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

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CBP
Cementitious Barriers Partnership

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")

Dome Model Description

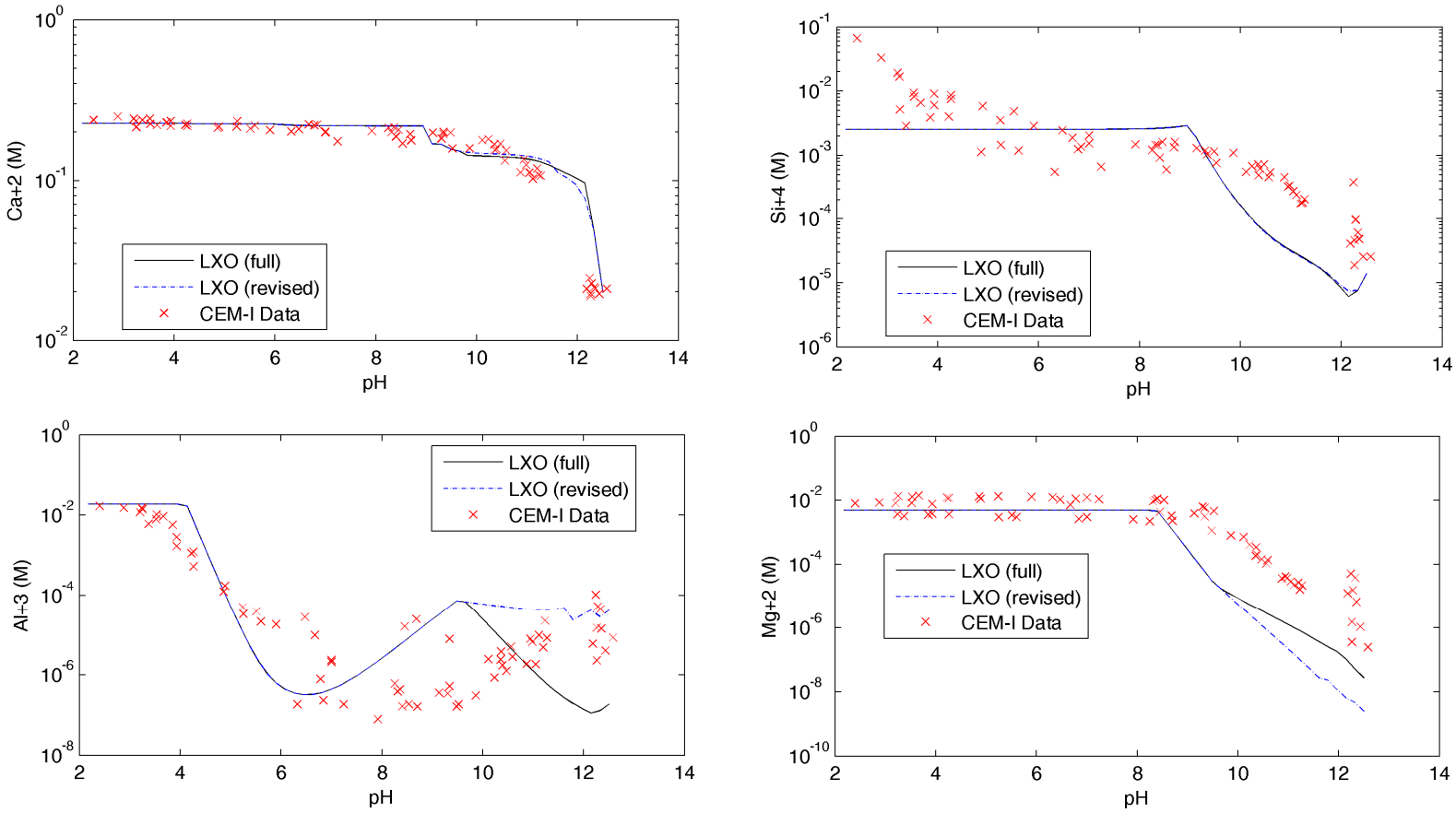
Thermodynamic model

- 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

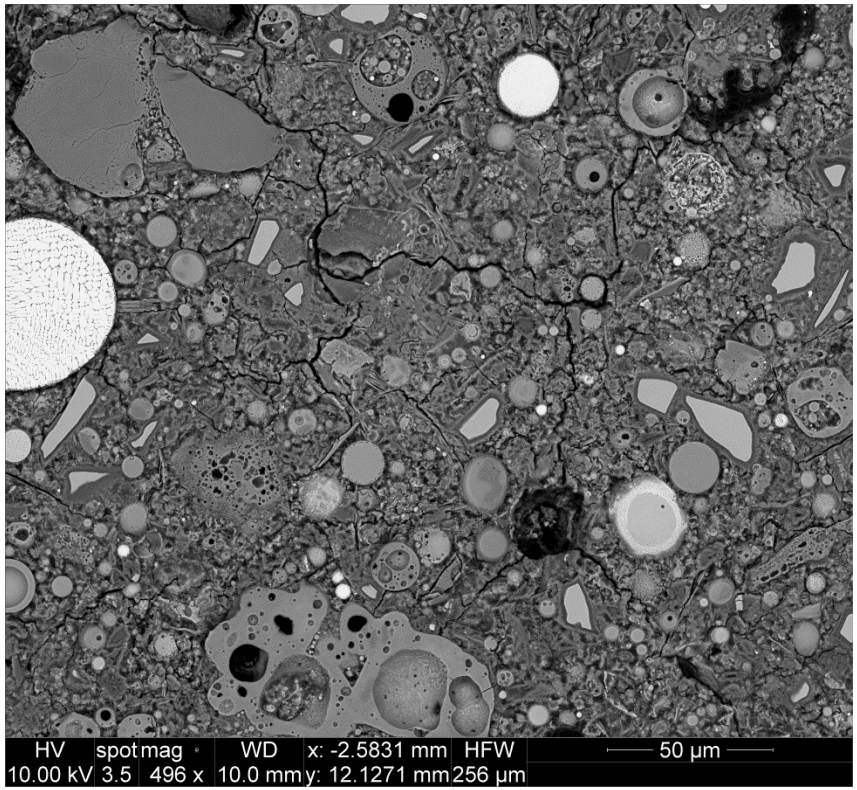
$Mg(OH)_2$ *Brucite*	$Ca(OH)_2$ *Portlandite*	C_3AH_6 *Hydrogarnet*	$C_4Ac_{0.5}H_{12}$ *Hemi-carbonate*	$C_6As_3H_{32}$ *Ettringite*
$CaSO_4 \cdot 2H_2O$ *Gypsum*	$CaCO_3$ *Calcite*	C_3FH_6 *Fe-hydrogarnet*	$C_4Fc_{0.5}H_{12}$ *Fe-hemi-carbonate*	$C_6Fs_3H_{32}$ *Fe-ettringite*
