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

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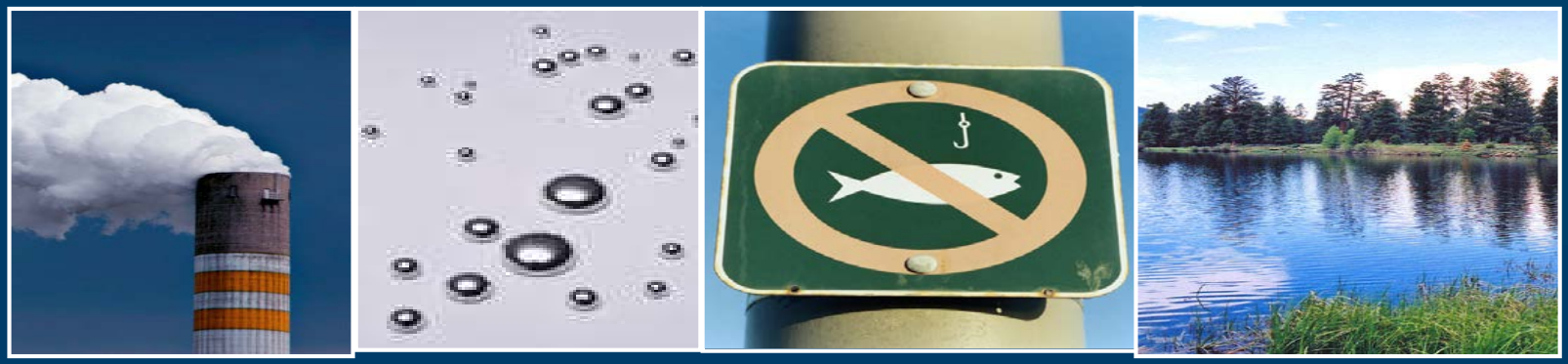
Presentation for 2nd Symposium of International Waste Working Group Asian Regional Branch



Office of Research and Development
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division

13 April 2015

Research Team

Vanderbilt University research team and collaborators:

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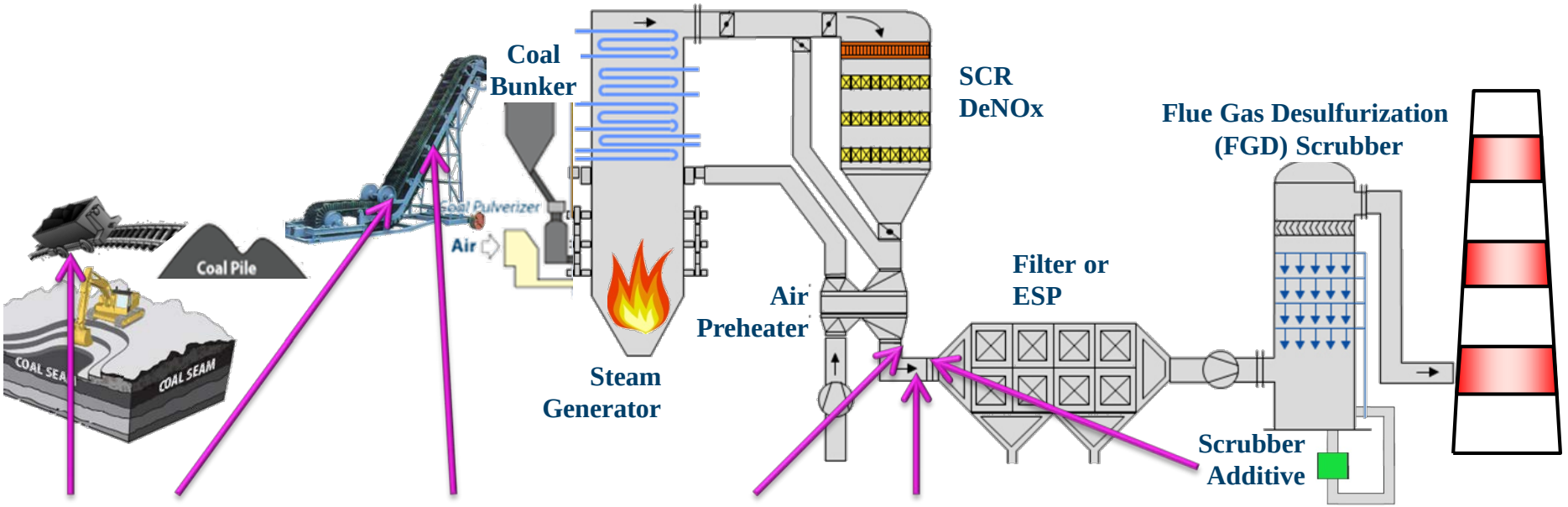
Background

- 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.

EPA United States Environmental Protection Agency

Control Technologies for Reducing Air Emissions at Coal-Fired Power Plants



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

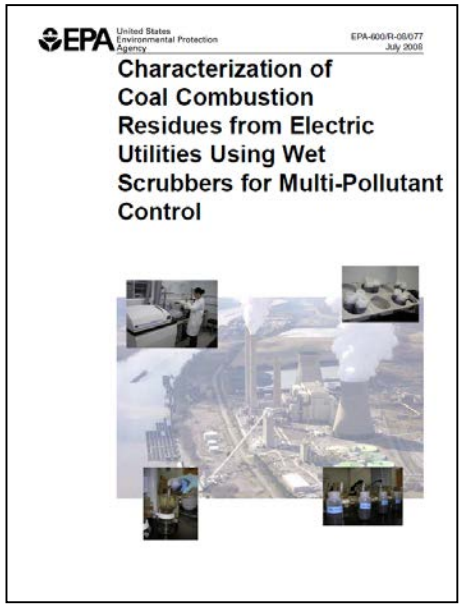
Posted as "New Methods" to SW-846 on Aug 2013

