

# Lab to field comparison - Leaching test relationships, laboratory-to-field comparisons and recommendations for leaching evaluation using the leaching environmental assessment framework (leaf)

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## 1 Objectives and Background

The primary objective of this report is to provide an evaluation of applicability and limitations of using laboratory leaching tests, as defined by the LEAF and LEAF-analogous methods, for estimating leaching of COPCs from a broad range of materials under field disposal and beneficial use scenarios. This evaluation is achieved by comparison of LEAF laboratory testing of “as produced” material using LEAF methods, laboratory testing of “field aged” material, and results from field leaching studies of the material. Interpretation of LEAF leaching data is conducted within the context of a defined conceptual leaching model and chemical speciation modeling is used as a tool to facilitate evaluation of scenarios beyond the conditions of common laboratory testing (i.e., normalize the laboratory data to the field conditions by estimating the impact of factors not practical to achieve in the laboratory, but which are known to occur and affect leaching). A second objective of this report is to provide recommendations on the selection and use of LEAF testing for different types of materials or wastes when evaluating disposal or use scenarios.

The Leaching Environmental Assessment Framework (LEAF) is fundamentally different than the defined simulation-based approach, such as the toxicity characteristic leaching procedure (TCLP)<sup>1</sup>, because it focuses on characterization of intrinsic material-specific leaching behaviors controlling the release of COPCs from solid materials over a broad range of test and environmental conditions, with application of the resulting leaching data to specific disposal or use conditions (Kosson et al., 2002). The framework consists of four laboratory leaching methods, data management tools, and leaching assessment approaches developed by Vanderbilt University in conjunction with U.S. EPA and international partners.

The four leach testing methods described in LEAF have been validated through interlaboratory studies (Garrabrants et al., 2012a, 2012b) and adopted into SW-846, the EPA compendium of laboratory tests (EPA, 2013a) as:

- Method 1313 or EN14429/ EN14997 – Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure
- Method 1314 or EN14405 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure
- Method 1315 or EN15863 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-Dynamic Tank Leaching Procedure
- Method 1316 (or to some degree EN12457) – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio in Solid Materials using a Parallel Batch Extraction Procedure

These tests may be applied to solid materials to determine fundamental leaching parameters including liquid-solid partitioning (LSP) of constituents as a function of pH and cumulative liquid-to-solid ratio (L/S) as well as the rate of constituent mass transfer from monolithic and compacted

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<sup>1</sup> TCLP was designed to simulate a plausible mismanagement scenario of co-disposal in a municipal solid waste landfill.

granular materials. Coordinated development of LEAF has occurred between research laboratories in the United States (U.S.) and the European Union (EU). The general approach and test methods described in this report also are applicable for assessing release of organic substances, radionuclides and nano-particles, although for the test methods additional consideration is needed with respect to compatibility of the constituents of interest to the container materials used.

Leaching tests are tools typically used for estimating the environmental impact associated with disposal or utilization of materials and wastes on the land (e.g., soils, sediments, industrial wastes, demolition debris, etc.). Results of leaching assessments based on testing and interpretive models provide a source term as one part of an evaluation of environmental safety. In addition to test results, integral factors in applicability assessment or criteria development for use and disposal include (i) definition and application of appropriate fate and transport models and (ii) establishment of risk-informed constituent concentration thresholds at defined points of compliance.

Characterization of leaching behavior using the LEAF tests along with scenario-specific information can be used to assemble a leaching “source term” for many environmental scenarios or levels of environmental assessment including:

- screening level assessments at a site-specific, regional or national scale;
- detailed site-specific evaluations;
- performance comparisons between different materials or treatment processes under specific disposal or use scenarios;
- development of chemical speciation based models to evaluate potential material leaching behavior under field conditions that may be difficult or impossible to reproduce in the laboratory.

Assessing the applicability and accuracy of any predictive leaching assessment approach, however, requires evaluation through the use of pilot- and full-scale field studies in which leaching predictions for a particular material based on laboratory testing may be compared to measured leachate concentrations for that material collected under field conditions. Field studies also provide information regarding the relative importance of natural processes on leaching of COPCs including water flow patterns, extent of local chemical equilibrium, and chemical changes due to aging or exposure to the environment.

This report facilitates understanding application and accuracy of the LEAF test methods by addressing the following important relationships of LEAF test data:

- within datasets from the different LEAF test methods conducted on the same material;
- compared to the results of test methods currently in more widespread use, specifically the Toxicity Characteristic Leaching Procedure (TCLP; EPA Method 1311) , EN 12457(2002) and the Synthetic Precipitation Leaching Procedure (SPLP; EPA Method 1312);
- relative to field leaching and material behavior over a wider set of disposal and use scenarios;
- in conjunction with chemical speciation modeling and other knowledge to evaluate leaching under conditions beyond typical laboratory testing conditions.

Furthermore, this report provides recommendations for how environmental scientists, engineers and regulators may use LEAF as part of their evaluation programs.

## 2 Evaluation Cases

In order to illustrate the relationship between laboratory data and field measurements, ten disposal and beneficial use cases for which both laboratory and field data exist have been identified and are presented in this report. These ten field evaluation cases consist of combinations of laboratory testing and field analysis for the following seven materials:

- coal fly ash (CFA; 3 cases);
- fixated scrubber sludge with lime (FSSL) produced at some coal-fired power plants by combining coal fly ash with flue gas desulfurization (FGD) scrubber residue and lime (1 case),
- municipal solid waste incinerator bottom ash (MSWI-BA; 2 cases);
- a predominantly inorganic waste mixture comprised of residues from soil cleanup residues, contaminated soil, sediments, construction and demolition (C&D) waste and small industry waste (IND; 1 case);
- municipal solid waste (MSW; 1 case);
- cement-stabilized municipal solid waste incinerator fly ash (S-MSWI-FA; 1 case);
- portland cement mortars and concrete (1 case).

