The Leaching Environmental Assessment Framework as a Tool for Risk-informed, Science-based Regulation

D.S. Kosson¹, A.C. Garrabrants¹, Hans van der Sloot², Susan Thorneloe³, Richard Benware⁴, Greg Helms⁴, and Mark Baldwin⁴

¹ Vanderbilt University, Nashville, TN
² van der Sloot Consultancy, Langedijk, the Netherlands
³ U.S. EPA Office of Research and Development, RTP, NC

19 June 2012
Presentation Outline

Introduction to Leaching Assessment

Overview of LEAF
  • Leaching Tests
  • Data Management

Overview of Interlaboratory Validation

Applicability to DOE Challenges

Conclusions
Materials Testing – Historically

1960s-1990s

Protection from hazardous wastes; waste minimization/conservation.
  • Classification of “hazardous” waste (RCRA Subtitle C/D landfills)
  • Acceptance criteria for disposal of treated wastes (Universal Treatment Standards)
  • Best demonstrated available treatment (BDAT)

1990s – present

Move toward integrated materials management; balancing overall environmental performance with materials costs and long-term liability
  • Global economic policy (resource costs, international trade)
  • Risk-informed waste management practices
  • Changing definition of waste materials (e.g., Dutch Building Materials Decree; U.S. definition of solid waste)
  • Applications for waste delisting and alternative measures of treatment effectiveness
  • Re-use of waste materials (mine reclamation, alternative construction materials)
What is Leaching?
Process by which constituents of a solid material are released into a contacting water phase

**Percolation Release**
- Water passes thru material
- Equilibrium
- High concentration

**Mass Transfer Release**
- Water flows around material
- Diffusion to material surface
- Lower concentration
Leaching - Controlling Factors

**Physical Factors**
- Particle size
- Rate of mass transport

**Site Conditions**
- Flow rate of leachant
- Temperature
- Bed porosity
- Fill geometry
- Permeability
- Hydrological conditions

**Chemical Factors**
- Equilibrium/kinetic control
- pH
- Liquid-solid ratio
- Complexation
- Redox
- Sorption
- Biological activity

**Release Mechanisms**
- Wash Off
- Dissolution
- Diffusion

- H⁺
- CO₂
- O₂

- Erosion

- Trace elements
- Soluble salts
- TOC (at high pH) → DOC
Total Content

Total Content **Does Not** Correlate to Leaching

![Graph showing correlation between As total content and eluate concentration](image)
Many Leaching Scenarios …

- landfill
- drinking water well
- road base
- contaminated soil
- agriculture
- coastal protection
- industrially contaminated soil
- factory
- seepage basin
- construction debris and run-off
- roof runoff
- municipal sewer system
Common Assessment Approach

- CCR Leaching
- CCR Leaching in Use Context
  - Use Source Term
  - Constituent Release from Use
    - Location DAF
    - Constituent Pt. of Compliance

Threshold Definition

Road base

A* A* B

A* B C

C

Location DAF

Constituent Pt. of Compliance
Leaching Tests

Total Content
- Correlation to leaching?

Regulatory Tests
- Comparison to limits
- Does not consider
  - Release Scenario
  - Time (kinetics)
  - Mass Transport

Characterization Tests
- Range of conditions
- Comparisons between
  - Materials
  - Treatments
  - Scenarios
Leaching Method Development

Leaching characterization applied to anticipated release conditions resulting in improved accuracy and more reliable environmental decision making


Parallel and coordinated methods development in the EU and US

Designed to address concerns of EPA Science Advisory Board

- Form of the material (e.g., monolithic)
- Leaching parameters (e.g., pH, liquid-solid ratio (L/S), release rate)

Intended for situations where TCLP is not required or best suited

- Assessment of materials for beneficial reuse
- Evaluating treatment effectiveness (determination of equivalent treatment)
- Characterizing potential release from high-volume materials
- Corrective action (remediation decisions)
Leaching Environmental Assessment Framework

LEAF is a collection of …
- Four leaching 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 associated use and disposal scenarios.

