life)
- Blending of materials
- External sources (leachant composition)

What about TCLP and SPLP?



Acetic Acid

- TCLP solution is not a relevant leaching condition

Liquid-to-Solid Ratio (mL/g)

- TCLP/SPLP at L/S 20
- M1313 at L/S 10
- M1316 at L/S 0.5-10

Final pH

- TCLP and SPLP recording final pH is not required

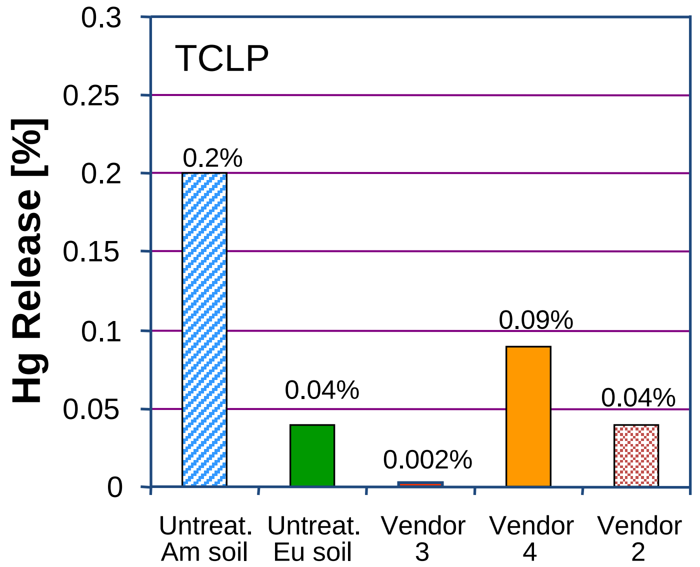
Comparison of Treatment Processes

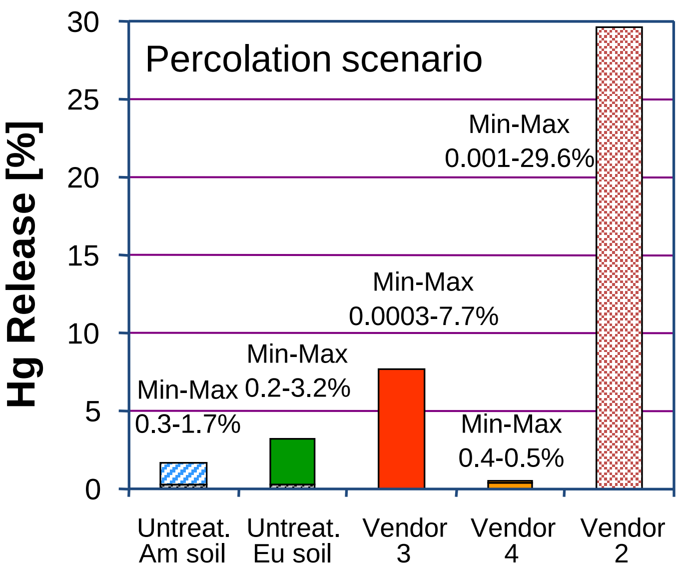
Mercury-contaminated Soil

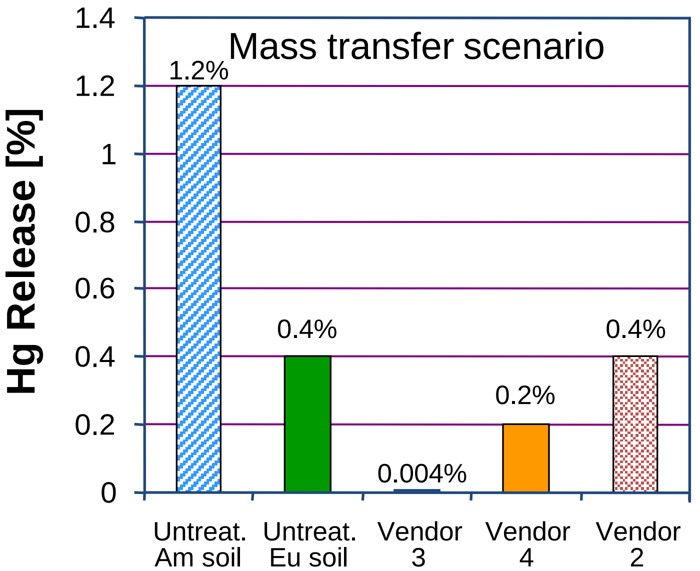
- 2 untreated soils (Am, Eu)
- 3 treated Am soils

  S/S: Vendors 2,3

  SPC: Vendor 4

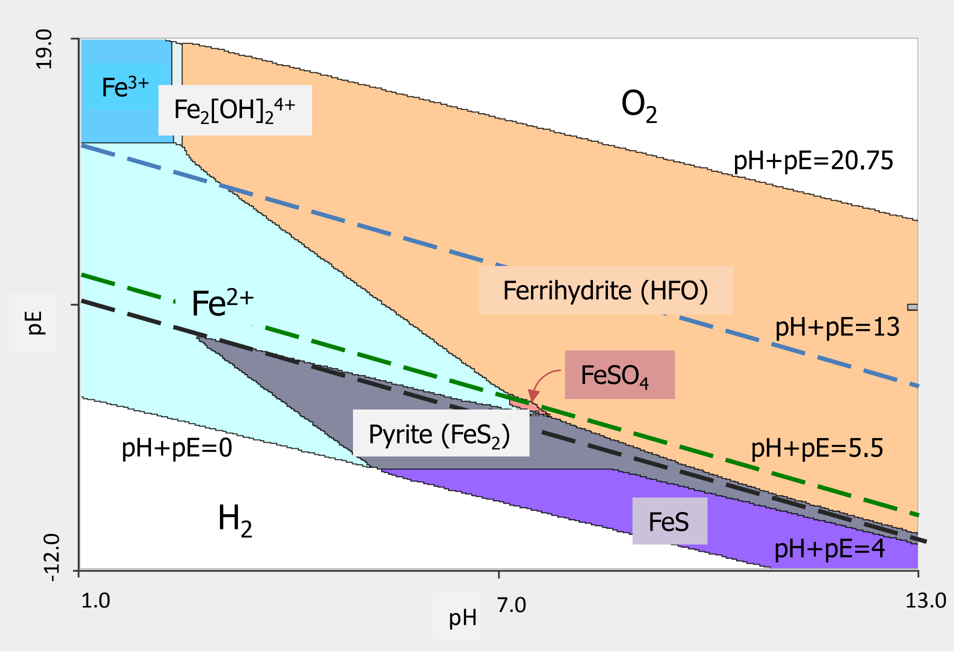




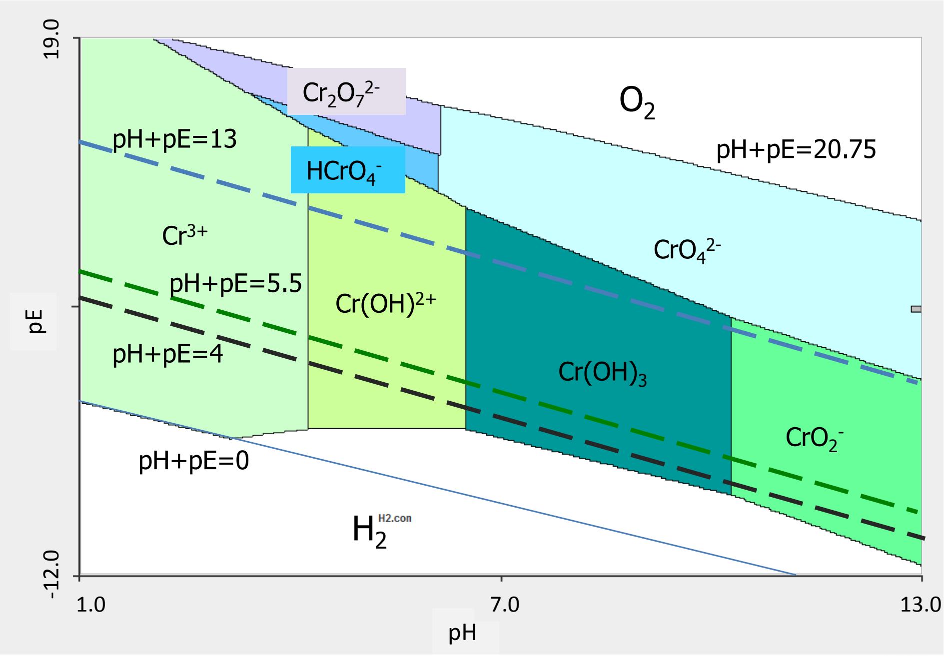


Effects of Redox Conditions (pH+pE)