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

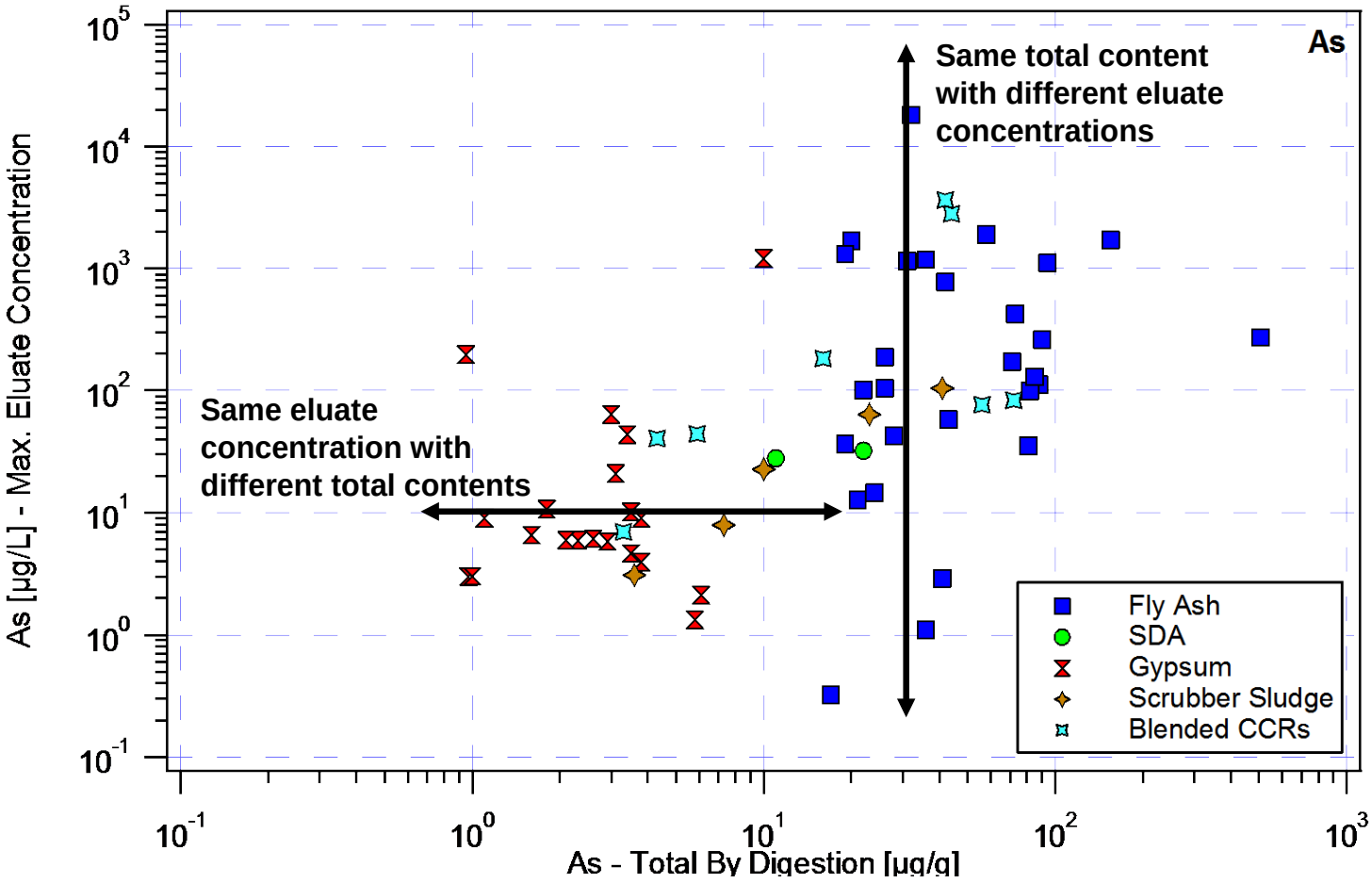
	Indicator Values		Fly Ash		FGD Gypsum	
	TC (µg/L)	MCL (µg/L)	Total Content (mg/kg)	Leaching Concentration (µg/L)	Total Content (mg/kg)	Leaching Concentration (µg/L)
Hg	200	2	0.1- 1.5	<0.01-0.50	0.01-3.1	<0.01-0.66
Sb	-	6	3-14	<0.3-**11,000**	0.14-8.2	<0.3-**330**
As	5,000	10	17-510	0.32-**18,000**	0.95-10	0.32-**1,200**
Ba	100,000	2,000	50-7,000	50-**670,000**	2.4-67	30-560
B	-	7,000*	NA	210-**270,000**	NA	12-**270,000**
Cd	1,000	5	0.3-1.8	<0.1-**320**	0.11-0.61	<0.2-**370**
Cr	5,000	100	66-210	<0.3-**7,300**	1.2-20	<0.3-240
Mo	-	200	6.9-77	<0.5-**130,000**	1.1-12	0.36-**1,900**
Se	1,000	50	1.1-210	5.7-**29,000**	2.3-46	3.6-**16,000**
Tl	-	2	0.72-13	<0.3-**790**	0.24-2.3	<0.3-**1,100**

* 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 H_2O equivalent level; MCL – Maximum concentration level

Total Content

Total Content **Does Not** Correlate to Leaching



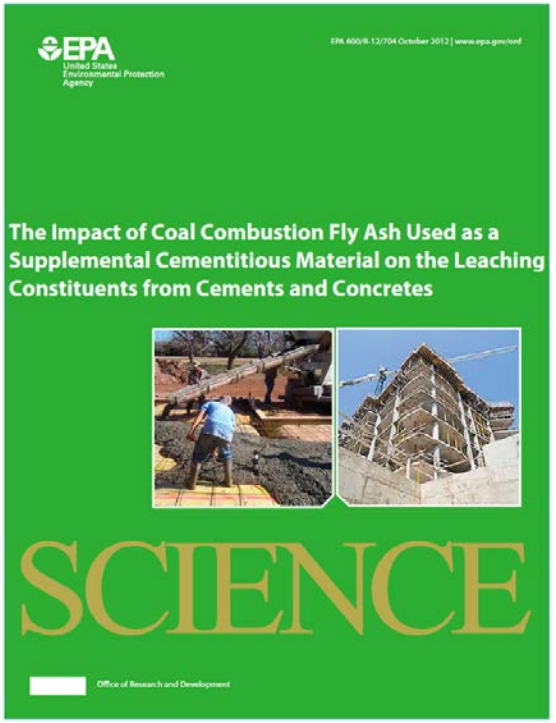
Evaluation of Fly Ash Use in Cement & Concrete

