Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework
Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework (LEAF)

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ABSTRACT

This report presents examples of the relationships between the results of laboratory leaching tests, as defined by the Leaching Environmental Assessment Framework (LEAF) or analogous international test methods, and leaching of constituents from a broad range of materials under disposal and beneficial use scenarios. A framework is defined for interpretation of laboratory testing results, including approaches for comparison of laboratory testing of fresh or field aged materials and leachate results from field applications. This report also illustrates the use of chemical speciation modeling for interpretation of leaching data and facilitated evaluation of scenarios beyond the conditions of laboratory testing. This report then provides recommendations for selection and use of the LEAF test methods, data interpretation, and chemical speciation-based models as tools for environmental leaching assessment.

Ten field cases were evaluated to illustrate how LEAF results can be used to compare to field leachate data for either the disposal or beneficial use of seven different materials. The field data presented in this report include leachate from field lysimeters, porewater from landfill or use applications, eluates from leaching tests conducted on sample cores taken from field sites, and leachate collected from landfills. The LEAF laboratory leaching tests in the comparisons are shown to be effective for estimating the field leaching behavior for a wide range of materials under both disposal and use conditions.

Interpretation of laboratory leaching test results to the field must be conducted within the context of the controlling physical and chemical mechanisms of the field scenario (e.g., pH, L/S, mode of water contact). The effects of field conditions that are beyond the physical-chemical domain of the laboratory test conditions can be evaluated through a combination of empirical calculations to extrapolate laboratory results and chemical speciation and reactive mass transport simulations that are calibrated based on LEAF testing results. Both direct laboratory testing results and outcomes from chemical speciation and reactive mass transport simulations can be used to provide a source term for subsequent fate and transport and risk assessment evaluations.
EXECUTIVE SUMMARY

ES-1 Objectives and Background

The primary objective of this report is to provide an evaluation of the applicability and limitations of using laboratory leaching tests, as defined by the LEAF and LEAF-analogous methods, for estimating leaching of constituents of potential concern (COPCs) from a broad range of materials under field disposal and beneficial use scenarios. This evaluation compares results from laboratory testing of “as produced” material using LEAF methods, laboratory testing of “field aged” material, and field leaching studies of the material. Interpretation of LEAF leaching data is conducted within the context of a defined conceptual leaching model. 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 simulation-based approach to testing, such as used for the toxicity characteristic leaching procedure (TCLP), 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 – Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure
- Method 1315 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-Dynamic Tank Leaching 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

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1 TCLP was designed to simulate a plausible mismanagement scenario of co-disposal in a municipal solid waste landfill.
cumulative liquid-to-solid ratio (L/S) as well as the rate of constituent mass transfer from monolithic and compacted 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 to assess release of organic substances, radionuclides and nano-particles. However, additional consideration is needed with respect to compatibility of the constituents of interest to the container materials used.

Leaching tests are tools 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 from the source to the points of compliance 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) 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.

**ES-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).

Table 1-1ES-1 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, 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 Table 1-1 include "pH" for pH dependent leaching data (e.g., from Method 1313 or equivalent), "L/S" for L/S-dependent leaching data (e.g., Method 1316 or equivalent), "Perc" for percolation column data (e.g., from Method 1314 or equivalent), and "MT" for mass transfer data (e.g., from Method 1315 or equivalent). 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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2 In this report, “as produced” materials refer to 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>
<thead>
<tr>
<th>Report Section</th>
<th>Case Name (Country)</th>
<th>Leaching Test Data</th>
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<td>MSW Incinerator Bottom Ash Used in Roadbase (Sweden)</td>
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<td>pH Perc</td>
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<td>4.7</td>
<td>Inorganic Industrial Waste Landfill (The Netherlands)</td>
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<td>MSW Landfill (The Netherlands)</td>
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<td>pH Perc MT</td>
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<td>pH</td>
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<td>Portland Cement Mortars and Concrete (Germany, Norway, The Netherlands)</td>
<td>pH (recycled concrete)</td>
<td>pH</td>
<td>pH</td>
</tr>
</tbody>
</table>

Notes:

pH = pH-dependent leaching data (e.g., EPA Method 1313, PrEN 14429, PrEN 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.

1 Site Materials refers to "as produced" source materials placed into the field application.
2 Analog Materials refers to comparative materials for cases where source material sample leaching characterization information was not available.
3 Field Materials refers to materials retrieved from a field application for laboratory testing.
The field component and laboratory testing comparison for each case is as follows:

**Case 1** (§ 4.1) 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.

**Case 2** (§ 4.2) compared the field leaching from large scale lysimeters over 7 years to results from laboratory percolation column tests.

**Case 3** (§ 4.3) 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.

**Case 4** (§ 4.4) 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.

**Case 5** (§ 4.5) 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.

**Case 6** (§ 4.6) 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. Single point leaching was carried out on an extensive set of samples (n=53) to evaluate the heterogeneity of material and exposure under field conditions.

**Case 7** (§ 4.7) focused on comparison of laboratory and field lysimeter results to leaching from a 12,000 m³ field pilot landfill for a mixture of predominantly inorganic wastes.

**Case 8** (§ 4.8) focused on a 45,000 m³ 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.

**Case 9** (§ 4.9) 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. In addition, laboratory leaching was carried on cores obtained from field testing after 10 years from a corresponding full-scale facility.

**Case 10** (§ 4.10) 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).

For each evaluation case, the following generalized approach was 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 L/S (e.g., from Method 1316 or Method 1314). [Field values for these parameters were also obtained]

(ii) **Dynamic Leaching** – percolation column leaching test results (e.g., from Method 1314) provide an understanding of percolation-controlled leaching of COPCs under idealized conditions, and/or mass transport leaching test results (e.g., Method 1315) 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, reliable (because of test conditions defined based on fundamental principles of environmental chemistry and mass transport) and robust (able to consider multiple or evolving physical-chemical conditions) than are obtainable using any single-point leaching test. Testing using LEAF is considered to be more accurate because of the ability to consider the range of anticipated environmental conditions and intrinsic leaching characteristics of materials.
ES-3 Leaching Fundamentals and Use of Laboratory Leaching Data

LEAF is described in detail within the report and provides a conceptual framework for interpreting characteristic leaching behavior and comparing LEAF laboratory test results to field leaching. 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 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 based on chemical thermodynamics). 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 and 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. For constituents with multiple valence states under 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) 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 (such as those present under field conditions) on LSP or with results from percolation column tests (e.g., Method 1314) or results from mass transport (e.g., Method 1315) 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.

3 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.
**ES-4 Case Summaries**

Each of the cases included consideration of multiple constituents (from 5 up to 29 per individual case) that illustrated each of the characteristic leaching responses indicated above and provided the basis for understanding relationships between laboratory test results and field data as a function of constituent, material and field management scenario. The observed field pH domain, constituents considered and the primary conclusions for each of the case studies are presented in Table ES-2. The observed field pH domain indicated for a specific case may be narrower than what would be considered the applicable pH domain for the material and field scenario when applied prospectively because (i) the range of material characteristics may be broader than the specific materials tested in individual cases (for example, coal fly ash may range from very alkaline to acidic, as indicated by Case 1 but the specific coal fly ash evaluated in Case 2 was alkaline), and (ii) the relatively short duration of field testing (i.e., typically less than 10 years) may not fully reflect the long-term aging of the materials (for example, strongly alkaline materials are expected to react with atmospheric or biogenic carbon dioxide to result in slightly alkaline pH of ca. 8-9).
Table ES-2. The observed field pH domain, constituents considered and the primary conclusions for each of the case studies.

<table>
<thead>
<tr>
<th>Report Section</th>
<th>Case Name (Country)</th>
<th>pH Domain</th>
<th>Constituents Considered</th>
<th>Primary Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Coal Fly Ash Landfill Leachate (U.S.)</td>
<td>6-13</td>
<td>Al, As, B, Ca, Cd, Co, Cr, Cu, F, Fe, K, Li, Mg, Mo, Mn, Na, Ni, Pb, S, Se, Si, Sr, Ti, V, Zn DOC</td>
<td>For a well-defined class of materials, the upper range of constituent concentrations from pH dependent testing over the relevant pH domain can be considered a conservative estimate of the upper limit of field concentrations constituents where solubility limits leaching. For highly soluble constituents, pH dependent test concentrations should be adjusted based on a correction factor between laboratory L/S and field pore water L/S. Field leachate concentrations lower than anticipated 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).</td>
</tr>
<tr>
<td>4.2</td>
<td>Coal Fly Ash in Large-Scale Field Lysimeters (Denmark)</td>
<td>11-13</td>
<td>Al, As, B, Ba, Br, Ca, Cd, Cl, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Sr, V, Zn; DOC</td>
<td>Laboratory percolation column testing provide a good estimate of initial leachate concentrations under field conditions. 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 reducing conditions.</td>
</tr>
<tr>
<td>4.3</td>
<td>Landfill of Coal Combustion Fixated Scrubber Sludge with Lime (U.S.)</td>
<td>6-12</td>
<td>Al, As, B, Ba, Ca, Cd, Cl, Co, Cr, Cu, F, K, Li, Mg, Mn, Mo, Na, Sb, Se, Si, Sr, Ti, Ti, V, Zn DOC</td>
<td>Carbonation of samples during field aging had 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). Higher concentrations of highly soluble species (i.e., potassium, sodium, chloride) observed in porewater compared laboratory testing can be readily estimated based on the ratio of laboratory L/S to field porewater L/S.</td>
</tr>
<tr>
<td>4.4</td>
<td>Coal Fly Ash Used in Roadbase and Embankments (The Netherlands)</td>
<td>8-12</td>
<td>Ca, Cr, Mo, S, Se,</td>
<td>The combined use of pH dependent leaching, percolation column leaching and chemical speciation simulations provided insights into the redox condition in the material (establishment of reducing conditions), 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.</td>
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<tr>
<td>Report Section</td>
<td>Case Name (Country)</td>
<td>pH Domain</td>
<td>Constituents Considered</td>
<td>Primary Conclusions</td>
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<tr>
<td>4.5</td>
<td>Municipal Solid Waste (MSW) Incinerator Bottom Ash Landfill (Denmark)</td>
<td>7-11</td>
<td>Al, Cd, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, P, Zn</td>
<td>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 dissolved organic carbon (DOC) complexation effects at the low L/S values associated with early leachate from MSW landfills.</td>
</tr>
<tr>
<td>4.6</td>
<td>MSW Incinerator Bottom Ash Used in Roadbase (Sweden)</td>
<td>7-10</td>
<td>As, Al, B, Ba, Br, Ca, Cd, Cl, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, V, Zn DOC</td>
<td>Laboratory testing of composite samples from field cores using pH dependent leaching and percolation column tests showed LSP and column elution consistent with leaching of MSW incinerator bottom ash from other sources 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). 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.</td>
</tr>
<tr>
<td>4.7</td>
<td>Inorganic Industrial Waste Landfill (The Netherlands)</td>
<td>6-9</td>
<td>Al, As, Ba, Ca, Cd, Cr, Cl, Cu, Fe, Hg, K, Mg, Mo, Na, Ni, P, Pb, S, Se, V, Zn DOC</td>
<td>Laboratory testing data obtained under oxidizing to mildly reducing conditions can be used in conjunction with chemical speciation modeling to estimate field leaching under mildly to strongly reducing conditions. 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...</td>
</tr>
<tr>
<td>Report Section</td>
<td>Case Name (Country)</td>
<td>pH Domain</td>
<td>Constituents Considered</td>
<td>Primary Conclusions</td>
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<tr>
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</tr>
<tr>
<td>4.8</td>
<td>MSW Landfill (The Netherlands)</td>
<td>5-9</td>
<td>Al, As, Ba, Ca, Cd, Cl, Cr, Cu, Fe, Hg, K, Mg, Mo, Na, Ni, Pb, Se, V, Zn</td>
<td>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. Chemical speciation modeling based on laboratory testing under oxidized conditions facilitated understanding of leaching under expected reducing conditions in the field.</td>
</tr>
<tr>
<td>4.9</td>
<td>Stabilized MSW Incinerator Fly Ash Disposal (The Netherlands)</td>
<td>8-13</td>
<td>Al, As, Ba, Ca, Cl, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, S, Se, Sr, V, Zn</td>
<td>The observed peak field leachate concentrations of anionic species such as sulfate and oxyanions of arsenic, molybdenum, selenium, are indicative of porewater (L/S ~ 0.2-0.5 mL/g, based on porosity of ca. 0.2-0.5) and are 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 chloride and 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) and were consistent with pH dependent leaching test results.</td>
</tr>
<tr>
<td>Report Section</td>
<td>Case Name (Country)</td>
<td>pH Domain</td>
<td>Constituents Considered</td>
<td>Primary Conclusions</td>
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<tr>
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<tr>
<td>4.10</td>
<td>Portland Cement Mortars and Concrete (Germany, Norway, The Netherlands)</td>
<td>7-13</td>
<td>Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, S, Sb, Si, Sn, Sr, Zn</td>
<td>Carbonation results in increased leaching of Ca, Ba, Sr and sulfate, consistent with loss of the ettringite mineral phase and pH dependent leaching test results. Increased leaching of oxyanions (e.g., molybdate, arsenate and chromate) also occurs with carbonation because of dissolution of the oxyanions substituted for sulfate in ettringite. pH dependent leaching test results on uncarbonated material can be used to estimate oxyanion leaching from carbonated materials at pH less than 10.</td>
</tr>
</tbody>
</table>
ES-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, including by reducing testing and evaluation costs for well-studied classes of materials.

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 previously evaluated material or material class; 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 anticipated 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, when warranted based on a screening assessment that includes laboratory characterization, 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 initial material characterization and 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 more realistic and refined, scenario-specific estimate of constituent leaching that can be used as a source-term for risk assessment. While the screening assessment is a bounding estimate of leaching potential, consideration of waste and scenario-specific information allows many conservative assumptions to be replaced with further testing data and mass transport modeling results.

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 its *Methodology for Evaluating Encapsulated Beneficial Uses of Coal Combustion Residuals* (2013b; also EPA, 2014) which describes a tiered approach that can be applied to a more limited set of uses of two secondary materials (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 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 for use of leach test data 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 in the vadose zone and groundwater or surface water 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). These evaluations can be incorporated into a model of constituent fate and transport leading to possible receptor exposure (e.g., groundwater transport to a drinking water well, with water ingestion as the exposure pathway).

**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 at 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)

Recommendations for use of LEAF testing in screening assessment (Tier 1) and equilibrium-based assessment (Tier 2) are provided in Table ES-3. Note that Tier 1 and Tier 2 assessments are independent of the physical form (i.e., granular or monolithic) of the material. A leaching screening assessment is based on the estimated maximum leaching concentration anticipated for each COPC that would leach assuming an infinite source. 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) 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)

An 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 results in conjunction with Method 1316 at L/S of 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) then measured from Method 1313 at the pH corresponding with the pH measured at L/S of 2 mL/g, then the Method 1313 results are considered to be availability constrained and the maximum concentration from Method 1313 over the applicable pH domain that is 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, then the COPC is considered solubility constrained and the maximum concentration over the applicable pH domain from Method 1313 is used as the peak source concentration.

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 (typically pH 2 for cations and pH 9 for oxyanions). 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 (Tier 2B) 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. However, prior knowledge from testing of analogous materials may reduce the need for or extent of characterization testing.

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4 For regulatory frameworks based on a source term concentration (typical in the United States), the maximum estimated leaching concentration is recommended for use in screening assessment. For regulatory frameworks based on the total mass of constituent potentially leached (as used in some international jurisdictions), availability is recommended for use in screening assessment.
Table ES-3. Tier 1 Screening Assessment and Tier 2 Equilibrium-Based Assessment - Summary of recommended test methods and analyses.

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tier 1 – Screening Assessment</strong>¹</td>
<td>Method 1313 (applicable pH range only²)</td>
<td>pH, Electrical conductivity (EC), COPCs, DOC</td>
<td>Maximum leachate conc.³ estimated as 20x or 10x maximum eluate conc. for highly soluble constituents in granular materials⁴,⁵ and the measured maximum eluate conc. for monolithic materials and solubility controlled constituents (all materials).</td>
</tr>
<tr>
<td><strong>Tier 2 – Equilibrium-based Assessment</strong></td>
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</tr>
<tr>
<td><strong>Tier 2A Compliance</strong></td>
<td>Method 1313 (applicable pH range + pH=2, 7, 9 if not included) Method 1316 (L/S=2 mL/g or lowest L/S eluate)</td>
<td>pH, EC (natural pH only), COPCs, DOC</td>
<td>Availability estimated as maximum release at measured pH intervals including pH=2 and 9; provides basis for finite source by assuming that availability is maximum cumulative release under field conditions. EC used to estimate ionic strength. Acid/base neutralization capacity to pH=7. Maximum leachate conc. estimated as determined from Tier 2B based on Method 1313 results over applicable pH domain. Method 1316 allows identification of solubility controlled vs highly soluble constituents.</td>
</tr>
<tr>
<td><strong>Tier 2B Characterization</strong></td>
<td>Method 1313 (full set of eluates) Method 1316 (full set of eluates)</td>
<td>pH, EC &amp; pE⁶ (natural pH only)⁷, COPCs, DOC, DIC, major and minor constituents (including P and S)</td>
<td>Availability as indicated in Tier 2A. Liquid-solid partitioning as a function of pH used for speciation assessment.⁸ Provides baseline understanding of material leaching behavior. Supports chemical speciation simulations to understand effects of changes in L/S, pH, redox, and reactive constituents (e.g., DOC, carbon dioxide, etc.). Maximum leaching concentration as indicated for Tier 1 or based on simulation results at L/S of the material pore solution. Method 1316 provides basis for determination of solubility control and verification of chemical speciation modeling at low L/S.</td>
</tr>
<tr>
<td><strong>Tier 2C Quality Control</strong></td>
<td>Method 1313 at natural pH, and pH=2, 7 and/or 9</td>
<td>pH, EC, relevant COPCs⁹ (natural pH and for availability) to meet environmental requirements and additional constituents to meet beneficial use requirements</td>
<td>Used to verify leaching over “applicable” pH range, acid/base neutralization capacity to pH=7, and availability of relevant COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Assumes definition after completion of Tier 2B and/or analogous prior information.¹⁰ Chemical analysis only for determination of leaching at natural pH and availability (2 or 3 extracts). Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>
Notes for Table ES-3:

1. For regulatory frameworks based on a source term concentration, the maximum estimated leaching concentration is recommended for use in screening assessment. For regulatory frameworks based on the total mass of constituent potentially leached, availability is recommended for use in screening assessment.

2. The applicable pH range is determined considering the material’s natural pH, changes in pH due to material aging processes, infiltration conditions, and interfaces or comingling with other materials.

3. "conc." is used as an abbreviation for concentration or concentrations.

4. Twenty times the maximum eluate concentration is recommended for highly soluble species when the material is homogeneous (e.g., coal fly ash) and ten times the maximum eluate concentration is recommended for heterogeneous materials (e.g., MSW incinerator bottom ash) where significant preferential flow is anticipated. Both multipliers are to account for the increased concentrations expected when estimating pore water concentrations (L/S=0.2 to 0.5 L/kg) from test conditions of L/S=10 mL/g).

5. Highly soluble species are Group IA elements (i.e., Na, K), anions (i.e., bromide, chloride, fluoride, nitrate), and oxyanions (i.e., As, B, Cr, Se, Mo, V).

6. Electron potential as a measure of oxidation reduction conditions (see § 2.2.3).

7. Determination of EC and pe is recommended for natural pH eluate only. The sensitivity and uncertainty of pe measurements are recognized but pe measurement will provide a useful indication of whether or not the material is inherently reducing under abiotic and anoxic conditions.

8. Speciation assessment refers to consideration of the effects of changes in pH, redox conditions, extent of carbonation, complexation with dissolved organic carbon, etc. which may be accomplished heuristically or in combination with geochemical speciation modeling.

9. Relevant COPCs are those constituents that are present in the material and have been found through Tier 2B characterization and/or prior information to leach at concentrations or release values that approach or challenge regulatory or quality control thresholds.

10. Prior information, such as characterization information from similar materials, may reduce or supplant the need for or extent of Tier 2B characterization.
Results from Method 1313 also can be used 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 or decreased leaching.

For periodic demonstration of compliance with regulatory thresholds, the extent of Method 1313 testing can be reduced to the applicable pH domain and regulatory COPCs, pH and conductivity. For quality control purposes, the extent of Method 1313 testing can be further reduced to only the natural pH value and along with the pH 2 and/or 9 as needed to measure availability for the relevant COPCs (those that are present and leach at concentrations that approach thresholds) 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. Summaries of recommended LEAF testing and evaluation are provided for percolation mass transport-based assessment and monolithic mass transport-based assessment in Table ES-4 and Table ES-5, respectively.

Percolation based regimes can be evaluated through use of the pH dependent test (i.e., Method 1313) in conjunction with the percolation column test (i.e., Method 1314 or Method 1316 for initial leachate concentrations). Considering the results of Cases 2, 5 and 8 (Sections 4.2, 4.5 and 4.8) initial eluates from Method 1314 or low L/S results from Method 1316 are good indicators of the anticipated COPC concentrations in initial field leachates and Method 1314 provides 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.

5 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.
### Table ES-4. Tier 3 Percolation Mass Transport-Based Assessment – Summary of recommended test methods and analyses.

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 3 – Percolation Mass Transfer Rate-based Assessment</td>
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<td></td>
</tr>
<tr>
<td>Tier 3A Compliance</td>
<td>Method 1313 (pH=2, 9, applicable pH domain) Method 1314 (to L/S=2 mL/g)</td>
<td>pH, EC (natural pH only), COPCs, DOC</td>
<td>Allows verification of liquid-solid partitioning at natural pH and availability (from Method 1313). Maximum leachate conc. estimated as established by Tier 3B as greater of either i) maximum conc. from Method 1314 up to L/S =2 mL/g, or ii) maximum conc. from Method 1316, or iii) maximum conc. from Method 1313 over applicable pH domain.</td>
</tr>
<tr>
<td>Tier 3B Characterization</td>
<td>Method 1313 (full set of eluates) Method 1314 (full set of eluates) Method 1316 (L/S=2)</td>
<td>pH, EC (natural pH only), COPCs, DOC, DIC, major and minor constituents</td>
<td>Availability and leaching as a function of pH and evaluation of potential changes in conditions as indicated for Tier 2B. Method 1314 provides leachate evolution as a function of L/S for source term based on test elution curve. Supports reactive transport simulations to consider sensitivity to field conditions such as infiltration chemistry, preferential flow and material aging. Provides basis for verification of chemical speciation modeling at low L/S.</td>
</tr>
<tr>
<td>Tier 3C Quality Control</td>
<td>Method 1313 at pH=2, 7 and/or 9 and Method 1316 at L/S = 2</td>
<td>pH, EC, COPCs (1313 for availability and 1314 at L/S of peak release) to meet environmental requirements, additional constituents to meet beneficial use requirements</td>
<td>Method 1313 extractions used to verify acid/base neutralization capacity to pH=7, and availability of selected COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Method 1314 extract at L/S of prior peak concentration to verify maximum leaching conc. Assumes definition after completion of Tier 3B Characterization. Chemical analysis only for determination of leaching at peak release conc. and availability (2 or 3 extracts). Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>
Table ES-5. Tier 3 Monolith Mass Transport-Based Assessment – Summary of recommended test methods and analyses\(^1\).

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 3 – Monolith Mass Transport-based Assessment</td>
<td>Tier 3A Compliance&lt;br&gt;Method 1313 (pH=2, 9, applicable pH domain)&lt;br&gt;Method 1315 (to 7 days)</td>
<td>pH, EC (natural pH for Method 1313 and all Method 1315 eluates), COPCs, DOC</td>
<td>Allows verification of liquid-solid partitioning at natural pH and availability (from Method 1313). Maximum leachate conc. estimated as established by Tier 3B as greater of either i) maximum conc. from Method 1314 up to L/S =2 mL/g, or ii) maximum conc. from Method 1316, or iii) maximum conc. from Method 1313 over applicable pH domain.</td>
</tr>
<tr>
<td>Tier 3B Characterization</td>
<td>Method 1313 (full set of eluates)&lt;br&gt;Method 1314 (full set of eluates)&lt;br&gt;Method 1315 (to 64 days)</td>
<td>pH, EC (natural pH only for Method 1313 and all Method 1314, and 1315 eluates), COPCs, DOC, DIC, major and minor constituents</td>
<td>Availability and leaching as a function of pH as indicated for Tier 2B. Method 1314 (crushed material) up to L/S=2 provides estimate of initial pore water composition. Method 1315 provides cumulative release as a function of leaching time for saturated and intermittent wetting conditions. Also provides basis for estimating reactive transport parameters (e.g., tortuosity) for simulation of evolving conditions (e.g., low liquid to surface area, external solution chemistry, carbonation, oxidation, intermittent wetting, etc.). Provides basis for Tier 3C quality control.</td>
</tr>
<tr>
<td>Tier 3C Quality Control</td>
<td>Method 1313 at pH=2, 7 and/or 9 and Method 1315 (to 7 days)</td>
<td>pH, EC, COPCs (1313 for availability and 1314 at L/S of peak release) to meet environmental requirements, additional constituents to meet beneficial use requirements</td>
<td>Method 1313 extractions used to verify acid/base neutralization capacity to pH=7, and availability of selected COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Method 1315 cumulative release to 7 days to verify consistency with characterization results (Tier 2B). Assumes definition after completion of Tier 3B Characterization. Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>

\(^1\)The cure time prior to testing of monolithic materials is an important consideration because for many cementitious materials, hydration and microstructure development continues for more than a one year, with initial cure times of 90 days recommended prior to Method 1315 testing.
Initial percolation characterization testing (Tier 3B) should include analysis of both major and trace constituents in all leaching test eluates (Methods 1313 and 1314 or 1316) because knowledge of the major constituents (such as Ca, Fe, DOC or SO₄) 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 (Tier 3A), Method 1313 can be used as described above (Equilibrium Based Assessment) and Method 1314 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.

Monolith regimes can be evaluated based on use of Method 1315 in conjunction with Method 1313 (Table ES-5). 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). An example approach for use of empirical data from Method 1313 (i.e., for availability) and Method 1315 (i.e., for estimated effective diffusivity) is provided for MSWI bottom ash scenarios in Kosson et al (1996). These approaches can also be used in conjunction with chemical speciation based mass transfer models (see Section 3) 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 and 1315) 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 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 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 reduced to only analysis of eluates up to 2 days for COPCs, pH and conductivity.

**ES-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 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.

As identified in table ES-1, ten field cases were evaluated using a combination of laboratory testing and field analysis for seven different materials: (i) coal fly ash (CFA), (ii) fixed 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 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 exposure and aging conditions that can occur and are reflected by 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 after initial curing periods (e.g., 90 days), 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 accurate estimates within defined uncertainty levels of maximum field leachate concentrations, extent of leaching and expected leaching responses over time and to changes in environmental conditions 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 plausible, 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 or international 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. The database would allow effective comparison of leaching (i) from materials produced over time from the same facility, (ii) commonality from similar materials from a diverse set of facilities, and (iii) from different types of materials considered for similar beneficial use applications.

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 modeling 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 insights into the expected leaching behavior over a range of field conditions that cannot be obtained otherwise. The resulting estimates of COPC release reduce the use of conservative assumptions in favor of more complete data and refined speciation models, and consequently expands alternatives and provides a sound scientific basis for making decisions about appropriate disposal or use of secondary materials under environmentally exposed conditions.
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ABBREVIATIONS AND ACRONYMS

BOD biological oxygen demand
C&D construction and demolition
CCR(s) coal combustion residue(s)
CEN Comité Européen de Normalisation, Brussels, Belgium
CFA coal fly ash
COD chemical oxygen demand
COPC(s) constituent(s) of potential concern
CSF chemical speciation fingerprint
DOC dissolved organic carbon
DNV Det Norske Veritas (a Norwegian classification society)
ECN Energy Research Centre of The Netherlands, Petten, The Netherlands
EPA U.S. Environmental Protection Agency
EPRI Electric Power Research Institute, Palo Alto, CA
ESP(s) electrostatic precipitator(s)
EU European Union
FGD flue gas desulfurization
FSSL fixated scrubber sludge with lime
HFO hydrous ferric oxide
IND small industry waste
ISO International Standards Organization, Geneva, Switzerland
LEAF Leaching Environmental Assessment Framework
L/A liquid-to-surface area ratio (mL/cm²)
L/S cumulative liquid-to-solid ratio (mL/g-dry or L/kg-dry; dry mass basis)
L/S_i interval liquid-to-solid ratio (mL/g-dry or L/kg-dry; dry mass basis)
LSP liquid-solid partitioning
meq milli-equivalents
MSW municipal solid waste
MSWI municipal solid waste incinerator
MSWI-BA municipal solid waste incinerator bottom ash
MW megawatt
NEN Nederlands Normalisatie Instituut, Delft, The Netherlands
NOK National Research Program Coal (The Netherlands)
ORD Office of Research and Development (U.S. EPA)
ORP oxidation-reduction potential
POM particulate organic matter
RCA recycled concrete aggregate
SHA solid humic acid
S-MSWI-FA stabilized municipal solid waste incinerator ash
SPLP Synthetic Precipitation Leaching Procedure (EPA Method 1312)
TCLP Toxicity Characteristic Leaching Procedure (EPA Method 1311)
U.S. United States
VU Vanderbilt University, Nashville, TN
1 INTRODUCTION

Leaching tests are tools typically used to estimate the environmental impact associated with disposal or utilization of materials and wastes on the land (e.g., soils, sediments, industrial wastes, demolition debris, etc.). However, the results of leaching tests are often used without sufficient consideration of the type of data available or the applicability of the available data for the chosen disposal or utilization scenario. Furthermore, results of leaching assessments based on testing and interpretive models only 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.