**Error! Reference source not found.** provides a summary of the cases and data sets evaluated in this report. In this table, the types of leaching test data (i.e., laboratory tests conducted on “as produced” site materials,<sup>2</sup> analog materials or field materials), field data (i.e., leachates collected from the field application) and case conditions are defined for each case.

The symbols representing leaching test data for the cases in **Error! Reference source not found.** include “pH” for pH dependent leaching data (e.g., from Method 1313 or EN14429/ EN14997), “L/S” for L/S-dependent leaching data (e.g., Method 1316), “Perc” for percolation column data (e.g., from Method 1314 or EN14405), and “MT” for mass transfer data (e.g., from Method 1315 or EN15863). For a few of the field case studies where laboratory test results were not available for the specific material present in the field, laboratory test results on closely analogous materials are used for comparison with field measurements. The field data presented in this report include (i) leachate from field lysimeters, (ii) porewater from landfill or use applications, (iii) eluate from leaching tests on sample cores taken from field sites, and (iv) leachate collected from landfills.

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<sup>2</sup> In this report, “as produced” materials refer to materials newly processed materials that are ready for disposal or beneficial use in a field application. This distinction is made relative to aged field materials that have been retrieved from a field application for testing in the laboratory.

**Table 1. Summary of Laboratory-To-Field Comparison Cases**

Report Section	Case Name (Country)	Leaching Test Data			Field Data	Case Conditions
		Site Materials <sup>1</sup>	Analog Materials <sup>2</sup>	Field Materials <sup>3</sup>	Leachates	
4.1	Coal Fly Ash Landfill Leachate (U.S.)	-	pH L/S Perc	-	Multiple landfills	Ox-Red, pH 6-13
4.2	Coal Fly Ash in Large-Scale Field Lysimeters (Denmark)	L/S	-	-	Lysimeters	Ox-Red, pH 11-13
4.3	Landfill of Coal Combustion Fixated Scrubber Sludge with Lime (U.S.)	pH L/S	-	pH L/S MT	Landfill	Ox, pH 6-12
4.4	Coal Fly Ash Used in Roadbase and Embankments (The Netherlands)	L/S	-	-	Roadbase, Embankment	pH 8-12
4.5	Municipal Solid Waste Incinerator Bottom Ash Landfill (Denmark)	-	pH Perc	-	Landfill	Reducing, pH 7-11
4.6	Municipal Solid Waste Incinerator Bottom Ash Used in Roadbase (Sweden)	-	pH Perc	pH L/S Perc	Roadbase test section	Ox-Red, pH 7-10
4.7	Inorganic Industrial Waste Landfill (The Netherlands)	pH Perc	-	pH L/S Perc	Lysimeters, Landfill	Ox-Red, pH 6-9
4.8	Municipal Solid Waste (The Netherlands)	pH Perc	-	pH L/S Perc	Landfill, Multiple landfills	Strongly Reducing, High DOC, pH 5-9
4.9	Stabilized Municipal Solid Waste Incinerator Fly Ash Disposal (The Netherlands)	pH Perc MT	-	pH	Pilot test cells, Landfill	Oxidizing, pH 8-13
4.10	Portland Cement Mortars and Concrete (Germany, Norway, The Netherlands)	pH (recycled concrete)	pH	pH	-	Oxidizing, Carbonation, pH 8-13

**Notes:**

pH = pH-dependent leaching data (e.g., EPA Method 1313, EN 14429, EN 14997).

L/S = L/S-dependent data with deionized or demineralized water (e.g., EPA Method 1316, EN 12547).

Perc = Percolation column data, up-flow or down-flow (e.g., EPA Method 1314, CEN/TS 14405).

MT = Monolith or compacted granular mass transfer data (e.g., EPA Method 1315, PrEN 15863).

Ox-Red = oxidized to reducing conditions.

<sup>1</sup>Site Materials refers to “as produced” source materials placed into the field application.

<sup>2</sup>Analog Materials refers to comparative materials for cases where source material sample leaching characterization information was not available.

<sup>3</sup>Field Materials refers to materials retrieved from a field application for laboratory testing.

For each evaluation case, the following generalized approach is used to compare laboratory test results for a material to its field leaching:

- (i) LSP Leaching – laboratory leaching results provide an understanding of the LSP for COPCs as a function of pH (e.g., from Method 1313 or EN14429/ EN14997) or L/S (e.g., from Method 1316 or EN12457 or Method 1314 or EN14405). [Field values for these parameters were also obtained]
- (ii) Dynamic Leaching – percolation column leaching test results (e.g., from Method 1314 or EN14405) provide an understanding of percolation-controlled leaching of COPCs under idealized conditions, and/or mass transport leaching test results (e.g., Method 1315 or EN15863) provide intrinsic COPC release rates.
- (iii) Laboratory-to-Field Comparison – laboratory LSP or dynamic leaching results (e.g., percolation or mass transport data) and conditions are compared with results and conditions measured in the field scenario to evaluate whether local equilibrium is controlling observed leaching under field conditions. If not, this comparison is used to determine the extent of preferential flow effects in percolation scenarios or limited water contact in mass transport scenarios.
- (iv) Chemical Speciation and Reactive Transport Modeling – a chemical speciation fingerprint (CSF) for the material of interest and subsequent reactive transport modeling (i.e., combination of speciation and mass transport models) are used to explore the extent that non-ideal conditions (e.g., preferential flow) and aging conditions (e.g., redox changes, carbonation, etc.) influence observed field leaching behavior.

