Update on Validation of Test Methods in the Leaching Environmental Assessment Framework

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Purpose

Purpose of this presentation is to provide LTIG with …

• Overview of Leaching Environmental Assessment Framework (LEAF) leaching test methods

• Update on validation of LEAF test methods
  □ Validation approach
  □ Status and schedule
  □ Example statistical analysis data

• Discussion of next-steps and the leach test validation group intentions to post two draft methods to SW-846 website (July 2011)
  □ Draft Method 1313
  □ Draft Method 1316
Presentation Format

Mark Baldwin (ORCR)
- Background on leach testing in solid waste management
- EPA’s involvement in new leach test development and LEAF
- Validation study structure and progress

Andy Garrabrants (Vanderbilt University)
- LEAF leach methods overview
- LEAF data management tools and LeachXS Lite
- Validation study results focusing on Method 1313 and Method 1316

Mark Baldwin (ORCR)
- Conclusions
- Next steps
Context for New Leaching Test Methods

TCLP

- Simulates plausible mis-management scenario for waste disposal (i.e., co-disposal with municipal solid waste) for TC, LDR regulations.
- Numerous non-hazardous waste disposal/use scenarios do not resemble TCLP conditions.
- EPA SAB (1991, 1999) expressed concern about over-broad use of TCLP.

Therefore …

EPA has initiated a program to identify and validate next-generation leach testing approaches.

- Goals in selection of appropriate tests included:
  1. General applicability to a broad range of wastes/secondary materials
  2. Consideration of test conditions that affect leaching
  3. Flexibility to allow tailoring for a range of applications
- Consultation with SAB (2003) on general approach and application to CCR evaluation.
What is the Leaching Environmental Assessment Framework?

LEAF is a collection of …

- Four leaching methods
- Data management tools
- Leaching assessment approaches

… designed to identify characteristic leaching behaviors in a wide range of materials.

Tiered testing and assessment

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
Leaching Method Development Approach

Characterization of Leaching Behavior (Kosson et al, 2002)
- Parallel and coordinated methods development in the EU
- Applied to anticipated release conditions – source term for release
- Goal to reduce uncertainties of environmental decision-making

Address Concerns of EPA Science Advisory Board
- Form of the material (e.g., monolithic, granular)
- Parameters that affect release (e.g., pH, liquid-solid ratio, release rate)

Intended for situations where TCLP is not required or best suited
- Assessment of non-hazardous materials for beneficial reuse
- Evaluating treatment effectiveness (determination of equivalent treatment)
- Characterizing potential release from high-volume materials
- Corrective action (remediation decisions)
Methods Validation Process

Based on “Guidance for Methods Development and Methods Validation for the RCRA Program”

Phase I – Demonstration of Proficiency

• Participating labs perform the test method on a single material to show that reliable results can be obtained

Phase II – Method Validation

• Advancing labs perform the test method on two additional materials.
• Final report to include Phase II and Phase I materials

EPA-ORD approved QAPP in place
Methods Validation Status

Method 1313 and Method 1316
✓ Phase I – completed in August 2010
✓ Phase II – completed in May 2011

Method 1315
✓ Phase I – completed in April 2011
• Phase II – scheduled for May 2011

Method 1314
• Phase I – scheduled for May 2011
• Phase II – scheduled for July 2011
Leaching Methods 1313 and 1316
Method 1313: pH-dependency test

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 1316: batch L/S test**

**Equilibrium Leaching Test**
- Parallel batch as function of L/S

**Test Specifications**
- 5 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**
Methods Validation Update
Methods Validation

11 Participating Labs

National Labs
- EPA-RTP (operated by ARCADIS)
- Oak Ridge National Labs
- Pacific Northwest National Labs
- Savannah River National Labs
- Energy Research Centre of the Netherlands

Academic Labs
- Ohio State Univ.
- Univ. of Wisconsin Madison
- Missouri Univ. of Science & Tech.
- Vanderbilt Univ.