The assumption that is often made, consciously or not, is that the leaching test “simulates” the release of constituents of potential concern (COPCs) as would happen in the application scenario and, therefore, the leaching test results represent the leachate that would occur in the field. Since many of the current leaching test methods are based on simulation of a particular pre-defined release scenario, the relevance of the leaching test results is restricted to the scenario being simulated. Furthermore, no single leaching test can encompass the range of conditions that a material or waste may be subjected to over the duration of use or disposal. Therefore, the applicability of the results of simulation-based leaching tests is often quite limited to the defined test conditions and relatively short assessment intervals. In order to address these limitations, a more robust science-based approach is needed for environmental leaching assessment that considers the impact on leaching of the chemical and physical characteristics of the tested materials and the range of environmental conditions likely to be encountered during disposal and utilization. These needs have been strongly articulated by the Science Advisory Board of the United States Environment Protection Agency (EPA) during reviews of regulatory leaching approaches (EPA, 1991, 1999).

1.1 The Leaching Environmental Framework

The Leaching Environmental Assessment Framework (LEAF) is fundamentally different than the defined simulation-based approach because it focuses on characterization of 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 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.

1.1.1 LEAF Leaching Methods

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 – Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure
• Method 1314 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure
• Method 1315 – Mass Transfer Rates 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 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 granular materials. Coordinated development of LEAF has occurred between research laboratories in the United States (U.S.) and the European Union (EU). Thus, LEAF analogous test methods have been or are being developed within the EU with minor differences intended to address the different regulatory contexts (e.g., quality control requirements, method description requirements, etc.)

1.1.2 Data Management with LeachXSTM

Typically, only those chemical species of environmental concern (e.g., heavy metals and select organic compounds) are measured under the current regulatory leaching structure, often for compliance purposes. However, the understanding of COPC leaching can be significantly increased if the release of major and minor species not typically studied are measured. For example, arsenic retention is often influenced by calcium and carbonate concentrations, while copper leaching concentrations are often influenced by dissolved organic carbon. Thus, examination of species that are not COPCs or other usual environmental analytes may provide insight into release mechanisms and the potential for changes in those release mechanisms for environmental COPCs. In addition, quantification of a broader range of constituents allows for chemical speciation modeling (see Section 3) and facilitates more fully descriptive leaching behavior modeling approaches. Therefore, the LEAF approach for environmental assessment is designed to provide a more complete evaluation of the leaching behavior which benefits from the analysis and evaluation of major and minor components of the solid matrix in addition to the typical species posing direct environmental concern.

However, the combination of multi-point leach testing and more comprehensive chemical analysis results in a considerable amount of data to be assessed, compared and reported. The leaching assessment and data management program, LeachXSTM, has been developed to facilitate leaching data management. The database driven program is integrated with the LEAF methods through Microsoft Excel spreadsheets used to upload laboratory and analytical data into the LeachXS materials database. In addition, display tools allow for comparison of leaching results for multiple materials and facilitated reporting of the large amount of data required for full characterization. LeachXS also serves as an interface for statistical evaluations of leaching results, chemical speciation modeling using ORCHESTRA (Meeussen, 2003), and advanced reactive transport modeling for several pre-defined release scenarios. LeachXS Lite is a freely-licensed, limited capability version of the full LeachXS program (van der Sloot et al., 2003; van der Sloot et al., 2008b)
focused primarily on uploading, comparing, and display of leaching data between materials and test types. The Lite version of LeachXS was developed, in part, to facilitate EPA characterization of coal combustion residues (CCRs) and associated reports (Sanchez et al., 2006, 2008; Kosson et al., 2009), but also is applicable to management and evaluation of LEAF data from a wide range of materials.

1.1.3 **Leaching Assessment**

Assessments based on the results of characterization-based leaching methods, such as LEAF and LEAF analogous methods, are more flexible than those from simulation-based tests because the data generated focus on relevant intrinsic leaching behavior independent of the disposal or utilization scenario. 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.

However, it must be recognized that leaching assessment only provides that source-term as part of the overall evaluation process, which also must consider dilution and attenuation from the source to the point of exposure or compliance, and the relevant risk-informed decision or compliance human health and ecological thresholds.

1.1.4 **Extension to Field Scenarios**

The robustness of the LEAF approach comes from using laboratory data that includes a range of limiting conditions (i.e., LSP and maximum leaching mass transport rates) in conjunction with models for estimating release under a range of field conditions and scenarios. 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. For example, leaching of alkaline materials such as some cement-stabilized materials may be altered by reaction with atmospheric carbon dioxide, resulting in a less

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6 LeachXS Lite, which is a collaboration of Vanderbilt University (VU), Energy Research Centre of The Netherlands (ECN), EPA Office of Research and Development (ORD) and ARCADIS-U.S., Inc., does not include the advanced formatting, statistical calculations, or chemical speciation and reactive transport modeling capabilities native to the full LeachXS version. The LEAF methods, Excel data templates and LeachXS Lite are available free of charge at www.vanderbilt.edu/leaching.
alkaline pH for leaching and altered chemical speciation for some constituents (e.g., formation of lead carbonate from lead hydroxide).

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) 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.

In this report, the liquid phase resulting from a laboratory leaching test is referred to as an “eluate” whereas liquid phase samples collect from field leachate samples are referred to as “leachate.” The term “constituent” refers to a component of a substance in the liquid or solid phase and is the analytical summation of the various speciation forms of that constituent in that phase. In contrast, a “species” refers to the chemical unit or speciation of an element in the solid or liquid phases. Thus, the measured concentration of a constituent (e.g., lead or Pb) in an eluate or solid material may result from the presence of multiple species containing that element in the designated eluate, leachate, or solid (e.g., Pb^{2+}, Pb(OH)_3; PbCl_2 or organo-Pb species). The “release” of a constituent is defined as the mass of a constituent leached per mass of solid material (mg/kg) and is calculated by multiplying the measured COPC eluate concentration (mg/L) by the associated extract or leaching L/S (L/kg) represented by the volume of liquid in contact with a unit mass of solid. Release is therefore on a solid phase unit basis and is used to represent the amount of a constituent that has or potentially may leach, rather than the more familiar liquid phase unit basis that is used to describe leachate or eluate concentrations.

1.2 Report Objectives and Approach

The primary objective of this report is to provide results from an evaluation of the 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.

1.2.1 **Field 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).

Table 1-1 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,\(^7\) 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 Table 1-1 include “pH” for pH dependent leaching data (e.g., from Method 1313), “L/S” for L/S-dependent leaching data (e.g., Method 1316), “Perc” for percolation column data (e.g., from Method 1314), and “MT” for mass transfer data (e.g., from Method 1315). 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.

\(^7\) 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 1-1. Summary of Laboratory-To-Field Comparison Cases

<table>
<thead>
<tr>
<th>Report Section</th>
<th>Case Name (Country)</th>
<th>Site Materials</th>
<th>Analog Materials</th>
<th>Field Materials</th>
<th>Leachates</th>
<th>Case Conditions</th>
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<td>-</td>
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<td>4.5</td>
<td>Municipal Solid Waste Incinerator Bottom Ash Landfill (Denmark)</td>
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<td>4.6</td>
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</table>

Notes:

- **pH** = pH-dependent leaching data (e.g., EPA Method 1313, PrEN 14429, PrEN 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.

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

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

3 Field Materials refers to materials retrieved from a field application for laboratory testing.
1.2.2 Evaluation Approach
For each evaluation case, the following generalized approach is used to compare laboratory test results for a material to its field leaching:

(v) **LSP Leaching** – laboratory leaching results provide an understanding of the LSP for COPCs as a function of pH (e.g., from Method 1313) or L/S (e.g., from Method 1316 or Method 1314). [Field values for these parameters were also obtained]

(vi) **Dynamic Leaching** – percolation column leaching test results (e.g., from Method 1314) provide an understanding of percolation-controlled leaching of COPCs under idealized conditions, and/or mass transport leaching test results (e.g., Method 1315) provide intrinsic COPC release rates.

(vii) **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.

(viii) **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 (see Section 3).

1.3 Data Quality and Quality Assurance
Two laboratories, Vanderbilt University (VU) and The Energy Research Centre of The Netherlands (ECN), were responsible for the laboratory leaching characterization of fly ash, cement mortars and concrete discussed in this report. VU carried out the leaching characterization of CBP fly ash, mortar and concrete samples, as well as the cement admixture paste sample (MBD2) as part of research on behalf of the Department of Energy, Office of Environmental Management. At VU, leaching procedures and chemical analyses were carried out under the same quality assurance and quality control procedures specified in the Quality Assurance Project Plan for characterization of CCRs for research carried out on behalf of USEPA (Kosson et al, 2009).

ECN carried out all leaching characterization of European cement and concrete samples included in this report. For more than two decades, ECN has been a national and international leader in developing and implementing leaching characterization methods. Since 1983, ECN has been actively involved in the development of leaching tests in support of national (The Netherlands) and European legislation (European Landfill Directive, 2002; Requirement 3 on Health and Environment in the Construction Products Directive, 1989; End of Waste Directive; in development) through chairmanship of working groups in the national standardisation body (Nederlands Normalisatie Instituut, NEN) and the European standardisation organisation CEN. ECN is a qualified laboratory for chemical analysis and for leaching tests under the Dutch quality assurance program RvA (Raad voor de Accreditatie) with annual external independent audits on the basis of NEN-EN-ISO 17025. ECN operates under ISO 9000 practice and has an ISO 9001 as well as an ISO 14001 certificate. ECN has participated in many
interlaboratory comparison (round-robin) studies for leaching characterization methods which has demonstrated its proficiency (van der Sloot et al., 1994, 1995, 2001b; Hohberg et al., 2000; de Groot et al., 1996). The interlaboratory validation studies for the LEAF test methods (Garrabrants et al., 2012a, 2012b), in which ECN participated and conducted LEAF-analogous European leaching methods in parallel demonstrated ECN’s proficiency in leaching characterization as well as the comparability of results between USEPA Method 1313 and the European pH-dependence methods, CEN/TS 14429 and CEN/TS 14497.

DHI works in accordance with the quality management system standard: ISO 9001 as certified by Det Norske Veritas (DNV). The certificate is covering the following products or services: Consulting, software, research & development and laboratory testing, analysis & products within the area of water, environment & health

1.4 Report Limitations

This report focuses primarily on the leaching behavior of inorganic constituents, along with the influences of solid phase and dissolved organic carbon on inorganic constituent leaching. This report does not include evaluation of the leaching of organic substances (e.g., polycyclic aromatic hydrocarbons, pesticides, pharmaceuticals, etc.) or radionuclides. Future work is needed to include organics contaminants, radionuclides, and nanoparticles into LEAF although some work is already progressing in Europe and the U.S. through commercial labs to include organic contaminants and radionuclides.

The cases evaluated in this report are based on studies carried out over approximately the last two decades. All the data presented herein should be considered “secondary data.” As such, the data were likely generated for purposes not specifically in support of this analysis. Nonetheless, these data are useful and broadly appropriate for use in this analysis with some limitations:

- Over the time period that is covered by these cases, the knowledge base for leaching assessment has grown considerably. Thus, if some of these studies were designed and carried out today, more extensive testing would be completed if necessary resources were available. However, many of the studies included complete characterization of the initial material, careful sampling and extensive laboratory leaching characterization in addition to carefully monitored field lysimeters and field, pilot-scale testing.

- Laboratory test methods have evolved since some of these studies were conducted with several of the most recent test methods standardized or in the process of being standardized in the U.S. and EU, respectively. In some cases, these studies were conducted using precursor methods that retain the objectives and general approaches of the standardized leaching tests. The results of analogous leaching tests (i.e., methods intended to determine the same leaching characteristic) have been shown to provide similar and directly comparable results despite minor variations in the procedure or test parameters (Garrabrants et al., 2012a; 2012b; Lopez-Meza et al., 2008; van der Sloot et al., 1995, 1997; van der Sloot 2010a; Hjelmar et al., 2012). Thus, the fundamental information and knowledge to be gained from past studies discussed in this report is still valid.
• In some cases, the collection and analysis of field data contain principal uncertainties including (i) the extent of preferential flow or dilution that may have occurred in sampling of landfill leachate, and (ii) the exact exposure and aging conditions that contribute to the field data. Therefore, for each case, the relevant attributes of each sample are summarized to the extent known or previously reported.

• The studies discussed in this report have been carried out by research groups in at least five countries, each with their own quality assurance and quality control requirements. These requirements are summarized in Section 4 and are discussed in more detail as part of the primary documents from which the cases are taken. However, all studies have been previously independently peer-reviewed as part of required publication processes.
2 LEACHING TESTS AND CONCEPTUAL INTERPRETATION FRAMEWORK

Leaching is defined as the release of constituents from a solid material to the aqueous phase when contacted with water. Release to the aqueous phase can be determined by constituent liquid-solid partitioning (including consideration of solubility, adsorption the solid phase, content available for leaching, aqueous complexation, etc.), the physical properties of the material that limit mass transport, the degree to which equilibrium is achieved, and the properties of the contacting liquid. The solid materials of interest may be soils or sediments (with or without known contamination), wastes (from municipal, industrial, construction, or nuclear material processing), treated wastes or waste forms (e.g., cement-stabilized wastes, vitrified wastes or products from a range of physical/chemical/thermal treatment processes), secondary materials under consideration for beneficial use (e.g., slags, flue gas desulfurization gypsum, coal fly ash), or construction materials. The contacting water may be from percolation through porous materials, flow around porous or nonporous (or fractured) monolithic materials, or from condensation processes. The material may be water-saturated or unsaturated. The source and fate of the water (and any leached constituents) may include precipitation, runoff, groundwater, surface water or collected leachate.

The goal of environmental leaching assessment is to provide an estimate of constituent leaching potential for materials under possible management scenarios that is as accurate as practical or needed, but also does not under-estimate release of COPCs. The intended use of assessments may be to evaluate the environmental safety of specific management options for a class of materials (e.g., beneficial use or disposal scenarios for coal combustion residues), evaluate a specific or set of use or disposal scenarios for a material (e.g., use of a particular coal fly ash in construction of a roadway, embankment or structural fill), establish classes or performance characteristics of materials that may be acceptable for use in defined use scenarios, compare the effectiveness of treatment processes for specific waste types (such as may be needed for regulatory determinations of equivalent treatment), delisting of materials categorized as hazardous wastes based on the material's origin, or to determine remediation goals for contaminated soils or sediments. The constituents identified as COPCs will be specific to the material being evaluated, with specific COPCs usually considered because of their inherent human or aquatic toxicity (e.g., arsenic, mercury, etc.). However, it is important to recognize that leaching of COPCs most often is strongly influenced by the leaching of other major and trace constituents in the material being evaluated and the constituents present initially in the contacting water, the general chemical state (e.g., pH, oxidation-reduction potential, and ionic strength) of the leachant in contact with the solid, and the physical characteristics of the material that impact water contact. All of the above factors influence the LSP of COPCs and the rate and extent to which equilibrium between the solid and liquid phase is approached.

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”
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 considered to be 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.

Several physical-chemical factors such as preferential flow and reducing conditions are known to significantly impact leaching and observed leachate conditions under field conditions but are not readily reproduced through routine laboratory testing (i.e., using standardized commercial test methods). As a consequence, while the LEAF test methods directly incorporate many of the important factors that impact leaching, additional factors such as reducing conditions and preferential flow are considered through chemical speciation and reactive mass transport simulations as discussed in later sections of this report.

### 2.1 LEAF and LEAF-analogous Leaching Tests

The LEAF test methods are presented in Table 2-1 by EPA method number along with a listing of analogous EU leaching methods. The LEAF methods are designed to measure fundamental leaching parameters including:

- LSP as a function of eluate pH;
- LSP as a function of L/S under percolation (column flow) or batch extraction testing;
- mass transfer rates from COPC leaching from monolithic or compacted granular materials.

Method 1313 and Method 1316 are parallel batch procedures intended to characterize the LSP at conditions approaching equilibrium as a function of final extract pH and liquid-to-solid ratio (L/S), respectively. Method 1314 and Method 1315 are test methods intended to measure the rate of constituent release under percolation or diffusive/dissolution mass transfer conditions, respectively. The test parameters and values specified in these methods have been described in a background information document on the LEAF leaching methods with fully validated methods available (Garrabrants et al., 2010; Garrabrants et al., 2012a; 2012b).

LEAF-analogous methods, also shown in Table 2-1, include leaching methods from the EU which are similar in structure and intent to the LEAF methods. Many of these EU methods have only minor deviations in test structure (e.g., the number of test fractions taken) or in test parameters (e.g., specified targets or time durations) from their LEAF counterparts. Documentation supporting the development and use of the EU test methods is available in the public literature (van der Sloot et al., 2012; Hjelm et al., 2012).

The following sections contain brief description of LEAF and LEAF-analogous methods, example outputs from LEAF testing, and comparison of the results of analogous EU and EPA method results using the same test material. More detailed comparison and information relevant to the precision of these methods also has been documented (Garrabrants et al., 2012a; 2012b).
Table 2-1. LEAF Test Methods and Analogous European/International Methods.

<table>
<thead>
<tr>
<th>EPA Method</th>
<th>Method Name</th>
<th>Short Name</th>
<th>Analogous EU and International Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>1313*</td>
<td>Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure</td>
<td>pH-dependence Test</td>
<td>PrEN 14429</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PrEn 14997</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ISO/TS 21268-4</td>
</tr>
<tr>
<td>1314</td>
<td>Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-Flow Percolation Column Procedure</td>
<td>Column Test or Percolation Test</td>
<td>CEN/TS 14405</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CEN/TC 351-TS-3</td>
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<tr>
<td></td>
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<td></td>
<td>ISO/TS 21268-3</td>
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<td></td>
<td></td>
<td>NEN 7343</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NEN 7373</td>
</tr>
<tr>
<td>1315*</td>
<td>Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure</td>
<td>Monolith Leach Test or Compacted Granular Leach Test (generally &quot;Tank Leaching Test&quot;)</td>
<td>PrEN 15863</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CEN/TC 351-TS-2</td>
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<td></td>
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<td></td>
<td>NEN 7345</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NEN 7375</td>
</tr>
</tbody>
</table>

Notes:
1. In Kosson et al. (2002) and other previous works, precursor methods with slightly different test conditions were used. These precursor methods include:
   - SR002 as a precursor to Method 1313 without specific target pH values.
   - MT01 (monolithic materials) and MT02 (compacted granular materials) as precursors to Method 1315 with minor interval duration changes.
   - SR003 as a precursor to Method 1316 with no significant changes.
2. The “PrEN” designation denotes a preliminary CEN standard method that has been approved by a CEN technical committee and has completed interlaboratory validation, but is in the final approval process for “EN” designation.
3. The “TS” designation denotes a “technical specification” which is a test method resulting from multi-national consensus and approved by a CEN technical committee, but has not yet completed interlaboratory validation or the final approval process for “EN” designation.
4. Specifications for the Compacted Granular Leach Test are under development.

2.1.1 pH-dependent Leaching Tests

The concentration of hydrogen ion in solution (i.e., pH) has a major influence on the dissolution of COPC-containing mineral phases as well as on the COPC speciation in aqueous solution and the extent of adsorption onto or ion exchange with reactive surfaces. Thus, pH is a master variable in leaching assessment and reporting of pH in the eluate or leachate (i.e., pH at the leaching test end point) is of critical importance because pH at the approximated chemical equilibrium conditions controls the observed liquid-solid partitioning behavior for many constituents. Tests that measure COPC leaching with respect to pH are an important class of equilibrium-based test methods where the pH of the final extract is controlled as an independent variable in order to characterize leaching over a broad range of pH values. The pH-dependent leaching tests tend to be parallel batch extraction tests (i.e., multiple batch extraction conducted at different test conditions) with specific target pH values intended for the final eluate pH. Control of pH typically is obtained either by initial acid addition or by automated acid/base addition. The resultant eluate COPC concentrations are
plotted as a function of final eluate pH and are interpreted as a continuum pH-dependent leaching curve.

**Method 1313: Liquid-Solid Partitioning as a Function of pH using a Parallel Batch Extraction Procedure**

Method 1313 consists of nine parallel batch extractions at targeted pH values and one extraction at the natural pH\(^8\) of the material. The solid material may require particle size reduction by crushing in order to facilitate the approach to solid-liquid equilibrium within a reasonable extraction timeframe. Dilute acid or base in deionized water is added to each extraction according to a pre-test titration in order to achieve final extract pH values at specified target values ranging between 2 and 13 at an L/S of 10 mL/g-dry. The extraction contact time ranges from 24 to 72 hours based on the grain size of the “as tested” material (i.e., the material after any particle size reduction or air drying required to improve the handling of the “as received” material). The pH and conductivity of the final extract solution are recorded and vacuum- or pressure-assisted filtration is used to separate the liquid and solid phases prior to chemical analysis of the eluate. This method also provides a titration curve of the solid material defined as the eluate pH response to additions of acid or base expressed in milli-equivalents (meq) of acid per gram of material with base additions shown on the x-axis as acid additions less than zero.

Eluate concentrations for constituents of interest are plotted as a function of eluate pH allowing for comparison to quality control and assessment values (e.g., quantitation or detection limits and waste disposal or utilization criteria). Eluate concentrations may also be interpolated to the target pH values to provide a uniform basis for comparison of results as the recorded eluate pH is likely to differ slightly from target values within specified pH tolerances. Example results for Method 1313 are shown in Figure 2-1 for arsenic leaching from a coal combustion fly ash, both as measured arsenic concentrations plotted as at measured eluate pH values (left) as well as arsenic concentrations interpolated to Method 1313 target pH values (right). In the figure, concentrations for the different parallel batch extractions of the test are connected with a line; however, this line should not be used as a functional trendline showing pH-dependent leaching between data points. A large circle is used to denote the natural pH extraction data.

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\(^8\)The natural pH, also referred to as "own pH", is the final eluate pH response of a deionized water extraction of a solid material (i.e., no acid or base added) conducted at an L/S 10 mL/g-dry.
**Figure 2-1.** Example of Method 1313 data in triplicate for arsenic pH-dependent leaching from a coal combustion fly ash showing measured data (left) and interpolated data (right). The figures have been modified from those in Garrabrants et al., 2012a.

EU pH-dependent Methods PrEN 14429 and PrEN 14997  
PrEN9 14429 and PrEN 14997 are European pH-dependent leaching tests developed by the Comité Européen de Normalisation (CEN) which are analogous to EPA Method 1313. Although initially designed to test waste materials, the approach of these methods has been adapted as ISO/TS 21268-4 under the International Standards Organization (ISO) program for soils and soil materials (ISO, 2007).

Separate sample portions are extracted in parallel at a fixed L/S ratio of 10 mL/g in dilute acid or base solutions in order to reach stationary pH values at the end of the extraction period. Sample portions of 15, 30, or 60 g (depending on sample heterogeneity and volumes of extractant required for chemical analysis) are prepared to have a grain size with 95% (m/m) less than 1 mm. Any particle size reduction is conducted by crushing. At least eight final pH values are required, covering at the minimum the range pH 4-12 (including the lowest value ≤4 and the highest value ≥12). The maximum pH differential between final pH points shall not exceed 1.5 pH units. The amounts of acid or base needed to cover the pH range can be derived from the results of a preliminary titration, from available experimental data on the material to be tested or from an arbitrary division of the predetermined maximum consumption of acid and base. The tests are carried out at a fixed contact time of 48 hours at which time equilibrium conditions are assumed for most constituents. The equilibrium condition is verified by a pH difference of less than 0.3 pH units between measurements taken after 44 hours and 48 hours. The results are expressed in mg/L of constituents for each final pH value. The quantity of acid or base that is added is recorded for each final pH value in mol H+/kg of dry material with base additions expressed as negative values.

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9 The PrEN designation denotes that a draft method which is in the final process for approval as a European standard (EN). PrEN methods have been developed from a multi-national consensus process, approved by a CEN technical committee, and completed interlaboratory validation studies to assess method precision. The PrEN designation does not carry the status of an EN, but the method may be adopted as national standard. With regard to LEAF-analogous methods, the U.S. EPA interlaboratory validation study on EPA Method 1313 (Garrabrants et al., 2012a) has been accepted by CEN as the basis for validation for PrEN 14429 and PrEN 14997.
The primary difference between these two EU methods is how the extraction solution is introduced to the test portion:

- PrEN 14429 (2005) – Test portions are contacted with extraction solutions in a closed vessel with acid/base introduction through initial addition of extraction fluid. At the start of the test, the extraction solutions are prepared and divided evenly into three fractions. A fraction of extraction solution is added to the extraction bottle at the start of the test, after 30 minutes, and after 2 hours.

- PrEN 14997 (2005) – Test portions are placed into an open vessel with reagent water and acid/base is introduced via automated pH control. The method specifies that acid or base addition between cumulative extraction times of 44 and 48 hours shall not exceed 2% of maximum of the total acid/base addition at 48 hours.

Comparison of pH-dependent Leaching Test Results

The interlaboratory validation program for Method 1313 (Garrabrants et al., 2012a) allowed for a comparison of leaching test results between Method 1313 and the precursor “technical specifications” of PrEN 14429 and PrEN 14997 (denoted as CEN/TS 14429 and CEN/TS 14997, respectively). A sample of the results for testing of a coal combustion fly ash is shown in Figure 2-2 for selected COPCs.

In general, all pH-dependence leaching tests characterize the LSP behavior of fly ash; however, in Figure 2-2, minor differences were observed in the pH range 6 < pH < 12. These differences are most likely attributed to kinetic effects where the approximate equilibrium in some tests may not be established over the test duration to the same degree.

2.1.2 L/S-dependent Leaching Tests

The amount of liquid in contact with a solid sample (i.e., L/S) is another critical parameter controlling the leaching of COPCs. At low L/S, liquid-solid partitioning and ionic effects in the aqueous solution control the release of COPCs while such solution chemistry effects are not significant at high L/S values where the mass of a COPC released into solution may be indicative of the total amount of COPC in the solid that is leachable. L/S-dependent leaching tests may be designed as batch extractions over a duration of time required to approach equilibrium or as percolation column tests at a flow rate low enough to approximate liquid-solid equilibrium. Eluate concentrations typically are expressed as a function of extraction L/S (for batch tests) or as cumulative L/S (for percolation tests).

Method 1314: Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using an Up-Flow Percolation Column Procedure

Method 1314 is an up-flow percolation column procedure used to evaluate the release of constituents from solid materials as a function of cumulative L/S. Relative to field conditions, L/S

10 Cumulative liquid-to-solid ratio will be denoted as L/S whereas the liquid-to-solid ratio for individual leaching intervals or test fractions will be denoted as L/S; where the value i represents the endpoint cumulative L/S. For example, L/S0.2 refers to first fraction of Method 1314 starting at L/S=0 mL/g-dry and ending at an L/S=0.2 mL/g-dry while L/S10 refers to the last fraction of the test starting at L/S=9.5 mL/g-dry ending at L/S=10 mL/g-dry.
can be a useful surrogate measure for time when infiltration rates are considered. In the context of the column test, L/S is defined as the volume of liquid passing through the column relative to the dry equivalent mass of test material in the column bed and is expressed in units of mL/g-dry. A sample of the solid material of approximately 300-600 grams is packed under moderate effort into a 5-cm diameter x 30-cm long column. Layers of clean silica sand are used at the top and bottom of the column to provide flow regulation on the inlet side and coarse filtration at the outlet. Leaching solution (elucent) is pumped upward through the material and eluate is collected as nine discrete volume fractions of the continuous elution volume. The up-flow percolation mode is intended to minimize air entrapment and flow channeling. The pump flow rate is adjusted to provide a volume of eluent equivalent to 0.75±0.25 L/S per day. For primarily inorganic materials, deionized water is used as the eluent for testing; however, a 1 mM solution of CaCl₂ may be used when testing certain materials (e.g., organic soils, clayey materials) where deflocculation of clay layers or dissolution of organic carbon may be a concern.

Method 1314 specifies nine eluate fractions collected at L/S values of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10 mL/g-dry. The eluate pH, conductivity and optionally oxidation-reduction potential (ORP) are recorded for each fraction prior to filtration through a 0.45-µm membrane and preservation of an analytical sample. After chemical analysis of analytical samples, cumulative

Figure 2-2. Comparison of pH-dependent leaching tests results for testing of a coal combustion fly ash using Method 1313, CEN/TS 14429 and CEN/TS 14997 (Garrabrants et al., 2012a).
release from the column at the specified L/S values is calculated from eluate concentrations and interval liquid-solid ratios (L/S). Thus, the measured eluate concentration for a given fraction represents the composite or integrated concentration over the designated cumulative L/S interval. Depending upon the intended use of the test results (e.g., when only cumulative release at specified L/S values is a concern), analytical samples may be composited to minimize analytical costs, but typically all eluate collections are analyzed for COPCs. For display purposes, eluate concentrations are typically graphed as a function of L/S, with the concentration of each individual fraction plotted at the cumulative L/S at the end of the fraction interval. A second useful representation of percolation test data is the cumulative release for each constituent (i.e., the cumulative amount of a constituent leached per mass of material tested) as a function of cumulative L/S. Cumulative release is accurately plotted at the end-point cumulative L/S for each fraction interval. Example outputs from Method 1314 testing of a contaminated soil from a smelter site are presented in Figure 2-3 and include the pH of the collected eluate fractions, the graphs of eluate COPC concentration, and cumulative release of the COPC.

![Figure 2-3](image-url)

Figure 2-3. Example Method 1314 results for arsenic leaching from a contaminated smelter site soil showing eluate pH in collected fractions from the column, eluate arsenic concentrations, and cumulative release of arsenic with L/S (Garrabrants et al., 2012b).