The broad range of potential uses of environmental leaching assessment implies that there is a need for a graded or tiered approach that provides for flexible, scenario-based assessments and allows tailoring of the needed testing and information based on the type of intended use of the assessment and available prior or related information. Furthermore, determination of constituent leaching estimates that are greater than or equal to the actual expected constituent leaching is necessary to maintain environmental protection in the face of uncertainty (often referred to as a “conservative” approach). The extent of the assessment bias toward over-estimation of COPC leaching should depend on the nature of the decision and the uncertainties regarding the available material and scenario information. However, even when used as a screening test, LEAF methods provide release estimates that are more accurate and reliable (i.e., less conservative, or less of an over-estimate) and robust (able to consider multiple or evolving physical-chemical conditions) than are obtainable using any single-point leaching test. Testing is more accurate because of the tailoring to the range of potential environmental conditions and intrinsic leaching characteristics of materials inherent in the design of LEAF, and is more reliably so because field conditions can be related to the test result for the relevant conditions.

### 3 Leaching Fundamentals and Use of Laboratory Leaching Data

Detailed material characterization consists of laboratory measurement (i) LSP as a function of pH (pH-dependent leaching), (ii) LSP as a function of L/S either by percolation column or by parallel batch procedures, and (iii) rates of mass transport under diffusion-controlled conditions.

Equilibrium-based leaching test measure LSP under specified test conditions. For example, Methods 1313 or EN14429/ EN14997 and 1316 determine the effect of pH and L/S, respectively, on LSP under

batch test conditions which are intended to approximate chemical equilibrium between the aqueous and solid phases (Garrabrants et al., 2010). Column percolation tests carried out at relatively slow flow conditions (e.g., residence time ~1 day or less) approximate local equilibrium between the pore solution and solid phase at any given point in the column. Column percolation tests also often are considered a surrogate for field leaching conditions for scenarios where infiltration or groundwater passes through a relatively permeable solid; however, field conditions are much more likely subject to preferential flow, and therefore infiltration bypassing the material in question results in lower observed concentrations in the field than the laboratory.

The following are characteristic responses of LSP observed from equilibrium-based leaching tests:

**Response 1. Total Content vs. Availability.** The fraction of the specific constituent that is not bound in recalcitrant phases and is released over the domain of leaching conditions (i.e., L/S=10 mL/g dry and pH between 2 and 13) is considered the available fraction of the total content in the material, often referred to as “availability.” The sum of the constituent incorporated into recalcitrant phases and the available content of that constituent is equal to the total content of the constituent in the material.

**Response 2. LSP less than Aqueous Solubility.** A constituent, or fraction thereof, may be present in one or more readily soluble solid phases that dissolve fully into the aqueous phase under the leaching test conditions with the resultant constituent concentration in the aqueous phase less than the aqueous solubility (i.e., an under-saturated solution). One example of this case is the dissolution of sodium chloride when the total amount of dissolvable sodium and chloride results in concentrations in the aqueous phase that are less than the respective solubility for each constituent. In this case, the available content of a constituent could be the limiting factor in the concentration seen in laboratory testing (referred to as “availability-limited” leaching).

**Response 3. LSP at Aqueous Solubility.** A constituent, or fraction thereof, may be present in one or more solid phases that will only partially dissolve into the aqueous phase under the leaching test conditions with the resulting constituent concentration in the aqueous phase at the aqueous solubility (i.e., a saturated solution). This phenomenon is referred to as “solubility-controlled” release.

**Response 4. Surface Interaction.** A constituent, or fraction thereof, may be present as a readily soluble species that is not initially present in the material as a distinct, precipitated solid phase. The constituent species may be present at a relatively low concentration associated with a reactive solid surface where the LSP is controlled by adsorption/desorption or ion exchange phenomena. Such reactive surfaces include oxide minerals (e.g., iron, manganese, or alumina (hydr)oxides), (ii) clay-like minerals, (iii) particulate organic carbon (such as from decay of plant matter), and (iv) particulate carbon (such as char from combustion or activated carbon).

For many constituents, the initial speciation (i.e., chemical forms) and distribution in the solid material are often a combination of two or more of the four phenomena described as characteristic responses above. Primary factors that can modify the LSP of a particular constituent are pH, eluate ionic strength and aqueous phase complexation.<sup>3</sup> For constituents with multiple valence states under

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<sup>3</sup> The final conditions achieved during a leaching test or field conditions define the LSP, not the initial test conditions, because these are the conditions that define liquid-solid equilibrium. Thus, the pH of an eluate at the conclusion of a leaching test defines LSP, not the initial pH of the eluent.

the range of oxidizing to reducing conditions observed in the field, the oxidation-reduction potential (ORP) of the porewater and bulk solutions in contact with solid materials can influence the resulting LSP and precipitated solid phases. The effect of redox conditions can also extend to constituents with only single valence state because of precipitation with reduced species (i.e., zinc precipitation with sulfides).

Laboratory leaching test results from pH dependent leaching (e.g., Method 1313 or EN14429/ EN14997) are used in this report in conjunction with other information known about a material (e.g., availability data, total carbon, etc.) to develop a “chemical speciation fingerprint” (CSF). This CSF includes the set of mineral phases, adsorbing surfaces, organic matter fractionation and the fraction of the total content of each constituent that is available for leaching. The resulting CSF may be used in conjunction with the results of L/S-dependence tests to assess the impact of low L/S ratios on LSP or with results from percolation column tests (e.g., Method 1314 or EN14405) or results from mass transport (e.g., Method 1315 or EN15863) to calibrate needed mass transport parameters for simulations of dynamic leaching tests (i.e., mobile-immobile fractions for percolation column tests or tortuosity for monolith diffusion tests). The resulting combination of the CSF and mass transport parameters may then be used in conjunction with one or more field conceptual models (i.e., percolation with preferential flow or diffusion controlled release from a monolith) and a variety of initial and boundary conditions (e.g., system geometry, infiltration rate and chemistry, redox state, etc.) to estimate release under a range of field scenarios. Characterization of uncertainty at each step is needed to understand the accuracy and limitations of each simulation.

