LEACHING ASSESSMENT AND DECISIONS FOR USE AND DISPOSAL OF COAL COMBUSTION RESIDUES

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Disclaimer

These are the results of research by the Vanderbilt research group and my opinions and this should not be construed to represent USEPA or any other organization.

No group - USEPA, industry or environmental advocacy organizations - have sought to influence or constrain my briefing today. However, I am in regular discussions with all of these groups.
Key Messages
Leaching Assessment and TCLP

Leaching assessment is an important tool for evaluating the potential for impact to water resources.

• Leaching is the release of constituents from a solid material into contacting water
• Leaching does not correlate with total content
• Leaching provides the source term for environmental assessment

TCLP was developed to evaluate co-disposal with municipal solid waste.

• Conditions for many disposal scenarios, including CCR disposal, are very different than MSW disposal
• Most currently used leaching tests evaluate only a single condition and do not provide information on the range of environmental conditions known to affect leaching
Key Messages
Leaching Assessment and LEAF

The Leaching Environmental Assessment Framework (LEAF)

- Evaluates leaching over a range of conditions for disposal and use scenarios
- Applicable to a wide spectrum of materials
- Allows distinction between management options
- Includes set of leaching test methods, data evaluation methods, and data management and analysis tools
- Considers range of pH, leaching mechanisms
- Major improvement on current practices, but development also required pragmatic choices to focus on the most important factors to provide tailored answers
- Parallel, coordinated development in EU and other countries
Key Messages
Testing Coal Combustion Residues

A large set of coal combustion residues (CCRs, including fly ash, gypsum and scrubber residues) have been evaluated using the LEAF methods.

LEAF Testing Results Indicate:

• Key Constituents of Potential Concern: arsenic, antimony, barium, boron, cadmium, chromium, mercury, molybdenum, selenium, thallium and vanadium

• There is a very wide range in leaching from fly ash samples from different sources (spans greater than 1000x)

• Different use and disposal options provide a wide range of attenuation factors (this also spans greater than 1000x); estimated attenuation includes consideration of design and location
Key Messages
Testing Coal Combustion Residues

Potential approaches to using LEAF in environmental protection decisions

• Screening, binning (yes/no/maybe) and site/scenario specific evaluations
• Evaluating individual CCRs for specific options
• Evaluating classes of materials or types for use at local, regional or national scales
• Guiding design criteria for engineered systems (e.g., roadways, structural fills, concrete, etc.)

Preliminary cost estimates for using LEAF as assessment & quality control tool

• $0.38 per ton produced
• $100,000 per annum per station
Key Messages
LEAF Status

Under development for more than 15 years for application to wide range of wastes and construction materials

Responsive to EPA SAB concerns regarding TCLP-based leaching assessment practices

Standard Methods planned for completion (Spring 2012)
  • Interlaboratory validation (round robin testing) in progress
  • Multiple EPA consultations and reviews completed; final reviews and NODA planned

Software tools available (beta versions) for aiding laboratory testing, data management and decision making

Implementation guidance is needed
LEAF Supporting Documentation


LEAF Reports in Preparation

Interlaboratory Validation of LEAF Method 1313 and Method 1316
• Fall 2011 release

Relationship Between LEAF Testing Results and Field Leaching
• Spring 2012 release

Interlaboratory Validation of LEAF Method 1315
• Spring 2012 release

Interlaboratory Validation of LEAF Method 1314
• Spring 2012 release

Application of LEAF Test Methods for Evaluating Use and Disposal of Coal Combustion Residues (CCRs)
• Summer 2012 release
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SUPPORTING INFORMATION

Potential Use of LEAF in CCR Management Decisions
(LEAF provides source term information)
Field Leaching Data for Landfills (Arsenic)
EPRI data in comparison with EPA Lab data

![Graph showing arsenic levels vs pH for different facilities](image)

- Facility 1 (subbit., western)
- Facility 2 (subbit., Wyoming)
- Facility 3 (subbit., Wyoming)
- Multiple facilities (single observation)
- BPT EPA CCR SR002
- GAB EPA CCR SR002

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Many Leaching Scenarios ...
Common Assessment Approach

Material Leaching in Context of Application
*(tests mimic scenario)*

Use as Source Term

Constituent Release from Application Scenario

DAF or Scenario Model

Constituent Concentration at Point of Compliance

road base
Enhanced Assessment Approach

Material Leaching Tests
Broad-based characterization of intrinsic leaching behavior

Material Characterization
(tests measure range of intrinsic behavior-LEAF)

Constituent Release from Application Scenario
Constituent Concentration at Point of Compliance

Material Leaching in Context of Application (EAF)
Use as Source Term
DAF or Scenario Model

road base

Threshold Definition

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Cost Estimate

Assuming:

- Quarterly Sampling
- Triplicate Method 1313 - $15,000 + administrative costs
- Analysis for 15 Constituents

American Coal Ash Association (ACAA)

- 72,500,000 tons of fly ash produced in 2008
- 274 coal-fired electric utility generating stations
- $20 to $45 per ton for cement quality fly ash in 2003

Costs of LEAF Testing

- Using ACAA data - 265,000 tons per station on average
- $100,000 (est’d) per annum per station
- $0.38 per ton produced
SUPPORTING INFORMATION

The Leaching Environmental Assessment Framework (LEAF)
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.