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11 Since the eluate concentration represents a mean concentration, a more accurate representation would be obtained by plotting the COPC concentration at the geometric mean L/S over the fraction interval.
Method 1316: Liquid-Solid Partitioning as a Function of Liquid-Solid using a Parallel Batch Extraction Procedure

Method 1316 is an equilibrium-based leaching test intended to provide eluates over a range of L/S values from 10 to 0.5 mL/g-dry using five parallel batch extractions in DI water. No acid or base is added to the extractions so that the results can indicate changes in eluate pH with L/S. Particle size reduction of the solid material may be required in order to facilitate the approach to solid-liquid equilibrium. The contact time for the extractions ranges from 24 to 72 hours based on grain size in a similar manner. The pH and conductivity of the final extract solution are recorded. Solid and liquid phases are separated by vacuum- or pressure-assisted filtration and prepared for chemical analysis. This method provides data on the changes in equilibrium chemistry (i.e., ionic strength, constituent concentrations) as the L/S value approaches that are found within the solid phase pore solution. Method 1316 output (see example in Figure 2-4) is similar to the output of Method 1314 with eluate pH, eluate COPC concentration and COPC release plotted as functions of L/S. COPC release results are similar to the results of Method 1316; however, eluate concentrations are typically higher in Method 1316 due of the natural of batch extraction process.

![Graphs showing pH, arsenic concentration, and arsenic release as functions of L/S.](image)

**Figure 2-4.** Example Method 1316 results for arsenic leaching from a contaminated smelter site soil showing eluate pH in collected fractions from the column, eluate arsenic concentrations, and cumulative release of arsenic with L/S (Garrabrants et al., 2012a).
**EU Percolation Method CEN/TS 14405**

CEN/TS 14405 (2004) is an up-flow percolation column test method designated as a “technical specification”\(^{12}\) by CEN for characterization of waste and has been adopted by ISO under ISO/TS 21268-3 for soils and soil materials (ISO, 2007). A very similar column test, CEN/TC351-TS-3, sponsored through the CEN Technical Committee 351 is undergoing robustness testing (Hjelmar et al., 2012). The Dutch standards NEN 7343 (1995) and NEN 7373 (2004) from the Nederlands Normalisatie Instituut (NEN), are precursors of the CEN/TS 14405 method.

The procedure for CEN/TS 14405 is similar in intent and procedure to Method 1314 with minor differences in the number of eluates collected and, hence, the prescribed L/S values. CEN/TS 14405 allows for collection of an eluate at 0.1 mL/g-dry that is not specified in Method 1314 due to limitations of eluate volume at this low L/S. In addition, while Method 1314 specifies a flow rate based on L/S passing through the column which is dependent on the mass of solid in the column, CEN/TS 14405 specifies flow rate in terms of eluate volume per time, which is independent of the solid mass. The CEN/TS 14405 method determines the release of constituents from granular material packed into a column with a leachant percolating through the column packing. The test conditions, including the flow rate of the leachant, enable conclusions to be drawn from the results as to which components are rapidly washed out and which components are released under the influence of interaction with the matrix.

Test material, with or without particle size reduction, is packed into either a 5-cm or a 10-cm diameter plastic or glass column that is 30-cm long. Packing is achieved in a standardized manner with a plastic rammer. Demineralized water leachant is percolated in up-flow through the column at a specified flow rate of 12 mL/h for a 5-cm diameter column or 48 mL/h for 10-cm diameter column. The eluate is collected at seven fixed values of cumulative liquid-to-solid ratio or L/S (i.e., 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL/g-dry). Each eluate is characterized physically and chemically for pH, conductivity and concentrations of constituents of interest according to existing standard methods. In the test procedure, equilibrium conditions at the outlet of the column are verified after an equilibration period by measuring a pH deviation. The results of the test are expressed as a function of L/S, in terms of both eluate concentration (mg/L) and cumulative mass release (mg/kg-dry).

**EU Batch L/S Method EN 12457**

EN 12457 is a European Standard consisting of a four-part batch leaching procedure in which particle size-reduced material is extracted with deionized or demineralized water at room temperature. Parts 1, 2 and 4 of the standard are single-batch extractions at difference L/S ratios and particle size requirements. Part 3 consists of a two-step test with re-extraction of the recovered

\(^{12}\) The “TS” designation denotes a CEN “technical specification” which is a method that has resulted from a multi-national consensus process and has been accepted by a CEN technical committee, but has not completed interlaboratory validation studies and final CEN approval. TS methods may be used as national standards. The U.S. EPA validation data for Method 1314 has been accepted as the basis for validation of CEN/TS 14405, but this method has not yet received the “PrEN” designation.
material from the first L/S 2.0 mL/g extraction in a second extraction step at L/S of 8.0 mL/g (cumulatively the L/S is equal to 10 mL/g). In comparison to the LEAF methods, EN 12457-2 is most similar to the L/S 10 target extractions in Method 1316 and the natural pH extraction of Method 1313.

**Comparison of L/S-dependent Leaching Test Results**

The results of Method 1314 and CEN/TS 14405 were compared during validation of the EPA percolation column test (Garrabrants et al., 2012b). In Figure 2-5, this comparison is shown for selected COPCs leached from a smelter site soil in terms of mass released from the column tests. Also include in this figure are the release values resulting from the batch L/S test, Method 1316, performed on the same material (Garrabrants, et al., 2012a). The three L/S-dependence tests result in very similar cumulative release data with all tests showing the same general behavior for each COPC. Differences in the cumulative release from these test methods were considered within the reproducibility values calculated for the individual LEAF tests (see Garrabrants et al., 2012a, 2012b for details on performance measurements).

![Comparison of L/S-dependent release](image)

**Figure 2-5.** Comparison of L/S-dependent release for a contaminated smelter site soil using Method 1314 (percolation), Method 1316 (batch L/S) and CEN/TS 14405 (percolation). Data taken from Garrabrants et al., 2012a, 2012b.
2.1.3 **Mass Transport-based Leaching Tests**

For materials with low hydraulic conductivity relative to their surroundings, the majority of any infiltrating water will not percolate through the material but will be diverted to “flow around” the material. Examples of such material would be clays and compacted granular materials and monolithic material derived from solidification/stabilization. When flow-around conditions exist, constituents must travel through the porous structure of the material to the bulk material surface in order to be release. Often, this mass transport through the material is the rate limiting factor in leaching assessments. The rate of mass transport may be characterized using tank leaching tests where a sample of monolithic or compacted granular material is suspended in a tank of leaching fluid over a specified leaching interval. The fluid is refreshed in order to maintain a concentration gradient between the material surface and the pore structure. This gradient is related the driving force for mass transport through the material. Refreshment of the leaching solution often is semidynamic, occurring in accordance with a specified refresh schedule, such that the leaching method appears as a large scale, sequential batch leaching procedure consisting of several leaching intervals that comprise a total or cumulative leaching time.

**Method 1315: Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure**

Method 1315 is a semi-dynamic tank leaching procedure used to determine the rate of mass transport from either monolithic materials (e.g., concrete materials, bricks, tiles) or compacted granular materials (e.g., soils, sediments, fly ash) as a function of time. Monolithic test specimens may be cylinders or parallelepipeds, cast in molds or cut/cored to size from larger samples. Granular materials are compacted into cylindrical molds at optimum moisture content by Proctor-type compaction methods such as ASTM D698 (2007) or ASTM D1557 (2009). Test specimens are leached in intervals in a series of tanks containing deionized water with each leaching interval having a specified duration. The volume of deionized water in each tank is based on the surface area of the test specimen at a liquid-to-surface area ratio (L/A) of 9 mL/cm². At the end of each leaching interval, the test specimen is removed from the tank, the mass of the test specimen is recorded, and the specimen is submerged into another new tank containing fresh deionized water. The cumulative times corresponding to the end of the nine leaching intervals are 2, 25, 48 hours, 7, 14, 28, 42, 49, and 63 days. For each tank eluate, the pH, conductivity, and optionally ORP are recorded prior to filtration through a 0.45-µm membrane and preservation of an analytical sample.

After chemical analysis, the mean flux of constituents in each interval (i.e., mass released per surface area per unit time of the leaching interval) and the cumulative release of constituents (total mass released per unit surface area as a function of time) are calculated from the eluate concentration, the volume of eluate collected for each interval, the geometry and mass of the test specimen, and the duration of each interval. In addition, mass transfer characteristics (e.g., diffusivity, tortuosity) may be calculated using assumed mathematical models. An example of the outputs of Method 1315 conducted on sample of a solidified waste analog (i.e., cement, coal water matrix spike with metal oxide powders) is shown in Figure 2-6 and include (i) the evolution of pH in test fractions, (ii) eluate concentrations for a selected COPC, (iii) the mean interval mass flux...
(mg/m² s) of the COPC as a function of cumulative leaching time, and (iv) the cumulative mass release (mg/m²) of the COPC as a function of cumulative leaching time. This test is used to assess the combined effects of pore water chemistry (e.g., dissolution, adsorption) and diffusion through a monolithic or compacted granular material.

Figure 2-6. Example Method 1315 test results for barium leaching from a solidified waste analog material showing pH evolution, eluate concentration, mean interval flux and cumulative release (Garrabrants et al., 2012b).

EU Mass Transport Methods PrEN 15863 and NEN 7375
The EU mass transfer leaching test, PrEN 15863 (2009) and the Dutch standard mass transfer test, NEN 7375 (NEN, 2004), are similar in intent and procedure to Method 1315. Differences include the total testing duration, the number and duration of the testing intervals, and the basis for determination of the amount of liquid used in each leaching interval as shown in Table 2-2. Currently, a similar procedure, CEN/TC 351-TS-2, is undergoing robustness testing for use with construction products under CEN Technical Committee 351 (Hjelmar et al, 2012). Dutch standards NEN 7345 (1995) and NEN 7375 (2004) are precursors of the PrEN 15863 method while CEN/TS 15863 is the technical speciation designation for PrEN 15863.
NEN 7375 Procedure

NEN 7375 is a test intended to define leaching from molded or monolithic materials under mass transfer conditions as a function of time. The test determines the nature and properties of the material matrix by placing a complete sample in a leaching fluid of demineralized water and replenishing the eluate at eight specified cumulative times of 0.25, 1, 2.25, 4, 9, 16, 36, and 64 days. Test specimens should have a minimum dimension of 40 mm and a geometric surface area of at least 75 cm². The volume of eluent for each leaching interval is based on the test specimen volume with 2-5 mL of eluent for every cm³ of test specimen. From analytical samples of each eluate collection, the composition of the eluate is determined using standard methods, and the leached quantity per unit area is calculated for each constituent. Parameters that can be deduced from the development of release of constituent over time include the extent of surface rinsing and the effective diffusion coefficient which can be used to estimate leaching over longer periods.

PrEN 15863 Procedure

PrEN 15863 is a procedure for leaching of a solid monolithic material in a similar manner as NEN 7375 or Method 1315. The test specifies that a regular shaped test specimen is prepared by cutting or coring in accordance with standard sampling methods. The test specimen is submerged in a tank of demineralized or deionized water for specified interval durations for a series of eight leaching intervals (see Table 2-2). Leachant is refreshed at cumulative times of 0.08, 1, 2.25, 8, 14, 15, 28, and 36 days. For each eluate, pH and conductivity are measured and recorded prior to preparation for chemical analysis using standard methods. The results of the test are the cumulative mass release (mg/m²) expressed as a function of time.

Table 2-2. Comparison of Method 1315 and EU Mass Transfer Test Parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method 1315</th>
<th>PrEN 15863</th>
<th>NEN 7375</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Test Duration (d)</td>
<td>63</td>
<td>51</td>
<td>64</td>
</tr>
<tr>
<td>Eluate Volume Basis</td>
<td>specimen surface area</td>
<td>specimen surface area</td>
<td>specimen volume</td>
</tr>
<tr>
<td>Liquid Volume</td>
<td>9±1 mL/cm²</td>
<td>8±1 mL/cm³</td>
<td>2-5 cm³/cm³</td>
</tr>
<tr>
<td>Number of Intervals</td>
<td>9</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Refresh Exchanges at Cumulative Times (d)</td>
<td>0.08 0.1 2.0 7 14 28 42 49 63</td>
<td>0.08 1.0 2.25 8 14 15 28 36 64</td>
<td>0.25 1.0 2.25 4 9 16 36 64</td>
</tr>
</tbody>
</table>
Comparison of Mass Transport Test Results

Figure 2-7 shows the comparison of interval mean flux for mass transport of selected COPCs in a solidified waste analog for EPA Method 1315, NEN 7375 and CEN/TS 15863 (the technical specification of PrEN 15863). This figure shows that the general trend of the interval flux is consistent despite the different interval durations of the tank leaching tests.

![Graphs showing Antimony, Arsenic, Chromium, and Selenium flux over time for different methods.](image)

Figure 2-7. Comparison of mean interval flux release results for testing of a solidified waste analog using Method 1315, CEN/TS 15863 and NEN 7375. Data taken from Garrabrants et al., 2012b.

2.2 A Conceptual Framework for Interpreting Leaching Test 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. Data sets from the currently-specified LEAF, EU and respective precursor test methods (Table 2-1) are the laboratory test results used in this report for comparison with field data. Laboratory leaching test results are used here primarily to illustrate a conceptual framework for the relationships between test method results and field data because more complete testing information is available for the
laboratory tests, including a wider range of test method results and constituents analyzed, than is available from reported field data and studies.

2.2.1 **Liquid-Solid Partitioning at Equilibrium**

Equilibrium-based leaching test measure LSP under specified test conditions. For example, Methods 1313 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). Similarly, 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. Therefore, eluates collected between two L/S values indicate the average release over that L/S interval. The primary distinguishing feature of a percolation test over that of a batch L/S procedure is the column test captures the effects of different elution rates of COPCs into the pore solution at different L/S values with the result that the local composition of the system changes as the amount of liquid passes through the column. Under the assumption of a constant flow rate, the cumulative L/S (e.g., the volume eluted from the column divided by the dry mass of solid material in the column) is used as a surrogate for elution time. 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.

For all equilibrium-based leaching tests, the approximation of local equilibrium is the result of pragmatic choices in selection of appropriate contact times, because attaining true chemical thermodynamic equilibrium would, in most cases, require test durations far longer than practical for routine implementation in a decision-making framework.

**Chemical Phenomena Affecting LSP**

The resulting LSP of constituents in a material at chemical equilibrium can be the result of several chemical phenomena that occur either individually, with one phenomenon dominant in the observed behavior, or with multiple phenomena occurring simultaneously with different phenomena controlling the observed behavior under different pH or L/S conditions.

To illustrate this concept, the several response types are used to describe dominant leaching mechanisms under common partitioning behaviors. Most of these response types can be distinguished based on examination of the results from one or more of the LEAF test methods, however, for some situations, chemical speciation may be needed to clarify the contributing

---

13 In many column test procedures, the number of pore-volumes eluting from the material is used as the comparison basis rather than cumulative L/S. Cumulative L/S was selected as the basis for comparison for Method 1314 because it is not dependent on system porosity and provides a convenient basis for comparing results of Method 1314 with Methods 1313 and 1316.

14 The extent of preferential flow during percolation can be evaluated based on the observed concentrations and elution profiles for highly soluble constituents such as sodium, potassium, chloride and nitrate. Greater extents of preferential flow result in lower peak concentrations and longer tailing of elution curves.
mechanisms (i.e., distinguishing between precipitation and adsorption at low constituent concentrations).

**Response 1. Total Content vs. Availability**
A constituent, or fraction thereof, may be incorporated into one or more solid phases or mineral structures that do not readily dissolve in water, thereby rendering that fraction of the constituent not available for leaching under reasonable environmental conditions and relevant time frames (e.g., years to decades). Although the solid phase or mineral structure containing the constituent may be dissolved over geologic time frames due to weathering and aging which may allow for leaching of the constituent in the long term, these time frames typically are long enough that leaching may have little impact on groundwater when carried through a risk assessment. One example of this response is the incorporation of lead into stable alumina-silicate phases where the alumina silicate phases must be dissolved to release the lead and have been found to be stable over geologic time frames (i.e., amorphous glassy phases and other mineral phases). The fraction of lead not bound in these recalcitrant phases is considered the available fraction of the total content in the material, often referred to as “availability.” The sum of the lead incorporated into recalcitrant phases and available content of lead is the total lead content in the material. Comparison of total content to maximum leaching concentration for a wide range of CCRs illustrated that total content and available content are not correlated (Thorneloe et al., 2010).

**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 undersaturated 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).

For many of these highly soluble species, the LSP curve is not a strong function of pH, and eluate concentrations remain relatively constant across the pH range. When availability-limited release is dominant, eluate concentrations increase with decreasing L/S (i.e., the same mass of constituent is released into less liquid), but mass release is independent of L/S (i.e., when normalized to the mass of the solid material tested, mass of the constituent release is relatively constant with changes in L/S). An illustration of availability-limited leaching as a function of pH and L/S is shown in Figure 2-8 using chloride release from a sample of unwashed flue gas desulfurization (FGD) gypsum with material code SAU (Kosson et al., 2009).
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. An example of this case is the dissolution of arsenic from a highly alkaline coal fly ash under neutral to alkaline pH (Figure 2-9).

When this phenomenon is dominant in leaching, eluate concentrations typically are strong functions of pH and are constant with decreasing L/S (i.e., the dissolution of the partial soluble solid phase controls the eluate concentration). As long as pH remains relatively constant with decreasing L/S, the constituent mass release will decrease with decreasing L/S at a rate approximately proportionate to the decrease in L/S (e.g., a reduction in L/S from 10 to 0.5 mL/g-dry will result in a 20x decrease in constituent). However, the greater ionic strength at lower L/S may also impact the amount leached. In addition, trace constituents may also coprecipitate with major element solid phases, resulting in solid solutions and more complex behavior where the observed liquid concentration for the trace species is proportional to the content of that species in the solid solution.
Figure 2-9. Arsenic as an example of solubility-controlled (saturated solution) leaching as a function of L/S and pH for a coal combustion fly ash (EaFA; after Garrabrants et al., 2012a).

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). When adsorption/desorption or ion exchange phenomena control constituent leaching, the constituent species of interest is fractionally distributed between the aqueous and solid phases at equilibrium, with the fractional distribution influenced by (i) the total available amount of the constituent in the liquid-solid system, (ii) the nature and amount of reactive solid surface in the system, and (iii) the aqueous solubility of the species at the test conditions.

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 above. Examples include (i) chloride present both in a relatively insoluble alumina-silicate phase and as sodium
chloride crystals (Responses 1 and 2, above; Figure 2-8), (ii) lead present both in a relatively insoluble alumina-silicate phase and as a lead molybdate phase (Responses 1 and 3, above), or (iii) arsenic present as several species with the resultant leaching behavior a combination of Responses 1, 2 and 4, as described above (Figure 2-9).

2.2.2 pH, Ionic Strength and Aqueous Phase Complexation as LSP Modifying Parameters

The above phenomena and resulting observed leaching behavior is further complicated by the following modifying factors:

Eluate pH

The solubility of some constituents, such as periodic table Group IA elements (e.g., sodium, potassium) and anions (e.g., chloride and nitrate), is not strongly affected by pH and, therefore, tends to have leaching characteristic behavior consistent with Response 2, above (Figure 2-8). In contrast, the solubility of some constituents is strongly dependent on pH and can exhibit behavior consistent with Response 2 over some pH domains and Response 3 over the remaining pH domains. For the example of a coal fly ash in Figure 2-10, magnesium is very soluble at pH < 8 (Response 2) while forming a saturated solution at pH > 9 (Response 3). Conversely, molybdenum is very soluble at pH > 8 while forming a saturated solution at pH < 6. This phenomenon allows the availability of many constituents to be estimated based on the maximum or asymptotic release over the domain of 2 < pH < 13.

![Figure 2-10. pH-dependent solubility of magnesium and molybdenum for coal fly ash sample TFA (after Kosson et al., 2009).](image)

Ionic Strength

The presence of other constituents in the aqueous and solid phases often influences the solid phases present for the constituent of interest (speciation of precipitated solids) and resultant solid phase solubility in the aqueous phase. One effect of the presence of highly soluble constituents is reflected in changes in ionic strength, which impacts solubility through changes in chemical activity (i.e., activity coefficients). Another effect might be precipitation of a constituent phase due to dissolution of a related phase through the presence of a common ion.
An example of the common ion effect is that barium will precipitate as barium sulfate as calcium sulfate dissolves, leading to apparent chemical interactions between calcium and barium leaching in the presence of sulfate.

**Complexation and Chelation**

Some constituents in solution may complex or chelate with a constituent of interest, shifting equilibrium toward the aqueous phase and increasing the LSP eluate concentration over the aqueous solubility afforded only by mineral dissolution. Examples of this include (i) complexation of cadmium by chloride at neutral to moderately alkaline pH, and (ii) the chelation of copper with DOC (e.g., humic and fulvic substances, especially in MSW landfill leachate) at moderately acid to alkaline pH (Figure 2-11).

![Figure 2-11. Illustration of the influence of organic matter and DOC on leaching of copper through three cases: (i) fresh municipal solid waste incinerator (MSWI) bottom ash, (ii) the same MSWI bottom ash heat treated at 500 °C to remove organic matter, and (iii) the heat-treated MSWI bottom ash from above with 1% compost added to provide organic matter (after van der Sloot et al., 2008c).](image)

In most cases, only the total concentration of a constituent, rather than the chemical speciation of a constituent, is measured in a leaching test eluate or leachate and in the solid material being evaluated because of analytical method limitations or cost. Thus, chemical speciation of individual constituents is most often only inferred based on empirical observations (i.e., characteristic liquid-solid partitioning behavior) or assessed by chemical speciation modeling (see Section 3).

### 2.2.3 Oxidation-Reduction Considerations for Leaching Tests and Leaching Assessment

For constituents with multiple valence states under 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. In the context of the case studies evaluated in this report, the most relevant constituents for reduction/
oxidation (redox) are Fe and S as species that control the LSP of other constituents and As, Cr, Cu and V as redox sensitive species that frequently are considered COPCs in environmental systems.

In order to provide context for redox relationships with respect to leaching and geochemical speciation modeling (Manahan, 1991):

\[
pE = \frac{F}{2.303RT} E_H = \frac{E_H}{0.0591} \quad \text{(at } 25 \text{ C}),
\]

where \( pE \) is the \(-\log\{\text{electron activity}\} \) or redox of the aqueous system at the stated conditions,

\( F \) is Faraday's constant,

\( R \) is the ideal gas law constant,

\( T \) is the absolute temperature, and

\( E_H \) is the measured half-cell potential against a standard hydrogen electrode (in contrast to use of a saturated calomel reference electrode as typically measured in the laboratory).

If the oxidized and reduced species (i.e., Fe\(^{3+}\) and Fe\(^{2+}\)) are both at unit activity\(^{16}\), than \( E = E^0 \) and \( pE = pE^0 \) at the stated temperature (usually 25 C). Values for \( pE^0 \) are available in standard tabulations (Pourbaix, 1963; Sillen and Martell, 1964). For conditions where the oxidized and reduced species are not at unit activity (which is typically the situation for leachates and other real aqueous solutions), then the value for \( pE \) can be calculated as follows:

\[
pE = pE^0 + \frac{1}{n} \log \left( \frac{[\text{oxidized species}]^a}{[\text{reduced species}]^b} \right)
\]

where \( a \) and \( b \) are the reaction stoichiometric coefficients for the redox half reaction and \( n \) is the number of electrons transferred.

The redox conditions for water are limited by the following oxidation and reduction reactions and resultant constraints:

**Oxidation**

\[
2H_2 \leftrightarrow O_2 + 4H^+ + 4e^- \\
\frac{3}{4}O_2 + H^+ + e^- \leftrightarrow \frac{1}{2}H_2O
\]

\[
pE^0 = 20.75 \quad \text{(at } 25 \text{ C})
\]

\[
pE = pE^0 + \log \left( \frac{P_{H^+}^{1/4}}{P_{O_2}^{1/2}} \right), \text{ assuming the partial pressure of oxygen, } P_{O_2} = 1
\]

\[
pH + pE = 20.75
\]

---

\(^{15}\) In the laboratory, \( E_H = E_{\text{measured}} + E_{\text{reference electrode}} \) where \( E_{\text{reference electrode}} \) is dependent on the type of reference electrode used.

\(^{16}\) Activity is the thermodynamic effective concentration in solution considering ion-ion interactions. In dilute solutions, activity is approximately equal to concentration, and unit activity is equal to a concentration of 1 mole/L.
However, in equilibrium with atmospheric oxygen, $P_{O_2} = 0.21$ and therefore

$$\text{pH} + \text{pE} = 20.59 \text{ (at 25 C)}$$

**Reduction**

$$2\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{H}_2 + 2\text{OH}^-$$

$$\text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{H}_2 \quad \text{pE}^0 = 0.00 \text{ (at 25 C)}$$

$$\text{pE} = pE^0 + \log([\text{H}^+])$$

$$\text{pH} + \text{pE} = 0 \text{ (at 25 C)}$$

The oxidation and reduction constraints imposed by the stability of water impose a plausible domain of pH + pE between 0 (fully reduced) and 20.75 (fully oxidized) as illustrated in Figure 2-12.

The actual redox of a system results from the combined effects of oxygen supply (i.e., atmospheric exchange, often limited by diffusion or barometric changes), oxygen consumption by microbial respiration and oxidation of organic matter (i.e., POM and DOC), anaerobic microbial respiration and fermentation (i.e., nitrate reduction (pE$^0$=21.05), iron reduction, sulfate reduction (pE$^0$=4.13) and carbonate reduction (pE$^0$=2.87), and/or the presence of reducing inorganic solid phases (i.e., sulfides, iron) which often result from high temperature processing (i.e., in slags from steel and iron production). Thus, reducing conditions in the field can result as a consequence of either the material being managed or imposed as a consequence of microbial processes and limited oxygen supply. Organic matter (i.e., POM and DOC) that provides the substrate (i.e., food source) for microbial processes can either originate from the material being managed (i.e., MSW, MSWI bottom ash, soils) or from external sources (i.e., decay of leaf litter or commingling of materials). During laboratory pH dependent testing (i.e., Method 1313), oxidizing to mildly reducing conditions (i.e., pH+pE ≥ 13) are most often present because of aerobic handling of materials and use of nitric acid to adjust pH, although more reduced conditions may result from highly reducing materials such as blast furnace slag. Percolation column testing (i.e., 1314) can result in an evolving redox condition as the test progresses for materials containing significant amounts of organic matter because initial conditions are oxic while microbial activity can deplete oxygen and produce reducing conditions as the test progresses over several days. The potential for redox changes should be considered when evaluating laboratory testing results and field scenarios. Consideration of potential effects of reducing conditions is most readily accomplished through sensitivity evaluation as part of chemical speciation modeling because accurate control of redox conditions in the laboratory presents many challenges that go beyond the capabilities of many commercial laboratories. Examples of using sensitivity analysis as part of chemical speciation modeling (i.e., varying the simulated conditions over a range of pH+pE values) is included in the discussion of many of the laboratory to field comparison cases in subsequent sections.

The relationship between pH and pE that results in the formation of a particular mineral phase depends on the stoichiometry of the reaction, and whether or not H$^+$ (or OH$^-$) is involved in the reaction as well as electron transfer (which is inherent in a redox reaction). For example, the reduction of iron according the reaction
\[
\text{Fe(OH)}_3(s) + 3H^+ + e^- \leftrightarrow \text{Fe}^{2+}_{(aq)} + 3H_2O
\]

includes the reduction reaction of \(\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}\), \(pE^0 = 13.2\) (at 25°C).

This results in the relationship for the observed Fe activity in solution (where activity is approximately equal to concentration in dilute solutions),

\[
3pH + pE = 17.16 - [\text{Fe}^{2+}].
\]

Within the discussion included in this report, the following redox reactions are important:

1. Iron reduction from \(\text{Fe}^{3+}\) to \(\text{Fe}^{2+}\) because \(\text{Fe}^{3+}\) in the form of hydrous ferric oxide (HFO) provides adsorptive surfaces for many species, thus impacting LSP. \(\text{Fe}^{2+}\) is relatively soluble at neutral to mildly acidic pH, while \(\text{Fe}^{3+}\) is essentially insoluble over the same pH range, so reduction of \(\text{Fe}^{3+}\) to \(\text{Fe}^{2+}\) results in increased solution concentrations of Fe and loss of adsorption of other constituents from solution to HFO surfaces, increasing the solution concentrations of these constituents. A predominance diagram, which is a presentation of the predominant speciation of a constituent (solid phases or dissolved phases as indicated by charged species) as a function of pH (x-axis) and \(pE\) (y-axis), is provided for iron (0.1 M) in the presence of sulfate (0.1 M) in Figure 2-12. The precise speciation, precipitated phases and transitions reflected in a predominance diagram is dependent on the presence and overall content of multiple constituents in the simulated system (i.e., iron, sulfate, carbonate, calcium, etc. usually reflected as a molar concentration (M) in the unit solid plus liquid simulated volume) and therefore simple systems are used here to illustrate general phenomena.

HFO predominates as the solid phase controlling iron solubility transitions to other phases between pH+pE between 5.5 and 4 at neutral to alkaline pH (orange region), becomes soluble \(\text{Fe}^{2+}\) between pH+pE between 5.5 and 13 and pH less than 7 (aqua region) and become completely solubilized at pH+pE greater than 4 and pH less than ca. 2.5. Iron precipitates with sulfide (produced from the concurrent reduction of sulfate) begins to form at pH+pE of 5.5 and predominates at pH+pE below approximately 4.

2. Sulfate reduction to sulfide (i.e., \(S^{2-}\) to \(S^-\) or \(SO_4^{2-}\) to \(HS^-\)) results in the precipitation of other constituents (i.e., Fe, Cu) as sulfide minerals that are relatively insoluble. The relationship between the sulfur species can be written as (Stumm and Morgan, 1996)

\[
\text{SO}_4^{2-} + 9H^+ + 8e^- \leftrightarrow \text{HS}^- + 4H_2O
\]

which results in the relationship

\[
1.125pH + pE = 1/8\log[\text{SO}_4^{2-}] - 1/8\log[\text{HS}^-]
\]

Figure 2-13 presents a Pourbaix diagram for sulfate (0.1 M) in the presence of iron (0.1 M). The aqua region (pH+pE greater than 5.5 and pH greater than ca. 3 indicates dissolved sulfate as the predominant speciation, while the red region that begins at pH less than 7 indicates a domain where reduced iron (Fe\(^{2+}\)) precipitates as iron sulfide (FeSO\(_4\)). At pH+pE less than 5.5 sulfate becomes reduced to sulfide and precipitates as iron sulfide species. In contrast, Figure 2-14, presents a predominance diagram for sulfate (0.1 M) in the presence of iron (0.1M) and now also with calcium (0.1 M). The addition of calcium to the system results in the formation of anhydrite (CaSO\(_4\) or gypsum, indicated by a blue region) which
limits the availability of sulfate to precipitate with iron (iron sulfate now only forms in a very small region indicated in orange).