## 4 Case Summaries

**Case 1** examined the leaching behavior of coal fly ash under landfill disposal conditions as a class of materials by comparing the leaching concentration ranges and pH dependent relationships for field leachates and pore water in comparison to laboratory test results obtained from LEAF testing of a wide range of coal fly ash samples. The applicable field leachate pH domain was from 6 to 13. Results of this case indicate that laboratory leaching characterization from a wide range of samples within a class of materials (i.e., coal fly ash) can be used to define the characteristic leaching behavior anticipated under field conditions (leachate concentration response as a function of pH and the anticipated ranges of concentrations, or bandwidth), associated with the response at specific pH values. The upper range of constituent concentrations from pH dependent testing (i.e., Method 1313 or EN14429/ EN14997) at a specific pH can be considered a conservative estimate of the upper limit of field concentrations, but laboratory concentrations of highly soluble constituents (i.e., availability limited) must be adjusted based on a correction factor between laboratory L/S and field pore water L/S. Field leachate concentrations lower than anticipated from laboratory pH dependent testing may be a consequence of either (i) reducing conditions (as seen for chromium and selenium) or (ii) common ion effects (as seen for barium in the presence of sulfate).

**Case 2** compared the field leaching from large scale lysimeters over 7 years to results from laboratory percolation column tests. The observed field leachate pH was between 11 and 12.8. Results of this case indicate that laboratory percolation column testing (e.g., Method 1314 or EN14405) can provide a good estimate of initial leachate concentrations under field conditions established in lysimeters. Initial concentrations from field lysimeters at very low L/S (i.e., <0.01 L/kg) of some species may be somewhat greater than observed from initial eluates of laboratory percolation column tests (i.e., molybdenum). Laboratory percolation column testing also provides a good approximation of the

evolution of leaching profiles as a function of L/S that would be expected under field conditions in the absence of preferential flow and establishment of strong reducing conditions.

**Case 3** compared field leaching, field pore water samples, and laboratory leaching test results on landfill core samples, laboratory leaching test results on fresh “as disposed” material for mixed coal fly ash and FGD scrubber residues, referred to as fixated scrubber sludge. The applicable field pH domain was from pH 6 to 9.5. Results from this case indicate that carbonation of samples during field aging can have a significant impact on the pH dependent leaching behavior of periodic table Group II elements (i.e., calcium, strontium) and some trace elements (i.e., arsenic). Water samples (i.e., landfill porewater) are more susceptible to carbonation because of air contact and low buffering capacity, and therefore care should be taken in sampling and data interpretation. Higher concentrations of highly soluble species (i.e., potassium, sodium, chloride) can be anticipated in porewater in comparison with laboratory testing but the extent of elevated concentrations can be readily estimated based on the ratio of laboratory L/S to field porewater L/S.

**Case 4** compared the results of field leaching over 2 years from a road base and embankment constructed with coal fly ash to percolation column results. Laboratory pH dependent leaching test results from an analogous material were also used for comparison. Results of this case illustrate the benefits of the combined use of pH dependent leaching and percolation column leaching in combination with chemical speciation simulations to understand field performance. Specifically, insights from the combined use of these tools provided insights into the redox condition in the material (establishment of reducing conditions), potential impacts of carbonation, and the resultant consequences for leaching of oxyanions (e.g., chromium). Percolation column experiments provided a realistic estimate of the upper bound concentration for leaching of COPCs, however, an initial delay was observed in the field before peak leaching concentrations were observed. The initial delay was attributed to the mass transport delay and attenuation associated with drainage materials (i.e., sand) underlying the primary fly ash fill. This highlights the need to carefully design and understand field monitoring strategies and their impact on field measurements.

**Case 5** focused on landfill leaching from combined MSWI bottom ash and MSWI fly ash that was deposited in layers and monitored for 30 years. Field leaching results were compared to laboratory leaching of core samples obtained from the landfill and laboratory pH dependent test and percolation column test results from analogous materials. The resulting applicable pH domain based on laboratory testing and field leachate samples is approximately pH 7 to 11. Results of this case illustrate that concentrations obtained from laboratory batch extractions at L/S of 2 mL/g can be used as an estimate of peak concentrations in leachate from a heterogeneous fill material. The L/S of 2 L/kg is greater than the expected porewater L/S of ca. 0.2 to 0.5 L/kg but reflects the impacts of preferential flow through a heterogeneous material in a landfill. Testing at L/S of 2 mL/g in conjunction with pH dependent testing (at L/S of 10 mL/g) provides an estimate of increased concentrations relative to pH dependent testing that would be expected for highly soluble constituents and resulting from DOC complexation effects at the low L/S values associated with early leachate from landfills.

**Case 6** focused on MSWI bottom ash used as a subbase below an unbound base course and surface asphalt layers that was cored and evaluated 15 years after the road construction. The resulting applicable pH domain was approximately pH 7 to 10. Single point leaching of an extensive set of samples (n= 53) illustrates the heterogeneity of material and exposure under field conditions.



Laboratory testing of composite samples from field cores using pH dependent leaching and percolation column tests showed LSP and column elution consistent with descriptions for other materials with respect to both highly soluble constituents (e.g., Na, K, Cl) and constituents where solubility limits LSP as a function of pH (e.g., Ca, Cu, Pb, Zn). A general CSF for MSWI bottom ash has been shown to provide a good description of release behavior of multiple major, minor and trace elements from MSWI bottom ash from several sources and indicates likely solubility controlling phases. Combined leaching test results and chemical speciation modeling illustrated (i) the effects of DOC complexation to increase aqueous concentrations of copper, lead and zinc, and (ii) the effects of L/S on the expected concentrations of highly soluble and solubility limited constituents as a function of pH, with lower L/S conditions resulting in increased aqueous concentrations when the constituent solubility is not limiting leaching.