LEAF facilitates integration of leaching methods which provides a material-specific “source term” release for support of material management decisions.

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

Note: Incorporation into SW-846 is ongoing; method identification numbers are subject to change
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 HNO₃ or NaOH
- 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 CaCl₂ (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/cm²
• 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

 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)
  - 10.0, 5.0, 2.0, 1.0, 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
Data Management Tools

Data Templates

• Excel Spreadsheets for Each Method
  □ Perform basic, required calculations (e.g., moisture content)
  □ Record laboratory data
  □ Archive analytical data with laboratory information

• Form the upload file to materials database

LeachXS (Leaching eXpert System) Lite

• Data management, visualization and processing program
• Compare Leaching Test Data
  □ Between materials for a single constituent (e.g., As in two different CCRs)
  □ Between constituents in a single material (e.g., Ba and SO₄ in cement)
  □ To default or user-defined “indicator lines” (e.g., QA limits, threshold values)

• Export leaching data to Excel spreadsheets
• Freely available at http://www.vanderbilt.edu/leaching
DRAFT METHOD 1313 (Liquid-Solid Partitioning as a Function of pH) LAB DATA

**Data Templates**

1) Enter particle size and solids content

2) Enter acid/base type & normality

3) Enter target equivalents from titration curve

4) Follow “set-up” recipe

5) Record pH, conductivity, Eh (optional)

6) Verify that final pH is in acceptable range
1) Set working materials database
2) Select material tests from database
3) Choose display options
4) Check comparison of materials for a single constituent
5) Bulk export one or more constituents to an Excel spreadsheet
LEAF Methods Validation
Study Materials

Coal Combustion Fly Ash
- Collected for EPA study
- Selected for validation of …
  - Method 1313
  - Method 1316

Solidified Waste Analog
- Created at Vanderbilt University
- Blast Furnace Slag, Class C Fly Ash, Type I/II Cement, Metal Salts
- Selected for validation of …
  - Method 1313
  - Method 1316
  - Method 1315

Contaminated Field Soil
- Copper smelter site
- Selected for validation of …
  - Method 1313
  - Method 1316
  - Method 1315
  - Method 1314

Brass Foundry Sand
- Selected for validation of …
  - Method 1315
  - Method 1314
Method 1313 Validation

Coal Combustion Fly Ash

Contaminated Field Soil

Reproducibility

Graphs showing data for Selenium and Arsenic (mg/L) across different pH levels, with lines indicating Mean, Overall SD, Between Lab SD, and Within Lab SD. MDL and ML values are marked on the graphs.
Data Processing

Log\(_{10}\)-Transform of Test Output
- Method 1313 – Eluate Concentration
- Method 1314 – Eluate Concentration, Cumulative Mass Release
- Method 1315 – Interval Mass Flux, Cumulative Mass Release
- Method 1316 – Eluate Concentration

Linear Interpolation and Extrapolation
- Collected Data Shows Variability
- Brings Data to Specified pH, L/S or Time
- Consistency in Comparisons

Implications for Compliance Standards
# LEAF Method Precision

<table>
<thead>
<tr>
<th>Method</th>
<th>Test Output</th>
<th>$RSD_r$ (%)</th>
<th>$RSD_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method 1313</td>
<td>Eluate Concentration (average over pH range)</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>Method 1314</td>
<td>Eluate Concentration (9th fraction at L/S=10)</td>
<td>13</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Mass Release (cumulative to L/S=0.5)</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Mass Release (cumulative to L/S=10)</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>Method 1315</td>
<td>Interval Flux (average excluding wash-off)</td>
<td>11</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Mass Release (cumulative to 7-days)</td>
<td>9</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Mass Release (cumulative to 63-days)</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>Method 1316</td>
<td>Eluate Concentration (average over L/S range)</td>
<td>7</td>
<td>17</td>
</tr>
</tbody>
</table>
Precision Comparison
(pH-dependence Tests)