3. Figure 2-15 presents a predominance diagram for arsenic (0.1 M) in the presence of sulfate (0.1 M). Arsenic is present in aqueous solutions as As(V) in the form of H$_2$AsO$_4^-$, HAsO$_4^{2-}$ or AsO$_4^{3-}$ (aqua, light green and light blue regions) and as As(III) in the form of H$_2$AsO$_3^-$ or HAsO$_3^{2-}$ (dark green regions), depending on the pH and pE of the system. At pH+pE less than 5.5, arsenic speciation transitions to As(III) precipitated with sulfide as the mineral orpiment (brown-gray region). Arsenic also precipitates with calcium and is adsorbed onto HFO surfaces when present (not included in Figure 2-15).

4. Figure 2-16 presents a predominance diagram for chromium (0.1 M). Reduction of Cr$^{6+}$ (usually as CrO$_4^{2-}$ in solution, light aqua region) to Cr$^{3+}$ dramatically changes Cr solubility at slightly acid to slightly alkaline pH, where Cr$^{3+}$ as Cr(OH)$_3$ is relatively insoluble near neutral pH (dark green region) while CrO$_4^{2-}$ is very soluble. Cr$^{3+}$ is soluble at both alkaline pH (as CrO$_2^-$, light green region) and acidic pH (as Cr(OH)$^{2+}$, light olive region, or Cr$^{3+}$, light green region).

5. Figure 2-17 presents a predominance diagram for copper (0.1 M) in the presence of sulfate (0.1 M). Copper redox reactions result with complex set of potential solid phases with the primary Cu reduction being:

$$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^{+} \quad \text{pE}^0 = 2.59$$

6. At pH+pE greater than 13, copper precipitates as tenorite (CuO) from over a wide pH range (dark blue region) or at pH+pE between approximately 5.5 to 13 as cuprite (Cu$_2$O). However, Figure 2-17 can be misleading because copper readily forms solution complexes with dissolved organic carbon (i.e., humic substances) and therefore much higher solution concentrations of copper are observed at near neutral pH in systems with significant amounts of organic carbon (i.e., soils and wastes) as discussed in later sections of this report. At pH+pE less than ca. 6, copper precipitates as sulfide mineral phases such covellite (CuS) and as Blaublei II (mix of CuS and Cu$_2$S).

7. For vanadium, multiple valence states and complex solution species are possible, with V(V) being the dominant valence state and present in solution as HVO$_4^{2-}$, HVO$_3^{3-}$, H$_3$V$_2$O$_7^-$ and VO$_2^+$ over alkaline to acidic pH, respectively (Figure 2-18). V(IV) as VO$_2^+$ (gray region) and V(III) as V$^{3+}$ (light gray region) also can be present in solution at acidic reducing conditions.
Figure 2-12. Predominance diagram for iron (0.1 M) in the presence of sulfate (0.1 M).

Figure 2-13. Predominance diagram for sulfate (0.1 M) in the presence of iron (0.1 M).
Figure 2-14. Predominance diagram for sulfate (0.1 M) in the presence of iron (0.1 M) and calcium 0.1 M).
Figure 2-15. Predominance diagram for arsenic (0.1 M) in the presence of sulfate (0.1 M).

Figure 2-16. Predominance diagram for chromium (0.1 M).
Figure 2-17. Predominance diagram for copper (0.1 M) in the presence of sulfate (0.1 M).
2.3 Relationships Between Results from the LEAF Leaching Tests

2.3.1 Equilibrium-based Leaching Tests

Eluate constituent concentrations from batch equilibrium-based leaching tests (e.g., Method 1313, Method 1316) should be consistent under the same test conditions within the range of documented inherent test variability (see Garrabrants et al., 2012a, 2012b). Therefore, COPC concentrations in the pH-dependent extraction at natural pH and L/S=10 mL/g are expected to be the same as COPC concentrations in an L/S-dependent extraction of the same material at L/S=10 mL/g. This can be demonstrated by plotting both pH- and L/S-dependent results as a function of eluate pH as shown in Figure 2-19 for leach testing of a contaminated smelter plant soil using Method 1313 and Method 1316.

The results of percolation tests may represent equilibrium between the solid and liquid phases or mass transfer of constituents from solid particles depending on test conditions (e.g., flow rate, column geometry, etc.). Initial interpretation of column percolation test results can be made based on the following:

- The two first eluate fractions collected as part of a percolation test, at cumulative L/S=0.2 and 0.5 mL/g-dry, provide a good estimate of constituent concentrations in the material porewater because of the pre-equilibration of the system prior to beginning eluent flow.
These two fractions also provide a useful estimate of the maximum expected initial leachate concentrations and porewater composition under field monofill conditions. The constituent release measured in the first two eluate fractions collected as part of a percolation test (i.e., Method 1314) also are comparable to the L/S=0.5 mL/g-dry eluate collected as part of the L/S dependence test (i.e., Method 1316), while the integrated concentrations measured in the first two eluate fractions of Method 1314 are comparable to the L/S=0.5 mL/g-dry eluate collected as part of Method 1316. For both tests, the system composition is similar because little elution has occurred from the column at low L/S.

- For constituents that follow Response 2 LSP (i.e., highly soluble constituent), the cumulative release from the percolation test at cumulative L/S=10 mL/g-dry should be comparable to the release observed at the natural pH of the material from the pH-dependence test (i.e., Method 1313; see Lopez Meza, 2008) and at L/S=10 mL/g for the L/S dependence test (i.e., Method 1316) because the system is relatively dilute under the batch conditions of the pH-dependence test and the L/S dependence test at L/S=10 mL/g and, therefore, interactions with other ions (e.g., ionic strength effects) often are not significant. Furthermore, the eluate concentration curve should follow “first flush” phenomena with a large decrease (i.e., one or more orders of magnitude) in eluate concentration by cumulative L/S=2 mL/g.

- For many Response 2 constituents, the release curve of the L/S-dependent leaching test appears to gradually approach a constant value. Often, the level of this asymptotic behavior roughly corresponds with the available content derived from the maximum of the pH-dependent leaching curve (see example boron release in Figure 2-19). Such behavior indicates a release-limiting case where the available content, or majority of the available content, has been released from the solid material.

- For constituents that follow Response 3 LSP (i.e., aqueous saturation), the percolation test eluate concentration is approximately constant as a function of cumulative L/S if the eluate pH is constant. The percolation test eluate concentration also should correspond with the pH-dependence test eluate concentrations at the corresponding eluate pH values. The resulting percolation test cumulative release curve has a slope of approximately 1.

- For constituents that follow Response 4 LSP (i.e., surface interaction), the percolation test eluate concentration profile will be variable between the profile observed for Response 2 and Response 3 LSP as described above because of adsorption-desorption partitioning which may result from either a linear or non-linear isotherm depending on the constituent, concentration and competing constituents. Similarly the slope for the cumulative release will be between that of Response 2 LSP and less than 1.

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17 Lower initial field leachate concentrations may be observed because of a greater extent of preferential flow or flow channeling under field conditions.

18 According to the Davies equation for activity coefficients (Sawyer et al, 2003), the impact of ionic strength effects will be less than 20 percent of the measured concentration for an individual constituent if the ionic strength of the solution is less than 0.06 M for monovalent ions and less than 0.002 M for divalent ions.
Figure 2-19. Comparison of eluate concentration (left) and release (right) for a Response 2 highly soluble species from pH-dependent (Method 1313) and L/S dependent (Method 1314 and Method 1316) leaching tests.
Further interpretation of percolation test results can be divided into understanding (i) the mass transfer behavior and (ii) the LSP behavior of constituents in the material during elution. The mass transfer behavior of a column is most easily determined based on the elution behavior of constituents that are highly soluble and have little pH-dependent leaching behavior (i.e., Response 2 from above). Thus, sodium, potassium or chloride often is the constituent selected to evaluate the mass transfer behavior observed based on results of a column test.

2.3.2 Mass Transfer-based Leaching and pH-dependent Leaching

Mass transfer-based leaching tests (e.g., Method 1315) are designed to measure the rate of mass transfer through the solid material to the bulk solid-liquid interface. Slow surface dissolution and/or internal resistance to constituent migration to the surface of the monolithic material reduces the leaching rate, which can be further reduced because of different chemical conditions within the matrix (i.e., pH, composition) than present at the surface-leaching fluid interface. Method 1315 is intended to assess the rate at which this occurs. A critical aspect of these tests is that the driving force for mass transfer (i.e., the concentration gradient between the solid and the bulk liquid phase) is maintained. Therefore, COPC concentrations in the bulk liquid phase should not approach equilibrium at the eluate pH value.
A first-order evaluation of whether or not the bulk liquid phase of a mass transfer-based leaching tests is at equilibrium is to compare eluate concentrations to the pH-dependent leaching data for the same material as a function of pH (Figure 2-21). Mass transfer data visually below the pH-dependent leaching curve indicates that equilibrium is not achieved during the leaching intervals of the mass transfer test. For most constituents of environmental concern, the example data shown for arsenic, cadmium, and boron in Figure 2-21 are typical when the leaching intervals specified in Method 1315 are followed. This comparison for constituents of the primary mineral phases of the material (e.g., calcium in the cement-based stabilized waste analog as shown in Figure 2-21) may appear to indicate that concentrations in the bulk liquid approach equilibrium; however, the results may reflect dissolution of minerals at the surface rather than mass transport through the material.

Figure 2-21. Comparison of mass transfer-based leaching data (single points) to pH-dependent leaching data (continuous series) as a check against equilibrium in the bulk liquid phase of the mass transfer test. Data is shown for a contaminated smelter site soil (CFS; top) and a solidified waste analog (SWA; bottom).
2.4 Relationships between LEAF Test Results and Single Batch Extractions

Many of the current leaching tests used to assess leaching from solid materials are single-batch extraction tests in structure. Thus, each test yields a single result for each COPC so that the result is limited to the test conditions under which the data point was derived. However, under the assumption that the single batch extraction obtains equilibrium over the extraction interval and if the pH of the final eluate solution is recorded, the results of single-batch tests may be compared to LEAF test results by plotting the results as a function of pH. In Figure 2-22, the results of Method 1313 and Method 1316 testing for a contaminated smelter site soil (CFS) and a solidified waste analog (SWA) are compared to the results of EPA leaching tests that are currently used for leaching evaluation, TCLP and SPLP. In order to compare these data, the procedure for TCLP (EPA Method 1311) and SPLP (EPA Method 1312) had to be modified to include recording of the final eluate pH.

![Graphs showing comparisons between LEAF test results and single-batch extractions for CFS and SWA](image)

Figure 2-22. Comparison of single-batch extractions (i.e., TCLP and SPLP) to pH- and L/S-dependent leaching results for a contaminated smelter site soil (CFS; top) and a solidified waste analog (SWA; bottom).

19 For example, TCLP specifies contacting particle size reduced material with a maximum particle size of 9.5 mm with either a NaOH buffered or unbuffered acetic acid leaching solution at an L/S of 20 mL/g-dry over an 18 hour period while SPLP specifies a similar particle size, L/S and duration conditions with a dilute nitric/sulfuric acid solution.
When compared to the LEAF test results, single-batch extraction results (e.g., TCLP and SPLP) often appear as another point along the pH-dependent trendline. For Response 2 species, TCLP and SPLP concentrations plot slightly below the pH-dependent trendline and are consistent with the increased L/S of the single batch tests. Species that follow solubility-controlled release (i.e., Response 3 species) have TCLP and SPLP data consistent with the pH-dependent trendline. Although the comparisons between single batch extractions and characteristic leaching tests are useful in interpreting COPC behavior, the single batch extraction data alone do not provide enough information to support such observations and therefore limit the ability to provide insight into leaching behavior for the broad set of disposal or utilization scenarios.

2.5 Determination of Constituent Availability

As discussed in Section 2.1.1, the amount of a constituent that partitions into the aqueous phase can be limited either by (i) the solubility of the constituent at the test conditions (resulting in a saturated solution at solid-liquid equilibrium), (ii) adsorption-desorption equilibrium partitioning between the aqueous solution and solid phases (i.e., sorption onto particulate organic matter or hydrous ferric oxide (HFO) surfaces), or (iii) the maximum leachable amount of the constituent. The maximum leachable amount may be either the total content, or often only a limited fraction of the total content because of constituent sequestration in relatively non-leachable phases such as durable glass phases or very poorly soluble alumina-silicate phases. Here, the maximum leachable quantity is referred to as the constituent availability. To measure or estimate constituent availability, test conditions must be established such that the aqueous phase solubility and adsorption processes do not limit leaching. Conditions to estimate availability can be established in test conditions either through (i) very large liquid-to-solid ratio, (ii) multiple extractions, (iii) use of chelating agents (e.g., EDTA) to increase aqueous solubility, or (iv) use of fundamental pH-solubility properties to select conditions of high solubility. Each of these approaches have been used with comparable results (NEN 7371, 2004; Garrabrants and Kosson, 2000; van der Sloot et al., 1997; Lopez Meza et al., 2008). From a practical perspective, it has been useful to integrate determination of constituent availability with pH dependence leaching (i.e., Method 1313). Constituent availability can be estimated from Method 1313 by selecting the maximum mass leached of each constituent over the pH domain from pH of 2 to 13. Most cationic elements will reach a plateau in leaching as pH decreases between pH 4 and 2. At pH 2, HFO phases are dissolved, resulting in leaching of adsorbed constituents. Most metal hydroxides (amphoteric constituents) will have a maximum solubility either at pH of 2 or approximately 13. Oxyanionic species (e.g., arsenate, molybdate, chromate) will have maximum solubility at mildly alkline pH (i.e., pH 9 – 10). Thus, the pH value at which availability is estimated will be constituent dependent.
3 CHEMICAL SPECIATION AND MASS TRANSPORT MODELING AS INTERPRETATION TOOLS

Often, leaching tests are used to characterize samples of materials that are either to be placed into a field scenario or material samples that are obtained from a field test location. However, understanding of field leaching behavior frequently requires consideration of the changes in material leaching over time due to aging of the material and/or due to release conditions that are representative of the field scenario, but are not readily reproduced in the laboratory. Material aging phenomena may include reaction with species from the surrounding environment (e.g., oxygen, carbon dioxide, sulfate), depletion of primary species through leaching (e.g., loss of calcium hydroxide from cementitious materials), and changes in the physical nature of the material (e.g., cracking). Scenario conditions that cannot be easily reproduced in the laboratory but may affect leaching include low L/S ratios, changes in chemical oxidation-reduction state (e.g., from either biotic or abiotic processes), and the presence/extent of preferential flow pathways.

One approach toward integrating aging phenomena and scenario conditions into the understanding of material leaching behavior is through the use of numeric models designed to simulate chemical speciation or reactive transport of COPCs for defined release conditions. Chemical speciation models simultaneously solve the chemical thermodynamic and kinetic equations representing the material mineralogy/adsorption/aqueous interaction reactions that allow for evaluation of equilibrium liquid-solid partitioning as a function of material and fluid phase composition, pH and redox state. The effects of physical parameters (e.g., monolithic nature of materials that divert infiltration or preferential flow during percolation) may be evaluated through coupling of the results of chemical speciation models with mass transport models, often called reactive transport models. Thus, chemical speciation and reactive transport models can be useful tools to prospectively or retrospectively evaluate (i) conditions not practically achievable in the laboratory on material leaching behavior, (ii) the aging of materials under factors that historically control leaching in the field, and (iii) integration between laboratory and field leaching data.

Using these tools, useful simulations of LSP and mass transport leaching are achievable for a wide range of materials to evaluate the impacts of varying laboratory and field conditions using idealized conceptual models. Interpretation of leaching data using chemical speciation and reactive transport models has been advanced by the development of extended thermodynamic databases and the evolution of descriptions of chemical interactions with reactive surfaces. However, like all numeric models, the results of these models are limited by the state of current knowledge or the availability of accurate data for the materials being tested (e.g., see Sarkar et al, 2012). For leaching assessment purposes, areas where limits in current knowledge or available data may increase uncertainty in chemical speciation and reactive transport model results include:

- chemical speciation of solid phases in materials and wastes;
- aqueous solution characteristics (e.g., dissolved or colloidal organic matter);
- thermodynamic data for solid mineral phases;
- adsorption onto solid surfaces;
- solution conditions (e.g., very high ionic strength solutions);
• physical mass transport conditions.

3.1 Modeling and Simulation Approach

Laboratory leaching test results from pH dependent leaching (i.e., Method 1313 or PrEN 14429) is used 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 (often referred to as “availability”). The resulting CSF may be used in conjunction with the results of L/S-dependence tests (e.g., Method 1316, EN 12457) to assess the impact of low L/S ratios on LSP or with percolation column tests (e.g., Method 1314, CEN/TS 14405, CEN/TS 16337-3) or mass transport (e.g., Method 1315, PrEN 15863, CEN/TS 16337-2) 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 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.

3.2 Chemical Speciation and Reactive Transport Modeling in LeachXS

Recent developments in chemical speciation codes such as ORCHESTRA (Meeussen, 2003), MINTEQA2 (Allison et al., 1991), PHREEQC (Parkhurst, 1995), Geochemist’s Workbench (Lee and Goldhaber, 2011) allow calculation of multi-element equilibrium concentrations based on available thermodynamic data and may include coupling with mass transport models.

The software package LeachXS™, used for data management and chemical speciation based simulations in this report, has the ORCHESTRA code embedded as the chemical speciation and reactive transport code for modeling experimental results and the chemical behavior of materials in specific application scenarios. ORCHESTRA can calculate chemical speciation in thermodynamic equilibrium systems using the same thermodynamic database format as PHREEQC or MINTEQA2, but also contains state-of-the-art adsorption models for oxide and organic surfaces as well as the ability to handle dissolution/precipitation of solid solutions.

Underlying chemical speciation models incorporate current knowledge about the chemical interactions between major, minor trace elements, such as mineral dissolution/precipitation, ion exchange, sorption and incorporation in solid solutions that result in the concentrations of elements in solution at liquid-solid equilibrium as a function of pH or L/S based on initial solid and liquid phase composition and redox state. A set of solid phases (i.e., minerals, solid solutions, adsorptive surfaces) and reactions (i.e., dissolution/precipitation, adsorption/desorption, reaction with carbon dioxide) in the form of reaction equations with corresponding thermodynamic equilibrium constants are solved simultaneously to calculate liquid-solid partitioning of major, minor and trace constituents including COPCs. Several books are available that describe the fundamentals of
chemical speciation and reactive mass transport modeling (Stumm and Morgan 1996; Appelo and Postma 2005).

In ORCHESTRA, ion adsorption onto organic matter is calculated with the NICA-Donnan model (Kinniburgh et al., 1999) using generic adsorption reactions (Milne et al., 2003). Adsorption of ions onto iron and aluminum oxides was modeled according to the generalized two layer model of Dzombak and Morel (1990). Aqueous speciation reactions and selected minerals were taken from the MINTEQA2 database (Allison et al., 1991). The MINTEQA2 database is internally consistent through use of a common set of primary entities and thermodynamic reference state; additional mineral reactions taken from literature were transformed into the same format by rewriting the reactions using primary entities in LeachXS-ORCHESTRA. For example, more recent thermodynamic data on solid phases relevant to cement, concrete and cement-stabilized waste forms has been obtained from Lothenbach, et al. (2008) and incorporated into the LeachXS-ORCHESTRA models used here. More detail on the use of the chemical speciation code can be found elsewhere (Dijkstra et al., 2006a, 2006b, 2008; Engelsen et al., 2009, 2010, 2012; Carter et al., 2008, 2009; van der Sloot et al., 2000, 2007, 2009, 2011; van der Sloot and van Zomeren, 2012; Sarkar et al, 2010; Sarkar et al., 2011; Sarkar et al., 2012).

3.2.1 Parameterization of ORCHESTRA

The input to the ORCHESTRA model to form a material-specific CSF consists of (i) element availability values, (ii) selected possible solubility-controlling minerals, (iii) definition of the reduction-oxidation state of the material, (iv) description of active Fe- and Al-oxide sites, and (v) a fractionation of organic matter between particular organic matter (POM) and reactive DOC concentration as a function of pH.

Availability
The maximum leached amount (mg of COPC/kg material) derived from pH-dependent leaching test concentrations between pH 2 and 13 is used as the concentration available for interaction under environmental conditions.

Possible Solubility-controlling Minerals
The chemical speciation model is used to generate saturation indices (SIs) for relevant mineral phases based on the eluate concentrations from pH-dependent leaching tests. From these SIs and prior knowledge of the material (e.g., previously identified mineral phases from speciation modeling or from published literature), solubility-controlling minerals are selected for possible inclusion in the definition of a CSF.

Reduction-oxidation State
The reduction-oxidation (redox) state of the material is specified as the sum of the electron activity (pE), which indicates the tendency for a solution to donate or accept a proton and pH. The numerical range for the sum pH+pE is based on the stability of water with values at between 0-20.75 for maximum reducing and oxidizing conditions (Stumm and Morgan, 1996). In pe vs. pH stability charts, this sum defines the upper and lower stability limits. For example, a pH+pE value of 10 represents slightly reducing conditions while a value of 15-16 represents
oxidizing conditions. The values for pH+pE selected for simulation may be either (i) based on measured laboratory or field values (with appropriate care taken to avoid sample changes during measurement and correction for the reference electrode used; see Section 2.2.3), (ii) based on observation of liquid-solid partitioning of iron, manganese and/or chromium as indicator species from field data and laboratory testing, or (iii) treated as a variable that is varied over a plausible range as part of a sensitivity study.

**Reactive Surfaces Description**

The surface area of reactive surfaces present in the solid is required in order to account for sorption of COPCs onto the solid surface. Reactive surface fractions are estimated from independent determinations of the test material or through selective chemical extractions on comparable materials. For example, the amount of amorphous and crystalline iron (hydr)oxide may be determined by a dithionite extraction (Kostka and Luther III, 1994), while amorphous aluminum (hydr)oxide may be determined by an oxalate extraction (Blakemore et al., 1987). In the CSF model, the extracted amounts of Fe and Al were summed and used as a surrogate for hydrous ferric oxides (HFO) as described by Meima and Comans (1998). Determination of HFO by ascorbic acid extraction has been standardized as ISO 12782-1 (2012).

**Organic Matter and Inorganic Carbon Descriptions**

POM and carbonate/bicarbonate content are either measured directly through total carbon analysis or estimated from the titration curve results of pH-dependent leaching tests. The total organic carbon in a solid can be divided into a solid fraction (POM) and a fraction that dissolves as a function of pH (DOC). DOC is available for interaction with COPCs in the eluate; however, the direct analysis of eluate DOC does not completely represent the reactive part of the dissolved organic matter. Based on experience with soil materials where the quantification between the hydrophilic fulvic, and humic acid fraction in DOC was estimated (van Zomeren and Comans, 2007), the reactive fraction of DOC is defined either as a constant value independent of pH or as a function of pH (i.e., with the lowest proportion of reactive forms at neutral pH and increasing towards both low and high pH). In the latter situation, a polynomial fit is created through eight data points to allow quantification of the reactive DOC at intermediate pH values in modeling (van Zomeren and Comans, 2007). Thus, the reactive component of the DOC used in chemical speciation modeling is parameterized as the solid humic acid (SHA) which represents the sum of the fulvic and humic fractions. In accordance with van Zomeren and Comans (2007), SHA is either (i) quantified by fractionation POM or (ii) assumed to be 20% of the total DOC, in case no data for the particular material were available.

Using the information specified above in conjunction with available prior knowledge of the material (such as previously identified mineral phases from speciation modeling or from published literature), the speciation of all elements is calculated in one problem definition in the Laboratory Simulation pH-Dependence Leaching Test model with the same parameter settings. This method of calculation limits the degrees of freedom in selecting parameter settings considerably, as improvement of the model description for one element may deteriorate the outcome for other elements.
3.3 Simulations in LeachXS

3.3.1 Laboratory Test Simulations

Laboratory testing results are used to calibrate and verify models (i.e., “laboratory simulations”) that then can be used for estimating system responses under anticipated field conditions. The specific types of simulation models currently included in LeachXS are as follows:

Chemical Speciation and Solubility Indices
Solubility index for possible minerals are evaluated in comparison to LSP data obtained from pH-dependent tests or L/S-dependent test for initial identification of relevant mineral phases based on LSP data.

pH-dependence Test and LSP Simulation
Based on identified mineral phases and other parameters (e.g., availability values, carbon fractionation, etc.), a CSF is developed to simulate results obtained from pH dependence tests. The parameters of this model can be varied to assess changes to LSP due to L/S (e.g., low L/S ratios found in field conditions), solution chemistry (e.g., high ionic strength solutions in cementitious materials), redox conditions (e.g., oxidation of reductive materials), the amount of iron hydr(oxide) and clay surfaces available for sorption, and the amount/fractionation of particulate organic matter (POM) and DOC.

Monolith Leaching and Mass Transport Rate Test Simulation
The CSF may be combined with diffusion models to determine mass transport parameters (e.g., effective tortuosity values, diffusivity) based on results from mass transport tests. The mass transport model segments a monolithic solid (i.e., a true monolithic form or a compacted granular material compacted to act like a monolith) into a series of layers from the external boundary to the interior core (Figure 3-1). Within each layer, the monolith segment is divided into aqueous and solid phases defined by the CSF. Local equilibrium between phases in the segment is calculated at each time step to account for changes in pH and local composition based on dissolved constituent mass transport between the layers by diffusion through the liquid phase. The external surface of the monolith is simulated as being in contact with a well-mixed bath of finite volume which is refreshed at time intervals defined by the leaching test conditions (e.g., Method 1315). This laboratory simulation model also can be used to evaluate the impacts to release rates from changes in eluate volume, eluate chemistry (e.g., influx of acid or sulfate attack), and layering of material composition and properties within a monolith (e.g., a carbonated surface layer with an un-carbonated core).
Percolation Test Simulation (mobile-immobile zones)
The CSF and percolation parameters may be used to evaluate the results of percolation column tests using the conceptual model of mobile and immobile zones. The conceptual model (Figure 3-2) consists of two zones segmented along the flow path, with one zone containing a mobile fluid phase in local equilibrium with the solid phase and the second zone containing an immobile fluid phase in local equilibrium with the solid phase. Within each column segment, each of the mobile and immobile zones are well mixed (i.e., uniform distribution of constituents within each of the solid phase and liquid phase orthogonal to the flow direction), and the mobile and immobile zones exchange dissolved constituents based on a mass transfer coefficient that can be considered an effective diffusion distance (van Genuchten and Dalton, 1986). This model is insensitive to percolation flow rate because homogeneity within the immobile zone is assumed. This model can be used for a first-order approximation of the effects of preferential flow in a percolation system, as well as the impacts of changes in redox and influent solution chemistry on the leaching of constituents.

Figure 3-1. Mass transport model (laboratory simulation) scenario.
Figure 3-2. Conceptual model of percolation with mobile and immobile zones shown for soil aggregates (left; van Genuchten and Dalton, 1986) and as a 1-dimension approximation in ORCHESTRA (right).

Percolation Test Simulation (percolation-radial diffusion)

The CSF and percolation parameters also may be used for evaluation of percolation column test results using the conceptual model of percolation with radial diffusion from porous solid particles. The conceptual model (Figure 3-3) consists of two zones segmented along the flow path, with one zone containing a mobile fluid phase in local equilibrium with the solid phase and the second zone containing porous spheres with an immobile fluid phase (in contrast to the previous model using an immobile zone which was well mixed). Mass transport within the spheres occurs by diffusion through the fluid phase with the boundary condition of equal fluid composition at the interface between the sphere surface and the mobile zone, and no diffusion at the center of the spheres (van Beinum et al., 1999; Sarkar et al., 2013). Thus, fluid phase constituents can diffuse into and out of the spheres based on concentration gradients, and within the spheres local solid-liquid equilibrium is maintained at each radial layer within the sphere. Within each column segment, each of the phases in the mobile zone are well mixed (i.e., uniform distribution of constituents within each of the solid phase and liquid phase orthogonal to the flow direction) and in local equilibrium between the solid and liquid phases. This approach is more accurately reflective of systems where the diffusion gradients within the immobile zone control release to the mobile zone. Thus, this model is sensitive to overall percolation flow rate and can be used to reflect the impact of fast infiltration that does not reach complete equilibrium between mobile and immobile zones. This model can also be used to evaluate leaching under the effects of preferential flow, cracking in monoliths, varying flow conditions (e.g., intermittent flow, different flow rates), and solution chemistry.
Figure 3-3. Conceptual model of percolation with radial diffusion in the immobile zone (Sarkar et al., 2013) shown as an up-flow column (left) and as flow through cracks in concrete (right).

3.3.2 LeachXS Field Test Simulations

In the different cases of laboratory to field evaluation data obtained from the field after a certain time of exposure to leaching under field conditions can be modeled just as was done for the laboratory test data. Results from laboratory testing and simulations described above can be used to parameterize the simulations for field scenarios and thus form a predictive estimate of field leaching under a range of conditions (i.e., “prediction scenarios”). Simulations of field scenarios illustrate the extent to which differences in field conditions compared to laboratory testing (i.e., contact water amounts and composition, and preferential flow) and changes in field conditions as a result of aging impact observed field leaching behavior. An illustration of this approach follows a description of prediction scenarios. For the illustration, the field data obtained in the pilot study on stabilized municipal solid waste incinerator (MSWI) scrubber residues (see Section 4.9) have been modelled using the same CSF as derived from the lab data. The main difference in this case is the higher carbonate level in the field exposed samples.