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

United States Environmental Protection Agency

- **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**

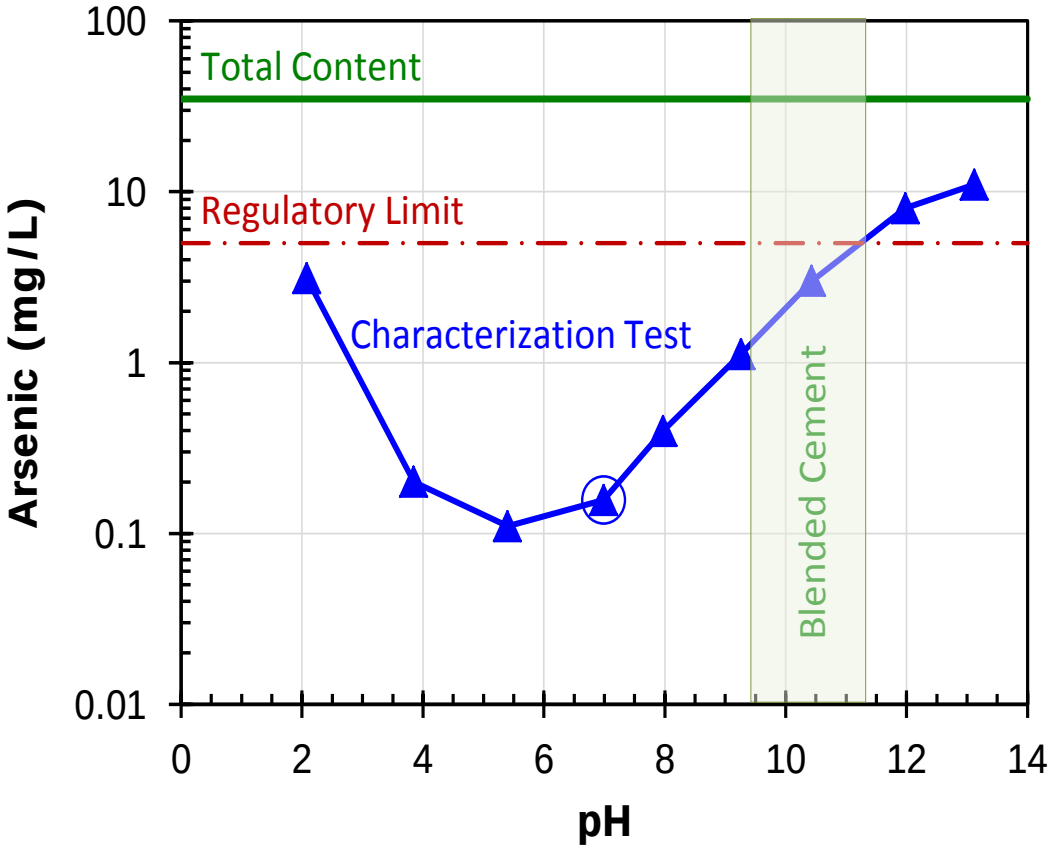
Leaching Tests

Regulatory Tests

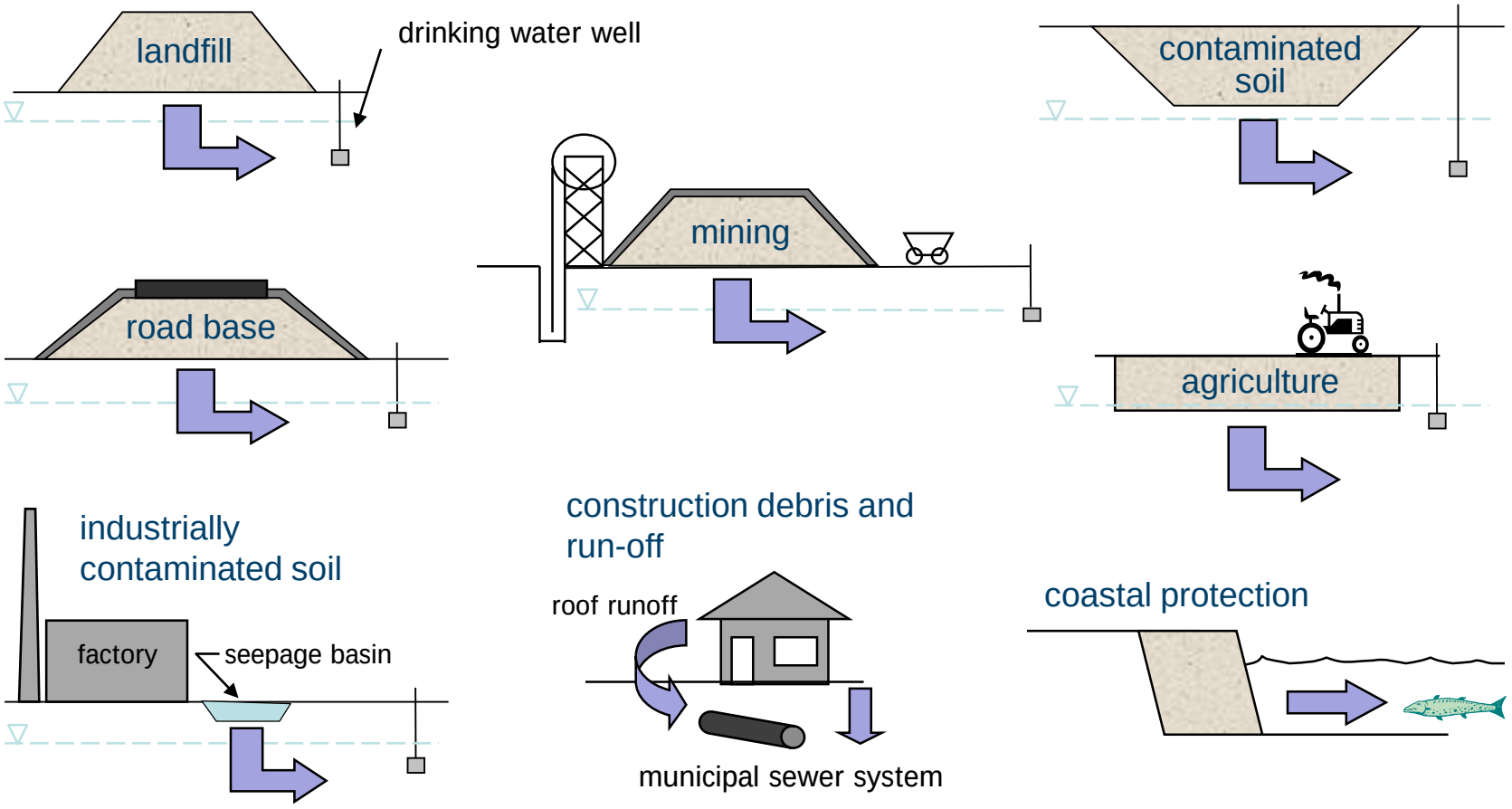
- Aim to bound risk by “plausible worst case”
- Comparison to limits
- Does not consider
  - Release Scenario
  - Time (kinetics)
  - Mass Transport

