Development and Use of the Leaching Environmental Assessment Framework in the United States

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Background

- Changes in air pollution control (APC) at power plants result in transferring metals from the flue gas to fly ash and other APC residues. The fate of these metals is tied to how coal combustion residues (CCRs) are managed.

- Key release route for land-managed CCRs is leaching to groundwater. Also of concern is release to surface waters, re-emission of mercury (e.g., cement kilns), and potential for bioaccumulation.
Control Technologies for Reducing Air Emissions at Coal-Fired Power Plants

- Coal Additive
- Refined Coal
- Flue Gas Conditioning
- Dry Sorbent Injection (DSI)
- Activated Carbon Injection (ACI)
- SCR DeNOx
- Filter or ESP
- Flue Gas Desulfurization (FGD) Scrubber
- Scrubber Additive
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
  • Integrated leaching assessment approaches

… designed to identify characteristic leaching behaviors for a wide range of materials and associated use and disposal scenarios.

Integration of leaching results provides a material-specific “source term” release for use in 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

Posted as “New Methods” to SW-846 on Aug 2013
Use of LEAF in the USA

- Guidance for use of LEAF is under development by U.S. EPA
- LEAF is being used with increasing frequency by state regulators and industry
- Current uses include:
  - Coal combustion residues (i.e., fly ash and scrubber residues) evaluation for disposal and beneficial use as part of new regulations development by the U.S. EPA
  - Contaminated site remediation (industry and state regulators)
  - Evaluation of treatment process effectiveness (EPA and industry)
  - Long-term performance of concrete and cementitious materials in nuclear energy and nuclear waste (U.S. Department of Energy)
  - Evaluation of leaching from use of fly ash in cementitious materials [study funded by EPRI] results published as 2 journal articles in Chemosphere;
Research to evaluate leaching from Coal Fly Ash and Scrubber Residues

- Coal Combustion Residues ~30 Facilities
  - Fly Ash – 34
  - Flue gas desulfurization (FGD) gypsum – 20
  - Scrubber Sludge – 7
  - Fixated Stabilized Sludge – 8

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

- Look for Commonalities in Performance …
  - Coal sources
  - Air pollution control in use
  - Other factors

- EPA Reports
  - EPA-600/R09/151
  - EPA-600/R-08/077
  - EPA-600/R-06/008
## U.S. range of observed total content and leaching test results (5.4 ≤ pH ≤ 12.4) for 34 fly ash samples and 20 FGD gypsum samples

<table>
<thead>
<tr>
<th>Indicator Values</th>
<th>Fly Ash</th>
<th>FGD Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC (µg/L)</td>
<td>MCL (µg/L)</td>
</tr>
<tr>
<td>Hg</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>As</td>
<td>5,000</td>
<td>10</td>
</tr>
<tr>
<td>Ba</td>
<td>100,000</td>
<td>2,000</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>7,000*</td>
</tr>
<tr>
<td>Cd</td>
<td>1,000</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
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<td>100</td>
</tr>
<tr>
<td>Mo</td>
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<td>200</td>
</tr>
<tr>
<td>Se</td>
<td>1,000</td>
<td>50</td>
</tr>
<tr>
<td>Tl</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

* Indicates DWEL value rather than MCL. **Bold** text indicates where leaching concentrations are greater than indicator values. Indicator values shown for comparison to leaching test concentration as an initial screening only (leaching results do not include dilution/attenuation considered in development of indicator values). From ES&T 2010 publication.

Indicator Values: TC = Toxicity characteristic value; DWEL – drinking H₂O equivalent level; MCL – Maximum concentration level
Total Content Does Not Correlate to Leaching

- Same total content with different eluate concentrations
- Same eluate concentration with different total contents

Legend:
- Blue squares: Fly Ash
- Green circles: SDA
- Red triangles: Gypsum
- Yellow pentagons: Scrubber Sludge
- Light blue diamonds: Blended CCRs

Graph: Log-log plot showing arsenic concentrations in eluate vs. total arsenic by digestion.
Evaluation of Fly Ash Use in Cement & Concrete

H. van der Sloot, D.S. Kosson, A. Garrabrants and J. Arnold
(EPA-600/R-12/704, 2012)

• Review of available world-wide data of cement mortars and concrete containing coal fly ash
• 31 mortars and concrete with fly ash, 21 mortars and concretes without fly ash

D.S. Kosson, A. Garrabrants, R. DeLapp, H. van der Sloot
(Chemosphere, 2014, 2 papers)

• 2 Concrete formulations x 4 fly ashes with controls, and mortars reflecting commercial usage in US
• Methods 1313 and 1315 used to characterize fly ash, reference materials without fly ash and materials with fly ash
Use of LEAF in EPA’s decision to support continued use of fly ash in concrete

• In response to concerns from the Inspector General and others, EPA conducted a study to evaluate high-volume use of fly ash as a cement replacement. The data used by the EPA study was from research conducted at Vanderbilt University using recently released and improved leaching tests.