SiO_2 (am) *Amorphous Silica*	C_2ASH_8 *Strätlingite*	$C_3AS_{0.8}H_{4.4}$ *Siliceous Hydrogarnet*	C_4AcH_{11} *Mono-carbonate*	$C_6Ac_3H_{32}$ *Tricarbo-aluminate*
$Al(OH)_3$ (am) *Amorphous Aluminum hydroxide*	C_2FSH_8 *Fe-Strätlingite*	C_4AH_{13} *Hydroxy AFm*	C_4FcH_{12} *Fe-mono-carbonate*	M_4AH_{10} *Hydrotalcite*
Al_2O_3 *Alumina*	C_2AH_8 *Unnamed meta-stable phase*	C_4FH_{13} *Fe-hydroxy AFm*	C_4AsH_{12} *Monosulfate*	M_4FH_{10} *Fe-hydrotalcite*
$Fe(OH)_3$ (mic) *Microcrystalline Iron hydroxide*	C_2FH_8 *Unnamed meta-stable phase*	***Solid Solution:*** $C_{1.67}SH_{2.1}$ *Jennite*	C_4FsH_{12} *Fe-monosulfate*	M_4AcH_9 *CO_3-Hydrotalcite*
Fe_2O_3 *Ferric oxide*	$CaSO_4$ *Anhydrite*	$C_{0.83}SH_{1.3}$ *Tobermorite*		