**Case 7** focused on comparison of laboratory and field lysimeter results to leaching from a 12,000 m<sup>3</sup> field pilot landfill for a mixture of predominantly inorganic wastes. The applicable pH domain for the material tested was 6.5 to 8.5. In summary, these results emphasize the importance of understanding the potential impacts of reducing conditions in the field that cannot be captured adequately during laboratory testing (but can be inferred by knowledge and simulation of chemical speciation under reducing conditions). Laboratory test conditions are likely to be oxidizing to mildly reducing, while field conditions for the same material can be mildly to strongly reducing depending on the extent of reducing constituents in the material, biogenic processes and exclusion of atmospheric oxygen. Reducing conditions in the pilot-scale landfill were most likely induced by microbial degradation of the limited amount of organic matter introduced with the waste because no reducing waste types (i.e., pyrites, slags) were included with the disposed materials. The effects of reducing conditions include (i) chemical reduction of iron resulting in loss of HFO sorptive surfaces and increased dissolved iron, (ii) increased biogenic DOC concentrations, and (iii) increased leaching of some species resulting from chemical reduction to more soluble species, loss of iron oxide sorption sites, and/or increased partitioning into the leachate by complexation with DOC. For several constituents (i.e., arsenic, barium, chromium, copper, iron, phosphorous) the maximum concentrations observed in the field pilot-scale landfill were significantly greater than maximum concentrations indicated by the laboratory column testing. These differing effects point to the need of *a priori* knowledge of the adsorption, solubilization and precipitation chemistry of different elements to interpret leaching results and the benefits of using chemical speciation modeling to facilitate interpretation. However, also shown in this case study is that leaching of many constituents was not impacted by the reducing conditions. This case also demonstrates that laboratory testing data obtained under oxidizing to mildly reducing conditions can be used in conjunction with chemical speciation modeling to provide an estimate of expected field leaching under mildly to strongly reducing conditions.

**Case 8** focused on a 45,000 m<sup>3</sup> pilot-scale landfill for MSW in Landgraaf, The Netherlands, that was filled with a mixture of sewage sludge, construction and demolition (C&D) waste, MSW, industrial waste, car shredder waste, foundry sand, and soil cleanup residue. The pilot study was established to evaluate the biodegradation of organic matter-rich waste by leachate renewal and recycling. The applicable pH domain was between 5.5 and 8.5 based on laboratory testing and field results. Peak concentrations for highly soluble species from laboratory percolation column at L/S 0.5 mL/g agreed well with peak leachate concentrations from the landfill and were a factor of 20 times greater than observed using pH dependent leaching test at L/S 10 mL/g. Reducing conditions in the landfill

resulted in higher concentrations in leachate than observed at corresponding pH values during pH dependent laboratory testing. These effects were entirely consistent with those observed for the predominantly inorganic landfill (Section **Error! Reference source not found.**) and were consistently estimated using a chemical speciation model for municipal solid waste. These results further support the use of chemical speciation-based simulations based on laboratory test results for evaluating the effects of reducing conditions established in the field.

**Case 9** focused on a pilot-scale field demonstration of near surface disposal of MSWI fly ash stabilized with a mixture of pozzolonic binders (i.e., multiple ash types). Initial samples of the stabilized material were subjected to laboratory leaching tests. Leachate and runoff was collected during that evaluation period of approximately 4 years, after which cores were taken of the stabilized material for laboratory leaching testing. Comparative results were also available from a full-scale monofill receiving the same stabilized waste. The applicable pH domain was between pH 12.5 for freshly stabilized material to pH 6 for field runoff. For several anionic species such as sulfate and oxyanions of arsenic, molybdenum, selenium, appreciably higher concentrations, by up to a factor of 20, are observed for field leachate and runoff samples than would be expected by direct comparison to laboratory pH-dependence test results and laboratory column test results due to two factors: (i) speciation is pH-dependent, and (ii) the species present at the field pH is highly soluble. As a result, the observed peak concentrations are indicative of pore-water (L/S ~0.2-0.5 mL/g, based on porosity of ca. 0.2-0.5) and are best approximated as 20 times the concentration observed at corresponding pH in the pH-dependence test (L/S=10 mL/g). Peak monofill leachate concentrations of highly soluble species (i.e., chloride, potassium) were approximately a factor of 10 greater than measured using pH dependent testing on freshly prepared material and approximately half of peak values from percolation column tests, likely because of diffusion controlled release and preferential flow. Carbonation at the surface of the stabilized material from reaction with atmospheric carbon dioxide resulted in lower pH (6-9) for runoff and leachate samples and characteristic reductions in leaching of calcium, barium and strontium. Field leachate concentrations indicate solubility controlled (local equilibrium with the surface) for several constituents (e.g., copper, chromium, manganese). Laboratory leaching of cores obtained from field testing after 10 years from the full-scale facility indicated that no significant leaching had occurred at a depth of 1 m. Chemical speciation modeling was used to illustrate the impact of carbonation on leaching of several constituents.

**Case 10** compared the leaching of cement and concrete samples with different aging periods, including 28 days (standard mortar), 4 years (recycled concrete aggregate), 40 years (field test site) and 2,000 years (Roman cement). As the concrete ages, the extent of carbonation from reaction with atmospheric carbon dioxide increases and reduces the natural pH of the material from an initial pH of 12-13 to a pH of approximately 9. Environmental leaching can result in further reduction to pH 7 through decalcification. Increasing extent of carbonation results in the loss of ettringite and the formation of calcite and barium and strontium carbonates, also resulting in decreasing solubility of calcium, barium and strontium at pH greater than 7 with increasing extent of carbonation. Increasing extent of carbonation also results in increases in sulfate solubility and leaching of oxyanions coprecipitated with ettringite (i.e., molybdate and chromate).