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

Measure intrinsic leaching characteristics of material

Evaluate release in the context of field scenario
  • External influencing factors such as carbonation, oxidation
  • Hydrology
  • Mineralogical changes

Geochemical speciation and mass transfer models to estimate release for alternative scenarios
  • Model complexity to match information needs
  • Many scenarios can be evaluated from single data set

Tiered approach to effective use prior data and reduce testing needs

*Do NOT mimic field scenarios with specific tests!*  
*Too many tests with limited data comparability!*

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; titles and 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
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 (e.g., As in two different CCRs)
  - Between constituents (e.g., Ba and SO₄ in a cement material)
  - 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 <em>(optional)</em></th>
<th>Test conducted by:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project</td>
<td>ABC</td>
<td>Example project</td>
</tr>
<tr>
<td>Material</td>
<td>XYZ</td>
<td>Example material</td>
</tr>
<tr>
<td>Replicate</td>
<td>A</td>
<td></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]

**Nominal Reagent Information**
- **Acid Type**: HNO3
- **Acid Normality**: 2.0 [meq/mL]
- **Base Type**: NaOH
- **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>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;As Tested&quot; Solid [g] <em>(±0.05g)</em></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>
</tr>
<tr>
<td>Reagent Water [mL] <em>(±5%)</em></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>191.80</td>
<td>189.80</td>
<td>185.80</td>
<td>178.80</td>
<td>200.00</td>
<td>181.00</td>
</tr>
<tr>
<td>Acid Volume [mL] <em>(±1%)</em></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
<td>4.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Base Volume [mL] <em>(±1%)</em></td>
<td>50.00</td>
<td>30.00</td>
<td>12.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19.00</td>
<td>19.00</td>
<td>19.00</td>
</tr>
<tr>
<td>Acid Normality [meq/mL]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td>Base Normality [meq/mL]</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</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**

<table>
<thead>
<tr>
<th>Water</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.80</td>
<td>12.20</td>
<td>10.80</td>
</tr>
<tr>
<td>9.20</td>
<td>7.80</td>
<td>5.98</td>
</tr>
<tr>
<td>4.79</td>
<td>3.60</td>
<td>2.30</td>
</tr>
</tbody>
</table>

**Eluate EC [mS/cm]**

<table>
<thead>
<tr>
<th>Water</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Eluate Eh [mV]**

<table>
<thead>
<tr>
<th>Water</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>

**Notes**
- pH out of range
- pH out of range

**required Contact Time**: 23-25 [hr]

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

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LeachXS Lite

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
Use of LEAF to Compare Performance of Coal Combustion Products
EPA Studies on CCR Leaching

Coal Combustion Products ~30 Facilities
- Fly Ash – 71
- FGD Gypsum – 33
- Scrubber Sludge – 14
- Fixated Stabilized Sludge ~20

Leaching Tests
- Method 1313 – pH Dependence
- Method 1316 – Batch L/S Dependence

Look for Commonalities in Performance …
- Coal sources
- APC practices
- Other factors

EPA Reports
- EPA-600/R09/151
- EPA-600/R-08/077
- EPA-600/R-06/008

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Total Content Does Not Correlate to Leaching


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Why is this LEAF approach needed?
Fly Ash Results

- **Arsenic (mg/L)**
  - pH vs. 5th and 95th %
  - 10x HBN and 100x HBN
  - AaFA - Median
  - BFA - Median
  - Own pH
  - All Fly Ash - Median
  - All Fly Ash - 95th %
  - Health Based Number (HBN)

- **Boron (mg/L)**
  - L/S (L/kg) vs. 5th and 95th %
  - 10x HBN and 100x HBN
  - AaFA - Median
  - BFA - Median
  - Own pH
  - All Fly Ash - Median
  - All Fly Ash - 95th %
  - Health Based Number (HBN)

**November 3, 2011**
Fly Ash Results

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Fly Ash Results

Graphs showing the concentration of Molybdenum and Selenium in relation to pH and L/S (L/kg) for different fly ash types and their respective Health Based Numbers (HBNs). The graphs include data for AaFA, BFA, and All Fly Ash with medians, 5th and 95th %, and various HBN concentrations.
Fly Ash Results

- Thallium (mg/L) vs pH
- Vanadium (mg/L) vs pH
- Thallium (mg/L) vs L/S (L/kg)
- Vanadium (mg/L) vs L/S (L/kg)

Legend:
- AaFA - Median
- BFA - Median
- own pH
- 5th and 95th % of pH
- Health Based Number (HBN)
- 10x HBN
- 100x HBN

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Statistical Representation

Fly Ash (Sub-bituminous Coal)

- Product type (e.g., fly ash, gypsum)
- Coal type (e.g., sub-bituminous)
- APC Equipment (e.g., SCRs)

Statistical Overlay

- Mean of Material Medians
- Median (50th percentile) of Material Medians
- 5th and 95th Percentiles of Material Medians
- 95% Prediction Interval
- Maximum Median Values
Arsenic Comparison By Product

- **Fly Ash - Bituminous Coal**
- **Fly Ash - Sub-bituminous Coal**
- **Gypsum (unwashed & washed)**
- **Scrubber Sludges**

**Graph Key:**
- ■ Mean of Material Medians
- † Median (50th percentile) of Material Medians
- — 5th and 95th Percentiles of Material Medians
- − 95% Prediction Interval
- × Maximum Median Values
Selenium Comparison By Product

Fly Ash - Bituminous Coal

Fly Ash - Sub-bituminous Coal

Gypsum (unwashed & washed)

Scrubber Sludges

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Conclusions

LEAF
- Evaluates leaching behavior using a tiered approach that considers the effect of pH, liquid-to-solid ratio, and material form on release
- Supporting software (LeachXS-Lite) available for data entry, analysis, visualization, and reporting
- Prepared for inclusion into SW846, EPA’s compendium of test methods for waste and material characterization

Comparison of Coal Combustion Products
- Statistical representations using LEAF data provides insights into conditions most-significantly affecting environmental performance
- Supports decision-making regarding optimization of processes and end use (e.g., disposal or reuse)