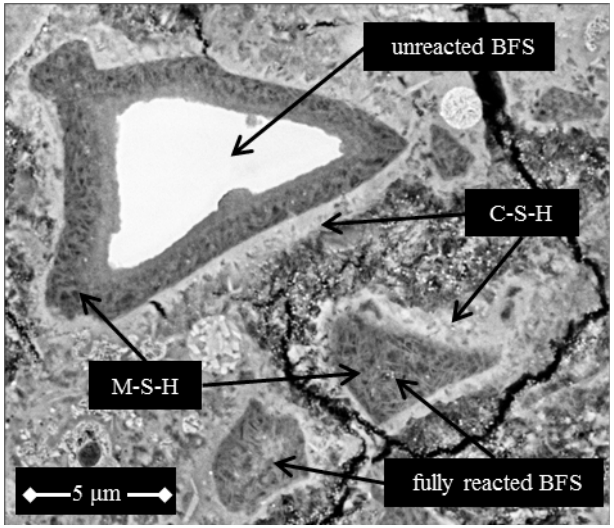
Comparison of 1313 Data and LXO Predictions



Experimental (CEM-I) data for HPC from USEPA Method 1313 (SW-846)

Partial Reaction of Binder Materials





L E A F

Leaching Environmental Assessment Framework

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)

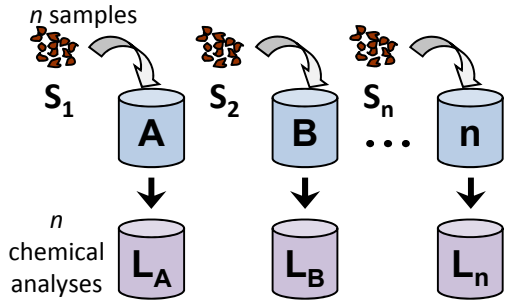
Method 1313 Overview

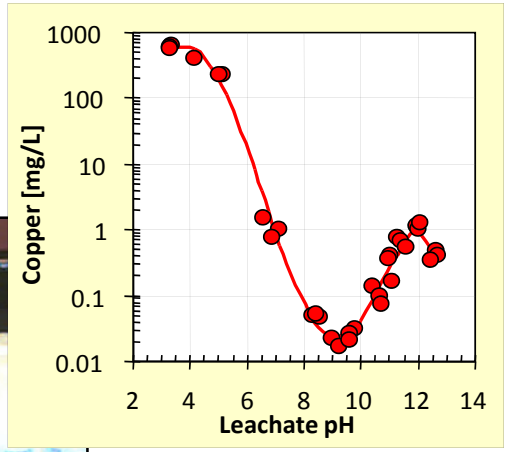
Equilibrium Leaching Test

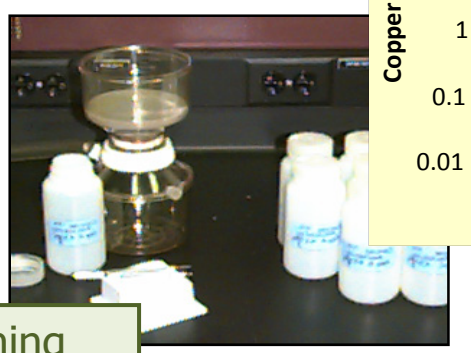
- Parallel batch as function of pH

Test Specifications

- 9 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 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

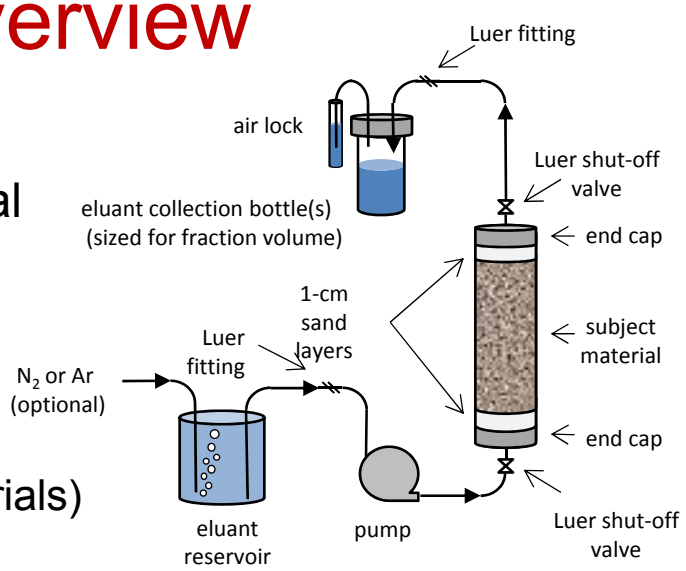
Method 1314 Overview

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 $CaCl_2$ (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

