Leaching Assessment as Data Input, Materials Testing and Data Management with LeachXS/ORCHESTRA

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Presentation Outline

- Use of Leaching Assessment for Chemical Speciation Modeling and Performance Assessment
- US EPA Leaching Environmental Assessment Framework (LEAF)
- Data Management using CBP LeachXS/Orchestra
Use of Leaching Assessment

• Calibration and Verification of Chemical Speciation Models
  – Need for multiple lines of evidence
  – Equilibrium partitioning as a function of pH, liquid-to-solid ratio (LS), system composition, pE
  – X-ray diffraction, SEM-EDS
  – Literature models (Lothenbach, et. al, etc.)
  – Mass of constituents available for reaction ("Availability")
**Thermodynamic model**

- LeachXS/ORCHESTRA:
  - Solves system of equations:
    - Conservation of mass
    - Laws of mass action
  - Yields solid, aqueous, and gaseous speciation

- C-S-H:
  - Ideal solid solution with Tobermorite- and Jennite-like end-members (from Lothenbach et al., 2008)
  - No adsorption and (some) additional minerals in the model
  - Dome construction material assumed to be Ordinary Portland Cement

**Mineral phases**

<table>
<thead>
<tr>
<th></th>
<th>Mg(OH)$_2$</th>
<th>Ca(OH)$_2$</th>
<th>C$_3$AH$_6$</th>
<th>C$<em>4$Ac$</em>{0.5}$H$_{12}$</th>
<th>C$_6$As$<em>3$H$</em>{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brucite</td>
<td>Portlandite</td>
<td>Hydrogarnet</td>
<td>Hemi-carbonate</td>
<td>Ettringite</td>
</tr>
<tr>
<td>CaSO$_4$·2H$_2$O</td>
<td>Gypsum</td>
<td>Calcite</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SiO$_2$ (am)</td>
<td>Amorphous Silica</td>
<td>C$_2$ASH$_8$</td>
<td>C$<em>3$AS$</em>{0.8}$H$_{4.4}$</td>
<td>Siliceous Hydrogarnet</td>
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</tr>
<tr>
<td>Al(OH)$_3$ (am)</td>
<td>Amorphous Aluminum hydroxide</td>
<td>C$_2$FSH$_8$</td>
<td>C$<em>4$AH$</em>{13}$</td>
<td>Hydroxy AFm</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Alumina</td>
<td>C$_2$AH$_9$</td>
<td>C$<em>4$FH$</em>{13}$</td>
<td>Fe-hydroxy AFm</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_3$ (mic)</td>
<td>Microcrystalline Iron hydroxide</td>
<td>C$_2$FH$_8$</td>
<td>C$<em>4$AsH$</em>{12}$</td>
<td>Monosulfate</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Ferric oxide</td>
<td>CaSO$_4$</td>
<td>C$<em>1.67$SH$</em>{2.1}$</td>
<td>Jennite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CA$<em>{2}$H$</em>{8}$</td>
<td>Anhydrite</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Solid Solution:</td>
<td></td>
<td>Solid Solution:</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C$<em>{1.67}$SH$</em>{2.1}$</td>
<td>Jennite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$<em>{0.83}$SH$</em>{1.3}$</td>
<td>Tobermorite</td>
<td></td>
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</tr>
</tbody>
</table>


Comparison of 1313 Data and L XO Predictions

Experimental (CEM-I) data for HPC from USEPA Method 1313 (SW-846)
Partial Reaction of Binder Materials
A Decision Support System for Beneficial Use and Disposal Decisions in the United States and Internationally...

- Four leaching test 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 scenarios.

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

*Posting to SW-846 as “New Methods” completed August 2013
Use of LEAF in the United States

- Guidance for use of LEAF is under development by 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 (EPA)
- Contaminated site remediation (Industry & State regulators, CERCLA?)
- Evaluation of treatment process effectiveness (EPA and Industry)
- Long-term performance of concrete and cementitious materials in nuclear energy and nuclear waste (DOE)
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, 5, 2, 1, 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
Study Materials for 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
## 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 (9$^{th}$ 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>

**Validation Reports**


What about TCLP and SPLP?

Acetic Acid
- TCLP solution is not a relevant leaching condition

Liquid-to-Solid Ratio (mL/g)
- TCLP/SPLP at L/S 20
- M1313 at L/S 10
- M1316 at L/S 0.5-10

Final pH
- TCLP and SPLP recording final pH is not required
Data Management in LXO

- **Databases**
  - Experimental data
  - Chemical speciation thermodynamics
  - Scenario case studies ("case files")

- **Data Input and Exchange**
  - Excel templates for testing results (3 versions)
  - XML files for exchange and building custom databases
  - Case file import/export tools

- **Data Evaluation**
  - Graphing, data comparison, model comparison (output to Excel files)
  - Statistical evaluations
  - Titration calculator (ANC/BNC)
  - ANS 16.1 Leaching Index *(in testing)*