3.3.3 LeachXS Prediction Scenario Models

Monolithic Diffusion Prediction Scenarios

- Leaching – one dimensional diffusion from a monolith where system size, material layers, time frames, water contact and composition at the boundary can be varied to represent field scenarios. Unsaturated cases also can be simulated but without consideration of gas phase transport and reaction processes (e.g., oxygen or carbon dioxide gas phase transport and reaction).

- Leaching with Carbonation and Oxidation – analogous to the Leaching model above, but also allows for consideration of gas phase transport and reaction processes to consider impacts of carbonation and oxidation (Brown et al., 2013).
- Sulfate Attack with Leaching – this simulation allows coupling of physical degradation through sulfate attack on cementitious materials with leaching (Sarkar et al, 2010, 2012).

**Percolation Prediction Scenarios**

- Mobile-Immobile Zones Dual Regime Leaching – this simulation is analogous to the percolation column test (mobile-immobile zones) model but with adaptation appropriate for evaluating field scenarios (van Genuchten and Dalton, 1986).

- Percolation with Radial Diffusion Leaching – this simulation is analogous to the percolation column test (percolation with radial diffusion) model but with adaptation appropriate for evaluating field scenarios (Brown et al., 2013; Sarkar et al., 2013).

### 3.4 Example of Model Development for a Stabilized Waste Material

The chemical speciation and reactive transport models described earlier are illustrated through application to cement-stabilized MSWI bottom and fly ash as described in Section 4.9. The data used in laboratory simulation and field simulation modeling is shown in Table 3–1 through Table 3–3 and includes (i) the model parameters from the pH-dependence, percolation and monolith models (Table 3-1), (ii) the availability data used to parameterize the CSF (Table 3-2), and (iii) the CSF mineral phases derived from saturation indices in conjunction with pH-dependent leaching test data (Table 3-3). Extensive literature on cement-stabilized materials and cements is available (van der Sloot et al., 2007; van der Sloot et al., 2011) and provides initial indications of the solid mineral phases that are applicable to the major components of the stabilized waste. However, most often very limited, if any information, is available with respect to identification based on direct measurements of the mineral phases controlling release of the trace constituents because they are present below the detection limits of available analytical instruments. As a result, the controlling mineral phases for COPCs must be inferred from the LSP as a function of pH and L/S.
Table 3-1. Model Parameters for CSF Definition for Stabilized MSWI waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH-dependent Model</th>
<th>Percolation Model</th>
<th>Monolith Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>L/S</td>
<td>10</td>
<td>varies</td>
<td>NA</td>
</tr>
<tr>
<td>Fraction DOC</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>pH+pE</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Clay (kg/kg)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HFO (kg/kg)</td>
<td>1x10⁻⁴</td>
<td>1x10⁻⁴</td>
<td>1x10⁻⁴</td>
</tr>
<tr>
<td>SHA (kgSHA/kgTOC)</td>
<td>2x10⁻⁴</td>
<td>2x10⁻⁴</td>
<td>2x10⁻⁴</td>
</tr>
<tr>
<td>Porosity</td>
<td>NA</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Density (kg/L)</td>
<td>NA</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Initial pH of Solid</td>
<td>NA</td>
<td>12.1</td>
<td>12.4</td>
</tr>
<tr>
<td>Initial pH of Leachant</td>
<td>NA</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Column Length (cm)</td>
<td>NA</td>
<td>25</td>
<td>NA</td>
</tr>
<tr>
<td>Relative Stagnant Volume (%)</td>
<td>NA</td>
<td>20</td>
<td>NA</td>
</tr>
<tr>
<td>Effective Diffusion Distance (cm)</td>
<td>NA</td>
<td>2</td>
<td>NA</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>NA</td>
<td>NA</td>
<td>1.5</td>
</tr>
<tr>
<td>Specimen Length (cm)</td>
<td>NA</td>
<td>NA</td>
<td>10.9</td>
</tr>
<tr>
<td>Specimen Width (cm)</td>
<td>NA</td>
<td>NA</td>
<td>9.57</td>
</tr>
<tr>
<td>Specimen Height (cm)</td>
<td>NA</td>
<td>NA</td>
<td>9.57</td>
</tr>
</tbody>
</table>

Note: NA=data not applicable for the type of model.

Table 3-2 Chemical Availability Values for CSF Definition of Stabilized MSWI Waste

<table>
<thead>
<tr>
<th>Species Name</th>
<th>Availability (mg/kg)</th>
<th>Species Name</th>
<th>Availability (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al⁺³</td>
<td>4,456</td>
<td>Mg⁺²</td>
<td>3,900</td>
</tr>
<tr>
<td>H₃AsO₄</td>
<td>0.15</td>
<td>Mn⁺²</td>
<td>170</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>59</td>
<td>MoO₄⁻²</td>
<td>7.7</td>
</tr>
<tr>
<td>Ba⁺²</td>
<td>19</td>
<td>Na⁺</td>
<td>26,000</td>
</tr>
<tr>
<td>Br⁻</td>
<td>830</td>
<td>Ni⁺²</td>
<td>9.3</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>84,000</td>
<td>PO₄⁻³</td>
<td>4.7</td>
</tr>
<tr>
<td>Cd⁺²</td>
<td>180</td>
<td>Pb⁺²</td>
<td>960</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>54,000</td>
<td>SO₄⁻²</td>
<td>11,000</td>
</tr>
<tr>
<td>CrO₄⁻²</td>
<td>9.7</td>
<td>Sb(OH)₆⁻⁷</td>
<td>4.9</td>
</tr>
<tr>
<td>Cu⁺²</td>
<td>360</td>
<td>SeO₄⁺²</td>
<td>0.46</td>
</tr>
<tr>
<td>F⁻</td>
<td>1,900</td>
<td>H₂SiO₄</td>
<td>3600</td>
</tr>
<tr>
<td>Fe⁺³</td>
<td>74</td>
<td>Sr⁺²</td>
<td>210</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>10,000</td>
<td>VO₂⁺</td>
<td>0.58</td>
</tr>
<tr>
<td>K⁺</td>
<td>34,000</td>
<td>Zn⁺²</td>
<td>8000</td>
</tr>
<tr>
<td>Li⁺</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3-3. Mineral Phases in CSF Definition for Stabilized MSWI Waste

<table>
<thead>
<tr>
<th>Chemical Formula*</th>
<th>Common Name</th>
<th>Chemical Formula*</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>2CaO-Al2O3·8H2O [s]</td>
<td></td>
<td>2CaO-2.4SiO2·3.2H2O</td>
<td>Tobermorite-I</td>
</tr>
<tr>
<td>2CaO-Al2O3·SiO2·8H2O [s]</td>
<td></td>
<td>0.83CaO-SiO2·1.3H2O</td>
<td>Tobermorite-II</td>
</tr>
<tr>
<td>2CaO-Fe2O3·8H2O [s]</td>
<td></td>
<td></td>
<td>Tricarboaluminate</td>
</tr>
<tr>
<td>2CaO-Fe2O3·SiO2·8H2O [s]</td>
<td>Ca3(PO4)2</td>
<td></td>
<td>alpha-TCP</td>
</tr>
<tr>
<td>3CaO·Al2O3·Ca(OH)2·0.5·(CaCO3)·0.5·11.5H2O [s]</td>
<td>Ba[Si,Cr]O4 [77% SO4]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Al2O3·6H2O [s]</td>
<td>Ba,SrSO4 [50% Ba]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Al2O3·CaCO3·11H2O [s]</td>
<td>Ca3(AsO4)2·6H2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Al2O3·CaSO4·11H2O [s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Fe2O3·Ca(OH)2·0.5·(CaCO3)·0.5·11.5H2O [s]</td>
<td>Cd(OH)2 [C]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Fe2O3·6H2O [s]</td>
<td>Cr(OH)3 [A]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Fe2O3·CaCO3·11H2O [s]</td>
<td>Cu(OH)2 [s]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3CaO·Fe2O3·CaSO4·12H2O [s]</td>
<td>FeVO4</td>
<td></td>
<td>Iron Vanadate</td>
</tr>
<tr>
<td>4CaO·Al2O3·13H2O [s]</td>
<td>Fe2O3·0.5H2O</td>
<td></td>
<td>Ferrhydrite</td>
</tr>
<tr>
<td>4CaO·Fe2O3·13H2O [s]</td>
<td>CaF2</td>
<td></td>
<td>Fluorite</td>
</tr>
<tr>
<td>Al(OH)3 [amorphous]</td>
<td>Gibbsite</td>
<td>MgCO3</td>
<td>Magnesite</td>
</tr>
<tr>
<td>CaSO4</td>
<td>Anhydrite</td>
<td>MnO(OH)</td>
<td>Manganite</td>
</tr>
<tr>
<td>Mg(OH)2</td>
<td>Brucite</td>
<td>Ni(OH)2 [s]</td>
<td></td>
</tr>
<tr>
<td>CaCO3</td>
<td>Calcite</td>
<td>Ni2SiO4</td>
<td></td>
</tr>
<tr>
<td>CaO·Al2O3·10H2O [s]</td>
<td></td>
<td>Pb(OH)2 [C]</td>
<td></td>
</tr>
<tr>
<td>Mg6Al2(CO3)(OH)16·4H2O</td>
<td>Hydrotalcite</td>
<td>Pb2V2O7</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)3 [microcrystalline]</td>
<td>Ferric hydroxide</td>
<td>Pb3(VO4)2</td>
<td></td>
</tr>
<tr>
<td>Al(OH)3</td>
<td>Gibbsite</td>
<td>PbCrO4</td>
<td></td>
</tr>
<tr>
<td>CaSO4·2H2O</td>
<td>Gypsum</td>
<td>PbMoO4 [C]</td>
<td></td>
</tr>
<tr>
<td>1.67CaO·SiO2·2.1H2O</td>
<td>Jennite</td>
<td>MnCO3</td>
<td>Rhodochrosite</td>
</tr>
<tr>
<td>MgCO3</td>
<td>Magnesite</td>
<td>SrCO3</td>
<td>Strontianite</td>
</tr>
<tr>
<td>Ca(OH)2</td>
<td>Portlandite</td>
<td>CuO</td>
<td>Tenorite</td>
</tr>
<tr>
<td>SiO2 [am]</td>
<td>Silica gel</td>
<td>Zn2SiO4</td>
<td>Willemite</td>
</tr>
<tr>
<td>K2Ca(SO4)2·H2O</td>
<td>Syntenite</td>
<td>ZnO</td>
<td>Zincite</td>
</tr>
</tbody>
</table>

Note: * - chemical formulae presented in cement-based notation or standard chemical format

For this illustration, the CSF that was developed from the pH-dependent model applied to pH-dependent test data subsequently was used in the percolation model (mobile-immobile zones) and the monolith model to simulate leaching under the conditions of respective percolation column and monolith diffusion tests. Results of the model simulations are provided in Figure 3-4 and Figure 3-5. The initial step toward assessing the simulation accuracy is the ability of the CSF to simulate the system response with respect to eluate pH, a master variable controlling leaching (see Section 2), for the pH dependent test, percolation column test and mass transport tests. In these figures, the pH titration curve is simulated to a high degree using the derived CSF and the eluate pH values for both percolation column and monolith leaching are well represented. For simulation of pH in the column test, peak pH response from the percolation model occurs at a lower L/S value than is indicated from the experimental data, most likely because of a greater amount of axial dispersion in the laboratory column which is not fully accounted for in the model. For the selected COPCs shown
in Figure 3-4 and Figure 3-5, the simulations provide a good representation of the experimental data for all three models, especially considering the uncertainties associated with both experimental data and simulations.

The effect of L/S on the pH-dependent model is shown in Figure 3-6. The results of the initial pH-dependent leaching test simulation at L/S of 10 mL/g-dry (solid, red line) are compared with results of the same CSF and model used to simulate LSP at 0.5 mL/g-dry (blue, dashed line). Also on the same graph, the simulation results are compared with experimental data from the pH-dependence test and percolation column test. Simulation results for Ca with an L/S of 10 mL/g-dry support the pH-dependent leaching data and indicate pH domains where Ca leaching is controlled by solubility (i.e., pH > 12) and by availability (i.e., pH < 12) as explained in Section 2. When the L/S decreases to 0.5 mL/g-dry, a similar pattern with a higher availability but the same solubility control is indicated. In Figure 3-6, this can be observed as the same Ca response for both simulations at pH greater than 12 while the simulation asymptotically approach different concentration values at pH less than 11. The difference in the concentration-based asymptote values is related to the L/S conditions under which the models were conducted (i.e., a similar mass released into less liquid at L/S 0.5 would result in a higher concentration). In contrast, potassium shows the behavior of a highly soluble species that exhibits LSP independent of pH and, therefore, a constant concentration as a function of pH. The pH-dependent model conducted at L/S 10 mL/g-dry is in good agreement with the pH-dependent test data and the simulation at the lower L/S of 0.5 mL/g-dry is in good agreement with the initial fraction observed from the percolation column test (i.e., the fraction collected at a cumulative L/S of 0.5 mL/g-dry). For selenium and molybdenum, the simulation and experimental results illustrate the more complex behaviors that can result as a function of pH and L/S.

For the four COPCs, experimental results for all eluates from the column test, ranging from L/S of 0.5 to 10 mL/g, are presented with the simulation results. When the eluate concentrations fall on the pH dependence curve for a range of L/S values this indicates that aqueous saturation of the constituent is controlling leaching within the column, as is the case for Ca. When initial percolation column test eluate concentrations correspond with the simulated values for the low L/S value (i.e., 0.5 mL/g) followed by continuous decrease in eluate concentration as is indicated for K and Se, this behavior is indicative of constituent release that is controlled by availability and depletion of the available fraction of the constituent as the percolation column test progresses.
Figure 3-4. Comparison of laboratory simulation results for a stabilized MSWI residue (van der Sloot et al, 2007). Multi-element, multi-phase chemical speciation modeling is shown for pH-dependent leaching data (left), percolation test data (middle) and mass transport test data (right).
Figure 3-5. Comparison of laboratory simulation results for a stabilized MSWI residue (van der Sloot et al, 2007). Multi-element, multi-phase chemical speciation modeling is shown for pH-dependent leaching data (left), percolation test data (middle) and mass transport test data (right).
Figure 3-6. Laboratory leaching test simulation shown pH-dependent leaching (model at L/S=10 L/kg) and percolation leaching (model at L/S=0.5 L/kg) for select species in a solidified MSWI residue (van der Sloot et al, 2007).
Figure 3-7. Chemical speciation and phase descriptions as a function of pH for a stabilized MSWI residue conducted on fresh material and aged (4 year) cores. Comparisons include pH-dependent model simulations (upper left), phase description for fresh material (upper right), phase description for aged material (lower left) and liquid phase fraction for fresh material (lower right).

3.5 A Comparison of Copper and Lead Speciation in Several Materials

Figure 3-8 through Figure 3-11 present chemical speciation modeling compared to experimental results of pH dependent leaching for copper and lead from cement mortar, coal fly ash, stabilized waste, municipal solid waste, predominantly inorganic waste, and municipal solid waste incinerator bottom ash. For all cases, the left graph compares the experimental results from pH dependent leaching at L/S=10 mL/g (red dots) and percolation column results, with L/S ranging from 0.2 to 10 mL/g (blue dots), to the modeled aqueous phase concentration at L/S=10 and 0.3 mL/g (red line and blue dashed lines, respectively). The right graph for each case presents the distribution of the constituent concentration in the liquid phase between the amount complexed with dissolved organic matter (DOC-bound, bright green) and other dissolved species (i.e., the sum of free and other complexed species, “Free” indicated in light blue-green), while the remaining colored areas indicate speciation in the solid phase. For the graphs on the right side, the units (y-axis) are moles per liter of the total unit volume (i.e., total volume of solid and liquid phases). The sum of the DOC-bound and the “Free” species is equal to the total dissolved concentration (for either Cu or Pb) as...
Figure 3-8. Geochemical model description of copper at L/S=10 with prediction to L/S=0.3 (left) and partitioning (L/S=10) based on multi-element geochemical speciation modelling (right). Data shown for cement mortar (top), coal fly ash (middle), and stabilized waste (bottom).
Figure 3-9. Geochemical model description of copper at L/S=10 with prediction to L/S=0.3 (left) and partitioning (L/S=10) based on multi-element geochemical speciation modelling (right). Data shown for municipal solid waste (top), predominantly inorganic waste (middle), and MSWI bottom ash (bottom).
Figure 3-10. Geochemical model description of lead at L/S=10 with prediction to L/S=0.3 (left) and partitioning (L/S=10) based on multi-element geochemical speciation modelling (right). Data shown for cement mortar (top), coal fly ash (middle), and stabilized waste (bottom).
Figure 3-11. Geochemical model description of lead at L/S=10 with prediction to L/S=0.3 (left) and partitioning (L/S=10) based on multi-element geochemical speciation modelling (right). Data shown for municipal solid waste (top), predominantly inorganic waste (middle), and MSWI bottom ash (bottom).
modeled at L/S=10 mL/g and indicated on the red line on the respective left side graph. In each right side graph, the remaining colored areas indicate the relative amount of the Cu or Pb associated with specific solid phases over the indicated pH range. For example, dark green indicates adsorption with particulate organic matter and red indicates adsorption onto iron oxide surfaces. For the graphs of Cu partitioning, yellow indicates precipitation as tenorite or copper hydroxide [Cu(OH)₂] depending on the material, while for the lead graphs, yellow indicates precipitation as lead hydroxide [Pb(OH)₂]. Purple indicates co-precipitation with ettringite and red indicates adsorption onto iron (hydr)oxide surfaces.

Examination of Figure 3-8 through Figure 3-11 elucidates several important phenomena:

- The specific chemical species that control LSP varies as a function of pH (as well as pE, as discussed in Section 2.2.3) and material type.

- Comparison of LSP as a function of pH and at different L/S values (i.e., 10 and 0.3 mL/g, left side graphs) provides clear indication of when solubility in solution (i.e., a saturated solution) vs. the amount of a constituent that is available for leaching (i.e., availability) controls the observed aqueous phase concentration. For example the aqueous phase concentration of Cu in most of the materials is controlled by solubility at pH greater than 4, while a plateau in aqueous concentration is present at lower pH values. Saturated solutions are typically indicated when the simulated LSP at L/S=0.3 and 10 mL/g coincide. Materials leaching in the pH domain where the simulated LSP at L/S= 0.3 mL/g results in substantially higher aqueous concentrations than the simulated LSP at L/S=10 mL/g can be expected to higher leachate concentrations at low L/S values (i.e., initial percolates) than observed from the pH dependent leaching test carried out at L/S=10 mL/g.

- Complexation with dissolved organic matter and adsorption onto solid organic matter is more important for Cu than Pb LSP, and plays a critical role between pH 6 to 12. The presence of more DOC increases the amount of Cu in solution.

- The same set of phenomena and solid phases (i.e., organic matter complexation, precipitated solid phases, adsorption onto iron surfaces) are responsible for a significant fraction of the LSP behavior in multiple materials, albeit to different extents.
4 LABORATORY AND FIELD DATA FOR EVALUATION CASES

4.1 Coal Fly Ash Landfill Leachate (United States)

The burning of coal for energy production results in several forms of CCRs, including (i) fly ash, which is the fine material entrained in combustion gases and typically collected by an electro-static precipitator (ESP) in the first stage of air pollution control; (ii) scrubber residues, usually collected in the second stage of air pollution control, which may include processes for removal of gaseous sulfur oxides in the form of calcium, sodium or magnesium sulfides and sulfates (depending on facility configuration), and mercury removal by adsorption onto activated carbon; (iii) FGD gypsum, which is produced when the scrubber is designed and operated to force sulfidic gas oxidation to sulfates and precipitation with calcium; and (iv) bottom ash, which is the post-combustion residue removed from the combustion grates or chamber. In addition, preprocessing of coal prior to combustion can result in the production of a "coal milling reject" stream often including pyrite minerals that have high concentrations of reduced sulfur species and are difficult to size reduce. Specific CCR streams from a coal combustion power plant may be managed separately (e.g., for beneficial use of one or more streams, such as fly ash or FGD gypsum) or together for disposal. The specific leaching characteristics of individual CCRs are a function of the coal type combusted and the combustion system design and operating conditions. Extensive discussion is available on coal combustion facilities and the leaching characteristics of individual CCRs (Sanchez et al., 2006, 2008; Kosson et al., 2009).

4.1.1 Case Description

Landfill leachates, porewater and lysimeter samples have been collected from multiple landfills and surface impoundments in the U.S. containing CCRs under an Electric Power Research Institute (EPRI) program (EPRI, 1988; 1998; 2006a; 2006b), and also by a U.S. EPA sampling program (EPA, 2000). The resulting set of field data was filtered to focus only on landfills receiving coal fly ash from coal combustion facilities without FGD scrubbers and not receiving coal milling rejects. In this way, the resulting set of data would reflect the range of landfill leachates produced from disposal environments where the fly ash predominated. It would not be possible to identify all disposal sites that receive only fly ash because most facilities co-dispose coal combustion bottom ash, although this waste stream is considered relatively inert. The resulting set of field data is compared to the range of pH-dependent leaching measured as part of a U.S. EPA study to characterize CCR leaching (Kosson et al., 2009) and a reference sample from an interlaboratory leaching test methods validation study (Garrabrants et al., 2012a; 2012b).

As part of the laboratory CCR characterization program, 35 fly ash samples were subjected to laboratory pH-dependent leaching by EPA Method 1313 and the corresponding precursor method SR002, as well as laboratory L/S dependent leaching by Method 1316 and the corresponding

20 Leachate samples typically are taken from leachate collection systems, which may include sumps, collection wells and/or drainage above liner systems. Porewater samples typically are collected under suction from porous sampling devices embedded in the field material or by taking core samples and then using centrifugation, compression or suction to express pore water from the solid samples. Lysimeters typically are small-scale (e.g., on the order of 1 to 10 m³) field test cells with liners and leachate collection intended to mimic larger field conditions.
precursor method SR003. Results of the laboratory testing program are summarized for each constituent as a function of pH or L/S based on the 5th, 50th, and 95th percentiles of the resulting data based on interpolation to common pH or L/S points (Garrabrants et al., 2012a) and graphed as either dashed (5th, 95th percentiles) or continuous lines (50th percentile). Field data are graphed as individual observations as a function of the measured sample pH along with the statistical (percentile) representation of the laboratory data.

4.1.2 Results and Discussion

A complete set of figures illustrating results from the field measurements in comparison to the statistical representation of the laboratory data is provided in Appendix A. The field sites and samples included can be summarized in Table 4-1. The field data includes core samples, pore water samples, leachates from lysimeter tests, leachates from well and leachate collection systems. The number of observations shown in Table 4-1 for calcium represents a high number of data points and full coverage of each site. The actual number of sites and data points for each COPC varies; thus, the ten total disposal sites are represented to various degrees.

Table 4-1. Summary of field sites and field data for calcium.

<table>
<thead>
<tr>
<th>Sponsor</th>
<th>Site</th>
<th>Solid Core</th>
<th>Lysimeter Leachate</th>
<th>Well Leachate</th>
<th>Leachate Collection</th>
<th>Pore water</th>
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The following are notable relationships between field leaching and leaching test results:

- Field leaching results for many constituents were well represented by the concentration as a function of pH domain of the laboratory leaching tests, considering the variability associated with the leaching behavior of fly ash from different facilities (Kosson et al., 2009). These constituents included aluminum, boron, calcium, copper, iron, potassium, magnesium, silicon, strontium, vanadium and zinc. Figure 4-1 illustrates this behavior for magnesium and vanadium. In most cases, there were a few data points that fell outside the laboratory distribution. For potassium, the laboratory distribution is skewed at alkaline pH because of the addition of potassium hydroxide during testing to achieve test pH values greater than the natural pH of the material.
The range of pH observed for field leachate samples is in agreement with the range of natural pH observed during laboratory testing of fly ash from multiple sources. However, more acidic natural pHs were observed during laboratory testing (Kosson et al., 2009), but probably were not present in the field samples because of exclusion of sites containing pyrites (coal mill rejects) which also would correlate with high sulfur coals.

For several constituents (e.g., arsenic, cadmium, chromium, manganese, nickel, and selenium), field leaching results exhibited bimodal behavior where one-third to one-half of the field results were well-represented by the domain of the laboratory concentrations as a function of pH domain, while the remaining data were significantly less than the laboratory testing results. Field concentrations that were less than the laboratory domain were also typically near detection limit values. Insufficient information was available to discern the cause of this response which may have been a result of relatively high detection limits, preferential flow or intrusion of dilution water. This bimodal behavior is illustrated in Figure 4-2 for arsenic, cadmium, chromium and selenium.
Figure 4-2. Bimodal behavior of field leaching results compared to pH-dependent leaching of arsenic, cadmium, chromium and selenium from CCRs.

- The upper range of field leaching concentrations for calcium and sulfate (Figure 4-3) reflects the solubility of calcium sulfate within the uncertainty of temperature and co-dissolved ions in solution (Marshall and Slusher, 1966). Note the 5th percentile dashed line for the laboratory extracts between pH 9 and 13 indicates a steep decrease in sulfate concentration with increasing pH. The decrease in sulfate at pH > 9 is consistent with the formation of ettringite, Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$.26H$_2$O, in some high calcium fly ash samples (e.g., material codes XFA, ZFA in Figure 4-4 as compared to material codes EaFA or UFA). The formation of ettringite results in decreased sulfate solubility at alkaline pH as well as a similar decrease in chromium and molybdenum leaching resulting from anion inclusion and isomorphic substitution into ettringite.
Figure 4-3. Comparison of field leachates to pH-dependent leaching for calcium and sulfate release from CCRs.

Figure 4-4. Effect of ettringite formation at alkaline pH on the leaching of chromium and molybdenum.
The upper range of field leaching concentrations for chloride (ca. 290 mg/L) is approximately 15 times greater than the chloride concentrations at the 95th percentile for chloride based on laboratory testing at L/S 10 L/kg (Figure 4-5, left). For sodium, the upper range of field leaching concentrations (2,900 mg/L) is approximately 17 times the concentration at the 95th percentile for the laboratory testing at L/S 10 L/kg (Figure 4-5, right). These observed field values are reasonable given that the field porosity\textsuperscript{21} is ca. 0.3 and a resulting multiplier of 33 is calculated if the assumption is made that all of the chloride or sulfate remains in solution (considering the porewater L/S would be approximately equal to the porosity, or 0.3 mL/g and the laboratory testing is at L/S = 10 mL/g, so the resulting correction factor would be 10/0.3 = 33. The results are also consistent with results of batch leaching as a function of L/S by Method 1316 and its precursor method SR003 (Kosson et al., 2002).

![Figure 4-5. Comparison of field leachates to pH-dependent leaching for chloride and sulfate release from CCRs.](image)

Field leaching results for barium generally were between 0.02 and 0.2 mg/L, while laboratory test results were between 0.1 and 2 mg/L, and correlates with relatively high sulfate concentrations (Figure 4-6). This result is likely because of the higher sulfate concentrations and low liquid-solid ratio in the field that reduces barium solubility based on Le Chatelier's principle.

\textsuperscript{21} “Field porosity” refers to the void fraction in the material under field conditions. Openshaw (1992) reported a compacted density of 1.3 g/cm\textsuperscript{3} for fly ash and a particle density of 1.9 g/cm\textsuperscript{3}, indicating a compacted porosity of 0.32.
4.1.3 **Case Summary**

Case 1 examined the leaching behavior of coal fly ash under landfill disposal conditions as a class of materials. The study compares 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) 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).
4.2  Leachate from Coal Fly Ash in Large-scale Field Lysimeters (Denmark)

4.2.1  Case Description

Large-scale lysimeter tests were carried out with coal fly ash in Denmark over the period of 1983 to 1990 (Hjelmar et al., 1991; Hjelmar, 1990). Individual lysimeters were 3 m x 3 m x 1.5 m deep (10 units) or 2.5 m deep (4 units) and used for a series of experiments, including those used for coal fly ash studies (Figure 4-7). Each lysimeter had a low density polyethylene liner and separate leachate collection. Filled lysimeters contained between 0.81 and 1.05 tonnes of fly ash and had 8-9 m² of surface area exposed to the atmosphere and natural precipitation. Two different fly ash materials, identified as HF1 and BF2, were obtained from different Danish power plants, each burning a different mixture of coal types. Results from BF2 as used in Lysimeters 4, 9 and 14 are the focus of the case comparison presented here. Similar results were obtained for HF1 and are available in Hjelmar (1990).

Fly ash samples HF1 and BF2 were also tested using laboratory percolation columns (Hjelmar et al., 1991). At the time of the testing, column test methods had not yet been standardized. For BF2, the column experimental conditions (identified as Column 4) were column diameter of 0.145 m, height of fly ash packing of 0.58 m for a total of 8.1 kg dry weight, and an influent velocity of 44-145 mm/day (up-flow). Similar column conditions were used for HF1. Column influent was a synthetic rainwater comprised of 0.5 mg/L NaCl, 0.19 mg/L NaHCO₃, 0.25 mg/L CaCl₂·2H₂O and 0.27 mg/L Na₂SO₄. However, the report also concludes, “Therefore, it makes little difference whether artificial rainwater (with limited buffering capacity, as above), demineralized water or slightly acidified demineralized water is used in leaching experiments, except perhaps at very high L/S values” (Hjelmar et al., 1991, p. 26).

Figure 4-7. Cross-section of large-scale field lysimeter construction (Hjelmar et al., 1991).
4.2.2 Results and Discussion

Only a limited set of analytes was measured in field leachate and laboratory column eluates; only one data point (at L/S ~0.002) was available for Lysimeter 4. A comparison of leachate composition from field lysimeters and laboratory column testing (Column-4) is provided in Figure 4-8 for pH and major constituents and in Figure 4-9 for trace constituents.