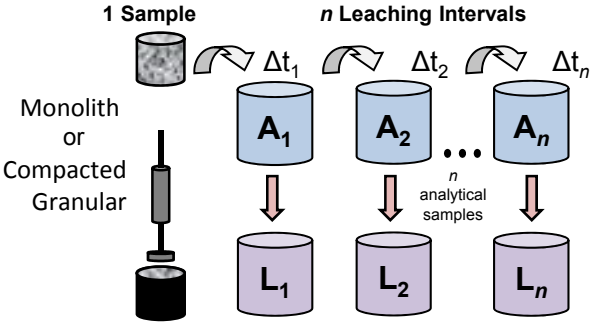
Method 1315 Overview

Mass-Transfer Test

- Semi-dynamic tank leach test

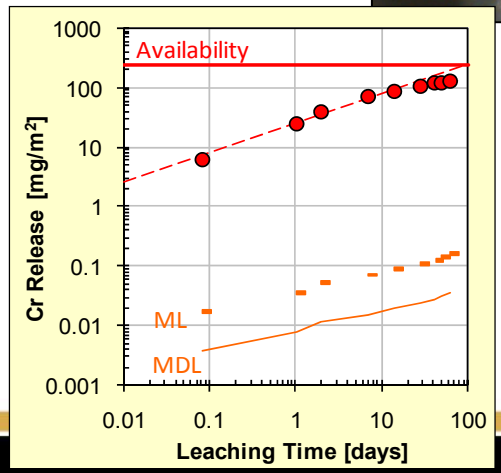
Test Specifications

- 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/cm^2
- 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



Monolithic

Granular



Flux and Cumulative Release as a Function of Leaching Time

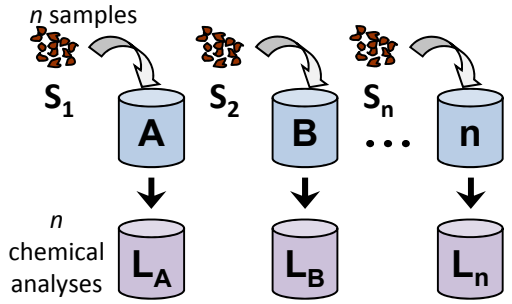
Method 1316 Overview

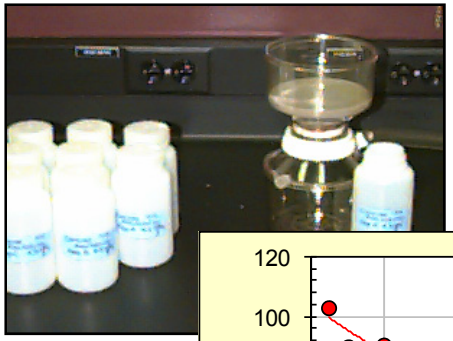
Equilibrium Leaching Test

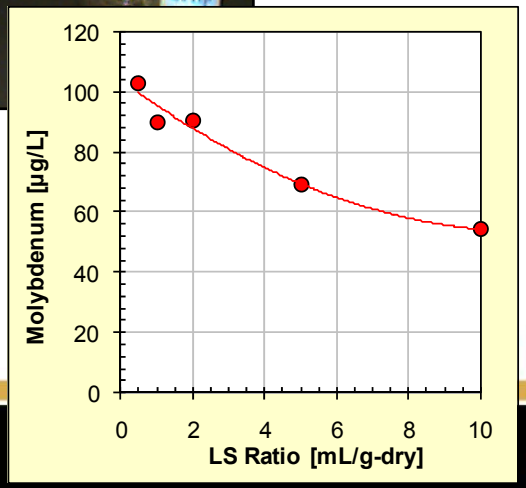
- Parallel batch as function of L/S

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

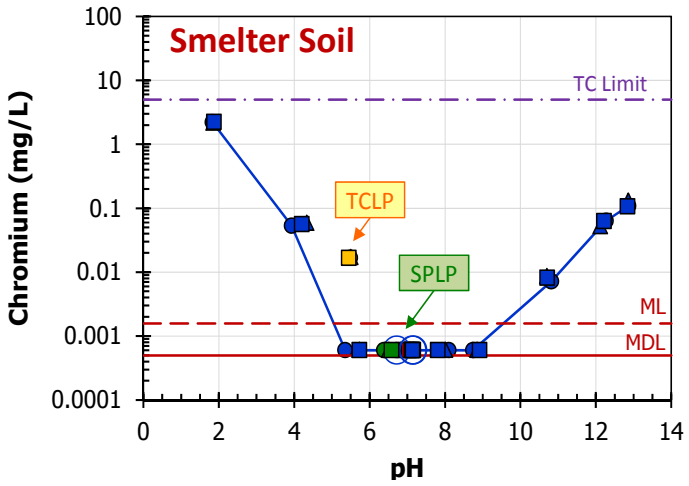
Method	Test Output	RSD_r (%)	RSD_R (%)
Method 1313	Eluate Concentration (average over pH range)	10	26
Method 1314	Eluate Concentration (9^{th} fraction at L/S=10) Mass Release (cumulative to L/S=0.5) Mass Release (cumulative to L/S=10)	13 7 5	28 18 14
Method 1315	Interval Flux (average excluding wash-off) Mass Release (cumulative to 7-days) Mass Release (cumulative to 63-days)	11 9 6	28 19 23
Method 1316	Eluate Concentration (average over L/S range)	7	17

