Application of New Leaching Protocols for Assessing Beneficial Use of Solid Wastes in Florida

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University of Florida

October 14, 2014 TAG Meeting
Presentation Objectives

• Review the objectives and methodology of the project
• Provide TAG with an overview of LEAF methods and questions that have been raised in our work
• Give examples of recent research
• Gather feedback from the TAG

• Michael Hoffmeister
  – Project objectives and tasks
• Justin Roessler, Dr. Ma
  – Examples of recent applications of LEAF as part of Florida beneficial use assessments
• B Intrakamhaeng, Weizhi Cheng
  – Observations from some recent work comparing LEAF with other leaching procedures
Uses of Leaching Tests

• Hazardous waste determination
  – TCLP is used to determine whether a solid waste is a toxicity characteristic hazardous waste (40CFR261)

• Waste treatment
  – TCLP is used to determine whether hazardous waste is sufficiently treated prior to land disposal (40CFR268)

• Beneficial use
  – SPLP is commonly used by regulatory agencies to assess leaching risk from beneficially used waste materials

• Other
Hinkley Center Evaluations of Beneficial Use

- Milled Asphalt
- Street Sweepings
- RSM from C&D Debris
- Drinking Water Sludge
Hinkley Center Evaluations of Beneficial Use

- Waste-to-Energy Ash
- Coal Ash
- Scrubber Residue
- Slag
Challenge

Promoting Recycling and Resource Conservation

Protecting Human Health and the Environment
Leaching Tests for Beneficial Use

• The TCLP may not be a good predictor since it is designed to simulate a landfill environment

• The SPLP is similar to the TCLP but it uses a simulated rainwater as the leaching solution.

• New EPA leaching tests in SW-846:
  – Leaching Environmental Assessment Framework (LEAF)
  – Provides a framework to characterize the waste under a larger scope of release conditions

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<thead>
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<th>Element</th>
<th>GCTL (mg/L)</th>
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<td>Aluminum (Al)</td>
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<td>Silver (Ag)</td>
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<tr>
<td>Vanadium (V)</td>
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</table>

**Example FL GCTLS**

**Typical practice is to compare leaching test results to GCTL or similar threshold**
What we are trying to assess?

Combustion Residual

Groundwater Well

Vadose Zone

Groundwater
Consider a Typical Leaching Test

Glass or Plastic Jar
Consider a Typical Leaching Test

100 g of residual
Consider a Typical Leaching Test

This is a batch test. Other types of leaching tests include dynamic batch tests and flow-through column tests.
Consider a Typical Leaching Test

\[ X_{\text{(dissolved)}} \]

\[ X_{(s)} \]
What Impacts Leaching?

Leaching Solution Chemistry

→ TCLP: Buffered acetic acid solution with pH = 4.8 or 2.3
→ SPLP: Unbuffered solution of nitric and sulfuric acid with pH = 4.2 or
Impact of pH

Maximum leachable concentration
Impact of pH: Soluble Salt

Maximum leachable concentration

Concentration vs. pH graph showing the impact of pH on the soluble salt concentration.
Impact of pH: Amphoteric

Maximum leachable concentration
Impact of pH

New CCA-Treated Wood (0.21 pcf)

% Leached

$\text{pH}$

Arsenic

Chromium
What Impacts Leaching?

Liquid to Solid Ratio

→ TCLP and SPLP: 20 to 1
What Impacts Leaching?

Decreasing L/S
Impact of Liquid to Solid Ratio
Impact of Liquid to Solid Ratio

Mass Released

Liquid to Solid Ratio
What Impacts Leaching?

Leaching Time

→ TCLP and SPLP: 18 +/- 2 hours
Impact of Time

Multiple Extraction Procedure (Arsenic)

Cumulative % Leached vs. Day

- Chipped Wood
- Wooden Blocks
What Impacts Leaching?

Redox Potential?

Oxidizing or reducing environment
EPA Leaching Tests

- **Method 1311** “Toxicity Characteristic Leaching Procedure”
- **Method 1312** “Synthetic Precipitation Leaching Procedure”
- **Method 1313** “Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure”
- **Method 1314** “Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure”
- **Method 1315** “Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure”
- **Method 1316** “Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure”
Method 1313

Parallel batch extraction done at a 10:1 liquid to solid ratio (10ml/g-dry) at up to 9 final pH values

Samples rotated for 24-72 hours

Goal: determine the leachability of the material for a range of pH values

Expected leaching within pH range

pH range of reuse scenario

Mass Leached

pH
Method 1314

Column leaching test with constant upward flow of pure water. Samples are taken at prescribed days to achieve specific L/S ratios

Goal: Determine which constituents wash out quickly and which dissolve into the water at a constant rate

![Graph showing Mass Released vs. L:S Ratio]

- **Slope ~ 1:** Mass release controlled by dissolution
  - Ex: As, Fe (mineral bound)

- Mass release controlled by surface availability
  - Ex: K, Na, Cl (very soluble elements)
Method 1315

Monolithic material sample (e.g. a brick) or a compacted granular material is submerged in a tank of water and allowed to soak for prescribed times. Water is periodically sampled and analyzed for constituents of concern. New water replaces the old.