Characterization Tests

- Allow scenario-specific release estimates and tiered approach
- Range of conditions
- Comparisons between materials, treatments, & management scenarios



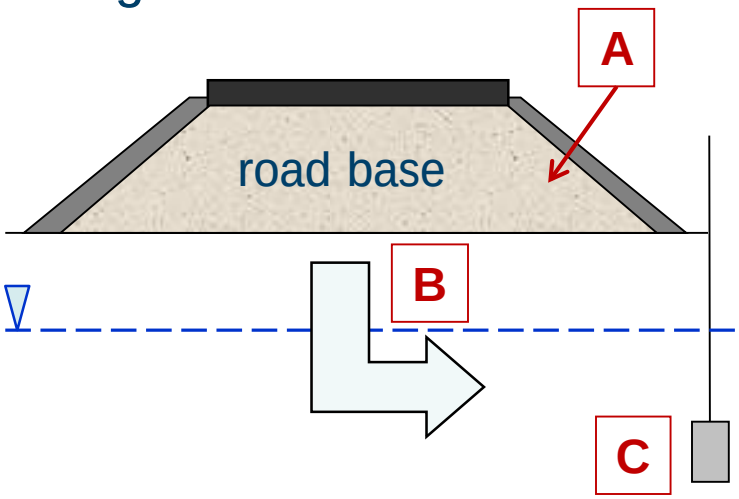
Many Leaching Scenarios …

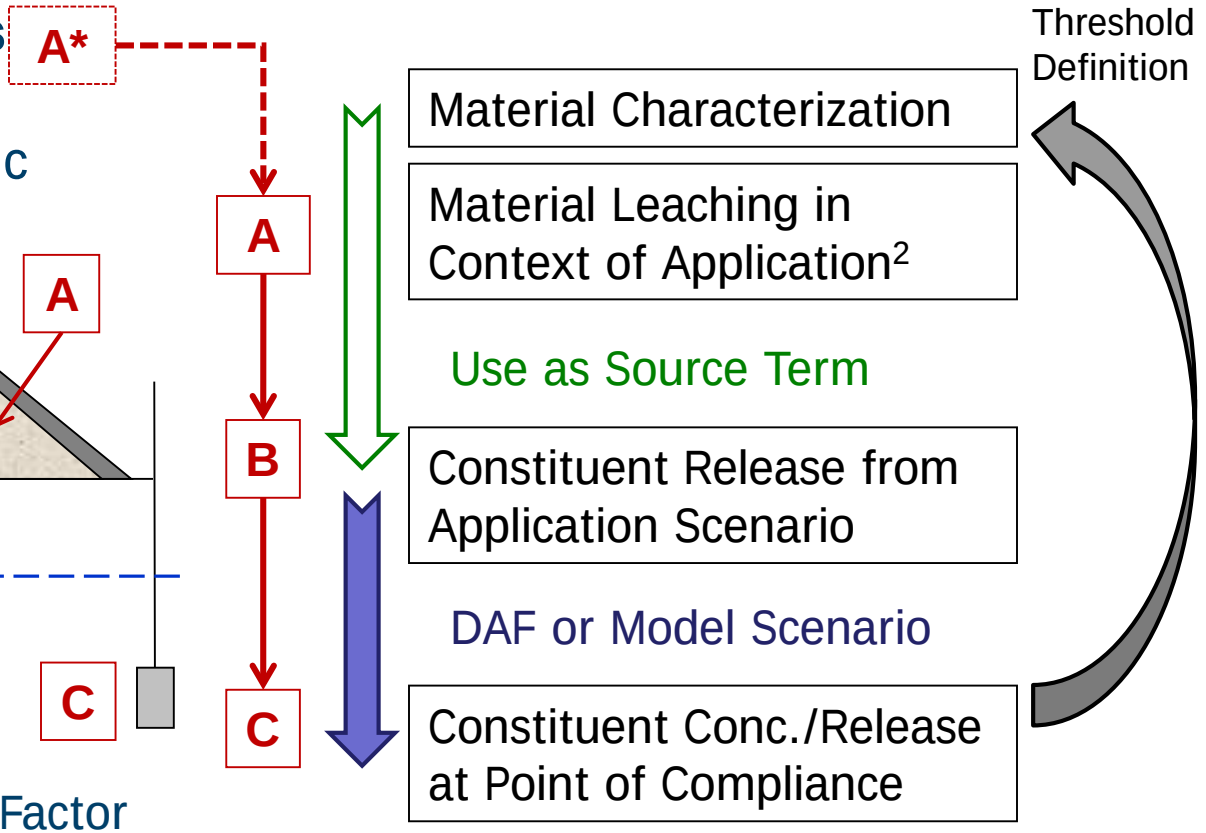


Assessment Approach

Material Leaching Tests

Broad-based characterization of intrinsic leaching behavior





DAF – Dilution-Attenuation Factor

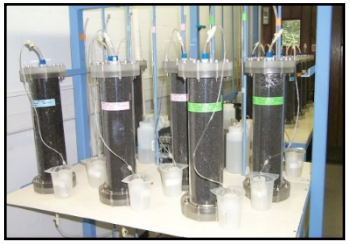
[2] by numerical modeling

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

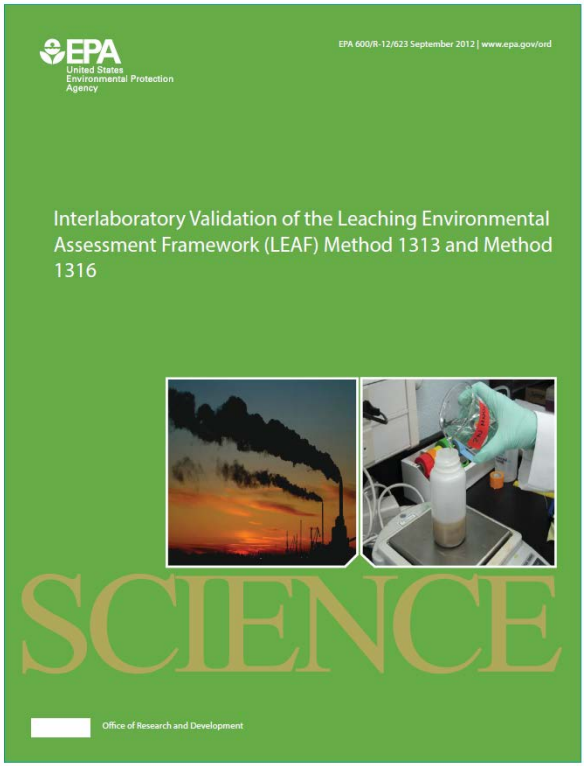
United States Environmental Protection Agency