Figure 4-8. Comparison of leachate composition from field lysimeters and laboratory column testing (Column 4, red symbols) for pH, sodium, potassium, calcium and sulfate.
Leachate pH values were lower for Lysimeter 14 than for Lysimeter 9 and Column 4, along with somewhat higher calcium and somewhat lower arsenic concentrations in Lysimeter 14 than the other results. Leachate constituent concentrations from Lysimeter 9 and eluate concentrations from Column 4 were nearly identical for all constituents and consistent with the single observation reported for Lysimeter 4. This information indicates that preferential flow was not a major factor in the field lysimeter performance. In addition, the common behavior between laboratory and field conditions for oxyanions (i.e., chromium and selenium) suggests that establishment of strongly reducing conditions in the field was not a consideration for the material tested.

![Graph of arsenic, chromium, molybdenum, and selenium eluate concentrations vs. L/S](image)

**Figure 4-9.** Comparison of leachate composition from field lysimeters and laboratory column testing (red symbols) for arsenic, chromium, molybdenum, and selenium.

### 4.2.3 Case Summary

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) 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.

4.3 Landfill of Coal Combustion Fixated Scrubber Sludge with Lime (United States)

4.3.1 Case Description
FGD filter cake and fly ash are typical CCRs requiring environmental characterization in conjunction with material management. Plant 14090 served as a test case for comparison of laboratory leaching tests of produced blended CCRs, laboratory leaching of core samples from the disposal landfill site for the blended CCRs, and field leachate samples (EPRI, 2012).

Plant 14090 is a 1,000+ megawatt (MW) power plant. The plant burns pulverized eastern bituminous coal in a boiler. Cold-side electrostatic precipitators (ESPs) are used on all units for particulate control. Selective catalytic reduction is used at the plant but was not active during collection of the materials used in this study. The wet FGD systems on two units are used to reduce SO₂ emissions via limestone slurry sorbents and an inhibited oxidation process. The FGD solids, consisting primarily of calcium sulfite, are pumped from the absorber to a thickener. Liquid overflow from the thickener is recycled back into the FGD system, and the thickened sludge is pumped to a series of drum vacuum filters for further dewatering. Water removed by the drum vacuum filters is recycled back into the FGD system, and the filter cake (FC) is taken by conveyor belt to a pug mill, where it is mixed with dry fly ash and dry quicklime for stabilization. The resulting FSSLs are taken by conveyor to a temporary outdoor stockpile and then transported by truck either to a utilization site or to an on-site landfill. After setting, the stabilized solid forms a weak monolithic material that has some degree of compressive strength and moderately high alkalinity.

“As produced” FSSL was sampled from Plant 14090 and evaluated as part of an EPA program on leaching characterization of CCRs and identified by material code “MAD” (Sanchez et al., 2008) and testing for pH-dependent leaching following method SR002 and L/S dependent leaching using method SR003.²² Core samples from the FSSL disposal landfill (designated “FCM”) also were characterized for pH-dependent leaching using SR002 and L/S dependent leaching using SR003. Porewater was collected from two locations in the landfill (designated “SCS-1” and “SCS-2”) between 2001 and 2007.

The concentrations of constituents in porewater samples collected from the FSSL landfill at Plant 14090 was compared as a function of pH to the equilibrium data from SR002 and SR003 tests.

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²² SR002 (abbreviated in figures as SR02) and SR003 (abbreviated in figures as SR03) are Vanderbilt University precursors of EPA Method 1313 and Method 1316, respectively. Although the general procedures and utilization of results are the same, these precursors differ from the current tests in the number of extracts and the exact target values (e.g., pH or L/S) required in each test.
Porewater was collected at two locations in the landfill (i.e., SCS-1 and SCS-2) from November 2001 through May 2007, providing 25 independent samples for analysis.

4.3.2 Results and Discussion

A complete set of figures illustrating results from the field porewater measurements in comparison to the laboratory leaching test results of “as produced” FSSL (i.e., MAD) and landfill core samples (i.e., FCM) is provided in Appendix B. The following are notable relationships among the testing results from the three types of samples:

- The average natural pH of the MAD material is approximately 11.9 and of the FCM material is 9.1 (based on replicate samples), whereas the average SCS sample pH is 7.4 with a span from pH 6-10. The high natural pH of the freshly mixed FSSL is due to addition of quicklime and the dissolution of Ca(OH)$_2$ at a pH of approximately 12.5. The decrease in natural pH from ca. 12.0 for MAD to 9.0 for FCM is consistent with the consumption of Ca(OH)$_2$ during carbonation of alkaline materials, including slower reactions with fly ash (natural pH 11.3) and scrubber solids (natural pH 8.9). Nominally, the natural pH of the field cored material should agree closely with the pH of landfill leachates. The discrepancy in pH readings may be caused by carbonation during handling and processing of landfill leachates. Based on the titration curve of FCM, approximately 0.5 milli-equivalents of acid per gram of material (meq/g) would be required to lower the pH of the FCM material to the mean leachate pH of 7.4. Considering the mass of FCM in the landfill, a significant amount of acid would be required to overcome the buffering capacity of the FCM material. However, considerably less acid (in the form of carbonation) would be needed to neutralize the porewater samples once they were no longer in contact (and therefore near equilibrium) with the solid phase. Therefore, porewater samples were likely neutralized through reaction with atmospheric carbon dioxide during collection and handling prior to analysis.

- The impact of aging and partial carbonation of field cores (FCM) in comparison to the “as produced” material (MAD) is apparent in the response of barium, calcium, magnesium and strontium between pH of 8 and 13, where FCM indicates decreased solubility relative to MAD (illustrated for barium, calcium and strontium in Figure 4-10). Porewater concentrations of these constituents are similar to or less than the concentrations measured for field core material. This is a typical response to carbonation and is consistent with other results for other materials presented in this report.

- Field porewater concentrations of barium are lower than measured in laboratory extracts of field cores and “as produced” material. This phenomena is similar to that observed for coal fly ash (see Section 4.1) and likely results from elevated concentrations of sulfate at the low L/S associated with porewater, thereby reducing barium sulfate solubility by common ion effects.
Figure 4-10. Comparison of pH-dependence testing of field-cored FSSL and “as produced” FSSL to field porewater samples showing the impact of aging and partial carbonation of field materials.

- When “as produced” and field core samples are compared, the coupling between chloride and cadmium leaching is evident (Figure 4-11). The higher chloride concentrations in the unaged “as produced” samples result in increased cadmium concentrations relative to the field cores. However, this effect of elevated chloride concentration increasing cadmium leaching is not evident when porewater samples are compared to laboratory results.
Figure 4-11. Comparison of chloride and cadmium leaching in field-cored FSSL and “as produced” FSSL to field porewater samples showing the impact of cadmium chloride chelation.

- The effect of dissolved organic carbon (DOC) concentrations resulting in increased copper concentrations is evident when comparing laboratory testing on the “as produced” material to field cores and porewater analysis at pH 6 to 8 (Figure 4-12).

Figure 4-12. Comparison of dissolved organic carbon and copper leaching in field-cored FSSL and “as produced” FSSL to field porewater samples showing the impact of complexation of dissolved organic carbon with copper.
Concentrations of oxyanions are either similar to or less than the concentrations measured by the laboratory pH-dependent leaching test at the corresponding pH. These leachate concentrations are more closely related to the laboratory testing of the field cores (i.e., aged FCM material) than to the concentrations from laboratory testing of the unaged “as produced” material (MAD). This relationship is observed for several analytes including arsenic, boron, antimony, molybdenum, selenium and vanadium (illustrated for arsenic, boron, molybdenum and selenium in Figure 4-13). Molybdenum is the only oxyanion for which aging of the material resulted in increased concentrations relative to the “as produced” material (at pH less than 8.

Figure 4-13. Comparison of arsenic, boron, molybdenum and selenium leaching in field-cored FSSL and “as produced” FSSL to field porewater samples.

Concentrations of highly soluble species, including chloride, potassium, lithium and sodium, are greater by up to a factor of 20 in the porewater (L/S less than 0.5 L/kg) than when measured by the pH-dependent leaching test at L/S of 10 L/kg. However, the porewater concentrations for these constituents are closely estimated by the laboratory batch L/S
dependent leaching test (i.e., SR03 or Method 1316; illustrated for potassium and sodium in

- Figure 4-14).

\[ L/S = 0.5 \text{ L/kg; } \text{Conc} = 20 \times 40 \text{ mg/L} = 800 \text{ mg/L} \]
\[ L/S = 10 \text{ L/kg; } \text{Conc} = 30 \text{ mg/L} \]
\[ L/S = 0.5 \text{ L/kg; } \text{Conc} = 20 \times 30 \text{ mg/L} = 600 \text{ mg/L} \]

\[ L/S = 10 \text{ L/kg; } \text{Conc} = 40 \text{ mg/L} \]
Figure 4-14. Comparison of potassium and sodium leaching in field-cored FSSL and “as produced” FSSL to field porewater samples (upper graphs). Lower four graphs present Method 1316 results applied to field core (FCM) and extrapolation to L/S=0.5 L/kg (dashed line) compared to result of 20x result from Method 1313 at natural pH.

4.3.3 Case Summary

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 fixed 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.
4.4 Coal Fly Ash Used in Roadbase and Embankments (The Netherlands)

4.4.1 Case Description
In the framework of the National Research Program Coal (NOK), studies were done to evaluate beneficial coal fly ash uses (Spee and Reintjes, 1986). Two applications were studied in full scale - a roadbase made with bound fly ash covered by asphalt and sintered paving bricks (road sections of 100 m long and 8 m wide) with cement-stabilized fly ash used as a base for an embankment (100 m long). Cross-sections for the roadbase and the embankment applications are presented in Figure 4-16 and Figure 4-15, respectively. Measurements were carried out over a 2 year period, starting in 1984.

![Cross section of roadbase constructed with cement stabilized coal fly ash](image)

Figure 4-15. Cross section of roadbase constructed with cement stabilized coal fly ash (same as for the embankment). The stabilized fly ash (0.8 m thick) is overlain with an asphalt layer in the road surface area and by clinker material (coarse aggregate) on the sloped road shoulder area, and underlain with a sloped sand drainage layer (0.30 m thick). A polyvinyl chloride plastic sheet underlies the sand drainage layer to ensure leachate collection in a collection sump (at left).

Leachate obtained from collection wells at the side of the road and at the foot of the embankment was analyzed for a selection of substances. The coal fly ash used was stabilized with addition of 5% cement. This mixture was tested separately in a column experiment.
4.4.2 **Results and Discussion**

Results for calcium, chromium, molybdenum and selenium from leachate collected from the roadbase, embankment and laboratory percolation column studies are presented in Figure 4-17. The set of data (dots) with the lowest L/S values represents concentrations in the leachate collected from the embankment, while the continuous lines represent concentrations obtained from the laboratory percolation column experiments.

![Figure 4-16. Cross-section of embankment constructed with cement stabilized coal fly ash as the core material and then covered with 0.3 m topsoil for growth of grass. A drainage sand layer underlies the stabilized coal fly ash, and a polyvinyl chloride plastic sheet underlies the sand drainage layer to ensure leachate collection through a drain (center bottom) and diversion to a collection sump (at left).](image)

Leachate concentrations emanating from the embankment initially have relatively low concentrations that increase significantly at L/S of ca. 0.005 L/kg. This delayed release reflects displacement of initial porewater in the underlying sand drainage layer and retardation by partial adsorption by the sand drainage layer. Similarly, there is an offset as a function of L/S of ca. 0.5 L/kg for the concentrations of constituents in leachates emanating from the roadbase in comparison to the percolation column results. This offset is attributed to the collection of samples at much lower L/S for the field conditions and integration of sample volumes over the collection intervals for the laboratory columns. This effect has been further confirmed through independent tracer studies (van der Sloot et al, 1991). Although this data set is sparse, it does indicate that the laboratory column experiments conservatively approximate the peak leachate concentrations observed in the field.
Figure 4-17. Field leachate concentrations from Dutch embankment and road base demonstration projects compared to laboratory percolation column experiments.

4.4.3 Insights Gained from Chemical Speciation of Coal Fly Ash Leaching

The following examples illustrate the impact of three common phenomena which strongly influence retention and leaching of COPCs – oxyanion substitution for sulfate in ettringite, carbonation due to uptake of CO₂, and oxidation/reduction. These phenomena are shown through comparison of leaching test data from a European coal combustion fly ash (pH-dependent and percolation column, material code CFA) to chemical speciation model results conducted at various L/S values. The presentation of chemical speciation results in these examples is similar to that used in comparison of materials.

In Figure 4-18 through Figure 4-20, leaching test results are presented along with chemical speciation modeling of LSP and associated phase partitioning of Cr, SO₄, and Mo. For each figure, the first panel compares pH-dependent leaching data (red dots) and percolation column data (blue triangles) to CSF model results at L/S 10 (red solid line) and L/S 0.3 (blue dashed line). The latter two panels of each figure show the relative contributions of mineral, carbon, and aqueous species.
that are responsible for the shape and magnitude of the CFS model results at L/S 10 and L/S 0.3. In particular, these figures for Cr, SO₄, and Mo in CFA fly ash illustrate the importance of oxyanion substitution for sulfate in ettringite, (CaO)₆(Al₂O₃)(SO₃)₃·32H₂O, as a retention mechanism for oxyanions such as molybdate and chromate in the pH range between 9 and 13.

Figure 4.18. Chemical speciation model results for chromium at L/S=10 and L/S=0.3 compared to pH-dependent (CEN/TS 14429) and percolation column (CEN/TS 14405) leaching results for coal fly ash (the Netherlands).
Figure 4-19. Chemical speciation model results for sulfate at L/S=10 and L/S=0.3 compared to pH-dependent (CEN/TS 14429) and percolation column (CEN/TS 14405) leaching results for coal fly ash (the Netherlands).
Figure 4-20. Chemical speciation model results for molybdenum at L/S=10 and L/S=0.3 compared to pH-dependent (CEN/TS 14429) and percolation column (CEN/TS 14405) leaching results for coal fly ash (the Netherlands).

Figure 4-21 and Figure 4-22 illustrate the impact of reaction with atmospheric carbon dioxide (i.e., carbonation) on the shift controlling mineral species. The two upper panels compare CSF model results at increasing degrees of carbonation (determined by CO₂ uptake between 1 and 7 wt %) to the leaching data for Ca and Ni. The lower figures show the phase partitioning that creates the CSF model LSP result. Figure 4-21 clearly demonstrates that increasing extent of carbonation yields a loss of ettringite and formation of calcite, CaCO₃, with a concurrent decrease in Ca solubility at pH greater than 7. In the case of Ni (Figure 4-22), increased carbonation increases the partitioning Ni into the aqueous phase due to the loss of oxyanion substituted ettringite and competition with carbonate adsorption onto HFO surfaces.
Figure 4-21. Effect of carbonation levels (wt% CO₃) on calcium model predictions and partitioning compared to pH-dependent (CEN/TS 14429) and percolation column (CEN/TS 14405) leaching test results.
Figure 4-22. Effect of carbonation levels (wt% CO₃) on nickel model predictions and partitioning compared to pH-dependence (CEN/TS 14429) and percolation column (CEN/TS 14405) leaching test results.

Figure 4-23 illustrates the impact of reduction/oxidation on the percolation leaching of Cr. The panels on the left side of the figure show the results of percolation column leaching tests (blue symbols) and model results conducted at three levels of pH+pE. For the model results, the orange
symbols indicate data points at target L/S values while the orange dashed line indicates continuous elution as a function of L/S. The right hand panels present the phase partitioning at each level of pH+pE. Figure 4-23 illustrates that as the reducing conditions (i.e., higher values of pH+pE) results in a decrease in Cr leaching due is the reduction of Cr(VI) to Cr(III) and the low solubility of Cr(OH)₃ at mildly alkaline pH. Comparison of the field embankment samples with the simulations indicates pH+pE in the embankment between 12 and 12.8 with Cr(OH)₃ as the controlling solid phase.
4.4.4 Case Summary

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.

4.5 Municipal Solid Waste Incinerator Bottom Ash Landfill (Denmark)

4.5.1 Case Description
A relatively small MSWI residue landfill, established between 1973 and 1976, has been monitored periodically for more than 30 years. The landfill is situated at Vestskoven in the western part of Greater Copenhagen in Denmark and contains approximately 10,000 m³ of bottom ash and fly ash from a nearby MSW incinerator (Hjelmar and Hansen, 2005; Hjelmar et al., 1991). During the initial period of operation, the amount and quality of the leachate generated was monitored. In December 2003, two borings were made into the site and several samples of the landfilled material were collected from different depths of the site. In addition, leachate was collected from one of the two borings. Solid samples obtained from the borings were subjected to leach testing in accordance with technical specification EN 12457-1, a single batch extraction leaching test with deionized water at L/S of 2 L/kg. Field leachate samples and leaching test extracts were then analyzed for constituents of interest.

4.5.2 Landfill Construction
In June 1973, a circular site was dug a few meters into the ground with the excavated soil used to construct a dike at the perimeter of the hole. The site was lined with reinforced PVC on top of which a protective 0.3 m drainage layer of sand was placed. The bottom liner slopes towards the center where a leachate collection tank was installed. Access to the collection tank was afforded by a well shaft, allowing the removal of leachate by pumping. The well shaft was adjusted in height as landfilling progressed until the landfill reached its final height. During the period July 11 to August 29, 1973, the site was filled to the top of the dike with approximately 6000 m³ of MSWI bottom ash and fly ash. The top of the site was then left open and exposed until 1976.

During the period January to June of 1976, an additional 4000 m³ of bottom and fly ash was placed on top of the site, forming a circular mound. A 1 m layer of topsoil was placed directly on top of the MSWI residues. Self-sown grass and bushes soon covered the surface of the site. Figure 1 shows a cross-section of the closed site while Table 4-2 provides some physical details on the size and shape of the site.
The landfilled material has been estimated to consist of approximately 85% of MSWI bottom ash and 15% of MSWI fly ash. Observations made during the drilling of boreholes in 2003 revealed that a substantial amount of scrap metal was also present and that the fly ash was deposited in distinct layers. Although the exact bulk density is unknown, the dry bulk density of the landfilled material was estimated to be 1000 kg/m³ in previously published information on the leachate development at the site (e.g., Hjelmar, 1989; Hjelmar, 1996; IAWG, 1997). Based on the information obtained in 2003, the estimate of the dry bulk density of the material in the monofill has been adjusted to 1,200 kg/m³. The calculated values of the L/S used in this report are based on the revised value of the dry bulk density. The landfill is thus estimated to contain approximately 12,000 tonnes of MSWI residues (dry weight).

**Table 4-2. Physical information about the Vestkoven MSWI monofill.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of MSWO residues</td>
<td>10,000 m³ (approximately)</td>
</tr>
<tr>
<td>Diameter of the site at the upper edges of the dike</td>
<td>52.4 m</td>
</tr>
<tr>
<td>Diameter of the site at the inner bottom of the dike</td>
<td>40 m</td>
</tr>
<tr>
<td>Surface area at the upper edge of the dike</td>
<td>2,157 m²</td>
</tr>
<tr>
<td>Surface area at the inner bottom of the dike</td>
<td>1,257 m²</td>
</tr>
<tr>
<td>Elevation of the bottom of the leachate collection tank</td>
<td>13.4 m above sea level</td>
</tr>
<tr>
<td>Elevation of the bottom liner</td>
<td>15.0 – 15.4 m above sea level</td>
</tr>
<tr>
<td>Elevation of the upper edge of the dike</td>
<td>18.4 m above sea level</td>
</tr>
<tr>
<td>Elevation at the top of the site</td>
<td>25.4 m above sea level</td>
</tr>
<tr>
<td>Maximum height of the MSWI at center</td>
<td>9.2 m (approximately)</td>
</tr>
</tbody>
</table>

**4.5.3 Leachate Quantity and Quality**

Since the landfill was established in 1973, the leachate produced has been pumped from the leachate tank at regular intervals. During the period from 1973 to 1977, the leachate was sprayed
onto the top of two adjacent MSWI residue landfills. From 1977 to 1980, the leachate was allowed to accumulate within the site. From 1980 to the present, the leachate has been pumped into tank trucks and removed from the site. The quantity of all leachate removed from site has been registered throughout its existence, and the leachate has been subjected to chemical analysis once a year (in the beginning more often). Water balances for the site have been calculated each year since 1980 and compared to precipitation data obtained from a nearby weather station (Hjelmar and Hansen, 2005). The results of the water balance calculations have shown that for the seven-year interval between 1998 and 2005, the leachate production has corresponded to 33% of the measured precipitation.

Leaching data were not available for the MSWI bottom ash and fly ash that was originally used in the MSWI landfill project. Therefore, a selection of leaching pH-dependent and percolation column test results from testing of MSWI bottom ash from Germany (Berger et al., 2005) and the Netherlands (van der Sloot et al., 2008c) are used as reference materials for this case.

4.5.4 Results and Discussion

A complete set of figures is provided in Appendix C for the comparison of Vestkoven monofill leachate concentrations (red circles) to laboratory results on Vestkoven core samples (grey diamonds) and off-site comparable materials from Germany, Italy, Austria, The Netherlands and the United Kingdom (solid symbols with lines). Laboratory data include (i) single batch extraction test results from EN 12457-1 testing of landfill cores and (ii) pH-dependent leaching test results for the reference materials, and (iii) percolation column testing for reference materials (Susset and Leuchs, 2008). Comparisons are shown as a function of pH (left) and L/S (right). Although the comparison materials represent the same class of materials placed into the Vestkoven landfill, the materials were not sampled from the monofill and, therefore, the results for comparison materials are provided only as an indication of expected leaching behavior.

The following are notable relationships between leaching test results for specific constituents:

- The batch extractions of cored samples at L/S 2 L/kg ranged from 7.6 to 11.6 which is consistent with the range of leachate pH values (Figure 2-5). Lower upper bound values of pH from field samples is expected because of reaction with carbon dioxide, either generated from decomposition of residual carbon in the fill material or from atmospheric exchange during leachate accumulation and sampling.
Figure 4-25. Eluate pH from leachates from the Vestkoven monofill (red circles) compared to the percolation column pH for comparable bottom ash samples (solid symbols).

- Analysis of batch extractions of core samples for arsenic was not available. Figure 4-26 presents the field leachate data in comparison to pH dependent test results and percolation column test results for the analogous reference materials. Maximum field leachate concentrations were approximately 10 times greater than anticipated based on pH dependent testing but consistent with column test results for the reference materials. Collectively, these results indicate that the fraction of arsenic not adsorbed to iron (the most likely retention mechanism for MSWI bottom ash) behaves as a highly soluble species, exhibiting higher concentrations at lower L/S.

Figure 4-26. Arsenic concentration results from the Vestskoven MSWI monofill leachate samples (red circles). Data are shown for pH-dependent leaching (left) and percolation column testing (right). These results illustrate typical relationships between pH-dependent and column testing of cored samples and leachate measurements.
The constituent concentration ranges from batch extractions of cored samples at L/S 2 L/kg also were consistent with the concentration ranges measured in the leachate samples obtained over several years of operation of the landfill (Figure 4-27). For many constituents (i.e., chromium, lead, potassium, sodium, chloride) the upper bound for extract concentrations from the core samples was greater than or similar to the upper bound for leachate concentrations, although both data sets exhibit considerable variability most likely resulting from heterogeneous water flow patterns through the landfill over the period of observation and the heterogeneity of the fill material. For zinc, the peak laboratory extractions at L/S 2 L/kg were up to an order of magnitude lower than the peak leachate concentrations at pH greater than 9; there is no clear explanation for this effect.

Increasing zinc concentration in leachate as a function of L/S reflects the concurrent decrease in pH and increased zinc solubility with decreasing pH (Figure 4-27). Other constituents that exhibit similar behavior include aluminum, cadmium, calcium, chloride, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel, lead, phosphorus, sulfur, and sulfate. In many cases, comparisons for many constituents cannot be made since data from the batch extractions of the core samples did not include analytical results for arsenic, mercury and selenium while leachate sample results did not include analytical results for barium, bromide, cobalt, lithium, molybdenum, antimony, selenium, silicon, tin, strontium, or vanadium.

Field leachate and core extract concentrations are consistent with pH dependent laboratory testing for chromium (apparently present predominantly as Cr(VI)) but were greater than pH dependent laboratory testing for lead and zinc because of DOC complexation at lower L/S but diluted at higher L/S (i.e., L/S of 10 mL/g used in pH dependent testing).

The L/S of 2 L/kg used in the batch extractions provides an accurate estimate, within approximately 2x uncertainty, of peak initial leachate concentrations of highly soluble species such as sodium, potassium and chloride (Figure 4-28). This observation is consistent with the earlier explanation (see Sections 2.1.2 and 2.3.1) that concentrations of highly soluble constituents can be substantially greater than measured at L/S of 10 L/kg as used in the pH-dependent leaching tests. Higher concentrations of highly soluble constituents (i.e, concentrations consistent with approximate porewater L/S of 0.2-0.5 L/kg) were most likely not observed because of material heterogeneity and preferential flow. The leachate concentrations for highly soluble constituents also follow the expected elution curve as a function of L/S as typified by the comparison materials (e.g., high initial concentrations that decrease by more than one order of magnitude prior to L/S of 2 L/kg.

4.5.5 Case Summary
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.
Chromium, lead and zinc concentration results from testing of cored materials from the Vestskoven MSWI monofill (grey diamonds) compared to leachate samples (red circles). Data are shown for pH-dependent leaching (left) and percolation column testing (right). These results illustrate typical relationships between pH-dependent and column testing of cored samples and leachate measurements.
Figure 4-28. Sodium, potassium and chloride concentration results from testing of cored materials from the Vestskoven MSWI monofill (grey diamonds) compared to leachate samples (red circles). Data are shown for pH-dependent leaching (left) and percolation column testing (right). These results illustrate leaching behavior of highly soluble species.
4.6 Municipal Solid Waste Incinerator Bottom Ash Used in Roadbase (Sweden)

4.6.1 Case Description

MSWI bottom ash has been evaluated extensively and demonstrated to have consistent, systematic leaching of individual constituents as a function of pH (IAWG, 1997; Sabbas et al., 2003; Dijkstra et al., 2006a; 2006b). The extensive use of MSWI in Europe has provided considerable focus on the potential for beneficial use of bottom ash, which is the heterogeneous material that is discharged from the incinerator grate and is the largest residue stream from MSWIs (the other large residue stream being air pollution control residues). Thus, the evaluation case described here is the result of evaluation of the use of MSWI bottom ash as a roadbase material in Sweden, referred to as Vändöra (Bendz et al., 2009).

The test road was constructed in 1987 in Linköping, Sweden (Lundgren and Hartlén, 1991) and was 15 years old at the time when the samples were taken (Bendz et al., 2009). Other studies were performed on this road in 1998 (Andersson et al., 1999) and in 2002 (Flyhammar and Bendz, 2006). In two of the test sections, MSWI bottom ash was used as a subbase below an unbound base course and surface asphalt layers. The bottom ash was poorly separated and contained large pieces of incineration residues (e.g., larger than a few decimeters). The test road has been in a rather bad condition during periods of time in its lifetime, with longitudinal cracks along the centerline of the road. Therefore, infiltration through the pavement is likely to have taken place.

This field study, Vändöra Q4-241, was carried out in September 2003 (Bendz et al., 2006). The unbound base course and asphalt layers were removed and three sample collection trenches were excavated into the road construction in different sections. In this report, results are discussed from the characterization of the subbase layer (bottom ash) as presented in Lundgren and Hartlén (1991) while the complete set of field data is presented in Bendz et al. (2006).

Fifty-three solid samples of approximately 250 mL each were collected from the subbase layer in a checker board pattern. One-step batch tests in deionized water at L/S 10 L/kg were conducted on all 53 samples according to the standard EN 12457-2. The minimum pH-value of the samples in deionized water at L/S 10 L/kg was 7.4 and the maximum pH value was 10.0 (Figure 4-29).

The collected samples were formed into four groups based on the range of pH values measured in single batch extractions. These four groups were 7.4-8.0 (n=16), 8.0-8.5 (n=21), 8.5-9.0 (n=12), and 9.0-10.0 (n=4). Samples within each group were mixed together to form composite samples for pH-dependent leaching and percolation column leaching (material codes Vändöra 1, 2, 3 and 4, respectively). Samples in the pH range 7.4 to 8.5 are indicative of a significant amount of natural carbonation during the road use. Leaching tests as a function of pH were carried out at L/S 10 L/kg on the four grouped samples according to technical specification CEN/TS 14997. For Vändöra composites from the first three pH intervals, extraction pH values of 2, 4, 5, 6, 7, 8, 10, 11 and 12 were tested. For the composite from the fourth pH interval, due to the smaller sample size, extraction pH values of pH 2, 4, 6, 8, 10 and 12 only were measured. Percolation tests were conducted on the grouped samples Vändöra 1, 2 and 3 according to technical specification CEN/TS 14405. The sample amount for Vändöra 4 did not allow for a percolation test. Sampling for Vändöra 1 and 2 was at L/S 0.1, 0.5, 1.0 and 2.0 L/kg (cumulative), and for Vändöra 3 at L/S 0.2, 1.0 and 2.0 L/kg (cumulative).
Leaching data were not available for the MSWI bottom ash that was originally used in the Vändöra project. Therefore, a selection of pH-dependent leaching and percolation column test results from testing of MSWI bottom ash from Germany (Berger et al., 2005) and the Netherlands (van der Sluot et al., 2008c) are used as reference materials for this case.

4.6.2 Results and Discussion

A complete set of figures illustrating results from the single extraction batch tests (deionized water at L/S of 10 L/kg), pH-dependent leaching tests and column tests for the comparison materials is provided in Appendix D.

Measured pH values from laboratory testing of reference bottom ash materials from Germany and The Netherlands are compared to pH measured in core samples from the Vändöra Roadbase in Figure 4-30. The lower field material pH shows the effect of carbonation in the field with pH values between 8 and 8.5, approximately equal to the saturation pH for calcium carbonate.