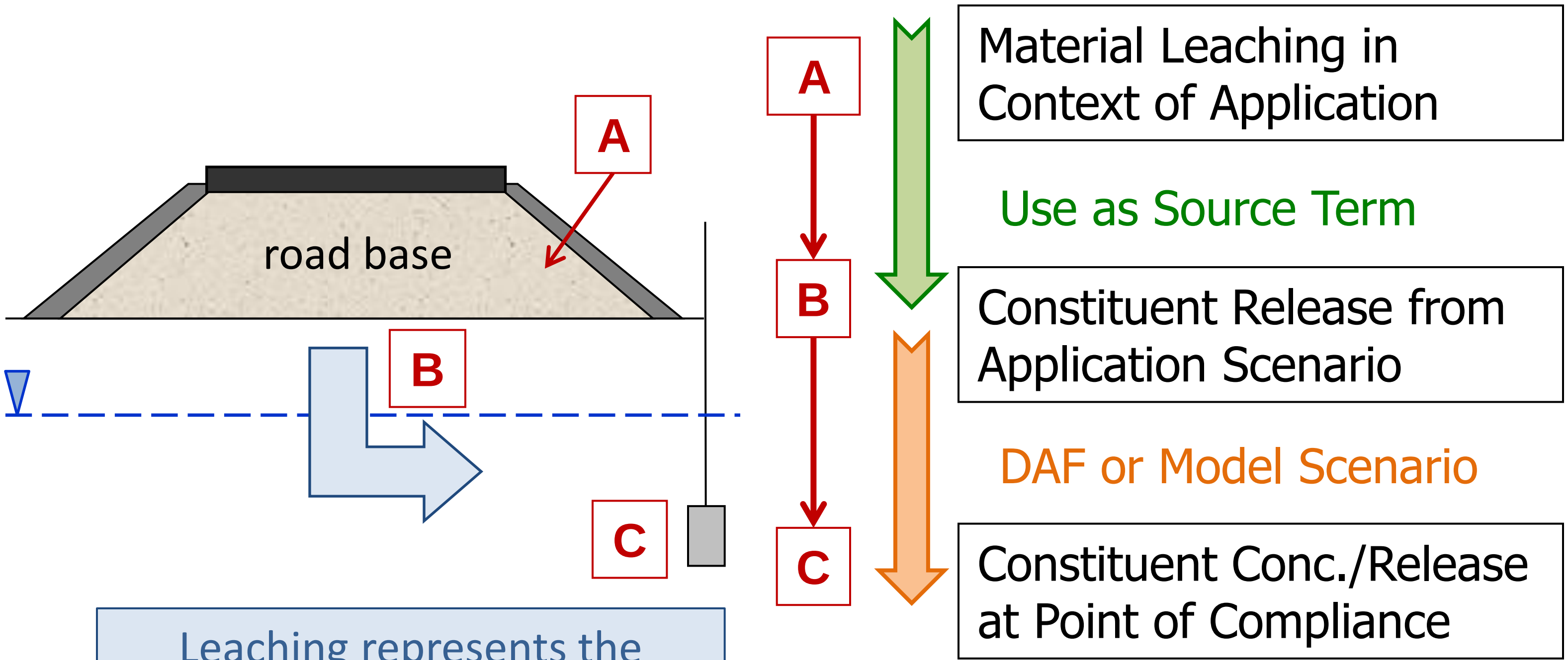
Iron



Chromium



Assessment Approach



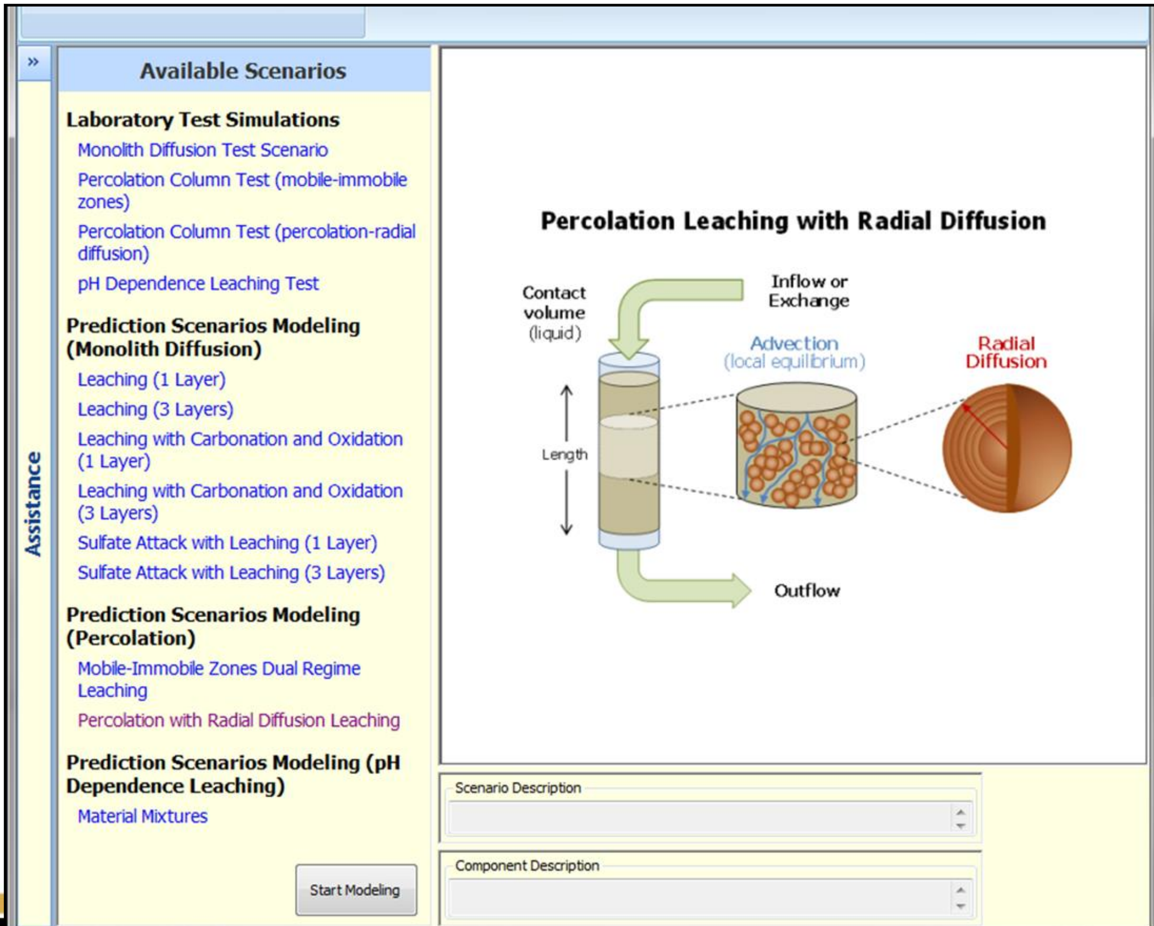
Leaching represents the "source term" for contaminant release into the near-field environment.

LeachXS™

Test Methods Support
Data Management
Statistical Analysis
Quality Control
Chemical Speciation
Scenario Modeling

LeachXS Lite
developed as free simplified version for data management in support of LEAF Methods use

Multiple, Flexible Base Models Available in LeachXS/ORCHESTRA



- Select general field or laboratory scenario to model
- Select from existing reference materials or customize materials
- Select interface conditions (e.g., fixed volume, continuous flow or intermittent flow/ exchange & solutions (e.g., “Hanford infiltration”)
- Resulting model transferable to GoldSIM simulations

Case 9 – Stabilized MSWI Fly Ash

Sustainable Landfill Project

- Cement stabilized monolithic wasteform
- S/S plant operating in Maasvlakte, The Netherlands

Project Goals

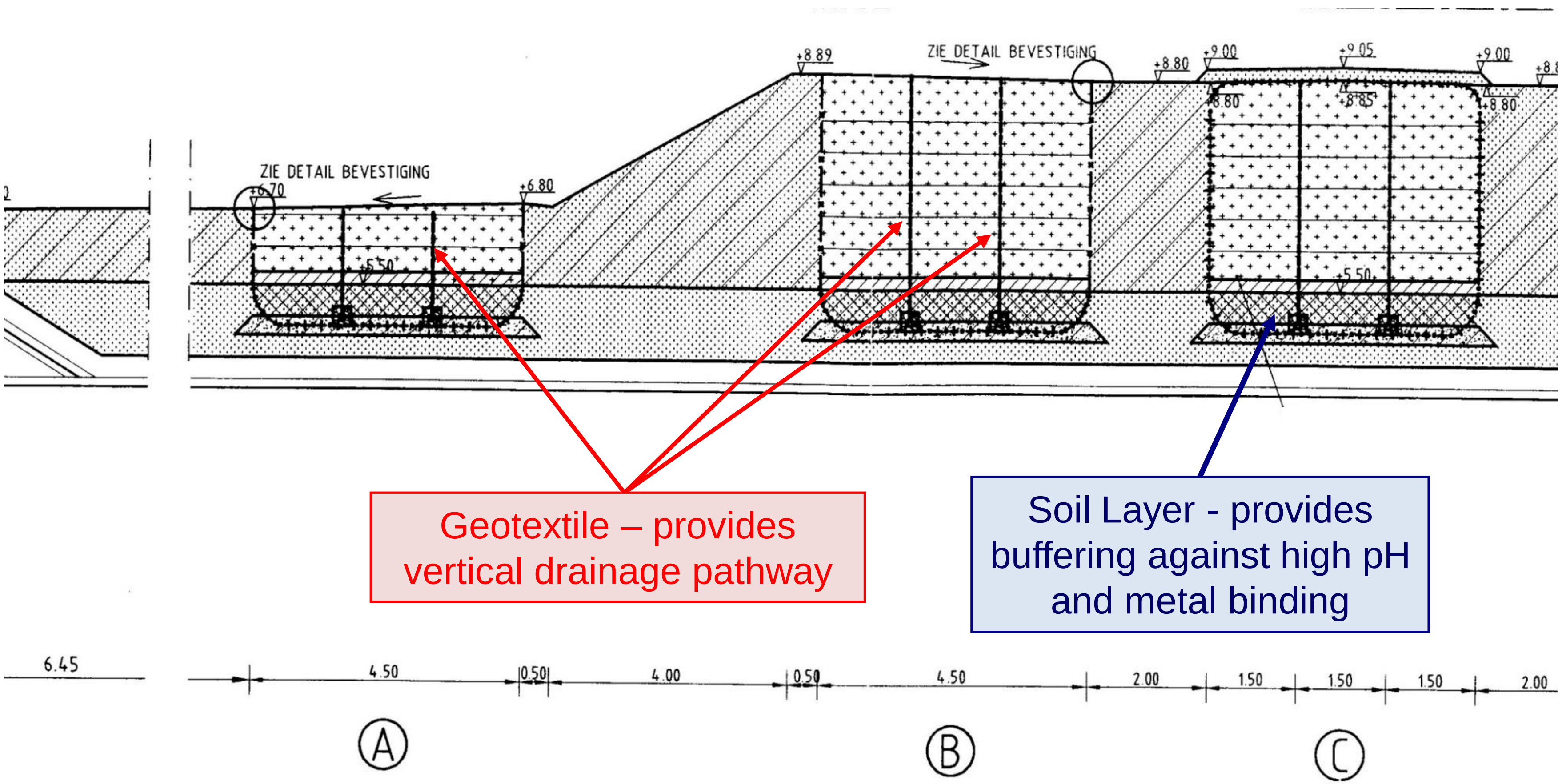
- Evaluate test methods for assessing long-term release behavior
- Functionality of current operational practices
- Development of a quality control procedure
- Chemical reaction/transport modeling (i.e., reactive transport modeling) to understand release controlling processes (chemical and physical)
- Evaluation of field leachate and testing at laboratory, pilot and field scale to improve prediction capabilities of long-term release

Sustainable Landfill Project (The Netherlands)
http://www.duurzaamstorten.nl/wawcs0122289/Home-page.html