Multi-lab Round-robin Testing

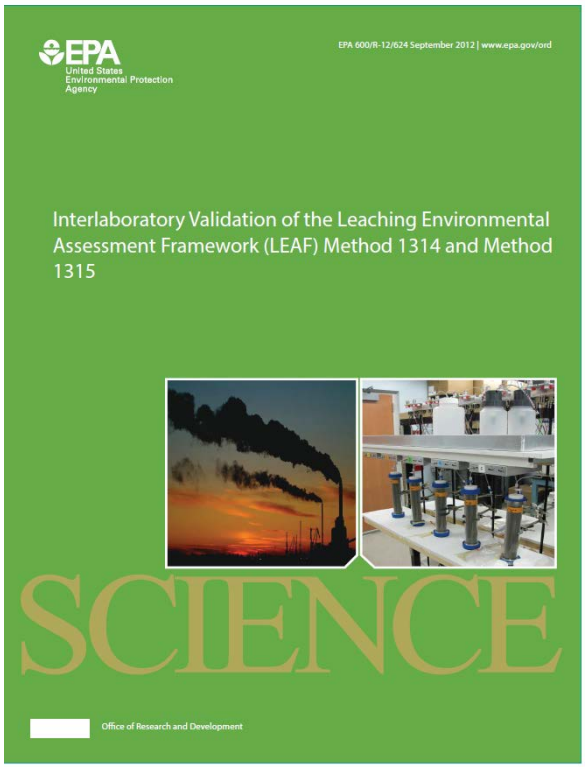
- Academic,
- Commercial,
- Government and
- International Labs

Materials

- Coal Fly Ash
- Contaminated Soil
- Solidified Waste
- Brass Foundry
- Sand



EPA 600/R-12/623



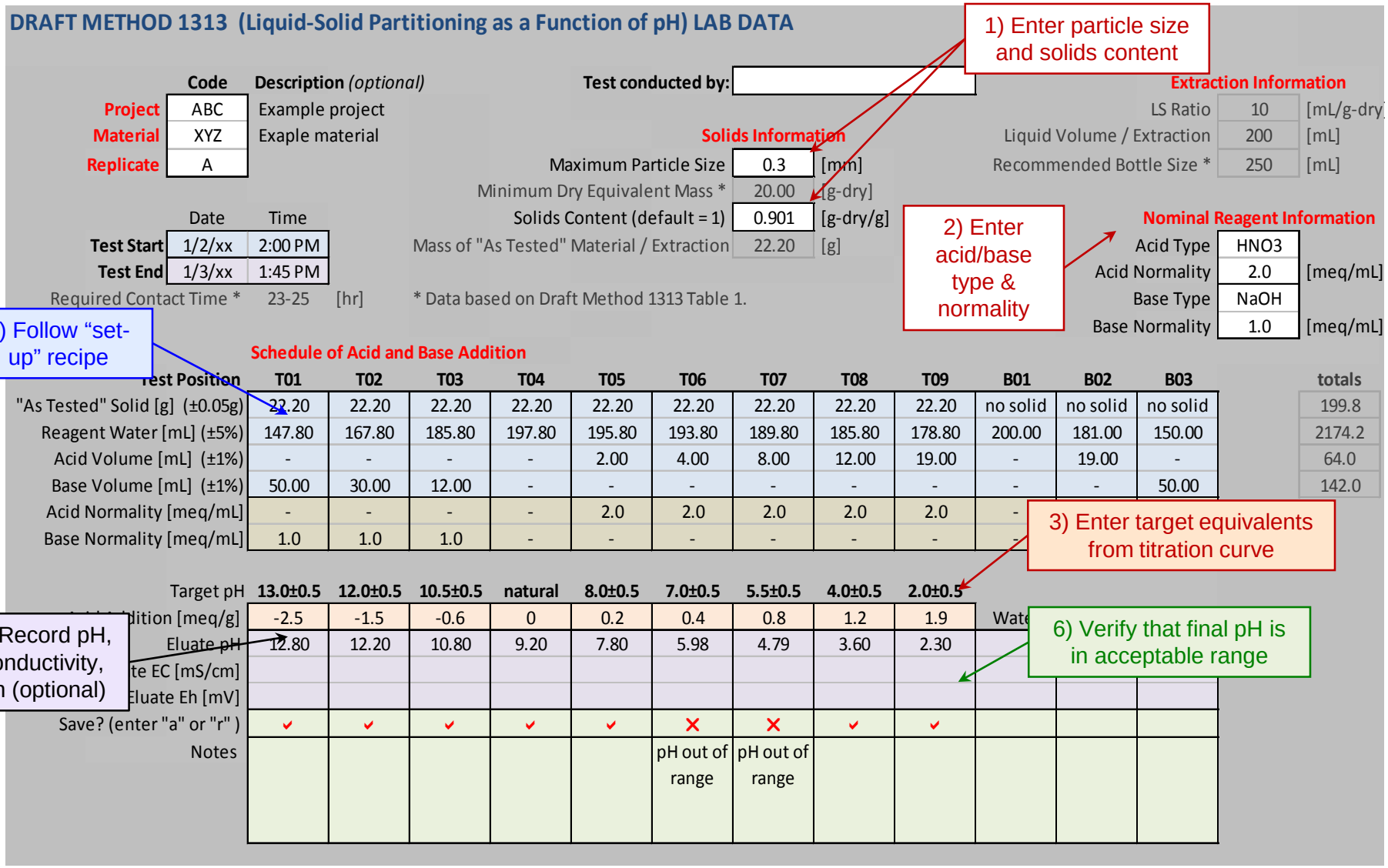
EPA 600/R-12/624

LEAF Data Management Tools

United States Environmental Protection Agency

- 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 SO_4 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