Figure 4-30. Measured pH in reference bottom ash and core samples from Vändöra roadbase.
For the comparison of leaching test eluates to field leachates, measured concentrations are displayed as functions of pH (left) and L/S (right). Single batch extraction test results (n=53, black circles) are plotted along with pH-dependent leaching test results for the four composite samples from the road subbase (red data sets) and the three reference materials (blue data sets); a sample key is provided Figure 4-30. In general, LSP was consistent between the single point extraction tests and the pH-dependent tests for the individual subbase samples, the composite subbase samples and the reference MSWI samples (Figure 4-31).

As expected, the individual subbase samples exhibit greater variability in pH and extract concentration because of differences in the extent of air exposure (i.e., carbonation, oxidation) and for more soluble species (i.e., chloride, potassium) different amounts of water contact because of preferential flow paths.

![Graphs showing pH and L/S for Cadmium and Nickel](#)

**Figure 4-31.** Cadmium and nickel results from pH-dependent leaching tests (left) and column leaching tests (right), illustrating consistency of results between field road subbase samples (16-year-old MSWI bottom ash) and for MSWI bottom ash reference samples.
The following are notable relationships between leaching test results for specific constituents:

- The effect of low liquid to solid ratio resulting in higher concentrations in initial column eluates as compared to pH-dependent leaching at L/S of 10 L/kg for highly soluble species is apparent for chloride and sodium (Figure 4-32). When estimating percolation concentrations at low L/S from batch extractions (typically at L/S of 10 L/kg), the upper bound for the expected concentration can be calculated by the ratio of the batch L/S to the initial column L/S or pore water L/S, whichever is greater. Thus, for a batch L/S of 10 L/kg and an initial column L/S of 0.5 L/kg, the initial column eluate concentration would be expected to be up to 20 times greater than the batch concentration (L/S 10 L/kg divided by L/S 0.5 L/kg). In many cases, this theoretical upper bound is not realized because of either preferential flow or the aqueous phase becoming saturated with respect to the constituent of interest.

Figure 4-32. Results from pH-dependent leaching test (left) and column leaching tests (right; chloride and sodium), illustrating higher initial eluate concentrations for highly soluble species from column tests (i.e., L/S < 0.2 L/kg) compared to pH-dependent leaching tests.
The effect of washout and depletion of highly soluble species during column testing or percolation compared with solubility controlled leaching during column testing is evident when comparing column test results for potassium and manganese (Figure 4-33).

Figure 4-33. Potassium and manganese results from pH-dependent leaching test (left) and column leaching tests (right) illustrating typical results for highly soluble species (potassium) compared to solubility controlled species (manganese).

As indicated earlier, potassium is a highly soluble species with initial column eluate concentrations significantly higher than measured from the batch pH-dependence test at L/S of 10 L/kg, and with eluate concentrations from the pH-dependence test essentially constant as a function of pH. As the column test progresses, potassium eluate concentration decreases rapidly with increasing cumulative L/S, decreasing by more than an order of magnitude by cumulative L/S of 2 L/kg. In contrast, the pH-dependent leaching test results indicate highly pH-dependent solubility for manganese between pH 5 and 13 with consistent results for the subbase composite samples (red symbols and lines) and reference materials (blue symbols and lines). However, column test results for manganese indicate
much higher concentrations for the subbase samples, consistent with manganese solubility at pH~8 compared with the concentrations for the reference samples where the column eluate concentrations are consistent with manganese solubility at pH 10-12.5. For manganese, changes in column eluate concentrations as a function of L/S are consistent with manganese LSP with the changes in eluate pH, rather than the rapid decrease in concentration noted for potassium.

- The effect of carbonation of field samples is evident in pH-dependent leaching of barium (not shown), calcium and strontium at pH greater than 7 by comparison of reference samples to the field subbase composites (Figure 4-34).

![Graphs showing pH and L/S effects on calcium and strontium concentrations.](image)

**Figure 4-34.** Calcium and strontium results from pH-dependent leaching test (left) and column leaching tests (right) illustrating the effects of carbonation to reduce solubility at alkaline pH.

- The effect of pH-dependent solubility on percolation results is evident for aluminum, magnesium, lead (Figure 4-35), and boron, manganese and zinc (not shown). Higher concentrations of lead at neutral pH than observed during pH dependent testing is likely the
result of complexation with DOC that was present in some individual samples and masked in the composites used for pH dependent testing (see Figure 4-36).

Figure 4-35. Aluminum, magnesium and lead results from pH-dependent leaching test (left) and column leaching tests (right) illustrating the effects of pH-dependent solubility on the eluate concentrations from column tests (also refer to Figure 4-30 for pH of column test eluates).
For aluminum, all of the column eluates for the reference materials are greater than for the subbase composites because the pH-dependent leaching indicates the same leaching as a function of pH, but the column eluates for the reference materials are between pH 10 and 12.5, where aluminum solubility is much greater than at the subbase column eluates between pH 8 and 8.5. A less pronounced but similar effect is observed for lead when comparing the single reference material that had column eluate with pH 12.5 (blue squares) in contrast to the other materials. The effect is less pronounced for lead than aluminum because of the column eluate pH values in comparison with the minimum in LSP that occurs at pH 8 to 10 for lead but at pH 6 to 8 for aluminum. Conversely, for magnesium, the column eluate concentrations for subbase composites are much greater than for the reference materials because magnesium solubility is much greater at pH 8-8.5 than at pH 10-12.5.

Figure 4-36. Copper and DOC results from pH-dependent leaching test (left) and column leaching tests (right) illustrating the effects of pH-dependent solubility on the eluate concentrations from column tests.
The effect of complexation leading to increased aqueous solubility is evident for copper leaching from the reference materials during the column tests when viewed in context with the DOC concentrations in column eluates (Figure 4-36).

Copper has been previously demonstrated to complex strongly with DOC from bottom ash (van Zomeren and Comans, 2004). Higher concentrations of copper are associated with higher DOC concentrations during column tests, with higher concentrations at low L/S decreasing with increasing cumulative L/S.

The single batch extractions for the individual subbase samples have anomalous results reported for arsenic, when compared to the composite samples, in that the individual samples indicate higher arsenic concentrations at the measured pH, however increased levels of carbonation can result in displacement of arsenic adsorbed to HFO.

4.6.3 **MSWI BA Chemical Speciation Insights**

Figure 4-37 presents data for pH dependence leaching of copper from MSWI BA (from The Netherlands) from a series of experiments (van der Sloot et al., 2001, van der Sloot et al., 2008). The uppermost red data series results from testing fresh MSWI BA, the lowest blue data series results after heat treating the same MSWI BA to 500 °C to remove organic carbon, and the middle green data series results after 1 wt% organic compost is added to the heat treated MSWI BA to add organic matter back into the material. Clearly, removal or addition of organic matter alters the concentration of copper in solution based on complexation with DOC.

![Figure 4-37](image)

**Figure 4-37.** pH-dependence leaching (CEN/TS 14429) data for MSWI bottom ash (Netherlands) as “fresh” material (red), MSWI BA after heat treatment at 500 °C (blue), and heat-treated MSWI BA with 1% compost added (green).

Figure 4-38 presents the experimental results of the same set of experiments along with results of using largely the same CSF for all three conditions, but varying the amount of organic matter in the system to correspond with experimental measurements of TOC and DOC for each experimental condition. Partitioning between POM and DOC plays a significant role in LSP between pH 7 to 13,
with increasing amounts of DOC responsible for increased Cu in solution. At a pH between 6 and 9.5, adsorption onto HFO surfaces represents a significant amount of Cu in the solid phase, while tenorite [CuO] or Cu(OH)$_2$ is present as a precipitated phased at pH greater than 7. Note that availability controls the observed Cu in solution at pH less than 6 based on simulation results, but experimental results indicate that the maximum available amount of Cu partitions into solution only at pH 3. This difference between simulation and experimental results suggests that either Cu dissolution is kinetically controlled during the test conditions, i.e., long enough leaching time is not provide to achieve equilibrium at low pH (Dijkstra et al., 2006) or a solid phase that is important between pH 3 and 6 has not been included in the simulation.
Figure 4-38. Chemical speciation modeling for MSWI bottom ash (Netherlands) as “fresh” material (upper), MSWI BA after heat treatment at 500 °C (middle), and heat-treated MSWI BA with 1% compost added (lower).

Figure 4-39 presents laboratory test data and simulations for pH dependent leaching of Cu from MSWI BA from Austria (van der Sloot et al., 2000). For this figure, the uppermost compares simulation of L/S=0.3 L/kg with experimental data obtained at L/S=10 mL/g, while the middle series provides simulation results at L/S=10 mL/g. This comparison indicates that increased Cu concentrations can be anticipated at lower L/S values because the same amount of Cu is available.
for leaching but increased DOC in solution at low L/S values results in increased Cu solubilization between pH 7 and 10, while the same mass of Cu in solution at low pH values results in increased Cu concentrations that are constrained by Cu availability. The bottommost two graphs present the fraction of dissolved Cu complexed with DOC (left graph) and the percent distribution between different solid phases as a function of pH (right graph). Dissolved Cu is predominantly complexed with DOC between pH 7.5 and 11.5, while uncomplexed Cu (“Free”) is present in solution outside of this pH range. Precipitated Cu(OH)₂ predominates between pH 8.5 and 13.5, while sorption to iron (hydr)oxide surfaces is important between pH 5.5 and 8.5.

Figure 4-40 through Figure 4-42 provide analogous information for Al, V and Zn, respectively, and provide similar insights into expected changes in observed LSP at L/S=0.3 vs. 10 mL/g and speciation in the solid and aqueous phases as a function of pH and L/S. Note that between pH 7 and 11, a significant amount of the Zn is present in solution as complexed with DOC (Figure 4-42, bright green area). Thus, increased amounts of DOC results in increased Zn concentrations in solution over this pH domain. Similar effects are observed for lead (not shown) and these effects are consistent with the field leachate concentrations observed in this case and the prior case (i.e., Figure 4-27 and Figure 4-35)
Figure 4-39. Chemical speciation modeling of copper in MSWI bottom ash (Austria) compared to pH-dependence (CEN/TS 14429) and percolation column (CEN/TS 14405) data.
Figure 4-40. Chemical speciation modeling of aluminum from MSWI bottom ash (Austria) at L/S=10 and L/S=0.3.
Figure 4-41. Chemical speciation modeling of vanadium from MSWI bottom ash (Austria) at L/S=10 and L/S=0.3.
Chemical speciation modeling of zinc from MSWI bottom ash (Austria) at L/S=10 and L/S=0.3.

Figure 4-43 and Figure 4-44 present pH dependent leaching data obtained at L/S=10 mg/L and percolation column data obtained from 0.3 to 10 mg/L for a group of selected COPCs. Simulation results are used to illustrate the effect of L/S on expected leaching. For example, sulfate is solubility controlled throughout the pH domain, as indicated by the overlap of simulation curves over the range of simulated L/S values. In contrast, K is availability controlled over the entire pH domain, as indicated by parallel simulation results at increased concentration with decreased L/S corresponding to the same mass of K partitioning into solution. Finally, Ca, Mg, and Mn are solubility controlled at pH greater than 12.5, 9.5 and 8.5 respectively, while they are availability controlled at lower pH values. When percolation column results align with pH dependence test results and simulated LSP, solubility control during percolation column leaching is indicated (e.g., for Ca, Mg, sulfate, Mn, Cu, Mo, Pb, Sb and Zn). However, percolation column results for K (a highly soluble species) indicates washout and depletion by the initial eluate concentration that corresponds with simulation results at L/S=1 (which is consistent with a loose packing for a course material such as bottom ash) and subsequent rapidly decreasing concentrations (also corresponding with decreasing eluate pH).
Figure 4-43. Chemical speciation modeling at different L/S compared to pH-dependence (CEN/TS 14429) and percolation column (CEN/TS 14405) data for MSWI bottom ash (Austria).
4.6.4 Case Summary

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.

### 4.7 Inorganic Industrial Waste Landfill (The Netherlands)

#### 4.7.1 Case Description

In the framework of a Dutch national research project on sustainable landfills, a landfill site in Nauernasche Polder, Nauerna, The Netherlands was the subject of a pilot scale demonstration project and lysimeters studies (van der Sloot et al., 2003; van Zomeren and van der Sloot, 2006b). In addition to the lysimeter and pilot landfill, laboratory experiments on landfill materials were conducted using the CEN/TS 14405 (2004) percolation column test and the CEN/TS 14429 (2005) pH-dependence test.

The filling of a 12,000 m³ pilot-scale landfill started in April 2000 and was completed in November 2001 (Figure 4-45). The pilot cell was isolated from the rest of the landfill site by a high-density polyethylene membrane. Leachate was collected in the lower corner of the test cell and the amount of leachate pumped out of the test cell was measured. A vertical drain (filled with coarse granular material) was installed in the center of the pilot cell to enhance the drainage of rainwater and to minimize the contact of rainwater with the waste material.

![Figure 4-45. Construction of the Nauerna pilot-scale landfill (van Zomeren and van der Sloot, 2006b).](image-url)
The material placed into the pilot cell was subject to more stringent acceptance criteria than currently required by waste regulation. The disposed material, characterized as "primarily inorganic waste" because it did not contain any municipal solid waste, included wastes from drilling mud (2.8 wt %), wastewater treatment sludge (0.1 wt %), foundry waste (0.5 wt %), blasting waste (1.7 wt %), residues from mechanical soil cleaning (10.2 wt %), contaminated soils, gravel and construction debris (7.2 wt %), mineral production waste (55.4 wt %), filter cake from waste processing (8.2 wt %), sludge from soil cleaning (11.4 wt %), waste from street cleaning (0.4 wt %) and miscellaneous materials (2.1 wt %) as reported in van der Sloot et al. (2003).

Samples were taken from all waste streams deposited in the cell and the landfilled weight of each stream was recorded. From all waste samples collected, a representative waste mixture was prepared by proportionately taking the waste sample mass per waste mass placed into the landfill into account. The resulting inorganic waste composite was used for the laboratory testing of pH-dependent leaching (CEN/TS 14429) and percolation column testing (CEN/TS 14405). In October 2001, representative waste samples were also used to fill three 1.5 m³ lysimeters with a representative waste mixture (Figure 4-46).

Figure 4-46. Nauerna landfill lysimeters.

The lysimeters were plastic containers of approximately 1 m height, open at the top surface to the atmosphere in order to receive natural precipitation. Leachates from the lysimeters were collected through a system of tubes and subsurface collection vessels. The lysimeters were located adjacent to the pilot landfill. The lysimeters were filled with test material as follows:

- Lysimeter 1 - disposal of wastes in order of delivery as practiced at Nauerna;
• Lysimeter 2 - encapsulation of more contaminated wastes in relatively low permeability wastes (soil cleaning residues); and,
• Lysimeter 3 - disposal of wastes in order of delivery as practiced at Nauerna with addition of 5 wt % each of sewage sludge and car shredder waste to increase organic matter loading.

The material placed into Lysimeter 1 and 2 were not significantly different and, therefore, leachate results are presented together for this evaluation. Lysimeter 3, however, contained a sufficiently different waste composition due to addition of organic matter. Therefore, the results from Lysimeter 3 are not considered for the purposes of this report. The studies at field, lysimeter and laboratory scale represent different time scales through the L/S to which the waste was exposed.

4.7.2 Results and Discussion
A complete set of figures illustrating results from the laboratory pH-dependent leaching tests and column tests of a sample of solid waste material (red solid dots) along with results from the combined Lysimeter 1 and 2 (orange open squares) and the pilot-scale landfill (purple open diamonds) is provided in Appendix E. Field lysimeter and pilot-scale landfill results are graphed both as a function of pH with the laboratory pH-dependent leaching test results (left) and as a function of L/S with the laboratory column test results (right).

An important distinction in redox within the material existed between the laboratory column tests, field lysimeters and pilot-scale landfill. Laboratory column leaching tests exhibited an initial ORP of -100 mV (pE -1.69) that increased to +250 mV (pE 4.23), presumably as a result of using oxygen-saturated water as the column eluent. The leachates from the field lysimeters had an initial ORP of -200 mV (pE -3.38) which increased to a stable value of approximately +200 mV (pE 3.38) after 1.5 years of testing. In contrast, the pilot-scale landfill maintained a relatively constant redox potential of -200 mV (pE -3.38) throughout the observation period of approximately 4 years (van Zomeren et al., 2005).

The following are notable relationships between leaching test and field results for specific constituents:

• There is a difference in the oxidation conditions for (i) the laboratory leaching tests and the field lysimeters where leaching occurs under oxidizing conditions, and (ii) the pilot-scale landfill where leaching occurs under reducing conditions. The difference in these conditions is most easily seen for iron leaching concentrations due to the increased iron solubility under reducing conditions (Figure 4-47, top). Unless a highly reducing material is being tested, oxidizing conditions prevail for most laboratory tests as materials are handled in open to laboratory atmosphere and the CEN/TS 14429 pH-dependent test uses mildly oxidizing nitric acid for pH adjustment. In the case of field lysimeters, the construction of the lysimeter most likely partially limited diffusion and barometric exchange of atmospheric oxygen into the system under unsaturated conditions. 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. Furthermore, biogenic reducing conditions are consistent with the observed increase in DOC landfill leachates compared to
the DOC concentrations in laboratory column eluates and lysimeter leachate (Figure 4-47, bottom).

Figure 4-47. Iron and dissolved organic carbon concentrations from Nauerna landfill study.

- Increased concentrations of chromium in leachate from the pilot-scale landfill are most likely the result of Cr(III) complexation with DOC (Figure 4-48, top); a similar effect is indicated for copper. Increased concentrations of arsenic in leachate from the pilot-scale landfill are most likely the result of loss of arsenic adsorption sites on hydrated iron oxide surfaces because of reduction and solubilization of iron (Figure 4-48, bottom).
In contrast, increased barium leachability in leachate from the pilot-scale landfill is most likely linked to increased solubilization of phosphate (shown as phosphorus) under reducing conditions (Figure 4-49). Vanadium also had higher concentrations in leachate from the pilot scale landfill under reducing/carbonated conditions than observed from the lysimeters and the laboratory column tests. For these constituents, 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.
Increased concentrations at low L/S indicated for chloride, magnesium, potassium, and sodium (illustrated for chloride, magnesium and sodium in Figure 4-50) are observed for leachates from the field lysimeters and the pilot-scale landfill, as well as the laboratory column tests when compared to pH-dependent test results at L/S of 10 L/kg. Peak pilot concentrations for chloride are consistent with laboratory column testing L/S of 0.5 mL/g and a peak concentration 20 times that observed from pH dependent testing at L/S of 10 mL/g. For these constituents, the concentrations in eluates at low L/S from laboratory column tests provide a reasonable indicator of the maximum field leachate concentrations.
Field lysimeter and pilot-scale landfill leachate concentrations for cadmium and zinc are indicated by initial solubility control followed by rapid washout of the fraction of the constituent available for leaching (Figure 4-51). The initial concentrations are similar to the laboratory pH-dependent leaching test results followed by a rapid decrease in concentration with increasing L/S.
4.7.3 Chemical Speciation Insights - Predominantly Inorganic Industrial Waste

Figure 4-52 through Figure 4-54 compare chemical speciation modeling results for Cr, Cu and Pb, respectively, with pH dependence and percolation column test results. In the left side of each figure, the chemical speciation results are compared to pH-dependent and percolation column test data (red circles and blue triangles, respectively) are compared to chemical speciation model results at L/S 10 mL/g and L/S 0.3 mL/g. The right side panels in each figure show the associate partitioning for controlling solid and aqueous phases. The phase partitioning panels for Cr (Figure 4-52) indicate that adsorption onto solid carbon or POM (dark green area) and complexation in solution with DOC (light green area) dominate the LSP at pH less than 10. This is consistent with the laboratory and field results presented in Figure 4-48. At pH greater than 10, amorphous chromium hydroxide [Cr(OH)₃(a)] is the prevalent solid phase. The effect of changing L/S from 10 to 0.3 mL/g on the Cr model result is relatively minor compared to other species.
Figure 4-52. Chemical speciation modeling of chromium from predominantly inorganic industrial waste at L/S=10 and 0.3 mL/g compared to pH-dependence and percolation column data.

In an analogous manner to Cr, Cu LSP behavior (Figure 4-53) is driven by association with POM and DOC; however, the role of DOC is significantly diminished at low L/S.
Lead LSP (Figure 4-54) is dominated by formation of crystalline lead hydroxide \([\text{Pb(OH)}_2(c)]\) (light yellow area) and hinsdalite \([(\text{Pb,Sr})\text{Al}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6]\) (pink area) at acidic and alkaline pH, respectively. Additionally, Pb LSP is affected by adsorption onto HFO surfaces (red area) and POM which playing significant roles at \(6 \leq \text{pH} \leq 11\).
The impact of redox condition on LSP is illustrated for Fe, Cu and total sulfur in Figure 4-55 through Figure 4-57. In each figure, chemical speciation model results are presented for mildly oxidizing (pH+pE=13), reducing (pH+pE=6) and strongly reducing (pH+pE=4) conditions. Comparison of simulations with experimental results from the pH dependence test suggests that the material is mildly reducing to slightly oxidized, most likely closer to pH+pE of 13 than 6 which is reasonable for the laboratory conditions and test method; however, the effect of increasing the reducing condition on the chemical speciation in this material is clear, as would occur to a limited extend during percolation column testing and to a greater extent under field conditions (i.e., between pH+pE of 4 and 6). As conditions become more reducing, Fe solubility increases at neutral to slightly acid pH with a corresponding loss of adsorptive surface area (see loss of ferricyrite in Figure 4-55) while metal precipitation with sulfides (e.g. pyrite [FeS2], blauleli [Cu0.6S0.8], galena [PbS]) becomes evident. Comparison of simulations with measurements for redox must be treated with a high degree of uncertainty because of the errors that may be introduced during sampling collection and measurement (these errors would bias experimental measurements towards more oxidizing conditions through the unintentional introduction of atmospheric oxygen).
Figure 4-55. Comparing effects of oxidizing and reducing conditions - chemical speciation modeling of iron from predominantly inorganic industrial waste at L/S=10 mL/g compared to pH-dependent and percolation column laboratory data and pilot leachates.
Figure 4-56. Comparing effects of oxidizing and reducing conditions - chemical speciation modeling of copper from predominantly inorganic industrial waste at L/S=10 mL/g compared to pH-dependent (PrEN 14429) and percolation column (PrEN 14405) data.
Figure 4-57. Comparing effects of oxidizing and reducing conditions - chemical speciation modeling of sulfur from predominantly inorganic industrial waste at L/S=10 mL/g compared to pH-dependent (PrEN 14429) and percolation column (PrEN 14405) data.

4.7.4 Case Summary
Case 7 focused on comparison of laboratory and field lysimeter results to leaching from a 12,000 m³ 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.
4.8 Municipal Solid Waste Landfill (The Netherlands)

4.8.1 Case Description
The pilot-scale landfill for MSW in Landgraaf, The Netherlands, was established to evaluate the biodegradation of organic matter-rich waste by leachate renewal and recycling. The test cell had a volume of 45,000 m³ and 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 (Table 4-3). Samples of all the wastes accepted at the landfill were sampled proportionally to obtain a representative mixture of the waste in the test cell for laboratory studies. The material collected was homogenized and reduced in volume to manageable quantities by cone and quartering. During the filling of the test cell, lateral infiltration pipes were placed to facilitate the efficient wetting of the waste. During the entire operation of the test cell, leachate samples were collected and analyzed for major, minor and trace elements, as well as parameters to monitor the degradation of waste, for example gas composition, chemical oxygen demand (COD), biological oxygen demand (BOD), DOC. Preparation for the pilot program started in 2000. The actual leachate collection started when the pilot was completely filled in May 2002 (Luning et al., 2006; van der Sloot et al., 2008a).

Table 4-3. Waste composition of the landfilled material in the test cell at Landgraaf (Luning et al., 2006).

<table>
<thead>
<tr>
<th>Material</th>
<th>Eural Code*</th>
<th>Fraction of Total (%</th>
<th>Quantity (tonnes)</th>
<th>Fraction on dry basis (%)</th>
<th>Dry Matter (tonnes)</th>
<th>Water as moisture content (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW</td>
<td>20.30.01</td>
<td>34.4%</td>
<td>9,000</td>
<td>36%</td>
<td>5,300</td>
<td>3,700</td>
</tr>
<tr>
<td>Industrial Waste</td>
<td>20.03.01</td>
<td>11.5%</td>
<td>3,000</td>
<td>12%</td>
<td>1,400</td>
<td>1,600</td>
</tr>
<tr>
<td>Shredder Waste</td>
<td>19.10.04</td>
<td>18.3%</td>
<td>4,800</td>
<td>19%</td>
<td>3,800</td>
<td>1,100</td>
</tr>
<tr>
<td>Cleaning Residue</td>
<td>19.12.09</td>
<td>6.9%</td>
<td>4,700</td>
<td>19%</td>
<td>3,700</td>
<td>1,000</td>
</tr>
<tr>
<td>Foundry Sand</td>
<td>10.09.08</td>
<td>18.3%</td>
<td>1,300</td>
<td>5%</td>
<td>1,300</td>
<td>13</td>
</tr>
<tr>
<td>C&amp;D Waste</td>
<td>19.12.09</td>
<td>7.3%</td>
<td>1,900</td>
<td>8%</td>
<td>1,600</td>
<td>330</td>
</tr>
<tr>
<td>Sewage Sludge</td>
<td>19.08.12</td>
<td>3.2%</td>
<td>380</td>
<td>2%</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100%</strong></td>
<td><strong>25,200</strong></td>
<td><strong>100%</strong></td>
<td><strong>17,400</strong></td>
<td><strong>7,800</strong></td>
</tr>
</tbody>
</table>

Note: * European waste code

The shape and layout of the drains and infiltration pipes is given in Figure 4-58. Nine leachate drainage pipes were installed in the bottom of the test cell, which drained into six collection wells. A buffer tank was used for recirculation of leachate, which was connected with the lateral infiltration pipes located at two depths in the landfill test cell. Different cycles of infiltration and discharge of leachate were used during the operation of the cell.

The pH-dependence test (CEN/TS 14429) and the percolation column test (CEN/TS 14405) were carried out on subsamples of the waste mixtures collected and homogenized during initial filling of the test cell. After eight years of operation, core samples of the waste in the landfill were obtained and composited into a sample subjected to pH-dependence and percolation testing using the same
procedures. In addition to the core composite, material from individual cores taken after eight years of operation were subjected to a single step batch leaching procedure in demineralized water at L/S 10 L/kg (EN 12457-2).

![Cross-section schematic layout of the landfill test cell with leachate collection drains and infiltration pipes.](image)

**Figure 4-58.** Cross-section schematic layout of the landfill test cell with leachate collection drains and infiltration pipes.

### 4.8.2 Results and Discussion

A complete set of figures illustrating results from the laboratory pH-dependent leaching tests and column tests along with results from the pilot-scale landfill test cell is provided in Appendix F. Comparisons are presented between laboratory test results and field results for the following datasets:

- initial composited waste sample (green triangles with a dashed line) using pH-dependence and percolation column tests,
- field materials composited from landfill cores taken after eight years (blue squares with solid line) using pH-dependence and percolation column tests,
- individual core samples (grey diamonds) using single batch extraction in deionized water at L/S of 10 L/kg
- leachate collected from the landfill (red, open circles).

For each analyte, data are presented as a function of pH (left) and as a function of L/S (right). Leachate concentrations are plotted as a function of leachate pH or as a function of the cumulative L/S of leachate from the landfill (based on collected leachate volumes).

In the context of the other cases discussed in this report, the MSW landfill has the greatest proportion of biodegradable organic matter and therefore has the greatest amount of DOC in the leachate as well as the most chemically reducing conditions within the test material. Interpretation of the constituent concentrations in the landfill test cell leachate is complicated by the recirculation of collected leachate back into the landfill. Leachate recirculation induces higher rates of microbial biodegradation, furthering reducing conditions, and also results in accumulation of soluble constituents in the leachate, rather than washing them out and observing declining concentrations as leaching from the system progresses.
The following are notable relationships between leaching tests and field results for specific constituents:

- Results for pH, DOC and iron are presented in Figure 4-59 and Figure 4-60. The pH as a function of L/S for the column test on the initial composite material indicates near neutral pH (i.e., 7.5) initially, followed by a temporary increase to 8.0, followed by a decrease to 7.0, indicative of the onset of acetogenesis as part of MSW biodegradation. In contrast, the column test on the composite of core samples after eight years was initially near neutral and then increased to pH 8.5 followed by a slight decrease in pH. This behavior was most likely the result of washout of accumulated biogenic volatile fatty acids. DOC and iron concentrations in the eluates further support this assumed behavior (note the increase in dissolved iron at L/S of 10 L/kg for the column test on the initial composite material, signaling the onset of strictly anaerobic biodegradation and strongly reducing conditions).

Figure 4-59. Eluate pH from leachates from the Landgraaf MSW landfill (red circles) compared to the pH from percolation column testing for initial material and landfill cores (solid symbols).
Maximum chloride, potassium and sodium concentrations in the initial column test eluates were good indicators of maximum landfill leachate concentrations, which were a factor of approximately 20 greater than observed in laboratory pH-dependent test eluates (Figure 4-61). This phenomenon was expected because the concentrations measured in leachate and laboratory test eluates reflect a similar mass per volume of constituent dissolved but at different L/S conditions. Unlike the values observed for other cases in this report, the landfill leachate concentrations did not decrease with increasing L/S because of leachate recirculation.
Figure 4-61. Concentrations of highly soluble constituents (chloride, potassium and sodium, upper, middle and lower graphs, respectively) from laboratory test eluates and leachate from the landfill test cell.

- Aluminum, calcium, nickel and zinc concentrations in landfill leachate were consistent with concentrations measured in pH-dependent test eluates, indicating solubility controlled
leaching (i.e., a saturated solution with respect to the constituent at the leachate pH); results for aluminum, calcium and nickel are provided in Figure 4-62).