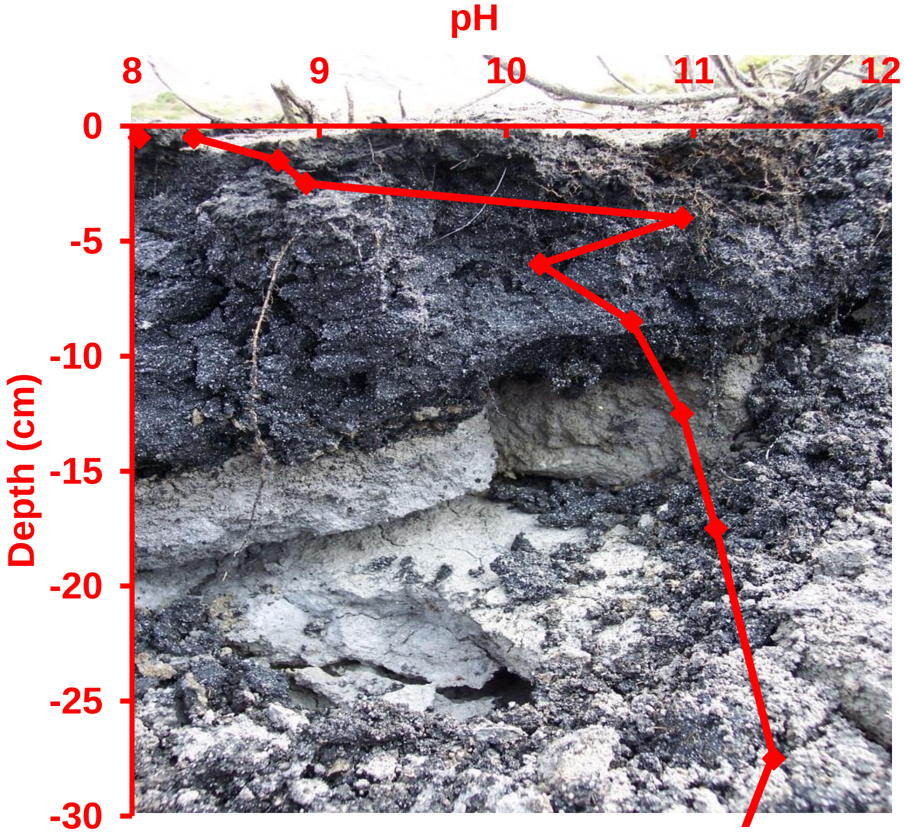
Pilot Experiment Preparation

A&G, Maasvlakte, The Netherlands

Pilot Experiment (front view)



Weathered Stabilized Waste

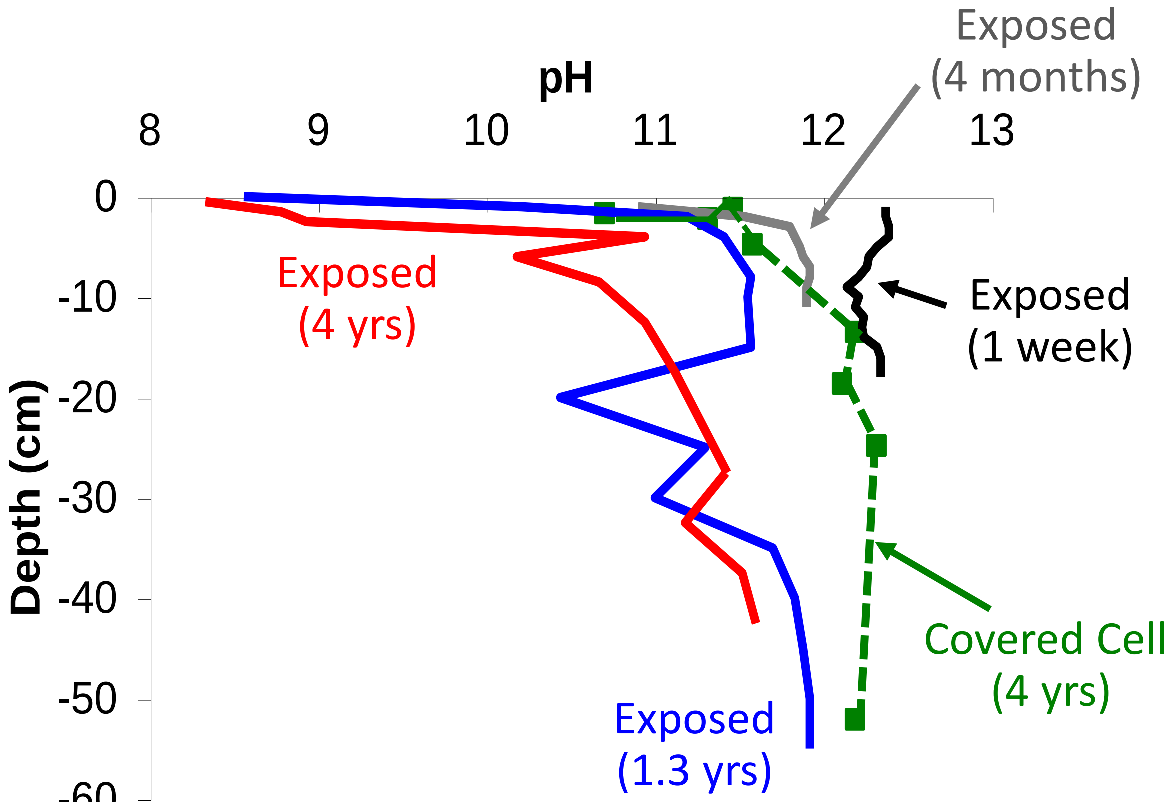


pH Profile measured after 4-yrs of atmospheric exposure

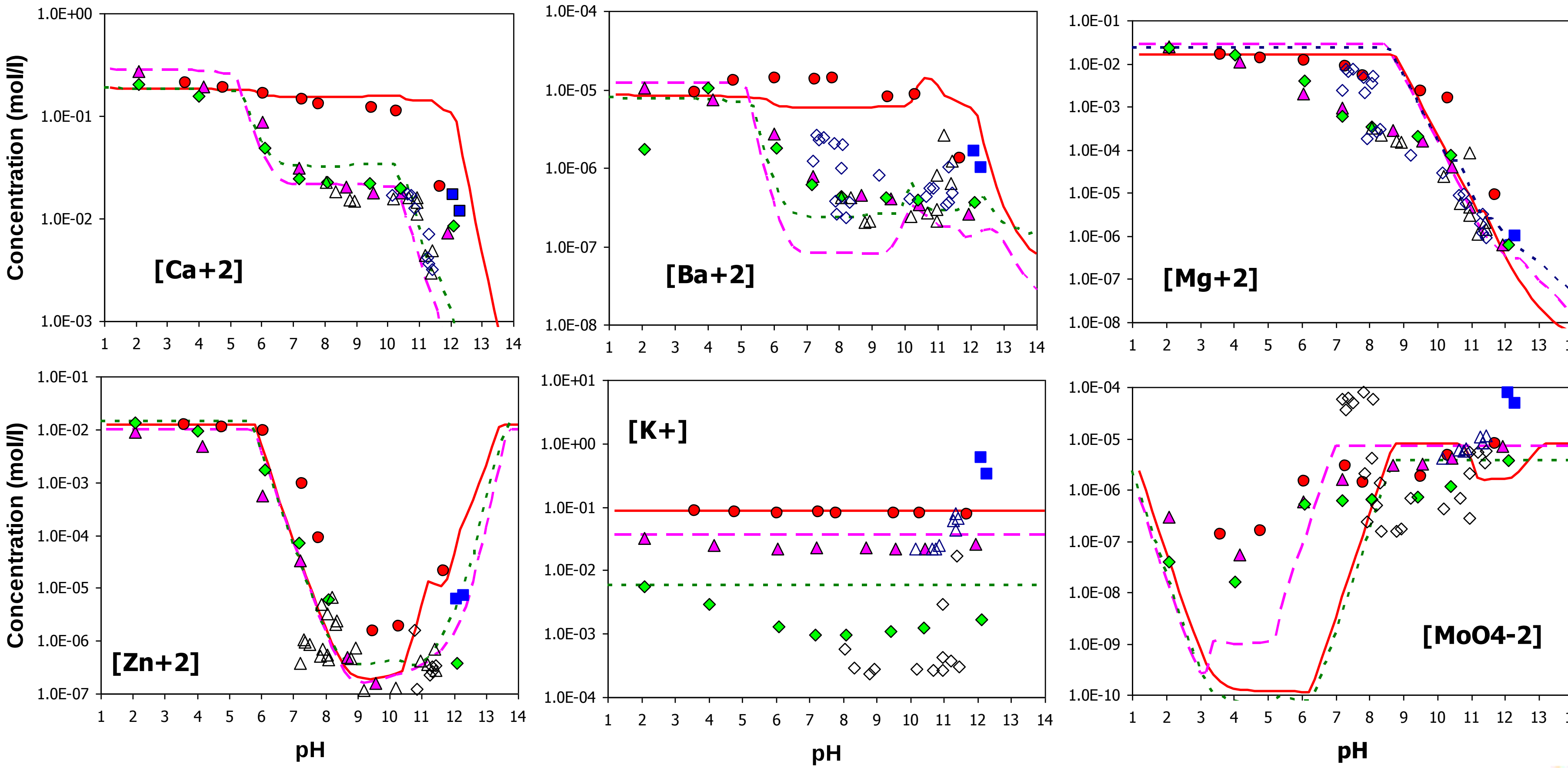
Weathered layer

- Carbonation effects
  - Neutralization to pH 8-9
  - $CaOH_2$ converted to $CaCO_3$
- Plant growth

pH Development in Solidified Waste



Integration of test results from lab, lysimeter, core sample leaching, field percolate and modelling



Red dots: pH dependence test TS14429 fresh
Blue square: percolation test TS14405 fresh
Purple triangle: Aged core material exposed TS14429
Green diamond: Aged core material sealed TS 14429
Open triangle: Core samples EN 12457-2
Open diamond: Core samples EN 12457-2

Red line: model prediction fresh
Purple broken line: model exposed cell
Green dotted line: modeling sealed cell