Excel Data Templates for each LEAF Method



DRAFT METHOD 1313 (Liquid-Solid Partitioning as a Function of pH) LAB DATA

1) Enter particle size and solids content

	Code	Description *(optional)*
Project	ABC	Example project
Material	XYZ	Exaple material
Replicate	A	

Test conducted by:

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]

Extraction Information

LS Ratio	10	[mL/g-dry]
Liquid Volume / Extraction	200	[mL]
Recommended Bottle Size *	250	[mL]

	Date	Time
Test Start	1/2/xx	2:00 PM
Test End	1/3/xx	1:45 PM

Required Contact Time * 23-25 [hr]

* Data based on Draft Method 1313 Table 1.

2) Enter acid/base type & normality

Nominal Reagent Information

Acid Type	HNO3	
Acid Normality	2.0	[meq/mL]
Base Type	NaOH	
Base Normality	1.0	[meq/mL]

4) Follow "set-up" recipe

Schedule of Acid and Base Addition

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03	totals
"As Tested" Solid [g] (±0.05g)	22.20	22.20	22.20	22.20	22.20	22.20	22.20	22.20	22.20	no solid	no solid	no solid	199.8
Reagent Water [mL] (±5%)	147.80	167.80	185.80	197.80	195.80	193.80	189.80	185.80	178.80	200.00	181.00	150.00	2174.2
Acid Volume [mL] (±1%)	-	-	-	-	2.00	4.00	8.00	12.00	19.00	-	19.00	-	64.0
Base Volume [mL] (±1%)	50.00	30.00	12.00	-	-	-	-	-	-	-	-	50.00	142.0
Acid Normality [meq/mL]	-	-	-	-	2.0	2.0	2.0	2.0	2.0	-			
Base Normality [meq/mL]	1.0	1.0	1.0	-	-	-	-	-	-	-			

3) Enter target equivalents from titration curve

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
dition [meq/g]	-2.5	-1.5	-0.6	0	0.2	0.4	0.8	1.2	1.9
Eluate pH	12.80	12.20	10.80	9.20	7.80	5.98	4.79	3.60	2.30
te EC [mS/cm]									
Eluate Eh [mV]									
Save? (enter "a" or "r")	✔	✔	✔	✔	✔	✘	✘	✔	✔
Notes						pH out of range	pH out of range		

5) Record pH, conductivity, Eh (optional)

6) Verify that final pH is in acceptable range

LeachXS™

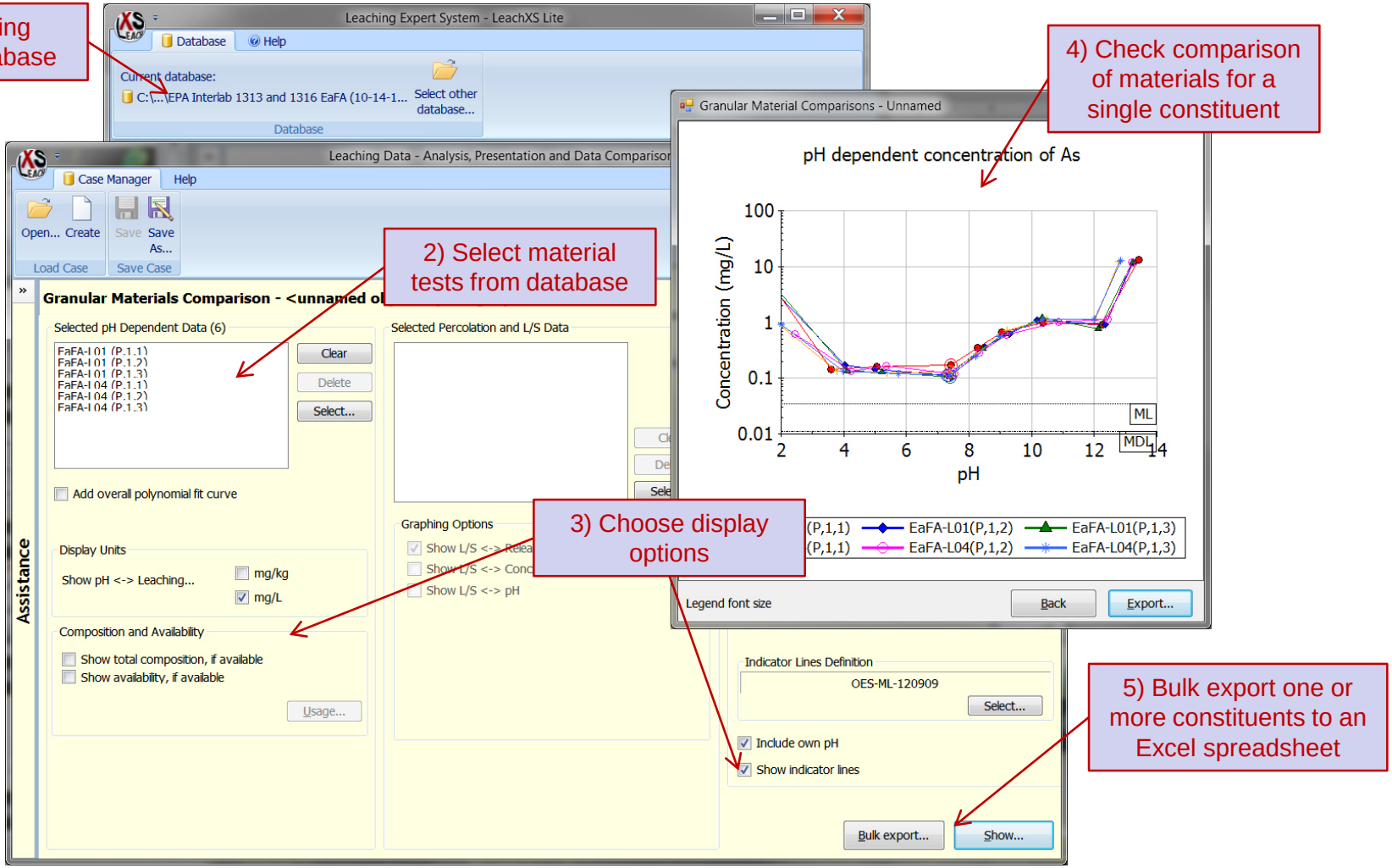
Test Methods Support
Data Management
Statistical Analysis
Quality Control
Chemical Speciation
Scenario Modeling