Goal: Determine time-dependent release rates under monolithic conditions

This information can help in predicting mass release in the long run
**Method 1316**

**Interpreting Results**

Parallel batch performed at five different liquid to solid ratios.

Similar to 1313 but more rapid.

**Expected leaching within L:S range**

**L:S range of reuse scenario**

**Concentration**

**L:S Ratio**
Example Questions

Analytical
• How do new tests compare to SPLP?
• What particle size is appropriate to use?
• How do the different filters impact the results?

Application
• Which pH regime should be the target regime?
• How do you evaluate leachate concentrations that change over time?
• For different reuse scenarios, what is the most appropriate test to use and how?
Project Objectives

• Document LEAF Methods
  – Testing procedures

• Guidance for practitioners
  – Intent
  – Differences
  – Application
Literature Review

- Application of leaching protocols
  - Refereed literature
  - Industry and government
  - International experience
- Identify candidate waste streams
Project Objectives

• Examine previous beneficial use assessments in Florida
Florida Beneficial Use Leaching Assessment

- Street sweepings
- Catch basin/SW sediments
- Waste-to-energy ash
- Milled asphalt pavement
- Coal combustion residuals
- Recovered waste-amended concrete

How may have LEAF impacted decision?
Project Objectives

• Perform leaching tests on three specific waste streams

• Selected from:
  • Previous assessments in FL
  • Feedback from project TAG
LEAF Testing

• LEAF tests
• SPLP and total concentration
• Answer questions from previous tasks:
  – How LEAF methods are applied
  – Added insight
Guidance Document

• Final Report
  – Utility of LEAF methods for beneficial use decisions

• Tutorial on LEAF methods
  – Differences from existing procedures
  – How they may be applied

• Potential ideas for guidance document
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</table>
How have we used LEAF?

• Several examples where LEAF has been used by our research team to help with a beneficial use assessment
  – Sludge from water treatment
  – Waste to energy ash
• We have also evaluated other wastes
  – Coal ash
  – Mining Waste
  – Electronic Waste
Our Approach

- SPLP testing still conducted
  - Screening tool
  - Needed for a comparison
- LEAF testing conducted to better assess contaminant release under specific reuse conditions
- LEAF testing conducted to examine waste treatment options
  - What can be done to make material leach less
Drinking Water Sludge
Drinking Water Sludge

• Assess the effect of additional treatment additives and possibility for use as a “clean fill” in water bodies
• Aluminum a potential concern with respect to leaching
• Consider the scenario where values are compared directly to target levels
Method Natural pH and SPLP

 Aluminum Concentration (mg/L)

Facility

GCTL = 0.2 mg/L

SPLP  1313 Natural pH
Leaching Results

Natural pH – pH when immersed in water at a liquid to solid ratio of 10

Method 1313 (Natural pH), Method 1316 (L/S – 10)

• Some would argue this is a more representative batch test than SPLP

• For some of the facilities tested SPLP concentrations were elevated when compared values at the natural pH

• In one instance method 1313 values were on different side of GCTL than SPLP
  – Mean and 95% UCL
pH - Method 1313 and SPLP

Facility

Leachate pH

SPLP  1313 Natural pH

A  C  D  J  O
Explaining Differences

• Differences in leachate pH between SPLP could explain discrepancy in concentrations
• SPLP test is conducted at a higher liquid to solid ratio and you would expect that pH would be lower
• Conduct Method 1316 – Batch Leaching as a function of liquid to solid ratio
  – Large number of facilities
  – Speed of testing, cost
Method 1316

![Graph showing the relationship between Aluminum Concentration (mg/L) and pH with Liquid to Solid Ratio on the x-axis. The graph illustrates an upward trend in both Aluminum concentration and pH as the Liquid to Solid Ratio increases.]
Drinking Water Sludge Summary

- SPLP and natural pH leaching can differ significantly
  - Implications for risk assessment
  - Which test is more representative?
- LEAF helps to demonstrate leaching of Al in pH range of water bodies below GCTL
Beneficial Use Assessment Pasco County – WTE Bottom Ash

- Conduct standard batch test SPLP
- Identify COPCs
  - GCTLS
- Which elements elevated above GCTLS?
  - Lead, Antimony, Molybdenum
What Can We Do to Decrease Leaching?