• Using concrete formulations representative of US residential and commercial applications, test monoliths were made without fly ash replacement (i.e., controls) and with 20% or 45% of the portland cement fraction replaced by fly ash from four coal combustion sources.

• The cumulative release results were consistent with previously tested samples of concretes and mortars from international sources.

• The overall results suggest minimal leaching impact from fly ash use as a replacement for up to 45% of the cement fraction in typical US concrete formulations.

• Scenario-specific assessment based on this leaching evaluation should be used to determine if potential environmental impacts exist.

• Results for this research are published in two Chemosphere journal publications (see reference list at end of presentation).
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 release

• Address Concerns of U.S. EPA Science Advisory Board
  • Form of the materials (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 use
  • Evaluating treatment effectiveness (equivalent treatment determination)
  • Characterizing potential release from high-volume materials
  • Corrective action (remediation decisions)

*TCLP – U.S. EPA Test Method – Toxicity Characteristic Leaching Procedure
Simulation vs. Characterization

• Simulation-based Leaching Approaches
  – Designed to provide representative leachate under specified conditions
  – Simple implementation (e.g., single-batch methods like TCLP or SPLP*) and interpretation (e.g., acceptance criteria)
  – Limitations
    • Representativeness of testing to actual disposal or use conditions
    • Results cannot be extended to scenarios that differ from simulated conditions

• Characterization-based Leaching Approach
  – Evaluate intrinsic leaching parameters under broad range of conditions
  – More complex; sometimes requiring multiple leaching tests
  – Results can be applied to “what if” analysis of disposal or use scenarios
  – Allows a common basis for comparison across materials and field conditions

*SPLP - Synthetic Precipitation Leaching Procedure
Regulatory Tests
- Aim to bound risk by “plausible worst case”
- Comparison to limits
- Does not consider
  - Release Scenario
  - Time (kinetics)
  - Mass Transport

Characterization Tests
- Allow scenario-specific release estimates and tiered approach
- Range of conditions
- Comparisons between materials, treatments, & management scenarios
Many Leaching Scenarios …

- Landfill
- Drinking water well
- Road base
- Contaminated soil
- Industrially contaminated soil
- Factory
- Seepage basin
- Mining
- Roof runoff
- Construction debris and run-off
- Coastal protection
- Municipal sewer system
- Agriculture
- Contaminated soil
Material Leaching Tests
Broad-based characterization of intrinsic leaching behavior

DAF – Dilution-Attenuation Factor
2 by numerical modeling
LEAF Leaching Tests*

• Equilibrium-based leaching tests
  – Batch tests carried out on size reduced material
  – Aim to measure contaminant release related to specific chemical conditions (pH, LS ratio)
  – Method 1313 – pH dependence & titration curve
  – Method 1316 – LS dependence

• Mass transport rate-based leaching tests
  – Carried out either on monolithic material or compacted granular material
  – Aim to determine contaminant release rates by accounting for both chemical and physical properties of the material
  – Method 1315 – monolith & compacted granular options

• Percolation (column) leaching tests
  – May be either equilibrium or mass transfer rate
  – Method 1314 – upflow column, local equilibrium (LS ratio)

*Posting to SW-846 as “New Methods” completed August 2013
Study Materials for LEAF Methods Validation

- **Coal Combustion Fly Ash**
  - Collected for 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 soil
  - Collection in process
  - Selected for validation of
    - Method 1313/1316 Phase II
    - Method 1315 Phase II
    - Method 1314 Phase II

- **Foundry Sand**
  - Collection in process
  - Selected for validation of
    - Method 1315 Phase II
    - Method 1314 Phase II
Validation of LEAF Test Methods

Multi-lab Round-robin Testing
Academic, Commercial, Government and International Labs

Materials
Coal Fly Ash
Contaminated Soil
Solidified Waste
Brass Foundry
Sand
LEAF 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](http://www.vanderbilt.edu/leaching)
Excel Data Templates for each LEAF Method

### 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>
<th>Extraction Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project</td>
<td>ABC</td>
<td>Example project</td>
<td>LS Ratio</td>
</tr>
<tr>
<td>Material</td>
<td>XYZ</td>
<td>Example material</td>
<td>Liquid Volume / Extraction</td>
</tr>
<tr>
<td>Replicate</td>
<td>A</td>
<td></td>
<td>Recommended Bottle Size</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]