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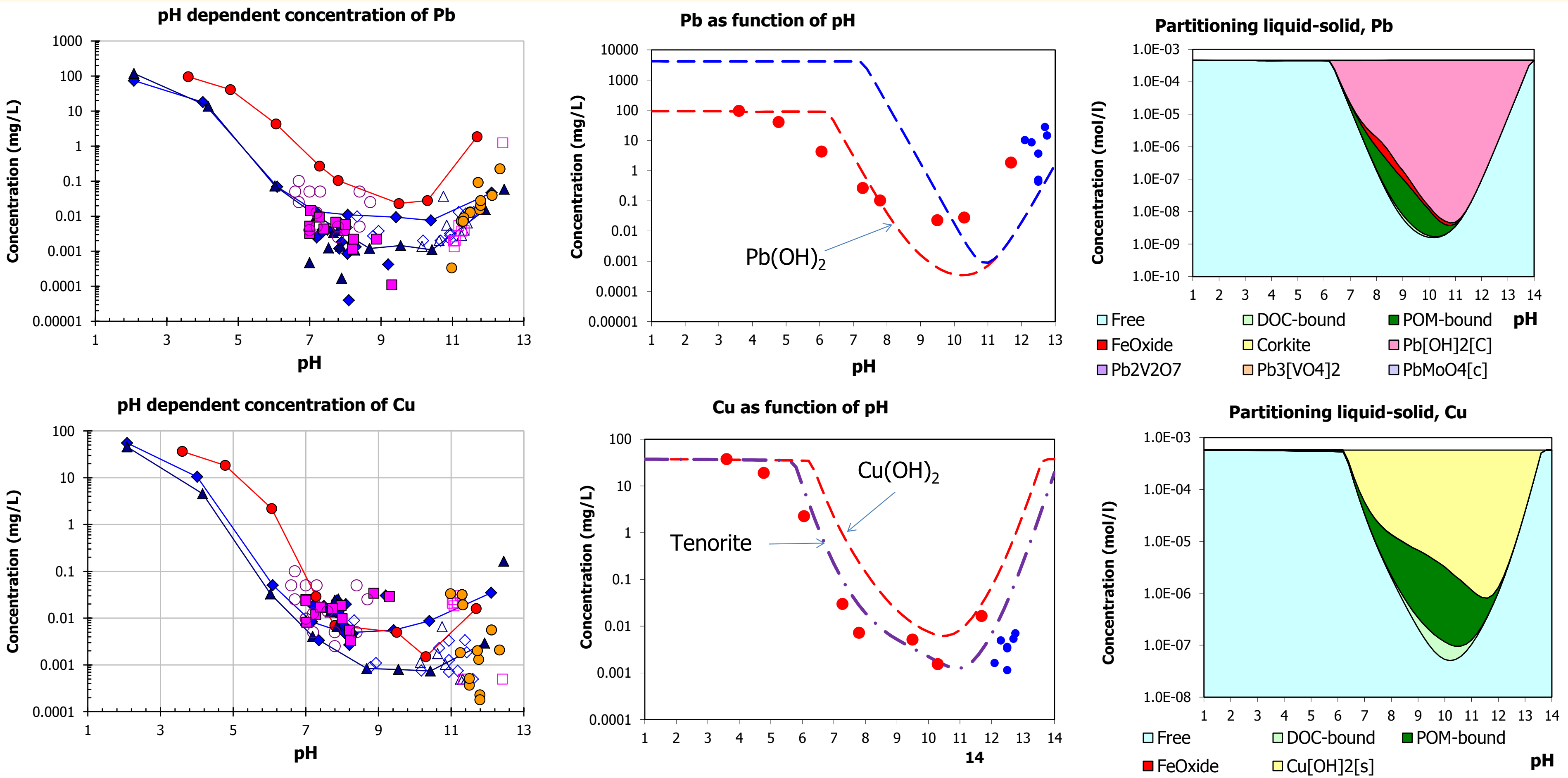


- Core sample composite Cell B (4 yrs)
- Core sample composite Cell C (covered; 4 yrs)
- Leachate Cell B
- Leachate Cell D
- Fresh stabilised waste NL
- Leachate full scale stabilised waste monofill
- Individual core sample Cell B (L/S=10; 4 yrs)
- Individual core sample Cell C (L/S=10; 4 yrs)
- Leachate Cell C
- Individual core sample Cell D (L/S=10; 4 yrs)
- Individual core samples full scale monofill (L/S=10; 10 yrs)

Case 1 - Coal Fly Ash - Landfill Disposal

Compared pH dependent relationships for field leachates and pore water to laboratory test results from a wide range of samples.

Results

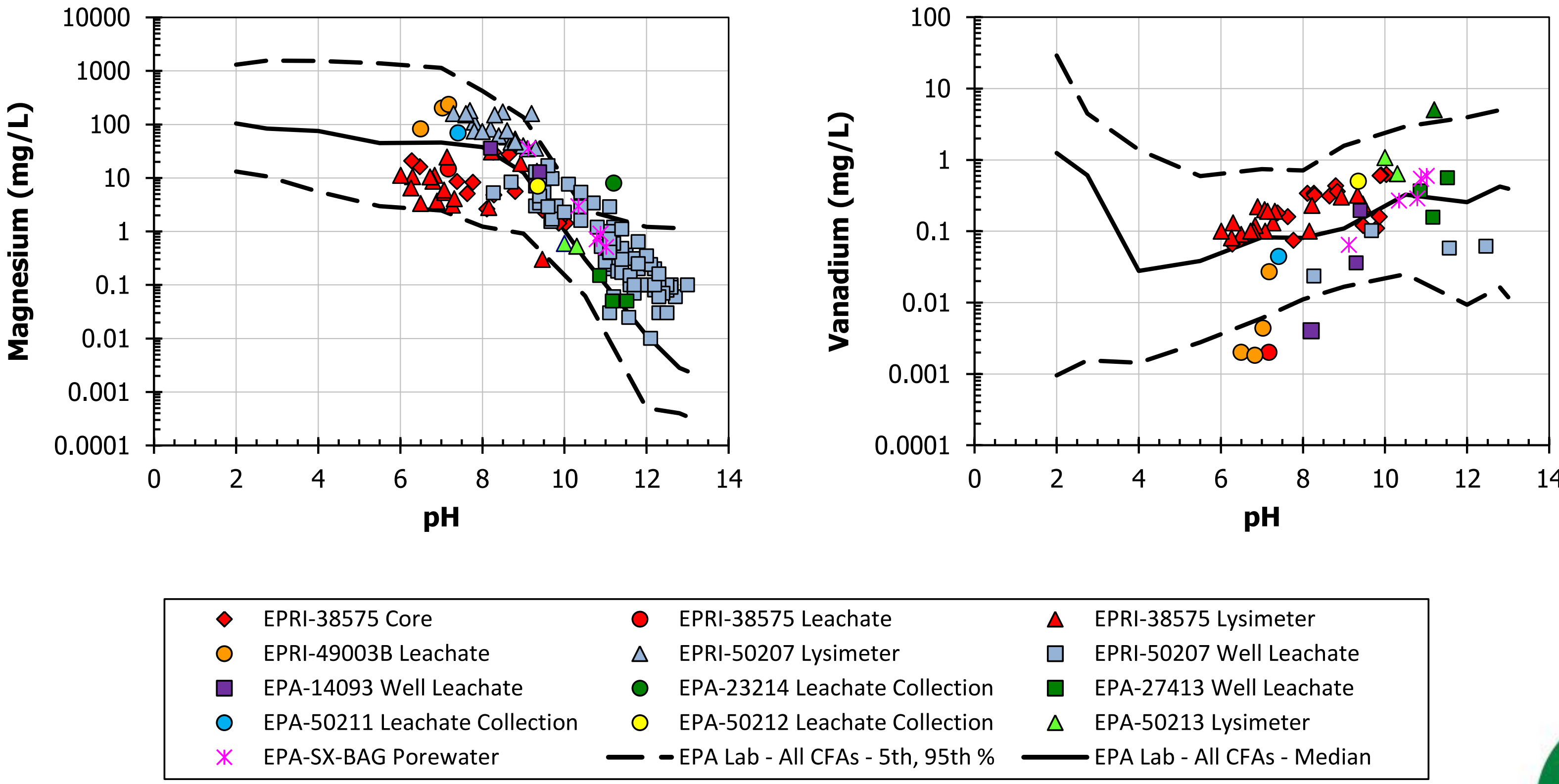
Applicable field leachate pH domain: 6 - 13.

Testing a wide range of samples within a class of materials can be used to define the anticipated field characteristic leaching behavior (pH dependent leaching and range of field of concentrations, or bandwidth).

Can be considered a conservative estimate of the upper limit of field concentrations, but laboratory concentrations of highly soluble constituents must be adjusted based on a correction factor between laboratory L/S and field pore water L/S.

Field leachate concentrations lower than anticipated may be a consequence of either (i) reducing conditions (e.g., Cr, Se), (ii) common ion effects (e.g., Ba), (iii) preferential flow.

Case 1 - Comparison of field leachates to pH-dependent leaching for Mg and V release from CCRs



Case 2 – Coal Fly Ash - Field Lysimeters

Compared large-scale lysimeters (7 years) to percolation column tests.

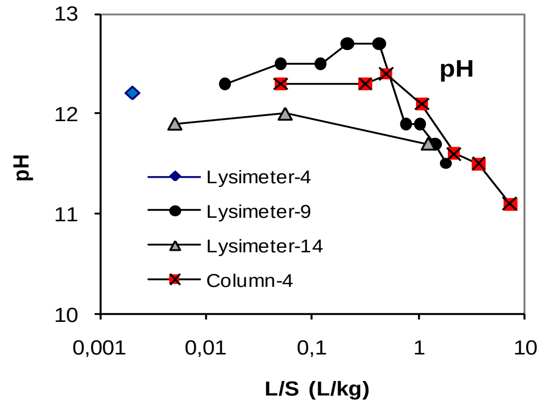
Results

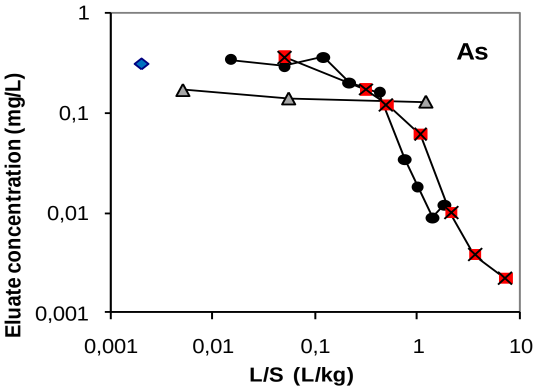
Applicable field pH domain: 11 – 12.8

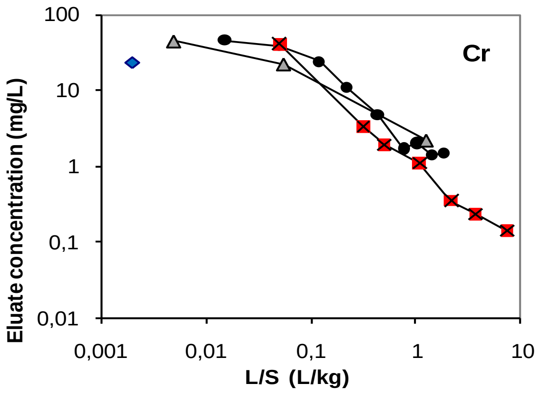
Percolation column testing can provide a good estimate of initial leachate concentrations under field conditions.