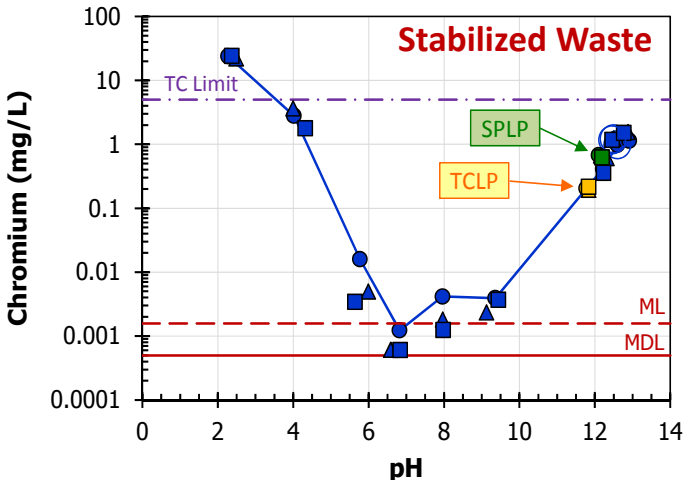
Validation Reports

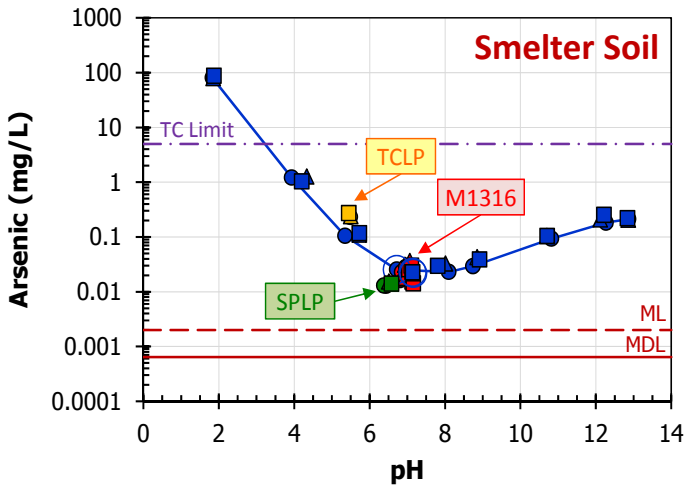
EPA-600/R-12/623 *"Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1313 and Method 1316,"* September 2012.

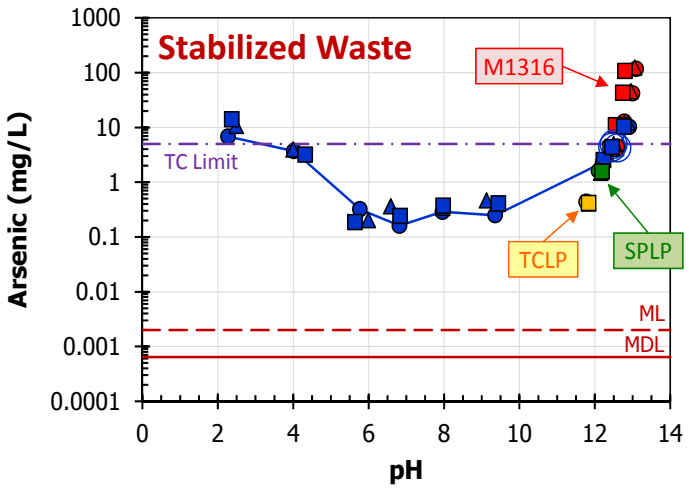
EPA-600/R-12/624 *"Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1314 and Method 1315,"* September 2012.

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)