• Aging has been demonstrated to reduce leaching of WTE ash
• Use LEAF to examine leaching of aged material
• pH changes due to carbonation
• Wash-off of elements due to precipitation
Method 1313 - Antimony

Antimony Concentration (mg/L)

Test pH

"Fresh" Ash pH
Method 1313 - Lead

Graph showing the relationship between lead concentration (mg/L) and test pH. The graph indicates that lead concentration decreases as the test pH increases, reaching a minimum around pH 6. The pH value corresponding to this minimum concentration is marked as "Fresh" Ash pH.
Optimum Final pH

Element Concentration (mg/L) vs. Test pH

Target pH Range
For Beneficial Use
Molybdenum Concentrations

- Initially elevated with respect to a direct comparison to GCTLs
- Concentration decreased throughout duration of column test
- Based on method 1313 data this is not expected to be related to pH changes
- “Surface Wash-Off” release mechanism
Method 1314- Molybdenum Leaching

The graph shows the relationship between Molybdenum Concentration (mg/L) and Liquid to Solid Ratio. The graph indicates a decreasing trend in Molybdenum concentration as the liquid to solid ratio increases. The GCTL - 0.035 mg/L line is also shown, indicating the guideline concentration level for molybdenum leaching.
What Did We Learn?

• LEAF allows us to better understand leaching of WTE ash
• pH changes influencing leaching
  – Lead, Antimony
  – Helped to select optimal pH range, ageing time
• Decrease in Molybdenum concentrations over time
  – Loss of Mo while “Aging”
  – Expected decrease over time
LEAF Assessment - Blending Coal Bottom Ash
Coal Bottom Ash

• Relatively inert material
• SPLP test results produced majority of leachate concentrations below GCLTs
  – Exception was Se within 10% of threshold
• Materials testing values (LBR) low
  – Experimented by blending bottom ash with lime rock to increase strength
• 50/50 blend able to achieve x2 strength
  – How would blending effect leaching?
Coal Bottom Ash-Lime Rock Blends

![Bar chart showing Selenium Concentration (mg/L) for different blends of coal bottom ash (BA).]

- **25% Coal BA**: Predicted Dilution and Measured Values are close, indicating minimal selenium concentration.
- **50% Coal BA**: Shows a higher selenium concentration compared to the other blends.
- **75% Coal BA**: The highest selenium concentration among the blends, with a significant predicted dilution.
- **100% Coal BA**: Similar to 25% Coal BA, with minimal selenium concentration.

Legend:
- Yellow: Predicted Dilution
- Green: Measured Values
Blending

• Trying to improve the structural characteristics of the material had unintended consequences

• Differences between SPLP and natural pH
  – SPLP pH – 5.3 “Natural” pH - 7.7
  – Natural pH selenium leaching:
    0.184 mg/L (3 x SPLP values)
  – 50:50 ash/lime rock blends: pH- 8.0

• By mass you would expect the concentrations of blends to be diluted
  – Better understanding because of LEAF testing and proper interpretation of results
Which Batch Leaching Test Best Represents Monofill Disposal Conditions?
Methodology

• Samples

Bottom Ash Greater 3/8”

Bottom Ash Less 3/8”

Mixed Ash

Fly Ash
Methodology

• Leaching method
  • Batch Tests
    • TCLP (EPA method 1311)
      • TCLP#1; (pH = 4.93±0.05)
      • TCLP#2; (pH = 2.88±0.05)
    • SPLP (EPA method 1312); (pH = 4.2)
Methodology

• Column test (EPA Method 1314)
An Example Result: TCLP/SPLP (Bottom Ash Less than 3/8”)

![Graph showing TCLP/SPLP results with concentration of Pb vs L/S (mL/kg-dry).](image)
An Example Result: Column Test (Bottom Ash Less Than 3/8”)
Concentrations Normalized to mg/kg

Bottom Ash Less Than 3/8”

Cumulative mass release (mg Pb/kg-dry)

L/S Ratio (mL/g-dry)

SPLP, pH = 12.23

TCLP#2, pH = 6.22

Final pH = 11.62

TCLP#1, pH = 11.67

Initial pH = 12.39
Comparing Leaching Tests

Bottom Ash Less Than 3/8”
EPA Method 1313 Bottom Ash Less Than 3/8”
EPA Method 1313 Bottom Ash Less Than 3/8”
Does the Particle Size Effect Trace Metal Leachability?
Comparing Particle Size

Bottom Ash Less than 3/8"

Cumulative mass release (mg Pb/kg-dry)

L/S Ratio (mL/g-dry)

Initial pH = 12.39

SPLP, pH = 12.23

TCLP#2, pH = 6.22

Final pH = 11.62

TCLP#1, pH = 11.67
Comparing Particle Size

Bottom Ash Greater 3/8”

- TCLP#2, Final pH = 4.74
- SPLP, Final pH = 11.47  Final pH = 11.00
- TCLP#1, Final pH = 6.7

Cumulative mass release (mg Pb/kg-dry)

L/S Ratio (mL/g-dry)

Initial pH = 11.98
Particle Size

• Batch test can’t account for all variables that affect leaching

• Many factors control leaching:
  • pH is a major factor
  • Specific element solubility
  • Particle size
Assessing the Differences Between the SPLP and LEAF Batch Leaching Methods
How Does SPLP Compare to LEAF?