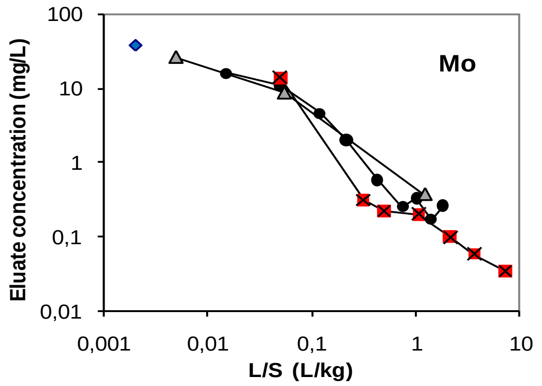
Percolation column testing provides a good approximation of the evolution of leaching profiles as a function of L/S that would be expected under field conditions in the absence of preferential flow and establishment of strong reducing conditions.

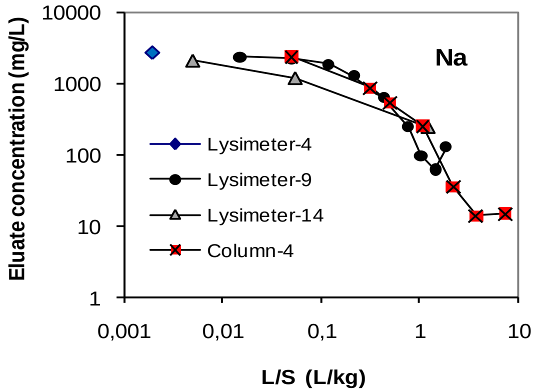
Case 2 – Coal Fly Ash - Field Lysimeters and Laboratory Column Testing











Case 3 – Fixated Scrubber Sludge Landfill

Compared field leaching, field pore water samples, and laboratory leaching test results on landfill core samples, and on fresh "as disposed" material

Results

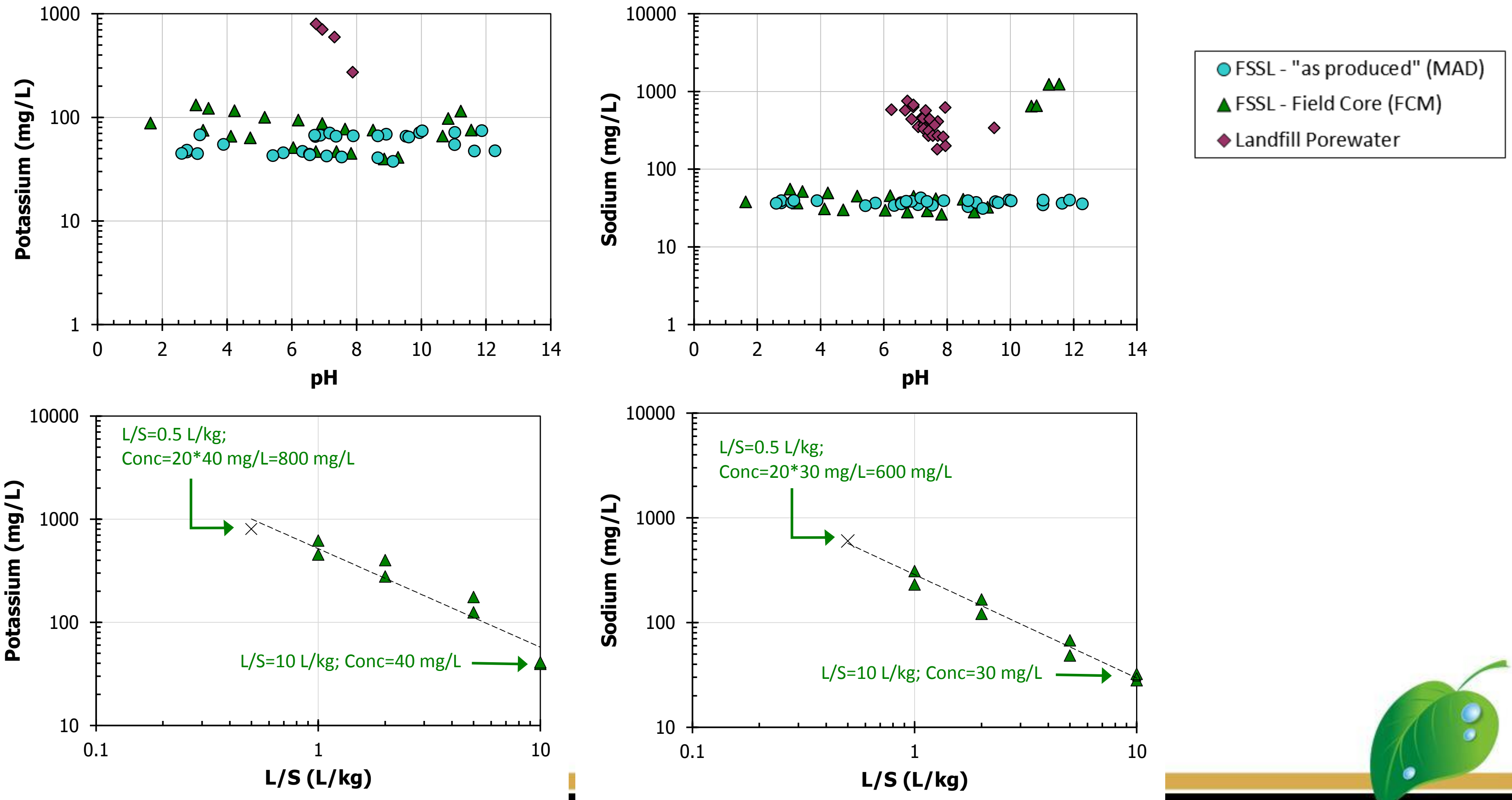
Applicable field pH domain: 6 – 9.5

Carbonation during field aging can have a significant impact on the pH dependent leaching behavior of periodic table Group II elements (i.e., Ca, Sr) and some trace elements (i.e., arsenic).

Water samples (i.e., landfill porewater) are more susceptible to carbonation because of air contact and low buffering capacity.

Higher concentrations of highly soluble species (i.e., K, Na, Cl) can be anticipated in porewater compared to laboratory testing. Elevated concentrations can be readily estimated based (L/S effect).

Case 3 – FSSL – Effect of L/S



Case 4 – Coal Fly Ash Road base and Embankment

Compared the results of field leaching over 2 years from a road base and embankment to percolation column results.

Results

Combined use of pH dependent leaching and percolation column leaching in combination with chemical speciation simulations to understand field performance.

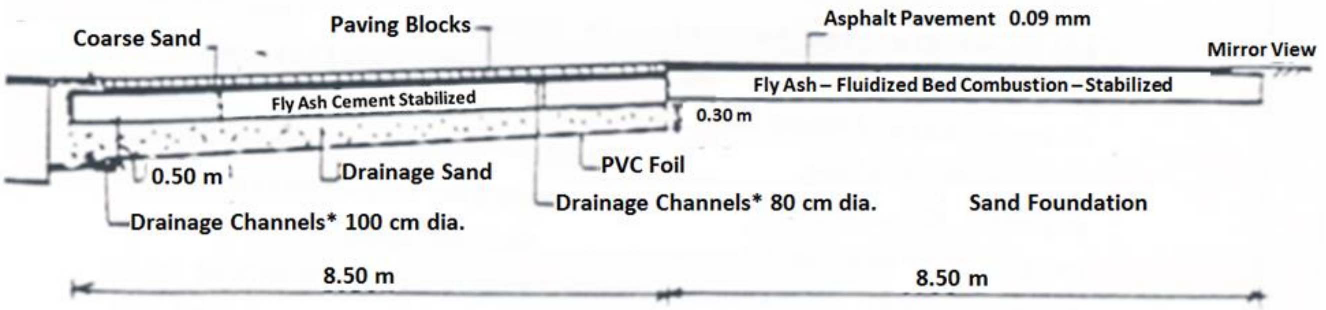
Reducing conditions and carbonation impact leaching of major species (e.g., Ca, Sr) and oxyanions (e.g., Cr).

Percolation column testing provided a realistic estimate of the upper bound concentration for leaching of COPCs.

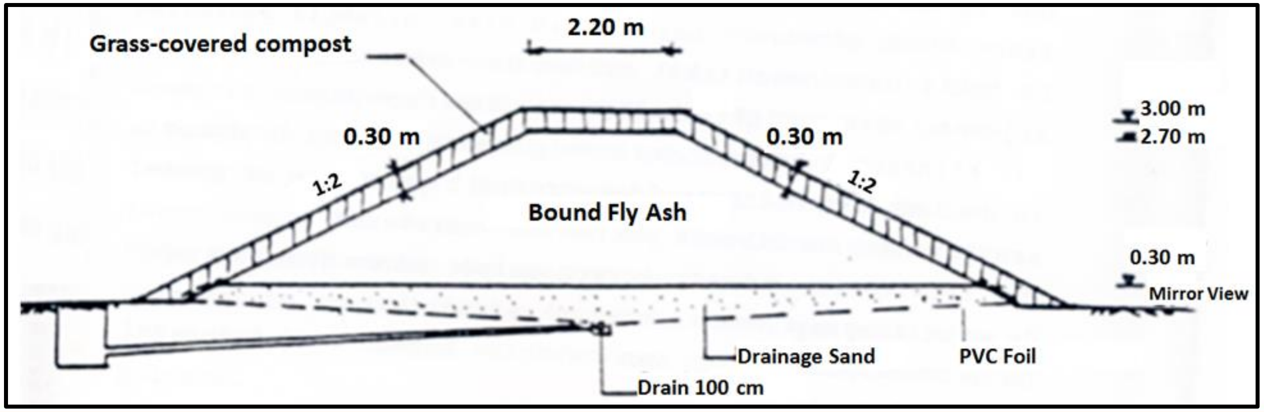
An initial delay in the field before peak leaching concentrations were observed was attributed to the mass transport delay and attenuation associated with drainage materials