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

LeachXS Lite

United States Environmental Protection Agency

1) Set working materials database



2) Select material tests from database

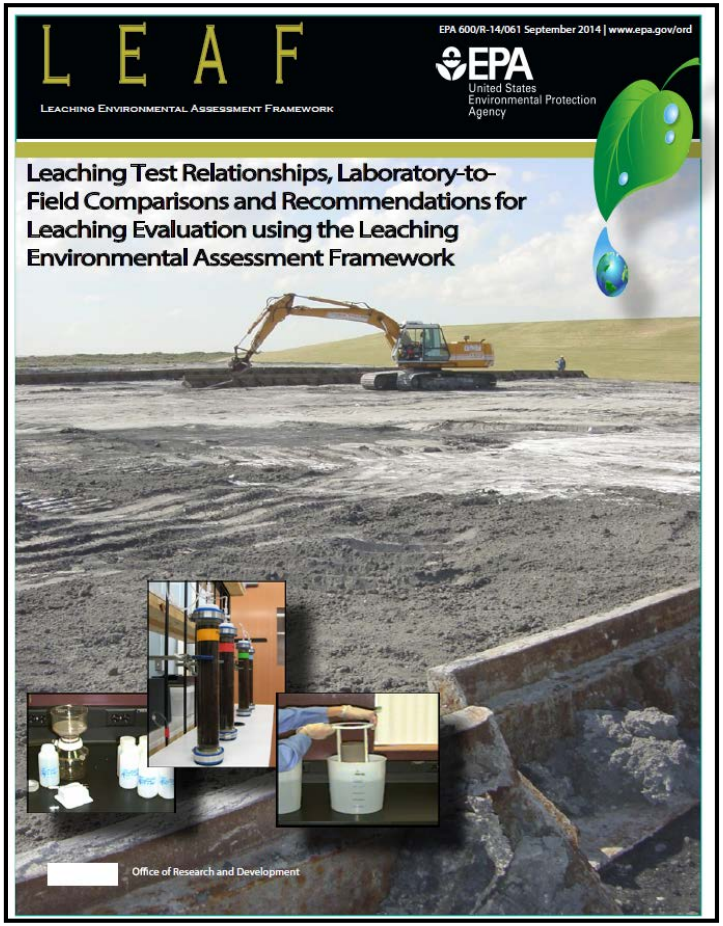
3) Choose display options

4) Check comparison of materials for a single constituent

5) Bulk export one or more constituents to an Excel spreadsheet

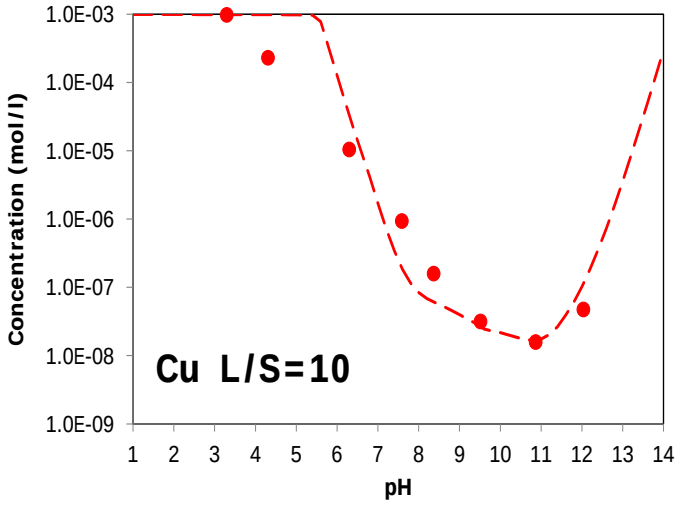
Laboratory-to-Field Relationships

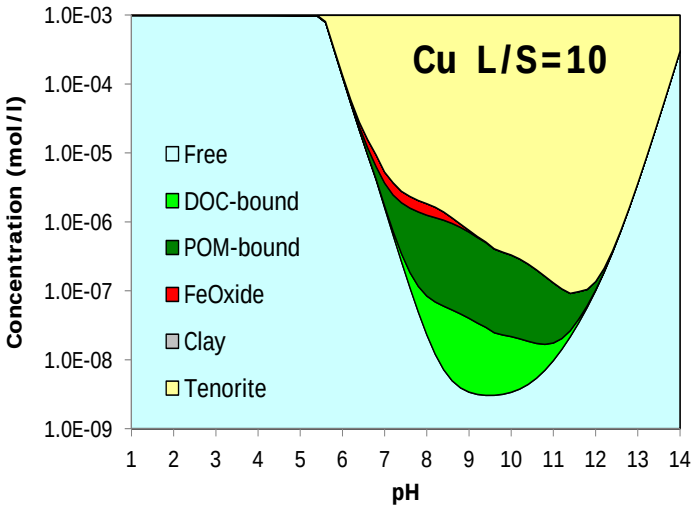
- Leaching Assessment Fundamentals
- 10 Cases of Large-scale Field Analysis Coupled with Laboratory Testing For 7 Materials
  - Coal combustion residues (fly ash, scrubber residues
  - Inorganic waste (mixed origin)
  - Municipal solid waste (MSW)
  - MSW incinerator bottom ash
  - Cement-stabilized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