## 5 Recommendations for Use of the LEAF Test Methods for Beneficial Use and Disposal Decisions

LEAF test results can be used to provide a reasonably conservative (upper-bound) source-term for a wide range of materials in use and disposal scenarios. The resulting source term should be used in conjunction with additional assessment steps that include consideration of dilution and attenuation from the source to receptor, and relevant receptor thresholds. Information presented in this report supports grouping individual sources of similar materials based on process origin and leaching behavior into material grouping or classes (i.e., coal fly ash from combustion of bituminous coal, coal combustion flue gas desulfurization gypsum, blast furnace slags, MSWI bottom ash, etc.). Accumulation of LEAF testing data for a range of materials and over time can provide useful estimates of uncertainty and variability associated with leaching from specific materials and material classes. Creation of one or more databases containing leaching data used in regulatory decision making and monitoring can facilitate efficient use of leaching data in future assessments.

### **Evaluating New Management Scenarios – Material Combinations and Pilot Studies**

Leaching assessment can present two forms of challenges:

1. Evaluating a new use or disposal scenario for a specific material or material classes; and,
2. Evaluating a new material class or specific material without prior characterization of materials within the same material class.

Careful consideration should be given to the extent of prior knowledge about both the material or class of material, and the use or disposal scenario before proceeding. Consideration should be given to the potential range and changes that may occur with respect to water contact, physical integrity of the material, blending or interfaces with other materials,, chemistry within the material and of contacting solutions, and evolution of pH and redox (e.g., from atmospheric exchange, carbonation, sulfide oxidation, organic matter degradation, etc.). Insufficient prior leaching characterization data or experience with sufficiently similar materials under analogous management scenarios should trigger use of a field pilot demonstration project to insure that a priori unforeseen conditions do not result in a significant shift in the phenomena controlling leaching for the material and scenario under consideration.

The case studies presented in this report provide the basis for recommending specific components and considerations for field demonstration projects

### **Estimating Leaching Source Terms**

In Kosson et al. (2002), leaching assessment using a performance or “impact-based approach” was proposed, that subsequently has been referred to as LEAF. The LEAF testing methodology allows for both empirical use of testing data for specific scenarios as part of a screening assessment, and use of the leaching test data in conjunction with chemical speciation and mass transport models to provide a less conservative and more refined, scenario-specific estimate constituent leaching that can be used as a source-term for risk assessment. A tiered-approach was proposed for developing the leaching source term, considering the type of evaluation being carried out, the level of information available, and the extent of conservatism embedded in the estimate. Subsequently, the EPA published *Methodology for Evaluating Encapsulated Beneficial Uses of Coal Combustion Residuals* (2013b; also EPA, 2014) provides a tiered approach specifically applied to a more limited set of uses of a two secondary material (i.e., coal fly ash use as a cement replacement in concrete and FGD gypsum use in gypsum board). The observations

and information gathered in this report provides a basis for more the more detailed recommendations provided on the use of LEAF test methods, consistent with the initially proposed methodology (2002) and the EPA methodology (2013). It must be emphasized that these recommendations only provide the approach for estimating the leaching source term (i.e., concentrations and amounts of a constituents leaching from the material under a specific scenario). Additional determinations are needed to define or account for (i) the location that serves as the basis for exposure assessment following constituent leaching release from a source scenario (e.g., point of compliance), (ii) dilution and attenuation from the point of release to the point of compliance, and (iii) appropriate exposure scenarios or reference thresholds (e.g., human health or ecological thresholds).

### **Scenario Definition**

Defining the material use or disposal scenario is the first step to selecting the appropriate leaching tests and basis for interpreting the resulting data. The extent of information needed as part of the scenario definition increases as the evaluation seeks to achieve a more detailed and refined estimate of constituent leaching. The initial scenario definition should as a minimum include determination of the applicable pH domain, range of oxidation-reduction conditions, and the primary mode and amount of water contact.

### **Screening Assessment (Tier 1)**

Leaching assessment for screening purposes can be based on the estimated maximum leaching concentration anticipated for each COPC. At this tier, maximum LSP is estimated based on the maximum concentration for each COPC measured over the applicable pH domain as defined by the scenario using the pH dependent leaching test (i.e., Method 1313 or EN14429/ EN14997) and then adjusted for the anticipated pore water L/S, unless it can be demonstrated that the specific COPC is solubility controlled throughout the applicable pH domain.

### **Equilibrium-based Assessment (Tier 2)**

Equilibrium-based leaching evaluation would consider LSP over the applicable pH and redox domains and the maximum amount of each COPC available for leaching. Method 1313 or EN14429/ EN14997 results in conjunction with Method 1316 or EN12457 at L/S of 2 mL/g or Method 1314 or EN14405 up to L/S 2 mL/g would be used to assess whether LSP for each COPC was constrained by aqueous solubility or availability. If the COPC exhibits significantly greater concentration at L/S of 2 mL/g (Method 1316 or EN12457) than measured from Method 1313 or EN14429/ EN14997 at the pH corresponding with the pH measured at L/S of 2 mL/g, then the Method 1313 or EN14429/ EN14997 results are considered to be availability constrained and the maximum concentration from Method 1313 or EN14429/ EN14997 over the applicable pH domain and then adjusted to the pore water L/S is used as the peak source concentration. If the COPC at L/S 2 mL/g is the same as (within uncertainty) the concentration measured at the corresponding pH from Method 1313 or EN14429/ EN14997, then the COPC is considered solubility constrained and the maximum concentration over the applicable pH domain from Method 1313 or EN14429/ EN14997 is used as the peak source concentration. The estimate of the peak concentration can be further refined based on the maximum between (i) the maximum concentration measured by Method 1314 or EN14405 (percolation column) and (ii) the maximum concentration measured over the applicable pH domain by Method 1313 or EN14429/ EN14997.