Industry and Commercial Labs
- Test America (TVA)
- URS Corporation

Validation Design

Test Replication
- Reference Lab – 6 test reps
- Participating Labs – 3 test reps

Analytical
- Conducted at Vanderbilt Univ.
- Full suite of ICP-OES elements

Statistical Analysis
- Len Stefanski, Dept of Statistics, North Carolina State University
- Implemented using LeachXS
- ~10 selected elements for report
Validation Study Materials

**Coal Combustion Fly Ash**
- Previous EPA study
- Selected for validation of …
  - Method 1313/1316 Phase I
  - Method 1314 Phase I

**Solidified Waste Analog**
- Cement/slag/fly ash spiked with metal salts
- Selected for validation of …
  - Method 1313/1316 Phase II
  - Method 1315 Phase I
  - Method 1314 Phase II

**Contaminated Field Soil**
- Smelter site soil
- Selected for validation of …
  - Method 1313/1316 Phase II
  - Method 1315 Phase II
  - Method 1314 Phase II

April 28, 2011
EPA-LTIG 13th Annual Meeting, Ft. Meade, MD
Data Interpolation

Raw Data

- Recorded data for M1313 varies
  - Difficult to precisely meet target pHs

Interpolated Data

- Log$_{10}$ transform and linear interpolation to pH target values
Statistical Analysis

Standard Deviations

- Interval bands about the mean
  - Within Lab (repeatability)
  - Between Lab (reproducibility)

95% Robust Confidence Limits

- Prediction interval - 95% lab means
  \[ RCL = \text{Med} \pm 1.96 \times C_n \times 1.483 \times \text{MAD} \]

- Median-based statistics considered more tolerant of outliers
Method 1313 Results

Phase I Completed Analysis
  • Coal Combustion Fly Ash

Phase II Partial Analysis
  • Solidified Waste Analog (preliminary results)
  • Contaminated Field Soil (reference lab only)
Method 1313 Phase I Fly Ash Results

- **Barium (mg/L)**
- **Chromium (mg/L)**
- **Boron (mg/L)**
- **Antimony (mg/L)**
- **Molybdenum (mg/L)**
- **Selenium (mg/L)**

Graphs showing the target pH levels and the concentration of different elements (Barium, Chromium, Boron, Antimony, Molybdenum, Selenium) with mean, between lab SD, within lab SD, and overall SD.
Method 1313 Phase II Solidified Waste Analog

Preliminary Results

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Method 1313 Phase II Contaminated Field Soil

Reference Lab Results

- Arsenic (mg/L)
- Barium (mg/L)
- Cadmium (mg/L)
- Copper (mg/L)
- Lead (mg/L)
- Thallium (mg/L)

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Method 1316 Results

Phase I Completed Analysis
  • Coal Combustion Fly Ash

Phase II Partial Analysis
  • Solidified Waste Analog (preliminary results)
Method 1316 Phase I Fly Ash Results

- Arsenic (mg/L)
- Boron (mg/L)
- Barium (mg/L)
- Molybdenum (mg/L)
- Antimony (mg/L)
- Selenium (mg/L)

Graphs show the relationship between L/S (L/kg) and the concentration of various elements (Arsenic, Boron, Barium, Molybdenum, Antimony, Selenium) with Mean, Between Lab SD, Overall SD, and Within Lab SD.
Method 1316 Phase II Solidified Waste Analog

Preliminary Results

- Arsenic (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD

- Chromium (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD

- Antimony (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD

- Selenium (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD

- Molybdenum (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD

- Vanadium (mg/L)
  - Mean
  - Overall SD
  - Between Lab SD
  - Within Lab SD
Lessons Learned to Date

Modifications to Methods

• Tolerances for contact time have been added
• Requirement that pH values to be measured within 1 hr after separation of solids and liquids due to lack of buffering in aqueous samples

Modifications to Data Templates

• Mandatory information has been highlighted
• Space added to document measured recipe values

Other Recommendations

• Reagents should be freshly prepared in vessels of compatible materials (e.g., strong alkalis should not be stored in borosilicate glass)
• Labs should establish a QC regiment to check the quality of reagent water (method blanks are important)
LEAF Data Management Tools
Data Management Tools

Data Templates– for managing data in the lab

• 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™ -- for data assessment

• Data 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 SO\textsubscript{4} 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
Data Templates

DRAFT METHOD 1313 (Liquid-Solid Partitioning as a Function of pH) LAB DATA

<table>
<thead>
<tr>
<th>Code</th>
<th>Description (optional)</th>
<th>Test conducted by:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project</td>
<td>Material</td>
<td>Replicate</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
</tbody>
</table>