- Correlation between laboratory leaching tests and beneficial use conditions

Aluminum concentration as a function of L/S ratio. SPLP result is added for comparison.
Differences Between SPLP and LEAF

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SPLP</th>
<th>LEAF (1313, 1316)</th>
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<tbody>
<tr>
<td>Solution</td>
<td>SPLP Solution (pH=4.2)</td>
<td>Reagent Water</td>
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<tr>
<td>Time</td>
<td>18 hours</td>
<td>Particle Size Dependent (Up to 72 hours)</td>
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<td>L/S</td>
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<td>Particle Size</td>
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<td>Filter</td>
<td>0.7 µm glass fiber</td>
<td>0.45 µm polypropylene</td>
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</table>

Table 1. Extraction Parameters as Function of Maximum Particle Size (LEAF)
Synthetic Precipitation Leaching Procedure (SPLP)

- A key leaching test in risk assessment for the beneficial use of solid waste materials
- Historically important in the field of solid waste management
- Simulates waste material exposure to slightly acidic rainfall conditions
- Results often compared to the GWCTL for decision making
LEAF Methods

• Provides a more robust dataset
• Wider range of pH and site-specific conditions

However....
• Lack of guidance on how to properly interpret the data
• Inappropriate use of the large volume of data is possible
• Increased range of pH may not be representative of actual site conditions
• May contradict SPLP data
• Inconsistency
# Materials

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<th>ID</th>
<th>Sample</th>
<th>Particle Size Reduction</th>
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<tr>
<td>1</td>
<td>Coal Fly Ash</td>
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<td>2</td>
<td>WTE Bottom Ash</td>
<td>3/8” and #4 Sieve</td>
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<tr>
<td>3</td>
<td>Electronic Waste</td>
<td>3/8” and #4 Sieve</td>
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<td>4</td>
<td>Mine Tailings</td>
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# Methodology

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</table>

S=Reagent Water   s=SPLP solution   T=72 hrs   t=18hrs   L=10.0 ml-eluent/g-dry material
l=2000 mL-eluent/100 g-wet material
Z=#4 sieve   z=3/8” sieve
F=0.45 μm   f=0.7μm
LEAF and SPLP Conducted by the Book
Influence of Extraction Time

Waste-to-Energy Bottom Ash #4

72 Hours Extraction (pH=10.09) (mg/L)

18 Hours Extraction (pH=10.51)

[Graph showing the influence of extraction time on various elements such as Al, Ba, Cr, Pb, Sb, Sr, V, B, Cu, Fe, Mg, Mo, Sn, Zn, and W in Waste-to-Energy Bottom Ash #4.]
Influence of Extraction Time

Waste-to-Energy Bottom Ash #4

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<thead>
<tr>
<th>Element</th>
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<th>WTE#4-18 hrs (pH=10.51)</th>
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<td>Ba</td>
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Extraction Time-Lead

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Influence of Extraction Solution

Mine Tailings

DI Water (pH=2.94) vs. SPLP Solution (pH=2.66) (mg/L)
Influence of Extraction Solution

Electronic Wastes #4

DI Water (pH=9.45)

SPLP Solution (pH=8.89) (mg/L)
Influence of Liquid to Solid Ratio

Waste-to-Energy Bottom Ash #4

Graph showing the relationship between SPIPLS (pH=10.16) (mg/L) and LEAFLS (pH=10.08) (mg/L) for various elements.
Influence of Particle Size

Waste-to-Energy Bottom Ash

Concentration (mg/L)

As, Cr, Mg, Mo, Ni, Sb, Sn, V, Zn

WTE3/8” (pH=10.45)
WTE#4 (pH=10.08)
Influence of Particle Size

Electronic Wastes

EW3/8*(pH=9.63)

EW#4 (pH=9.45)
Influence of Filter

Mine Tailings

Concentration (mg/L)

As, B, Ba, Be, Cd, Cr, Cu, Mg, Na, Ni, Pb, Sb, Se, Sn, Sr, V
Influence of Filter

Electronic Wastes #4

[Bar chart showing the concentration of various elements using LEAF Filter and SPLP Filter.]

- Cu
- Fe
- Mg
- Mn
- Mo
- Ni
- Pb
- Sb
- Se
- Sn
- V
- Zn
Feedback from TAG

• What information would you like to see?
• What is the best way to present the information so that the Florida solid waste community can readily access and utilize?

http://pages.ees.ufl.edu/townsend/

http://pages.ees.ufl.edu/townsend/research/hc14/