The maximum amount of a COPC that is available to leach per unit mass of material (i.e., “finite source”) is based on the maximum constituent release (i.e., mg/kg) over the entire pH domain of Method 1313 or EN14429/ EN14997 (i.e., pH 2-13). The amount of each COPC that leaches should be estimated based on the amount of contacting water per unit time (i.e., L/S per year) times the estimated peak concentration.

Initial characterization testing should include analysis of both major and trace constituents in all leaching test eluates because knowledge of the major constituents that control release of the trace constituents provides insights into the factors that may result in changes in leaching and allow for calibration of chemical speciation models. For compliance testing, the extent of Method 1313 or EN14429/ EN14997 testing can be reduced to the applicable pH domain and the relevant COPCs, pH and conductivity<sup>4</sup>. For quality control purposes, the extent of Method 1313 or EN14429/ EN14997 testing can be further reduced to only the pH values that result in peak concentrations over the applicable pH domain and the relevant COPCs and conductivity.

Knowledge of the chemical behavior of the COPCs and the scenario should be used to evaluate if higher leaching concentrations are anticipated because of changes in redox conditions. Anticipated changes in leaching because of changes in L/S, redox or chemical conditions can also be evaluated using chemical speciation modeling as demonstrated for the evaluation cases in this report.

### **Mass Transport-based Assessment (Tier 3)**

Mass transport-based assessment can be divided into two distinct regimes: (i) percolation through the material as the predominant leaching mechanism, and (ii) mass transport from monolithic materials where diffusion to the exterior surface of the bulk material and surface dissolution control constituent leaching. Intermediate conditions between the percolation and monolith regimes, such as for large aggregates and cracked monolithic materials also exist, but are beyond the scope of this discussion.

Percolation based regimes can be evaluated through use of the pH dependent test (i.e., Method 1313 or EN14429/ EN14997) in conjunction with the percolation column test (i.e., Method 1314 or EN14405). Considering the results of Cases 2, 5 and 8 (Sections **Error! Reference source not found.**, **Error! Reference source not found.** and **Error! Reference source not found.**) initial eluates from Method 1314 or EN14405 are good indicators of the anticipated COPC concentrations in initial field leachates and the evolution of the leachate concentrations over prolonged periods based on the progression of the L/S based on the field material geometry and annual infiltration rates. Results from Method 1313 or EN14429/ EN14997 can be used to determine the availability for each COPC based on the maximum value for each COPC over the domain of pH 2-13, and to indicate where increased leachate concentrations can be anticipated if there is a shift in field pH from the initial pH to other conditions over the range of pH defined for the specific scenario being evaluated. Chemical speciation modeling or other knowledge of the system should then be used to determine if changes in redox or other conditions (i.e., carbonation, infiltration chemistry) are likely to result in increased leaching.

Initial percolation characterization testing should include analysis of both major and trace constituents in all leaching test eluates (Methods 1313 or EN14429/ EN14997 and 1314 or EN14405) because knowledge of the major constituents that control release of the trace

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<sup>4</sup> Measurement of conductivity is recommended as an indicator of total ionic strength and therefore can also provide an indication if there is a significant change in leaching of total salts over the monitoring interval.

constituents provides insights into the factors that may result in changes in leaching and allow for calibration of chemical speciation models. For compliance testing, Method 1313 or EN14429/ EN14997 can be used as described above (Equilibrium Based Assessment) and Method 1314 or EN14405 analysis can be simplified to analysis of eluates as prescribed as Option E in Table 1 of the method (i.e. at L/S=0.2 and along with two composite samples) for COPCs, pH and conductivity, thus providing peak eluate concentrations and cumulative release. For quality control purposes, either Method 1313 or EN14429/ EN14997 reduced to only the pH values that result in peak concentrations over the applicable pH domain and the relevant COPCs or Method 1314 or EN14405 testing as described for compliance testing can be used.

Monolith regimes can be evaluated based on use of Method 1315 or EN15863 in conjunction with Method 1313 or EN14429/ EN14997. A detailed example of use of this information for evaluation of use of coal combustion fly ash as a substitute for Portland cement in concrete considering intermittent water contact via precipitation is available (EPA, 2013a). This approach can also be used in conjunction with chemical speciation based mass transfer models to provide insights into potential changes in leaching that may occur in response to changing conditions within or on the external surface of the material being evaluated.

Initial monolith characterization testing should include analysis of both major and trace constituents in all leaching test eluates (Methods 1313 or EN14429/ EN14997 and 1315 or EN15863) because knowledge of the major constituents that control release of the trace constituents provides insights into the factors that may result in changes in leaching and allow for calibration of chemical speciation models. For compliance testing, Method 1313 or EN14429/ EN14997 should be used to assess availability and solubility at the natural pH of the material (i.e., no acid or base addition) and Method 1315 or EN15863 analysis can be simplified to analysis of eluates at exchange up to 7 days for COPCs, pH and conductivity. For quality control purposes, Method 1315 or EN15863 reduced to only analysis of eluates up to 2 days for COPCs, pH and conductivity.

## 6 Conclusions

This report evaluated the relationships between laboratory leaching tests as defined by the Leaching Environmental Assessment Framework (LEAF) or analogous EU/international test methods and leaching of constituents of potential concern (COPCs) from a broad range of materials under disposal and beneficial use scenarios. This evaluation was achieved by defining a framework for interpretation of laboratory testing results, comparison of laboratory testing on “as produced” material, laboratory testing of “field aged” material, and results from field leaching studies, and illustrating the use of chemical speciation modeling as a tool to facilitate evaluation of scenarios beyond the conditions of laboratory testing.