Case 4 – Coal Fly Ash Road base and Embankment

Road Base

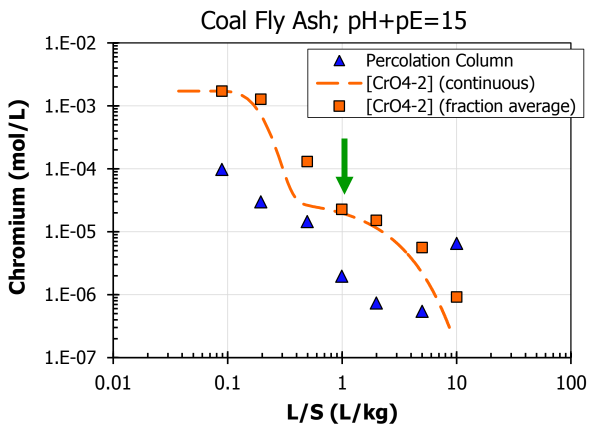


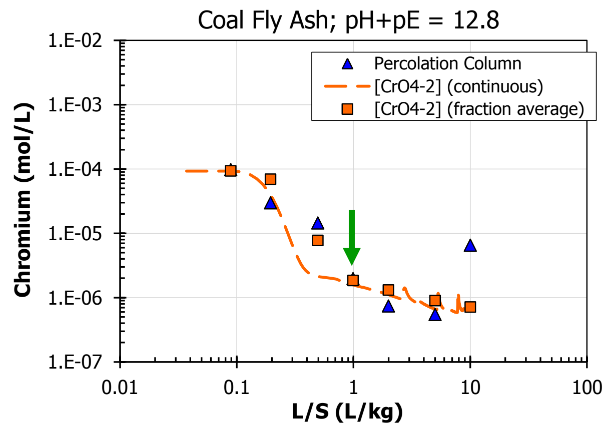
Drainage channels through the fly ash stabilization layer filled with a 2cm/6cm mix of coarse granular aggregate

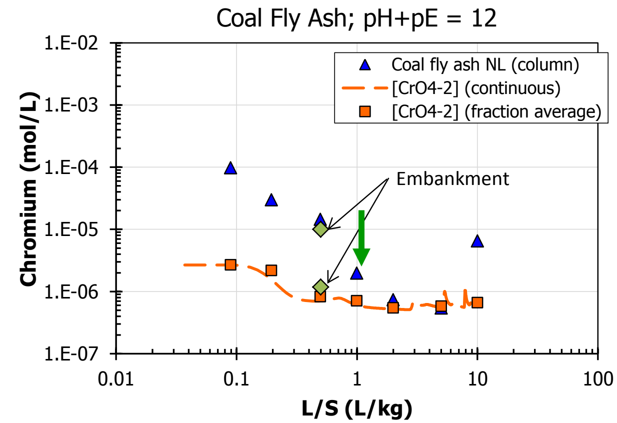


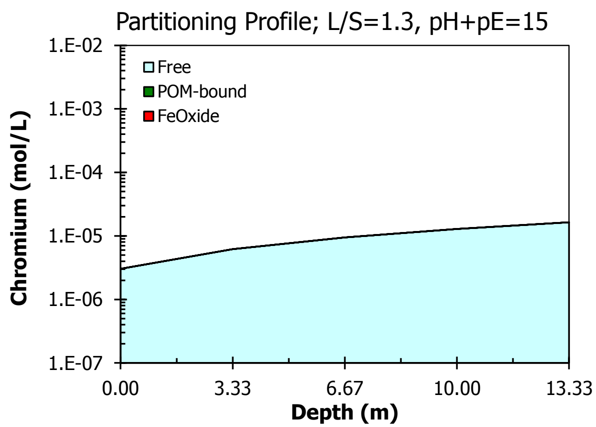
Embankment

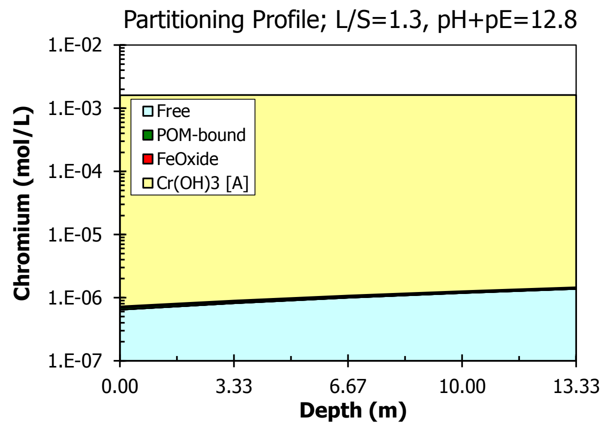
Case 4 – CFA Road Base and Embankment
Effect of Redox Conditions

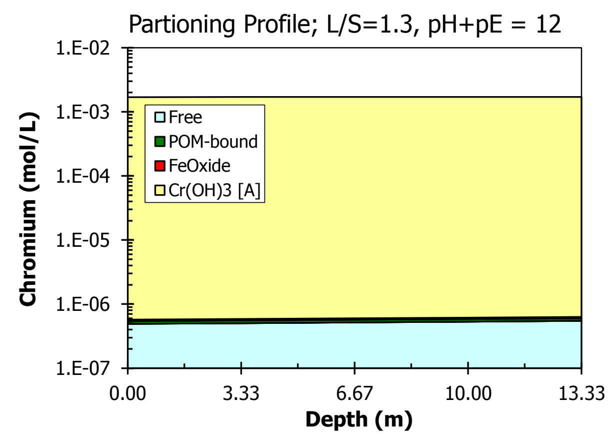








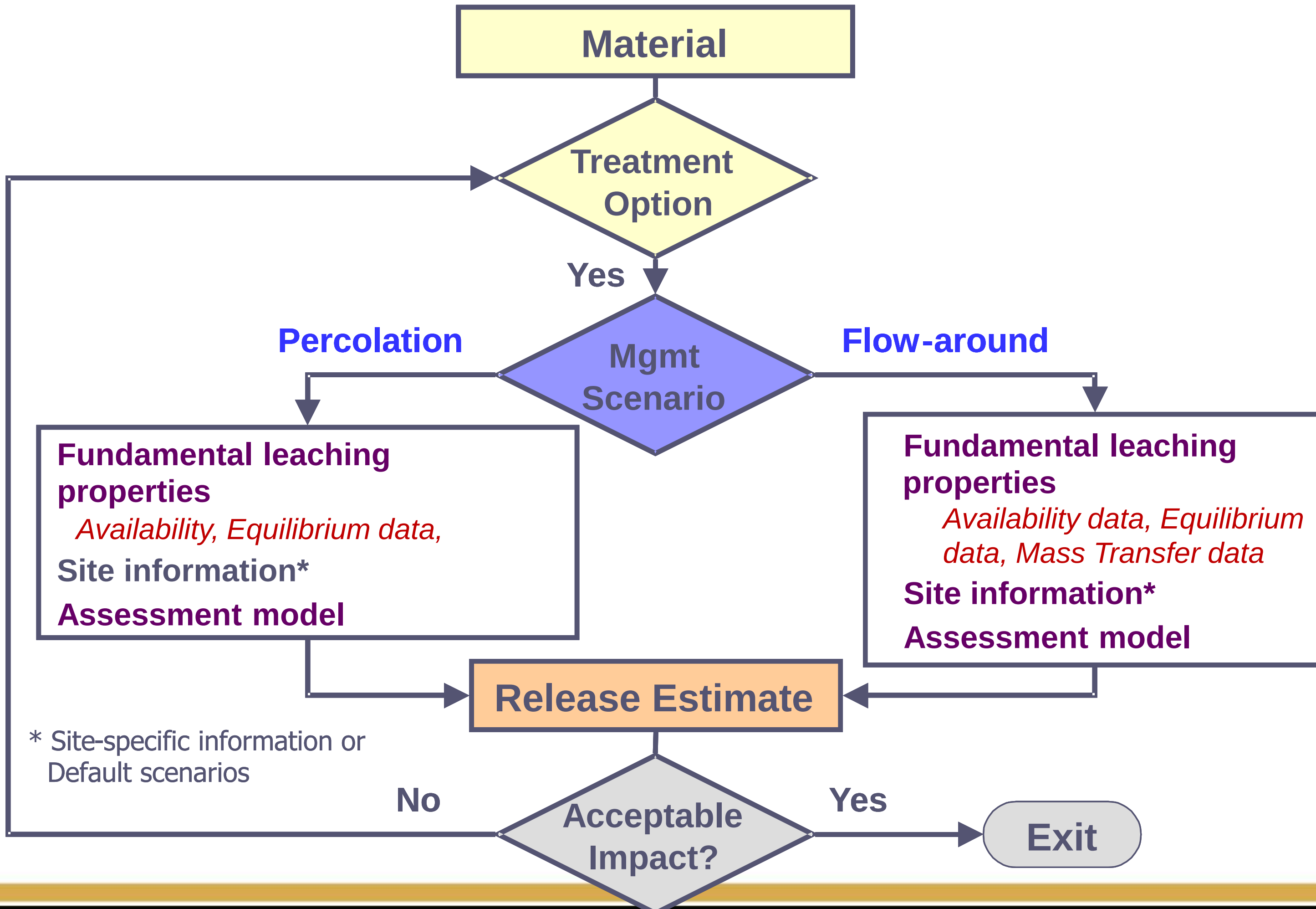




Conclusions

- LEAF can be used to provide a reasonably conservative (upper-bound) source-term for a wide range of materials in use and disposal scenarios.
- Interpretation of the leaching test results should be in the context of the controlling physical and chemical mechanisms of the field scenario.
- Leaching test results should be evaluated with consideration of the potential for changes in leaching conditions
  - pE changes (oxidation of reduced materials, reduction of oxidized material)
  - Carbonation
  - DOC from external sources
- Chemical speciation modeling can be used to consider field conditions beyond the domain of laboratory test conditions.

Selecting Methods and Data Use



Conclusions

- The leaching source term should be used in conjunction with additional assessment steps that include consideration of
  - the location that serves as the basis for exposure assessment (e.g., point of compliance),
  - dilution and attenuation from the point of release to the point of compliance, and
  - appropriate exposure scenarios or reference thresholds (e.g., human health or ecological thresholds).
- Field testing of new use or disposal scenarios or new classes of materials to be used or disposed in new ways is very beneficial to understanding the factors that control leaching for the specific scenario.