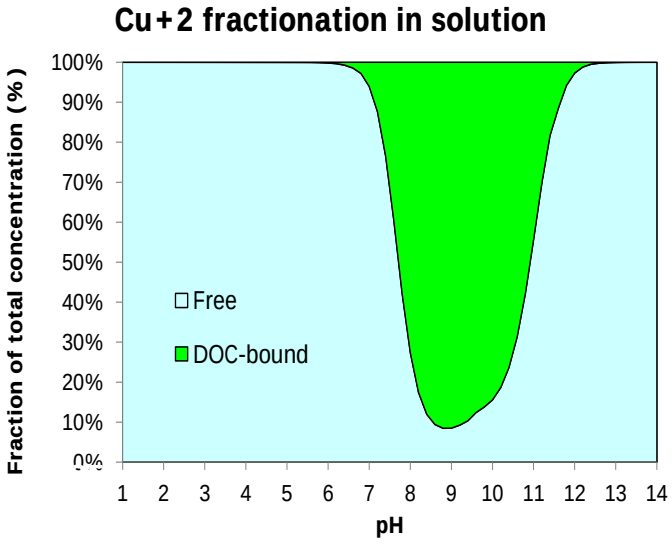


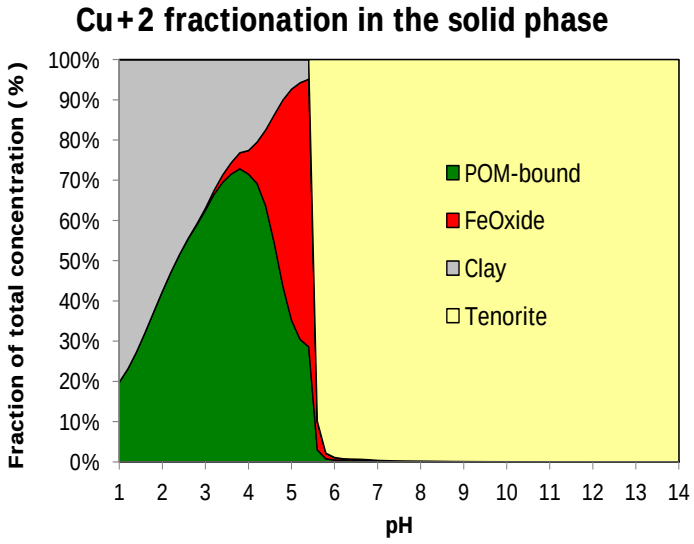
EPA 600/R-14/061

Geochemical Speciation Modeling







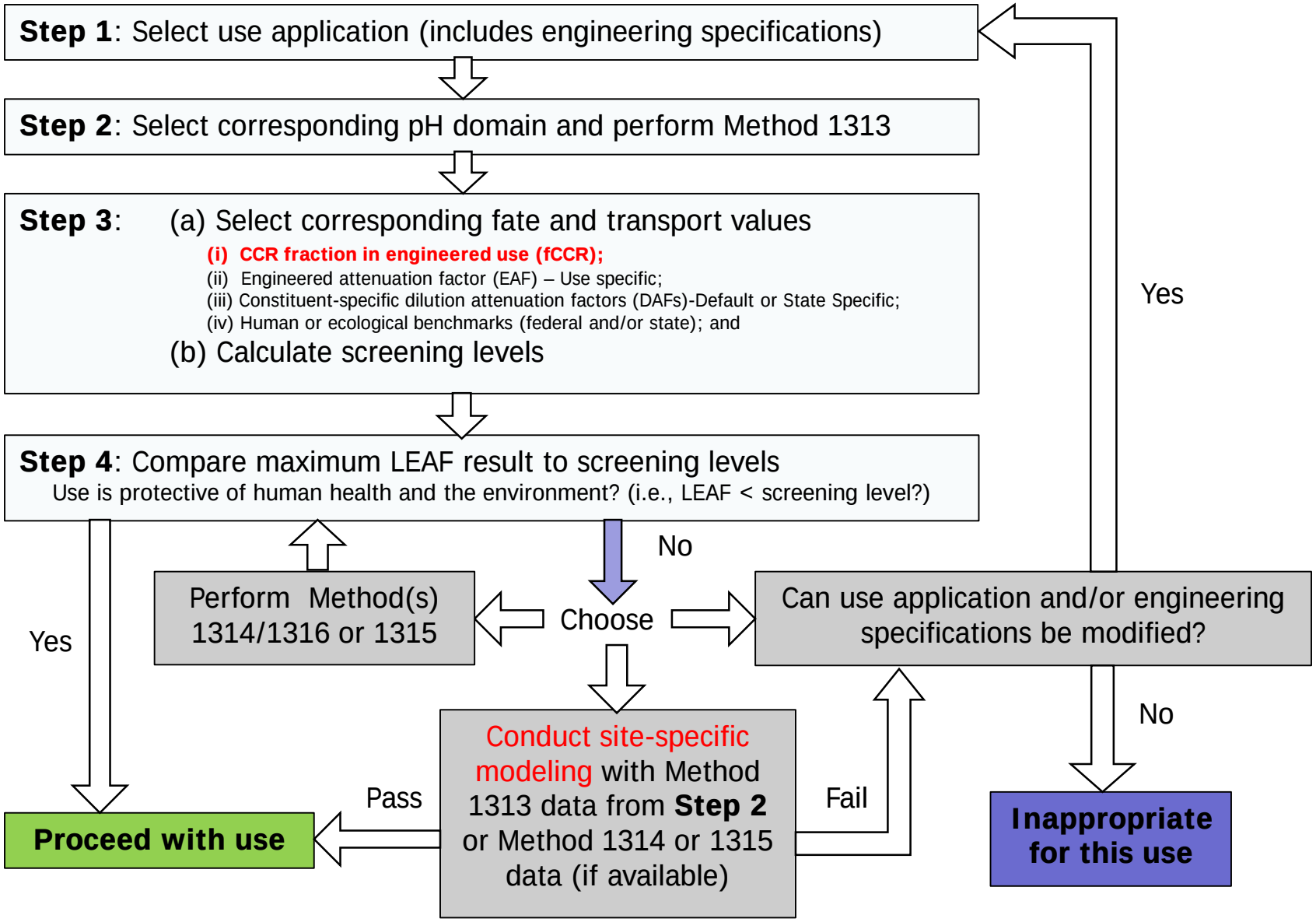


Model description for Cu in MSW combustion bottom ash reheated to 500°C in comparison with pH- dependence test results (e.g., EPA Method 1313)

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



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
  - *New Methods* in SW846 – EPA's compendium of test methods for waste and material characterization: http://epa.gov/wastes/hazard/testmethods/sw846/new_meth.htm
  - 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

- Laboratory-to-Field Comparisons for Leaching Evaluation using the Leaching Environmental Assessment Framework (LEAF), EPA 600/R-14/061, Sept 2014.
- 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
- Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1313 and Method 1316, EPA 600/R-12/623, Sept 2012
- Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1314 and Method 1315, EPA 600/R-12/624, Sept 2012

Supporting Documentation (Cont.)

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