Ten field evaluation cases for disposal or beneficial use that have a combination of laboratory testing and field analysis were considered that included the following materials: (i) coal fly ash (CFA), (ii) fixated scrubber sludge typically produced by combining coal fly ash with acid gas scrubber residue and lime at some coal fired power plants (FSSL), (iii) municipal solid waste incinerator bottom ash (MSWI-BA), (iv) a predominantly inorganic waste mixture comprised of residues from soil cleanup residues, contaminated soil, sediments, C&D waste and small industry waste(IND), (v) municipal solid waste (MSW), (vi) cement-stabilized municipal solid waste incinerator fly ash (S-MSWI-FA), and (vii) portland cement mortars and concrete. The field data presented in this report include (i) leachate from field lysimeters, (ii) porewater from landfill or

use applications, (iii) eluate from leaching tests on sample cores taken from field sites, and (iv) leachate collected from landfills. Principal uncertainties for field data in many cases include (i) the extent of preferential flow or dilution that may have occurred during water contact within the material and in sampling of landfill leachate, and (ii) the exact exposure and aging conditions that contribute to the field data.

Primary aging processes and reactions that can impact leaching are (i) establishment of reducing conditions from biogenic processes (i.e., degradation of organic matter), (ii) oxidation from atmospheric exchange, and (iii) carbonation from either atmospheric exchange, dissolved carbon dioxide (or carbonates) in contacting water, or reaction with biogenic carbon dioxide. Other slow mineral formation processes, such as with stabilized waste, may result in relative small changes in leaching relative to freshly prepared material. Constituents in infiltrating or contacting water, either from natural processes (e.g., DOC in the form of humic substances from leaf decay) or from anthropogenic origin (e.g., leaching from up gradient disposed materials) may have a substantial effect on leaching.

Based on the above comparisons and observations along with results discussed in earlier sections, the following conclusions and recommendations are drawn:

1. The combination of results from pH-dependent leaching tests (i.e., EPA Method 1313 or CEN/TS 14429 or CEN/TS 14997) and percolation column tests (i.e., EPA Method 1314 or CEN/TS 14405) can be used to provide reliable estimates of field leachate concentrations under both disposal and use scenarios. Leaching test results should be evaluated with consideration of the potential for changes in leaching conditions that are beyond the domain of laboratory test conditions, such as oxidation of reduced materials, reduction of oxidized material, carbonation and introduction of DOC from external sources. When field conditions beyond the domain of laboratory test conditions are expected, chemical speciation modeling can be used to consider the magnitude of effects from the postulated changing conditions. Peak leaching concentrations and availability of COPCs estimated from laboratory testing can be used to provide a conservative estimate (i.e., reasonable upper bound) of anticipated field leaching. Results from batch testing at low L/S ratios (i.e., EPA Method 1316 or EN 12457) can also be used in place of column test results when column testing is impractical. Thus, the LEAF laboratory leaching tests can be used effectively to estimate the field leaching behavior of a wide range of materials under both disposal and use conditions. Interpretation of the leaching test results should be in the context of the controlling physical and chemical mechanisms of the field scenario.
2. Field testing of new use or disposal scenarios or new classes of materials to be used or disposed in new ways is highly beneficial to understanding the factors that control leaching for the specific scenario. Thereafter, materials within a given class can be anticipated to behave similarly under the established use or disposal scenario and the LEAF testing approach can be used to distinguish “acceptable” versus “unacceptable” materials and use conditions within the general class of materials and scenario. The EPA guidance on beneficial use of coal fly ash in concrete (EPA, 2014) provides an example of the use of LEAF test results in such decisions.
3. Establishment of a national database of LEAF laboratory leaching test results for materials and leaching observed under field conditions would provide useful insights for evaluation of new cases and material use and disposal decisions.

4. Field testing should include (i) sampling and leaching characterization of the initial material, including pH-dependent, column and monolithic mass transfer rate (where applicable) testing; (ii) field leachate collection and monitoring over extended time frames (i.e., several years); and (iii) collection and characterization of test materials after prolonged field exposure (i.e., core samples from field test sites). Sample collection systems and subsequent handling need to be designed to avoid sample changes prior to analysis that degrade the representativeness of the samples and can result in misleading results (e.g., sample oxidation or carbonation during collection or handling resulting in changes in pH and constituent speciation). Furthermore, sample analysis should include a full suite of major and trace constituents that influence and provide a context for understanding COPC leaching.
5. Chemical speciation modeling of liquid-solid partitioning can be used for understanding the mechanisms (e.g., mineral phases, sorption and aqueous phase complexation phenomena) controlling leaching of the full range of constituents in the laboratory and the field, and understanding material leaching under conditions that are not readily subject to testing. Although the general behavior of many of the major and trace constituents are reasonably represented in relevant scenarios, application of chemical speciation modeling to waste management currently is constrained by the availability of test data for identifying important solid phases and the range of available thermodynamic data available for model parameters. Application of chemical speciation as a tool for understanding waste management should be expanded, along with underlying research to fill data gaps.
6. Single point leaching tests and other common leaching assessment approaches cannot provide needed insights into the expected leaching performance of materials under the range of expected field conditions. The LEAF integrated evaluation of multiple types of leaching test data (i.e., pH dependent LSP along with percolation and/or monolithic mass transport behavior) and field data within the context of understanding fundamental leaching behavior (i.e., processes controlling liquid-solid partitioning and mass transport rates), along with use of chemical speciation based modeling provides extensive insights into the expected leaching behavior over a range of field conditions that cannot be obtained otherwise.

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