Repeatability
- Max SWA Sb @ pH 2 RSDr = 130%
- Max CFS Ba @ pH 13 RSDr = 114%

Reproducibility
- Max SWA Sb @ pH 2 RSDn = 500%
- Max CFS Ba @ pH 13 RSDn = 300%
- Max RSDn = 124%
- Max RSDn = 118%

Method Precision
- Method 1314 Eluate Concentration (2 ≤ pH ≤ 13)
- EN12457 Eluate Concentration (natural pH)
- TCLP Eluate Concentration (acetic acid buffer)
Precision Comparison
(Percolation Tests)

Repeatability

Reproducibility

Method Precision
- Method 1314: Cumulative Release at L/S = 10 L/kg
- DIN 19528: Cumulative Release at L/S = 4.0 L/kg
- TCLP: Eluate Concentration (L/S = 20 L/kg)
EPA Database Field leachate samples for fly ash only comparison with LEAF (EPA-600/R-09/151) All Fly Ash 5th, 50th, 95th percentiles and maximums
Comparison of Laboratory and Field Results

Consistent behaviour in different scales of testing
Generic Vault Disposal System

- Muli-layer Cap and Infiltration Control
- Clean Grout (high strength)
- Reinforcing Steel
- Infiltration
- Perched Water Seepage
- Drainage Layer or Capillary Break
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 – release based on local equilibrium

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 simplistic and may not be realistic
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

Needed Information

- External stresses
  - External loads
  - Differential settlement
- Material strength (e.g., Young’s Modulus)
- Material pore structure
- Internal stresses
  - Shrinkage/dehydration
  - Expansive reactions within pores
**Moisture Transport**

- **Full Saturation**
- **Capillary Saturation**
  - Continuous Liquid
  - Discontinuous Gas

- **Transition Zone (b)**
  - Continuous Liquid
  - Continuous Gas

- **Insular Saturation (c)**
  - 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)
  - Percolation (degraded matrix)
- Water content determines
  - Gaseous degradation processes (oxidation, carbonation)
  - Constituent diffusion pathways

**Impact**

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

- **Full Saturation**
  - Continuous Liquid
  - Discontinuous Gas

- **Capillary Saturation**
  - Continuous Liquid
  - Continuous Gas

- **Transition Zone**
  - Continuous Liquid
  - Continuous Gas

- **Insular Saturation**
  - Discontinuous Liquid
  - Continuous Gas

- **Completely Dry**

---

**Needed Information**

- Water producing & water consuming reactions
- Water retention curves (capillarity)
- Relative humidity-material saturation equilibrium
- Drying rates
- Permeability (water)
- Boundary conditions
  - Episodic infiltration
  - Relative humidity
Oxidation Rates and Extent

Conceptual Model
- Waste form pores – two phase system of gas and liquid; depends on moisture content (saturation)
- O₂ transport via gaseous diffusion may be important depending on saturation.
- Oxidation may lead to change in leaching behavior
  - Increased Tc-99 release; other redox sensitive constituents

Impact
- Gas phase transport must be considered
  - Flux of O₂ (gas) \( \sim 10^5 \) > liquid phase flux

<table>
<thead>
<tr>
<th>D₀₂ [cm²/s]</th>
<th>Air</th>
<th>Water</th>
<th>Ratio (A/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.21</td>
<td>0.000019</td>
<td>1.1E+04</td>
</tr>
<tr>
<td>8.9E-03</td>
<td>2.6E-04</td>
<td>1.4E+01</td>
<td></td>
</tr>
</tbody>
</table>

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

Needed Information
- Reducing capacity & redox titration
- Moisture status
- Gas phase diffusivity \( f(\text{saturation}) \)
- Liquid phase diffusivity \( f(\text{saturation}) \)
- Boundary conditions
Carbonation