Solids Information
- Maximum Particle Size: 0.3 [mm]
- Minimum Dry Equivalent Mass: 20.00 [g-dry]
- Solids Content (default = 1): 0.901 [g-dry/g]
- Mass of "As Tested" Material / Extraction: 22.20 [g]

Extraction Information
- LS Ratio: 10 [ml/g-dry]
- Liquid Volume / Extraction: 200 [ml]
- Recommended Bottle Size: 250 [ml]

Nominal Reagent Information
- Acid Type: HNO3
- Base Type: NaOH
- Acid Normality: 2.0 [meq/mL]
- Base Normality: 1.0 [meq/mL]

Schedule of Acid and Base Addition

<table>
<thead>
<tr>
<th>Test Position</th>
<th>T01</th>
<th>T02</th>
<th>T03</th>
<th>T04</th>
<th>T05</th>
<th>T06</th>
<th>T07</th>
<th>T08</th>
<th>T09</th>
<th>B01</th>
<th>B02</th>
<th>B03</th>
<th>totals</th>
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</thead>
<tbody>
<tr>
<td>&quot;As Tested&quot; Solid [g] (±0.05g)</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>22.20</td>
<td>no solid</td>
<td>no solid</td>
<td>no solid</td>
<td>199.8</td>
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<tr>
<td>Reagent Water [ml] (±5%)</td>
<td>147.80</td>
<td>167.80</td>
<td>185.80</td>
<td>197.80</td>
<td>195.80</td>
<td>193.80</td>
<td>189.80</td>
<td>185.80</td>
<td>178.80</td>
<td>200.00</td>
<td>181.00</td>
<td>150.00</td>
<td>2174.2</td>
</tr>
<tr>
<td>Acid Volume [ml] (±1%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>64.0</td>
</tr>
<tr>
<td>Base Volume [ml] (±1%)</td>
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<td>30.00</td>
<td>12.00</td>
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<td>142.0</td>
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<td>Acid Normality [meq/mL]</td>
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<tr>
<td>Base Normality [meq/mL]</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Target pH
- 13.0±0.5
- 12.0±0.5
- 10.5±0.5
- natural
- 8.0±0.5
- 7.0±0.5
- 5.5±0.5
- 4.0±0.5
- 2.0±0.5

Acid Addition [meq/g]
- -2.5 | -1.5 | -0.6 | 0 | 0.2 | 0.4 | 0.8 | 1.2 | 1.9 |

Eluate pH
- 12.80 | 12.20 | 10.80 | 9.20 | 7.80 | 5.98 | 4.79 | 3.60 | 2.30 |

Notes
- pH out of range
- pH out of range

2) Enter acid/base type & normality

4) Follow “set-up” recipe

3) Enter target equivalents from titration curve

5) Record pH, conductivity, Eh (optional)

6) Verify that final pH is in acceptable range
1) Select a 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
Conclusions, Next-Steps, and Schedule
LEAF Reports in Preparation

Results of Inter-laboratory Validation of LEAF Test Methods

• Projected release of 3 report drafts:
  - July 2011 Batch Equilibrium Tests (Methods 1313 and 1316)
  - September 2011 Mass Transfer Test (Method 1315)
  - January 2012 Column Test (Method 1314)

Relationship Between LEAF Testing Results and Field Leaching

• Winter 2011 release

Application of LEAF Test Methods for Evaluating Use and Disposal of Coal Combustion Residues (CCRs)

• Spring 2012 release
Conclusions

The LEAF test methods:

- Evaluate leaching behavior using an approach that considers the effect of leaching on pH, liquid-to-solid ratio, and material form
- Prepared for inclusion into SW-846, EPA’s compendium of test methods for waste and material characterization
- Supporting software (LeachXS-Lite) available for data entry, analysis, visualization, and reporting
Next Steps

SW-846 Methods Team to post batch LEAF methods as EPA Draft Methods (pending completion of validation report; Summer 2011):

• **Method 1313** – Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure

• **Method 1316** – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

Subsequent postings following completion of validation study

• **Method 1315** – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank

• **Method 1314** – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio (L/S) using an Up-flow Percolation Column
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Tennessee Valley Authority               Jacqueline Broder & Anne Aiken
LEAF Supporting Documentation