Conclusions

- Individual sources of similar materials based on process origin and leaching behavior can be grouped into material classes for assessment purposes
- Accumulation of LEAF testing data for a range of materials and over time can provide useful estimates of uncertainty and variability associated with material classes.
- Creation of one or more databases containing leaching data used in regulatory decision making and monitoring can facilitate efficient use of leaching data in future assessments
  - More robust assessments
  - Reduced testing and evaluation costs

Conclusions

- Single point leaching tests and other common leaching assessment approaches cannot provided needed insights into the expected leaching performance of materials under the range of expected field conditions.
- The combination of results from pH-dependent leaching tests and percolation column tests (or monolith leach tests) can be used to provide reliably conservative estimates of field leachate concentrations under both disposal and use scenarios.

Acknowledgements

Vanderbilt University research team and collaborators:

D.S. Kosson (USA lead)[1], A.C. Garrabrants[1*], H.A. van der Sloot[2] (EU Lead), R. DeLapp[1], D. DeLapp[1], S. Sarkar[1], K. Brown[1], P. Seignette[3], O. Hjelmar[4], J.C.L. Meeussen[3]

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[7] ARCADIS-US, Inc., RTP, NC

Thank you

for your attention and invitation to participate in this workshop!

Questions?

Additional Supporting Information

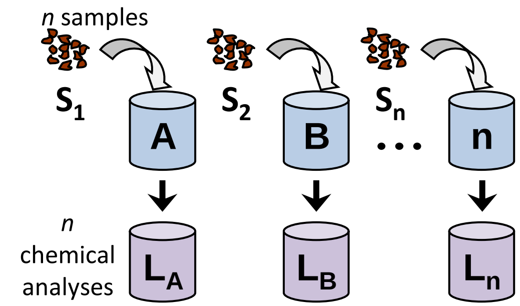
Method 1313 Overview

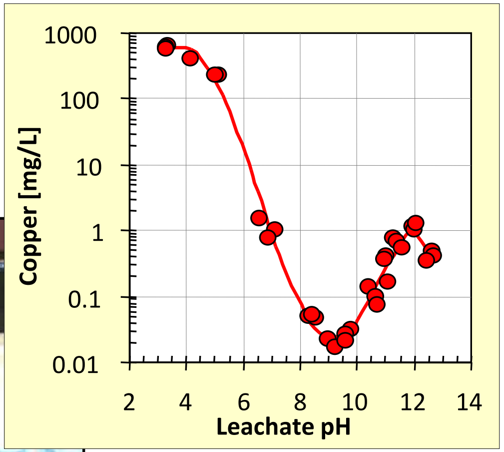
Equilibrium Leaching Test

- Parallel batch as function of pH

Test Specifications

- 9 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 or KOH
- Contact time based on particle size
  - 18-72 hours
- Reported Data
  - Equivalents of acid/base added
  - Eluate pH and conductivity
  - Eluate constituent concentrations





Titration Curve and Liquid-solid Partitioning (LSP) Curve as Function of Eluate pH

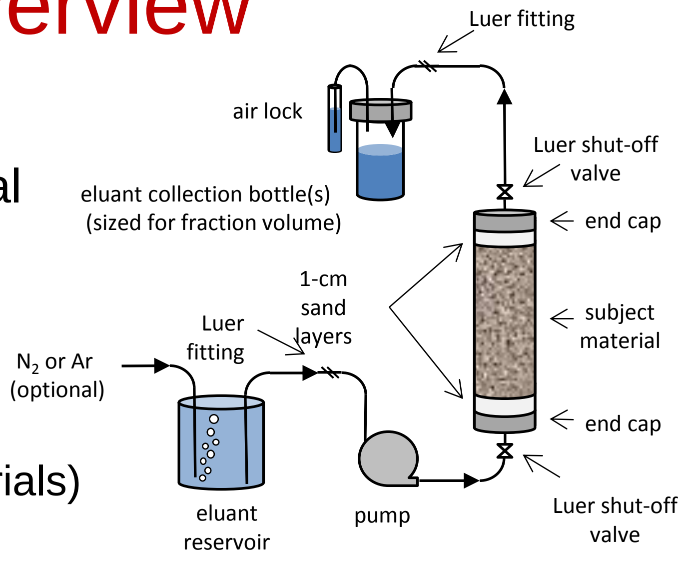
Method 1314 Overview

Equilibrium Leaching Test

- Percolation through loosely-packed material

Test Specifications

- 5-cm diameter x 30-cm high glass column
- Size-reduced material
- DI water or 1 mM $CaCl_2$ (clays, organic materials)
- Upward flow to minimize channeling
- Collect leachate at cumulative L/S
  - ❑ 0.2, 0.5, 1, 1.5, 2, 4.5, 5, 9.5, 10 mL/g-dry
- Reported Data
  - ❑ Eluate volume collected
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations



Liquid-solid Partitioning (LSP) Curve as Function of L/S; Estimate of Pore Water Concentration

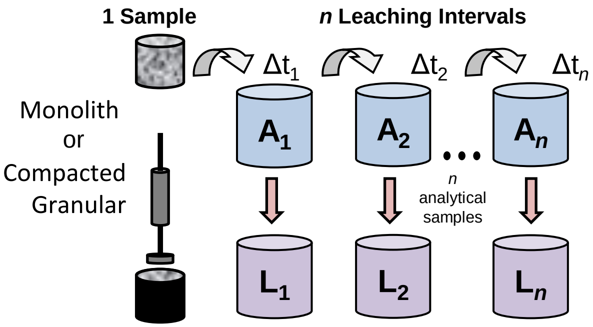
Method 1315 Overview

Mass-Transfer Test

- Semi-dynamic tank leach test

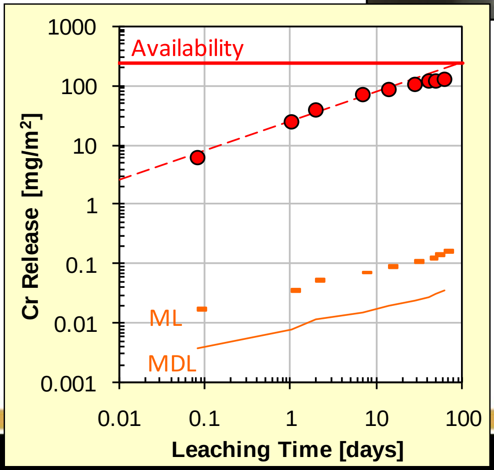
Test Specifications

- Material forms
  - ❑ monolithic (all faces exposed)
  - ❑ compacted granular (1 circular face exposed)
- DI water so that waste dictates pH
- Liquid-surface area ratio (L/A) of 9±1 mL/cm^2
- Refresh leaching solution at cumulative times
  - ❑ 2, 25, 48 hrs, 7, 14, 28, 42, 49, 63 days
- Reported Data
  - ❑ Refresh time
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations



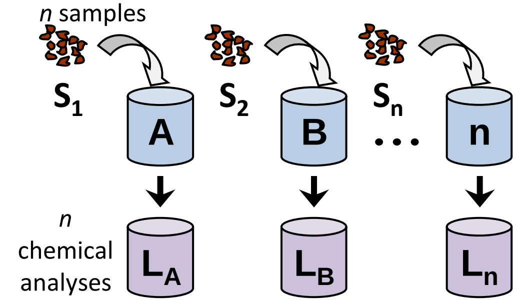
Monolithic

Granular



Flux and Cumulative Release as a Function of Leaching Time

Method 1316 Overview

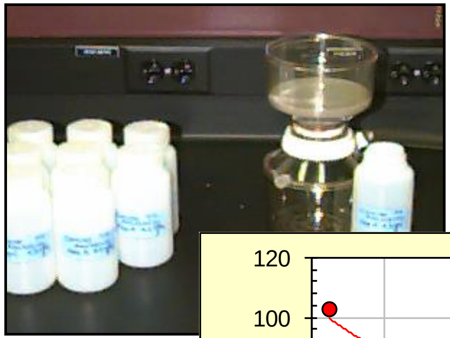


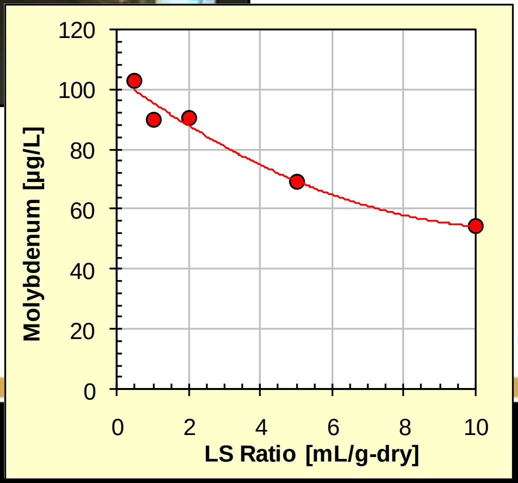
Equilibrium Leaching Test

- Parallel batch as function of L/S

Test Specifications

- Five specified L/S values (±0.2 mL/g-dry)
  - 10, 5, 2, 1, 0.5 mL/g-dry
- Size-reduced material
- DI water (material dictates pH)
- Contact time based on particle size
  - 18-72 hours
- Reported Data
  - Eluate L/S
  - Eluate pH and conductivity
  - Eluate constituent concentrations



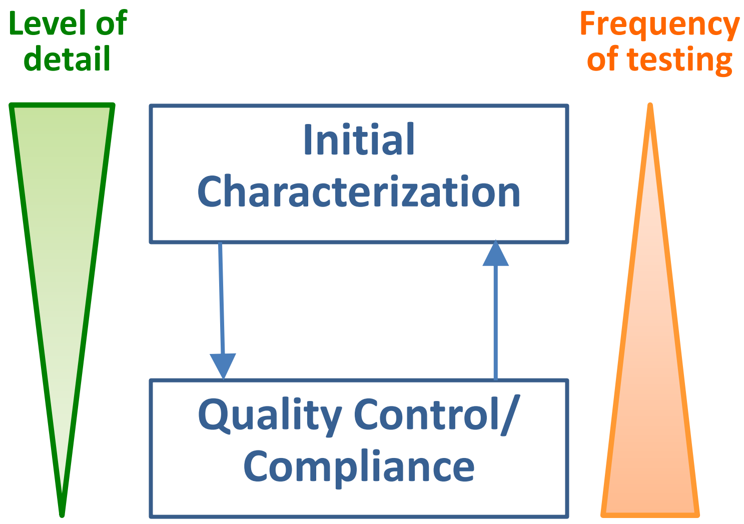


Liquid-solid Partitioning (LSP) Curve as a Function of L/S; Estimate of Pore Water Concentration