**Conceptual Model**
- $\text{CO}_3^{2-} + \text{Ca}^{+2} \rightarrow \text{CaCO}_3 \ (s)$
- Gas phase diffusion of $\text{CO}_2$
- Liquid phase diffusion of $\text{HCO}_3^{-}$
- 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)
- Impact on sorption sites
- Pore structure changes
- May have either positive (e.g., pore capping) or detrimental (i.e., increased solubility) impacts
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 may not reflect the dynamic chemistry and mineralogy of the waste form.
- Release rates and extents mechanistically different from simplified assumptions, effecting predictability.
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 over- or under-predict release
Needed Information

- pH dependent equilibrium
- Column test
  - Pore water
  - LS evolution
- Analysis of
  - pH, EC, Eh
  - Full suite of cations and anions
  - TOC, TIC, DOC, DIC
- Boundary Conditions!
A Possible Approach to Beneficial Use Screening Levels

**Step 1:** Select use application (includes engineering specifications)

**Step 2:** Select corresponding pH domain and perform Method 1313

**Step 3:**
(a) Select corresponding fate and transport values
   (i) CCR fraction in engineered use (fCCR);
   (ii) Across-the-board engineered attenuation factor (EAF);
   (iii) Default constituent-specific dilution attenuation factors (DAFs);
   (iv) Human or ecological benchmarks (federal and/or state); and

(b) Calculate screening levels

**Step 4:** Compare maximum LEAF result to screening levels
Use is protective of human health and the environment? (i.e., LEAF < screening level?)

- Perform Method(s) 1314/1316 or 1315
- Choose
- Can use application and/or engineering specifications be modified?
  - Yes
  - No

**Proceed with use**

**Conduct site-specific IWEM modeling with Method 1313 data from Step 2 or Method 1315 data (if available)**

**Inappropriate for this use**
Supporting Documentation


Benefits to Use of LEAF

• Provides standardization in leach testing and comparability in resulting data for use across different materials and management scenarios

• Analytical work complete for all four methods as part of the interlaboratory validation for inclusion into SW-846

• Comparable methods being used abroad enable more robust data sets that provide better characterization across material types and management scenarios

• Provides data needed for binning materials into categories that enable more efficient beneficial use decisions (no or less stringent testing required depending upon the leaching behavior of the material)
Benefits to Use of LEAF

• Industry that generates CCRs and other industrial by-products has clarity in what is required and access to labs across the U.S.

• Provides objective and independent analysis of claims made by producers or technologies

• LEAF allows one to understand the mechanistic behavior of materials across a range of management scenarios across long terms (can not use snap shot approach that doesn’t consider future environmental conditions)

• Provides robust source term for risk assessment by considering physical and chemical factors that control leaching behavior over time
Conclusions

The LEAF test methods

- Can be used to evaluate leaching behavior of a wide range of materials using a tiered approach that considers the effect of leaching on pH, liquid-to-solid ratio, and physical form
- Prepared for inclusion into SW846 – EPA’s compendium of test methods for waste and material characterization
- Supporting software (LeachXS-Lite) available for data entry, analysis, visualization, and reporting
- Demonstrated relevance for assessing release behavior under field conditions for use and disposal scenarios

Current efforts

- Complete interlaboratory validation for Method 1314 and Method 1315
- Provide information on
  - Relationship between the LEAF testing results and field leaching
  - Application of LEAF test methods for evaluating CCR use and disposal
Acknowledgements

Participating Laboratories

- Oak Ridge National Lab
- Pacific Northwest National Lab
- Savannah River National Lab
- ARCADIS-US, Inc.
- Test America, Inc.
- URS Corporation, Inc.
- Ohio State University
- University of Wisconsin (Madison)
- Missouri Univ. of Science & Tech.
- Vanderbilt University
- ECN
- DHI

Funding and Support

- U.S. EPA, Office of Research and Development
- U.S. EPA, Office of Resource Conservation and Recovery
- U.S. DOE, Office of Environmental Management
- Consortium for Risk Evaluation with Stakeholder Participation (CRESP)