#### 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] (±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>
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<td>no solid</td>
<td>no solid</td>
</tr>
<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>
</tr>
<tr>
<td>Acid Volume [mL] (±1%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
<td>4.00</td>
<td>8.00</td>
<td>12.00</td>
<td>19.00</td>
<td>-</td>
<td>19.00</td>
<td>-</td>
</tr>
<tr>
<td>Base Volume [mL] (±1%)</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>-</td>
<td>-</td>
<td>50.00</td>
</tr>
<tr>
<td>Acid Normality [meq/mL]</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</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>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Target pH and Other Parameters
- Water pH: 7.20
- Mass of "As Tested" Material / Extraction: 22.20 [g]
- Required Contact Time: 23-25 [hr]

#### Notes
- pH out of range
- Conductivity: 5.0 [mS/cm]
- Eh: 50 [mV]

**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**
LeachXS™

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

LeachXS Lite is considered a research version and has not yet undergone EPA review; developed as free simplified version for data management in support of LEAF Methods use
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
Laboratory-to-Field Relationships

- Leaching Assessment Fundamentals
- 10 Cases of Large-scale Field Analysis Coupled with Laboratory Testing For 7 Materials
  - Coal combustion residues (fly ash, scrubber residues)
  - Inorganic waste (mixed origin)
  - Municipal solid waste (MSW)
  - MSW incinerator bottom ash
  - Cement-stabilized MSW incinerator fly ash
  - Portland cement mortars and concrete
- Recommendations for Use of LEAF
Geochemical Speciation Modeling

Model description for Cu in MSW combustion bottom ash reheated to 500°C in comparison with pH-dependence test results (e.g., EPA Method 1313)
Approach to Risk Informed Evaluation

• Leaching Source Term Based on Leaching Test Results
  • Consideration of water contact mode (percolation or flow around)
  • Infiltration amount and frequency
  • Leaching concentration (percolation), mass release rate mixed into infiltration (monolith)

• Dilution and Attenuation Based on Transport to Point of Compliance
  – Protection of groundwater and/or surface water
  – Immediate underlying groundwater, property boundary, or other definition

• Thresholds Based on Human Health and Ecological Standards
  • Impact to water quality
  • Drinking water standards
  • Risk-based thresholds based on exposure scenarios
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) Engineered attenuation factor (EAF) - Use specific;
   (iii) Constituent-specific dilution attenuation factors (DAFs)-Default or State Specific;
   (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?)

Yes:
- Conduct site-specific modeling with Method 1313 data from **Step 2** or Method 1314 or 1315 data (if available)
- Can use application and/or engineering specifications be modified?
  - Yes: Perform Method(s) 1314/1316 or 1315
  - No: Inappropriate for this use

No:
- Choose
  - Pass
  - Fail

**Proceed with use**
Benefits to Use of LEAF and EU Methods

• Accepted Leaching Methods for EPA SW-846
  • Interlaboratory validation completed
  • Comprehensive documentation

• Standardization in Leaching Characterization
  • Comparability across different materials and management scenarios
  • Leverage of international available data from comparable methods
  • Potential for “binning” assessment (e.g., “go”, “no go”, “need more info”)

• Allows for Mechanistic Understanding of Leaching Behavior
  • Range of management scenarios
  • Range of time frames (e.g., range of future environmental conditions)
  • Provides robust “source term” for risk assessment (considers physical and chemical factors that control leaching behavior over time)
  • Most efficient when used in conjunction with speciation modeling
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


  – Demonstrated relevance for assessing release behavior under field conditions for use and disposal scenarios

  – Use of LEAF provided critical data to EPA’s decision to support continued use of fly ash as supplemental material for concrete
Supporting Documentation


- Kosson et al., pH-dependent leaching of COPCs from concrete materials containing coal fly ash, Chemosphere, 2013.

- Garrabrants et al., Effect of coal combustion fly ash use in concrete on the mass transport release of constituents of potential concern, Chemosphere, 2013.

- The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching of Constituents from Cements and Concretes, EPA 600/R-12/704, Oct 2012


Supporting Documentation (Cont.)


- Background Information for the Leaching Environmental Assessment Framework Test Methods, EPA/600/R-10/170, Dec 2010

- Characterization of Coal Combustion Residues from Electric Utilities - Leaching and Characterization Data, EPA-600/R-09/151, Dec 2009


- Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb 2006