Tiered Approach in Testing

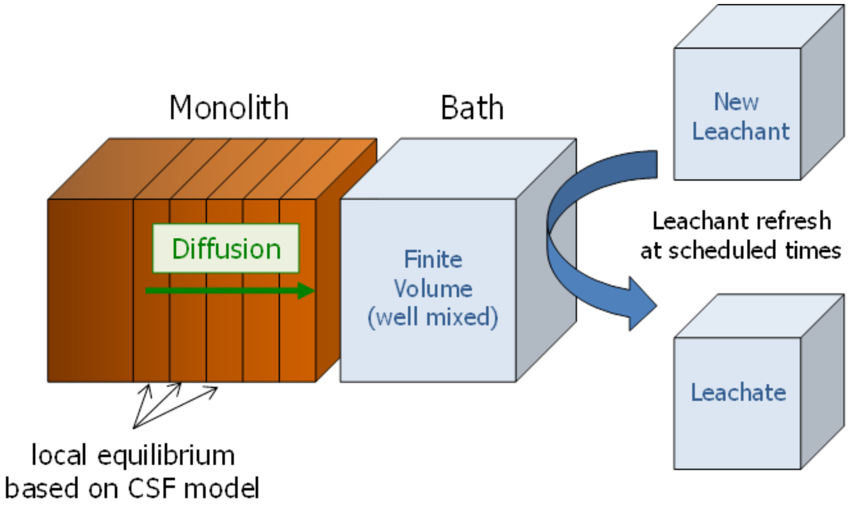
Goal: Efficient use of testing to minimize cost

- Different users and evaluation steps have different information needs.
- Once the release characteristics of a product type or class are established, simpler screening or conformity testing will suffice for critical parameters.



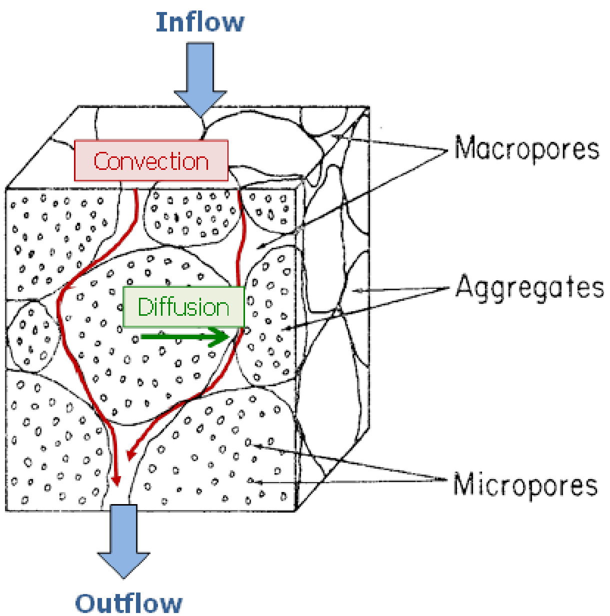
- Testing frequency based on the risk of exceeding limit values.
- Using a limited part of the full characterization testing for screening or compliance simplifies evaluation

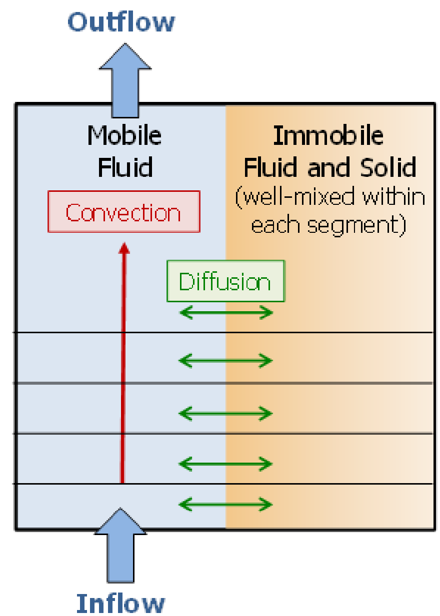
Monolith Diffusion



- Laboratory and field simulations
- Variable water contacting sequence, chemistry
- Saturated or unsaturated
- Carbonation, oxidation ingress
- Sulfate attack with leaching

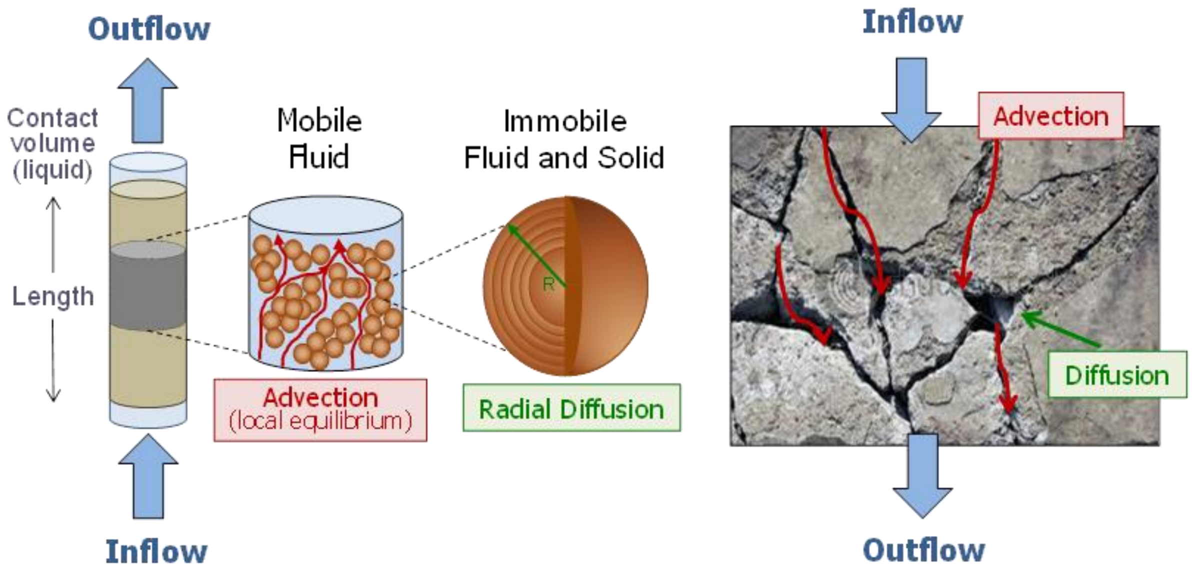
Percolation with Mobile-Immobile Zones





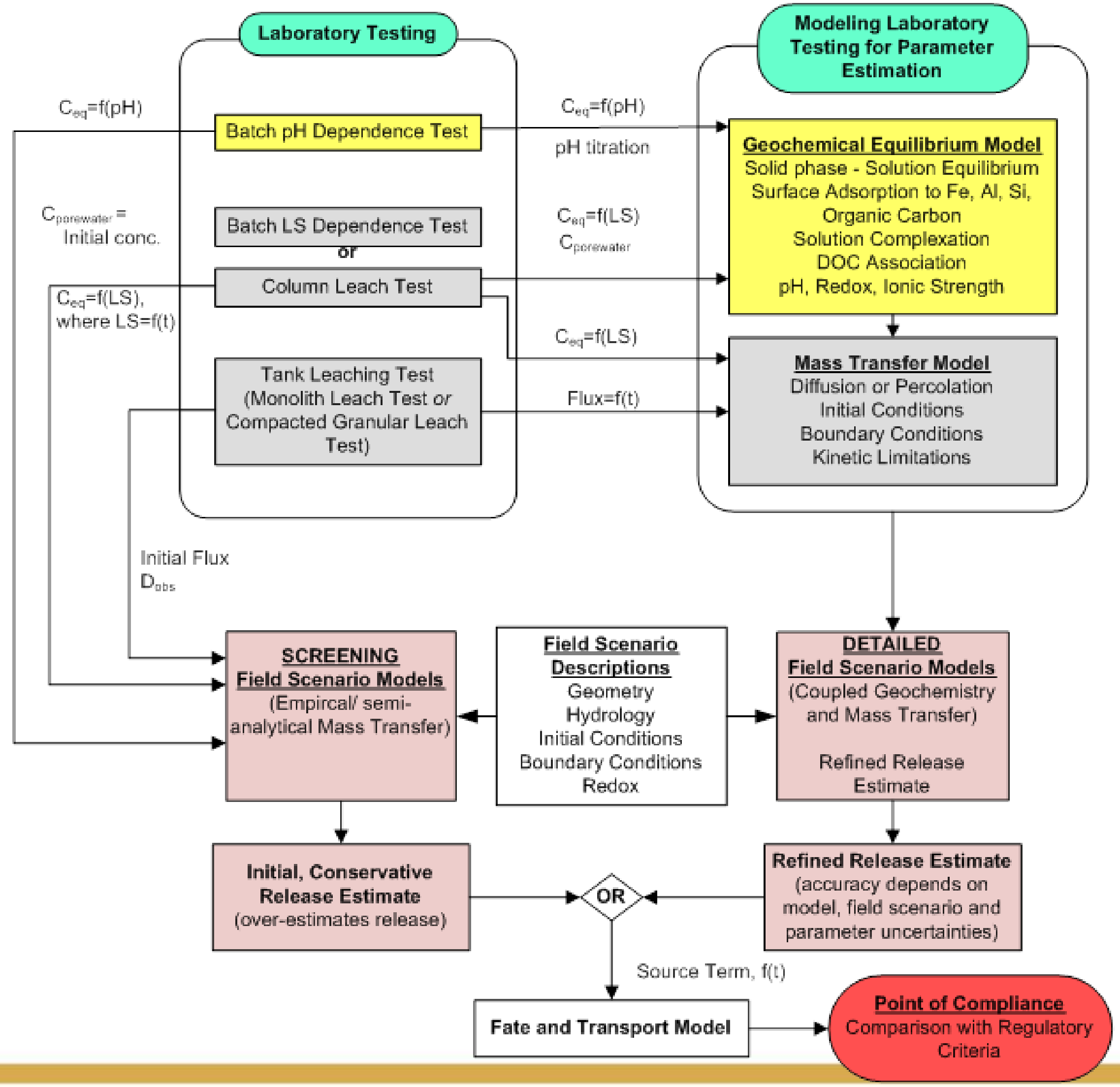
- Laboratory and field simulations
- Variable water flow rate, chemistry
- Effects of preferential flow

Percolation with Radial Diffusion



- Laboratory and field simulations
- Cracked materials or packed beds
- Effects of preferential flow
- Variable water flow rate, chemistry

Data Flow



- Results may be used empirically or with chemical speciation based models
- Screening is often based on peak concentration
- Definition of range of field conditions is critical