Figure 4-62. Examples of solubility-controlled leaching whereby the measured concentration in leachate and laboratory column tests is closely aligned with results from the pH-dependent leaching test (illustrated by aluminum, calcium and nickel, upper, middle and lower graphs, respectively).
Increased concentrations of chromium in leachate from the landfill test cell are most likely the result of complexation of Cr\(^{3+}\) with DOC (Figure 4-63, top). Increased concentrations of arsenic in leachate from the pilot-scale landfill are most likely the result of loss of arsenic adsorption sites on hydrated iron oxide surfaces because of reduction and solubilization of iron (Figure 4-63, bottom).

![Graphs](image)

**Figure 4-63.** Complex interactions as a result of reducing conditions are illustrated by chromium (DOC complexation) and arsenic (loss of iron adsorption), resulting in higher leachate concentrations than indicated by pH-dependent and laboratory column tests.

In contrast, increased barium leachability (Figure 4-64, top) in leachate from the pilot-scale landfill is most likely linked to increased solubilization of phosphate under reducing conditions (Figure 4-64, bottom).
Vanadium also had higher concentrations in the leachate from the pilot scale landfill under reducing conditions than observed from the lysimeters and the laboratory column tests (Figure 4-65). High vanadium is likely due to a shift in oxidation state from $V^{5+}$ to $V^{4+}$ (see Section 2.2.3).
Figure 4-65. Increased vanadium concentrations under reducing conditions, likely the result of chemical reduction of V$^{5+}$, also resulting in higher leachate concentrations than indicated by pH-dependent and laboratory column tests.

For these constituents, 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 (see Section 2.2.3 and Section 3).

- The strongly reducing conditions existing in the MSW landfill also favor the conversion of sulfate to sulfides with the concurrent precipitation of some metal sulfides. Decreasing sulfur in solution and leachable sulfur from composite samples is a reflection of conversion from sulfate (soluble) to sulfide (insoluble) as a result of biodegradation processes (Figure 4-66, top). The effect of these processes competing with increased solubilization by either DOC complexation for copper or chloride complexation for cadmium results in decreasing concentrations with increasing L/S when leachate results and laboratory column results on eight-year-old material to laboratory (pH-dependent and column testing) on the initial landfill composite (Figure 4-66, middle and bottom).
Figure 4-66. Decreasing sulfur in leachate from the landfill test cell and lower initial sulfate concentrations in eluates from laboratory column testing on core samples after eight years indicates conversion of sulfate to sulfides (top) with decreased solubility of copper (middle) and cadmium (bottom).
4.8.3 Chemical Speciation Insights – Municipal Solid Waste Landfills

An extensive review MSW leachate compositions is available (Robinson, 1995). MSW is anticipated to initially be at oxidizing (i.e., pH+pE=13-15) because of open air handling combined with initial biodegradation processes. However, under landfill conditions gradients from mildly reducing to strongly reducing conditions (i.e., pH+pE=5.5 as indicated by sulfate reduction) are present. Thus, chemical speciation modeling of pH dependent test results are simulated at pH+pE=13 (Figure 4-67 and Figure 4-68), while percolation column conditions can rapidly evolve from oxidizing to reducing conditions because of inherent microbial activity (initially aerobic to sulfate reducing or methanogenic) and field conditions are simulated at reducing conditions. Figure 4-67 (Cd, Ni, Pb, Zn) and Figure 4-68 (sulfate, Ca, Cr, F) left side graphs compare simulation of pH dependent leaching at L/S=10 (red line) and 0.3 mL/g (blue dashed line) with pH dependent leaching test data (red dots) and percolation column data (blue triangles) and simulated speciation at L/S=10 mL/g. As indicated with earlier examples, areas where the simulated results at L/S=10 and 0.3 mL/g coincide are anticipated to be solubility controlled pH domains for the indicated element. Domains where simulated concentrations L/S=0.3 mL/g are much greater than simulated concentrations at L/S=10 mL/g can be expected to exhibit higher concentrations in initial percolation column eluates, as indicated for sulfate results. Decreasing concentrations of Cd, Ni, Pb and Zn during the progression of column leaching is a consequence of depletion of the soluble species at near neutral pH, either because of limited available content or transformation under reducing conditions such as formation of a metal sulfide precipitate (i.e., Cd, Ni, Pb, Zn).
Figure 4-67. Chemical speciation modeling under reducing conditions (pH+pE=13) of municipal solid waste (the Netherlands) compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).
Figure 4-68. Chemical speciation modeling under reducing conditions (pH+pE=13) of municipal solid waste (the Netherlands) compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).
The upper panels of Figure 4-69 and Figure 4-70 present the changes in simulated Fe and Cu LSP, respectively, as a function of pH+pE between 13 and 4. The left side panels show the model conducted at L/S=10 while the right side panels shown the model conducted at L/S=0.3. In Figure 4-69, Fe solubility increases at neutral to slightly acid pH values with progressively more reducing conditions in response to the greater solubility of Fe$^{2+}$ compared to Fe$^{3+}$. Cu solubility (Figure 4-70) decreases with more reducing conditions because of the formation of blaublei [Cu$_{0.6}$S$_{0.8}$] and cuprite [Cu$_2$O]. The lower panels in these figures present simulated LSP at L/S=10 indicating dominant speciation in aqueous and solid phases (left side) and fractional distribution of controlling solid phases (right side). POM and DOC association are important contributors to overall observed LSP for both Fe and Cu. Pyrite is an important Fe solid phase at strongly reducing conditions, while the demarcation between the formation of blaublei and cuprite shifts to a higher pH as more strongly reducing conditions are simulated.
Figure 4-69. The effect of oxidation-reduction (redox) on the chemical speciation of iron from municipal solid waste (the Netherlands).
Figure 4-70. The effect of oxidation-reduction (redox) on the chemical speciation of copper from municipal solid waste (the Netherlands).
Figure 4-71 and Figure 4-72 illustrate that impact of biodegradation that results in removal of POM and DOC from the system under initially oxidizing conditions (pH+pE=13) and under reducing conditions (pH+pE=5.5), respectively. Progressive loss of DOC decreases DOC-associated Cu in solution and overall Cu solubility, shifting increasing amounts of Cu to adsorption to TOC and HFO under oxidizing conditions (Figure 4-71) while resulting in amounts of blaublei and cuprite under reducing conditions (Figure 4-72). Also note that initial percolation column eluate concentrations coincide with the simulation under oxidizing conditions with high POM and DOC concentrations while the final percolation column eluate concentrations coincide with reducing conditions where POM and DOC have been substantially depleted.
Figure 4-71. Chemical speciation of copper at pH+pE=13 during degradation of municipal solid waste (the Netherlands) through loss of POM and DOC under oxidizing conditions.
Figure 4-72. Chemical speciation of copper at pH+pE=5.5 during degradation of municipal solid waste (the Netherlands) through loss of POM and DOC under reducing conditions.

Figure 4-73 presents field leachate data in comparison with simulated aqueous concentrations of Fe and Cu based on laboratory testing. The observed field leachate concentrations correspond well with simulations at pH+pE=5.5, with the results for Cu also reflect a range in the amount of DOC present to complex with Cu and increase overall Cu solubility (ranging from coincidence with initial pH dependent leaching test results to orders of magnitude lower concentrations as DOC is depleted).
**Figure 4-73. Comparison of field leachate concentrations (multiple sources) for Fe and Cu with pH dependence laboratory test data and simulated concentrations at pH+pE=5.5 and L/S=10 and 0.3.**

4.8.4 **Case Summary**

Case 8 focused on a 45,000 m³ 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 4.7) 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. Chemical speciation modelling and experimental results also illustrated the importance of particulate organic matter and dissolved organic carbon on the leaching of several trace and major constituents in MSW.
4.9 Stabilized Municipal Solid Waste Incinerator Fly Ash Disposal (The Netherlands)

4.9.1 Case Description

A pilot experiment with four stabilized waste compartments has been carried out in The Netherlands using cement solidified/stabilized municipal solid waste incinerator fly ash (van Zomeren and van der Sloot, 2006a; van der Sloot et al., 2007). Details of the stabilization formula are proprietary but the formulation included portland cement and fuel ash derived pozzolans. Results are also available for the full-scale landfill receiving the same materials after ten years of operation (Keulen, 2010; van Zomeren et al., 2011). Laboratory results from pH-dependence testing and percolation testing on “as produced” cured and crushed material, along with laboratory monolith testing is compared to field pilot results based on leachate and testing of core samples after four years and full-scale landfill leachate and testing of core samples. Laboratory testing consisted of pH-dependent leaching using CEN/TS 14429, up-flow percolation testing using CEN/TS 14405, and monolith mass transfer rate using (NEN 7375, 2004). A full-scale landfill received the same material as the pilot system and was subject to core sampling after ten years of operation. Individual core samples were leached according to EN 12457-2 using single point batch extractions at L/S of 10 L/kg with demineralized water.

A schematic showing the design of the field pilot system is presented in Figure 4-74. Four hydraulically isolated test cells (Cells A to D) were used for the solidified/stabilized waste to examine the effects of waste depth, carbonation and mixing of stabilization formulations.

![Figure 4-74. Schematic illustration of the front view of the pilot scale experiment using stabilized waste (from van der Sloot et al., 2007). Each test cell was 8 m long, and the space between test cells was filled with sand to maintain physical stability.](image-url)
The waste was stabilized in situ in layers of approximately 0.5 m. Geotextile membrane was placed vertically at 1.5 m intervals to create preferential flow channels through the stabilized fly ash, facilitating infiltration flow around the monolith at the waste-geotextile interface rather than percolation through the material and thus establishing a “flow around” with diffusion to the interface scenario. A portion of the rainwater that falls on top of the stabilized waste evaporated because of the relatively high porosity of the surface layer and the low permeability (possibly even partial pore sealing) of the deeper layers in the stabilized waste monofill. A layer of mildly contaminated soil underlies the stabilized waste layer for protection of the bottom liner system. This soil layer also had the potential to neutralize the alkaline percolate water and possibly bind leached contaminants (Rietra et al., 2001).

After four years of operation, the four pilot landfill cells were visually inspected and demolished using a hydraulic excavator (van Zomeren et al., 2007). Bulk samples were taken at various spots within the stabilized waste and cores were drilled to sample detailed waste profiles. The three exposed cells (Cells A, B and D) were heavily weathered to a depth of 20-30 cm such that material could be easily removed with a spade. Cracking and swelling of the material was visible on the exposed surfaces. The outer first centimeter was light grey in color and then the material was dark grey to black to a depth of 20-30 cm. The material became much more solid below 40 cm depth. Plant roots grew in the stabilized waste to a depth from a few centimeters (Cell B) to 10-15 cm (Cell D). The material from Cell D (mixed waste) crumbled easily when removed while the material from Cell B below 50 cm was removed as blocks of about 20-50 cm in diameter that also crumbled readily under the bucket of the hydraulic excavator. The unexposed cell (Cell C) was visually unchanged in comparison with the initial condition after placement. The material was solid, grey in color and had no cracks or swelling. The unexposed material came out as large blocks (up to 0.5 m³) which did not break when they were dropped (on the sand) from 3-4 meter height. These blocks did break after (repeated) hitting with the bucket of the hydraulic crane. These observations clearly showed a significant difference in material properties (i.e., hardness, weathering, color, cracking) between the exposed and unexposed stabilized waste.

4.9.2 Results and Discussion

A complete set of figures showing the results from the laboratory pH-dependent leaching tests and column tests along with results from the pilot-scale test cells and the landfill are provided in Appendix H. Results are presented in the form of concentration as a function of pH (left graphs) including pH-dependent test results on freshly stabilized waste following a 28-day cure interval (connected orange dots), compositied core samples obtained after four years from test Cell B (connected blue diamonds) and test Cell C (connected green triangles), leachates from the test cells (individual filled blue, green and fuchsia symbols), leachate from the full-scale landfill (open red circles), single point extractions on test cell cores (open blue diamonds, green triangles and fuchsia squares) and single point extractions on landfill core samples (gold dots). Results are also presented in the form of concentration as a function of L/S (right) including column test results on freshly stabilized waste following a 28-day cure interval (connected orange dots), test cell leachates (open blue diamonds, green triangles and fuchsia squares) and the first fraction at L/S of 0.1 of a column test on two core samples from the landfill (gold dots).
The pH of the fresh material (one week old) in demineralized water was between 12 and 12.5, whereas the pH of the older samples (four months) increased with depth from 10.9 to 11.9 (van der Sloot et al., 2007). After six months, the pH of the stabilized waste at 15–25 cm below the surface had decreased to about 11.7. After four months, Cl was depleted from at least the first 10 cm of the stabilized waste, indicating substantial washout of this mobile element.

The depletion of mobile constituents and, possibly, enhanced carbonation of the outer layer was determined to be due to increased porosity and were the main processes responsible for the observed material properties (van Zomeren et al., 2007). Related research on intermittent wetting and carbonation of solidified/stabilized waste by Garrabrants et al (2002, 2003) and Sanchez et al (2002) indicated that relaxation of internal constituent gradients during non-wetting periods and solubility constrained leaching (i.e., local equilibrium at the surface in the presence of small volumes of contacting water) has a significant impact on leaching under these circumstances. A conceptual model of the processes that occurred during the pilot field experiment is illustrated in Figure 4-75.

![Figure 4-75. Conceptual model of processes occurring during the field pilot study of monolithic waste disposal (from van der Sloot et al., 2007).](image)

The following are notable relationships between leaching test and field results:

- Leachate and runoff from the field pilot and landfill was $6 < \text{pH} < 9$ while laboratory column tests indicated $12 < \text{pH} < 13$ (Figure 4-76). This difference was most likely due to carbonation on the surface for runoff and a combination of carbonation and neutralization by the underlying soil/buffer material for leachate in the field. Leachate pH values from the full-scale disposal cell were consistent with the values observed from the pilot cells.
Figure 4-76. Comparison of pH for laboratory testing of waste materials and landfill cores to landfill leachate pH for stabilized waste.

- Reaction of the field material with atmosphere carbon dioxide (i.e., carbonation) is demonstrated by the decreased concentrations of barium, calcium and strontium at $6 < \text{pH} < 10$ for the field cores as compared to the initially prepared samples (see calcium and strontium in Figure 4-77). The decrease in concentration for these analytes in this pH range is a typical result of the formation of carbonates of barium, calcium and strontium.
Figure 4-77. Calcium and strontium leaching from laboratory and field materials showing decrease in concentrations in the pH range $6 < \text{pH} < 10$ consistent with carbonate formation.

Similarly lower concentrations are indicated by pH-dependent leaching testing for lead from aged core samples compared to freshly stabilized material resulting from carbonation to form lead carbonate (see Figure 4-78).
Figure 4-78. Lead leaching from laboratory and field materials showing decrease in concentrations in the pH range 6 < pH < 10 consistent with carbonate formation.

Lower concentrations in pH-dependent solubility curves for core samples from field test after four years indicate effects of washout of highly soluble constituents like chloride, potassium and sodium (see Figure 4-79). However, several other elements are essentially unchanged (i.e., Al, Cu, Mg, S). Similarly, comparison of eluate concentrations from column testing with pH-dependence test results for highly soluble species (e.g., Cl, K, Na) indicates rapid washout as a nearly vertical response at the eluate pH, although initial eluate concentrations from the column test are greater than the concentration indicated by the pH-dependence test results. The initial eluate concentrations from laboratory column tests at L/S≤0.5 mL/g are consistent with the peak concentrations in field leachate and runoff from the pilot and full-scale cases. For column tests, concentrations decline by greater than an order of magnitude by L/S=2 mL/g. Scatter in field leachate and runoff concentrations is attributable to diffusion-controlled release during larger precipitation/infiltration events, dilution and depletion. Although peak concentrations are similar for pilot-scale and full-scale leachate samples, the rate of release of highly soluble salts is substantially slower than observed in laboratory column studies. Peak concentrations reflect pore water equilibration, while extended infiltration events result in a concentration gradient within the monolith, slowing release which is controlled by diffusion within the monolithic material. Dilution is caused by preferential flow paths channeling around the material.
Figure 4-79. Chloride and potassium leaching from laboratory and field materials showing washout of highly soluble species.

- 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).

- Laboratory column test results on freshly stabilized waste (near pH 12) are equal to or less than indicated by pH-dependence test results on laboratory samples for several elements, indicating depletion of the soluble species of the element at the eluate pH conditions (e.g., As, Cr, Mo, Se, V); this behavior is typical for oxyanion species. Vanadium and selenium (Figure 4-80) are examples where the more soluble speciation as an oxyanion (e.g., V$_2$O$_5$) appears to have been washed out as indicated by the decrease in the near neutral pH range.
(e.g., pH 6-8 for vanadium and pH 7-10 for selenium) based on pH-dependent leaching test results on core samples taken after four years compared to freshly stabilized waste.

Figure 4-80. Vanadium and selenium leaching from laboratory and field materials showing washout of more soluble oxyanions.

- For many elements, where solubility is highly pH-dependent, the distinctions between laboratory column test results and field leachate and runoff can readily be understood based on the difference between eluate pH under laboratory column test conditions (12<pH<13) and field conditions (6.5<pH<9) as a result of carbonation. These elements and species include aluminum, barium, calcium, chromium, magnesium, manganese, nickel, lead, strontium and zinc. Essentially no change in the pH-dependent solubility curves for several constituents (e.g., copper, chromium and manganese) from core samples after four years compared to freshly stabilized waste indicates solubility controlled leaching behavior (Figure 4-81). Similarly, laboratory column test results are entirely consistent with the pH-dependence test results on laboratory samples, indicating solubility controlled leaching.
Field leachate and runoff results were consistent with the pH-dependence test results for solubility-controlled species but a distinction must be made for elements that are not affected by carbonation and elements significantly affected by carbonation (e.g., Ba, Ca; compare with pH-dependence results of field cores).

Figure 4-81. Copper, chromium and manganese leaching from laboratory and field samples of stabilized waste.
Field leachate and runoff results for highly soluble species, oxyanions of arsenic, chromium and molybdenum (Figure 4-82), selenium and vanadium as well as highly soluble species such as chloride, potassium, and sodium, exhibited consistent behavior with column test results although when plotted with pH-dependence results display nearly vertical scatter shifted to correspond with the field pH (e.g., 6 < pH < 9).

Figure 4-82. Molybdenum leaching from laboratory and field samples of stabilized waste.

Laboratory leaching of the core samples obtained at depths from 1 to 12 m from the full-scale disposal site after eight years of operation indicated that no significant leaching of any constituents had occurred at a depth of 1 m (minimum sample depth) or greater, including highly soluble salts, and that carbonation had not occurred at that depth (van Zomeren, 2011).

For several elements (i.e., Al, Ba, Ca, Cu, Fe, Mg, Pb, and Zn), laboratory monolith test results (green squares) fall either on or close to the pH-dependent solubility curve (red lines), indicating chemical saturation in aqueous solution rather than diffusion-controlled constituent release under the test conditions for the monolith test.

For several elements (i.e., Cd, Cr, Mo, Na, S and Se), the laboratory monolith test results (green squares) are significantly less than the pH-dependent solubility curve (red lines), indicating that either the dissolution rate or diffusion-controlled constituent release dominates leaching of at the test conditions of the monolith test.

4.9.3 Chemical Speciation Insights – Stabilized Waste

Figure 4-83 through Figure 4-85 present chemical speciation modeling results at L/S=10 and 0.3 mL/g for Cu, Pb and SO₄ in comparison to (i) laboratory pH dependent leaching test data from fresh
stabilized waste (ca. 28 days cure) and core samples taken after 4 years from the field test site (i.e., Cell B, Cell C and Cell D) and after 10 years from the full-scale monofill (i.e., Monofill), (ii) leachate from the field test site, and from the full-scale monofill, and (iii) laboratory column percolation data from testing the fresh stabilized waste after curing and crushing. Figure 4-83, providing results for Cu, also compares chemical speciation modeling when the assume copper precipitate is either copper hydroxide [Cu(OH)₂] or tenorite [CuO] which are very similar with tenorite being a more stable mineral form. Leaching test results from fresh and aged stabilized waste suggests transformation from copper hydroxide to tenorite as the material ages but this has not been independently confirmed. Comparison of leaching test results for lead from fresh and aged samples also suggests that more stable states as represented by the chemical speciation are formed as the material ages.

Figure 4-83. Chemical speciation modeling at L/S=10 and 0.3 mL/g for copper from stabilized waste (the Netherlands) compared to field leachate data, laboratory pH dependence test data (CEN/TS 14429) on fresh stabilized waste (ca. 28 day cure) and field core samples after 4 years, and percolation
column data on fresh stabilized waste (CEN/TS 14405). Also included is a comparison of assuming Cu precipitation as Cu(OH)$_2$ and as tenorite [CuO].

Figure 4-84. Chemical speciation modeling at L/S=10 and 0.3 mL/g for lead from stabilized waste (the Netherlands) compared to field leachate data, laboratory pH dependence test data (CEN/TS 14429) on fresh stabilized waste (ca. 28 day cure) and field core samples after 4 years, and percolation column data on fresh stabilized waste (CEN/TS 14405).
Figure 4-85. Chemical speciation modeling at L/S=10 and 0.3 mL/g for sulfate from stabilized waste (the Netherlands) compared to field leachate data, laboratory pH dependence test data (CEN/TS 14429) on fresh stabilized waste (ca. 28 day cure) and field core samples after 4 years, and percolation column data on fresh stabilized waste (CEN/TS 14405).
Figure 4-86 through Figure 4-90 compare the impact of carbonation from reaction of atmospheric carbon dioxide with the alkaline stabilized waste for Ca, Cu, Cr, Mg and Zn. Most notable is the impact of the loss of ettringite and the formation of calcite reducing the solubility of Ca at alkaline pH with an analogous but less pronounced effect on Mg speciation and solubility. In case of Mg, a significant transformation of the solubility-controlling phases occurs upon carbonation, as brucite effectively disappears and is replaced by CO$_3^-$-hydrotalcite. The main effect of carbonation is expected for Group II elements of the periodic table (e.g., Mg, Ca, Sr, Ba). Carbonation has minimal impact on Cu and results in increased Zn leaching over the pH domain from 8 to 11. However, a substantial impact is observed for Cr, where initial oxyanion substitution for sulfate in ettringite is lost with progressing carbonation.

**Figure 4-86.** Chemical speciation modeling for calcium from stabilized waste (the Netherlands) at different carbonate levels compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405) for cement stabilized fly ash (the Netherlands).
Figure 4-87. Chemical speciation modeling for copper from stabilized waste (the Netherlands) at different carbonate levels compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).
Figure 4-88. Chemical speciation modeling for chromium from stabilized waste (the Netherlands) at different carbonate levels compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).
Figure 4-89. Chemical speciation modeling for magnesium from stabilized waste (the Netherlands) at different carbonate levels compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).
Figure 4-90. Chemical speciation modeling for zinc from stabilized waste (the Netherlands) at different carbonate levels compared to pH-dependence data (CEN/TS 14429) and percolation column data (CEN/TS 14405).

4.9.4 Case Summary

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.

4.10 Portland Cement Mortars and Concrete

4.10.1 Case Description
One high-volume end use for secondary materials (e.g., coal fly ash, granulated blast furnace slag) is
as substitutes for portland cement or admixtures in cement and concrete construction products. In
addition, some secondary materials may be used by being included in cement-based materials as
fine or coarse aggregate. For example, more than 11 million tons of coal fly ash were used as a

A review of LEAF-analogous laboratory leach testing for portland cement-based mortars and
concretes made with and without fly ash indicated that pH-dependent leaching and monolith
leaching of COPCs is systematic and fairly consistent between non-amended and fly-ash amended
materials with up to approximately 30 wt% of fly ash substituted for cement (van der Sloot et al.,
2012). Laboratory testing of commercial formulations of blended concretes and microconcretes
(i.e., those where a portion of portland cement is replaced with coal fly ash) using EPA Method 1313
for pH-dependent leaching and EPA Method 1315 for monolithic mass transfer rate leaching
demonstrated the following (Kosson et al., 2014 and Garrabrants et al., 2014):

- The pH-dependent leaching of COPCs in amended materials, with up to 45 wt% substitution
  of fly ash for portland cement and three-month cures, was controlled by the cement
  chemistry and was significantly different from the LSP measured for the component fly ash
  material incorporated into the blended sample,

- Eluate concentrations for COPCs in monolithic mass transfer leaching decrease when
  amended cement-based materials with substitution rates up to 45 wt% fly ash are allowed
to cure beyond the typical 28-days used for physical testing of cement-based materials,

- The combination of concrete chemistry and physical retention (e.g., observed diffusivity and
tortuosity) provided by the portland cement paste in the blended material controlled the
monolithic mass release of COPCs from concrete materials, and
• Most COPCs (e.g., Al, As, B, Ba, Cd, Cr, Mo, Pb, Sb, Se, Tl and V) are well-retained in fly ash-amended concrete materials, resulting in observable monolith leaching from concretes containing 45 wt% fly ash substitution for only a few analytes (e.g., Al, Ba, Cr, Sb and V).

Unanswered questions in the studies described above are the impact of sample aging processes (i.e., carbonation and decalcification) that have the potential to alter the chemistry and physical retention of the concrete.

The laboratory-to-field comparisons for concretes and mortars are based on pH-dependence testing of laboratory prepared concretes and mortars to pH-dependence testing of field samples that have been “in service” for extended time intervals:

1. Two sets of core samples of concrete in place for 40 years obtained from a test site in Stuttgart, Germany (Schießl, 2003)
   a. Core samples from a surface that has been exposed to rain and other weather variations,
   b. Core samples from a surface that was permanently immersed in fresh water.
2. Core samples from a Roman aqueduct, aged for approximately 2,000 years (van der Sloot et al., 2011),
3. Recycled concrete aggregate (RCA) that was used as roadbase in a test road in Norway (Engelsen et al., 2009; 2010)
   a. Fresh recycled concrete sampled from material used in the road base during the field test site preparation,
   b. Field samples of the recycled concrete aggregate from the roadbase after four years of roadway use, < 10 mm sieved from the field material (therefore more carbonated),
   c. Field samples of the recycled concrete aggregate from the roadbase after four years of roadway use, 20-120 mm sieved from field material (and then size-reduced for laboratory testing).

Testing results from these field samples are compared to two laboratory-prepared reference mortars from Germany (sample: Cement mortar CEM I DE) and Norway (sample: Cement mortar CEM I NO).

4.10.2 Results and Discussion
A complete set of figures illustrating available pH-dependent leaching behavior for the comparison materials is provided in Appendix H. In general, LSP was consistent between materials cured for short times (i.e., 28 days) and materials exposed to field conditions for extended time periods (Figure 4-91).
Figure 4-91. Aluminum, antimony, copper and zinc as example results from pH-dependent leaching tests on field core samples of concrete of different ages and exposure conditions in comparison with reference mortars. LSP was consistent between reference materials cured for short times (i.e., 28 days) and materials exposed to field conditions for extended time periods.

The following are notable observed effects of field aging:

- Arsenic and chromium leaching are shown in Figure 4-92. For arsenic, elevated and more erratic leaching was observed for the Roman cement (entire pH domain), possibly the result of combined carbonation and decalcification, and the German reference mortar. Chromium leaching was greatest at neutral to alkaline pH for the Norwegian reference mortar. The German reference sample contained a reducing agent to decrease chromate content to meet EU regulations on occupational exposure.
- The effect of carbonation (Figure 4-93) to decrease leaching of barium, calcium and strontium at neutral to alkaline pH is evident, with assumed increasing extent of carbonation from short cure time reference samples (minimal carbonation), four-year-old Norwegian recycled concrete, and 2,000-year-old Roman cement (complete carbonation).
Figure 4-92. Arsenic and chromium results from pH-dependent leaching tests on field core samples of concrete of different ages and exposure conditions in comparison with reference mortars.

Figure 4-93. Calcium and strontium results from pH-dependent leaching tests on field core samples of concrete of different ages and exposure conditions in comparison with reference mortars. The effect of carbonation to decrease leaching at neutral to alkaline pH is evident.
Figure 4-94 presents the impact of progressive extent of carbonation on the observed solubility of Ca (upper left graph) and the change in solid and liquid phase speciation at different extents of carbonation (i.e., 1, 2.85 and 6 percent by mass total carbonate in the initial solid phase). As the extent of carbonation progresses as a result of the alkaline cement material reacting with carbon dioxide (most frequently from either atmospheric or biological sources), the solubility of Ca decreases over the pH domain from 6 to 14. Progressive extent of carbonation results in the conversion of ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26(H₂O)], portlandite [Ca(OH)₂] and calcium oxide-aluminates and other alkaline cement phases to calcite [CaCO₃].
Figure 4-94. Chemical speciation modeling of the impacts of carbonation on solubility of Ca and the resulting solid and aqueous phase speciation compared to pH-dependence leaching test data on portland cement CEM I standard mortar after 28-day cure.
Figure 4-95 compares the laboratory testing and chemical speciation results (from Figure 4-94) for Ca with pH dependence leaching test data from samples of cementitious materials with a range of extent of aging. Older materials are expected to have greater extents of carbonation.
because of prolonged exposure. Included in Figure 4-95 are a CEM I standard mortar after 56 days of curing (least extent of carbonation and similar to the CEM I standard mortar in Figure 1), a recycled concrete aggregate (0-32 mm diameter) after field exposure through use in a roadbed for 4 years with Ca leaching behavior similar to 2.7% carbonate content, and Roman cement that had been in service for approximately 2,000 years with Ca leaching behavior similar to between 3 and 6% carbonate content.
compared to chemical speciation modeling of the impacts of carbonation on solubility of Ca and pH-dependence leaching test data on portland cement CEM I standard mortar after 28-day cure.

Figure 4-96 presents the impact of progressive extent of carbonation on the observed solubility of Ca, sulfate, Mo and Cr in comparison to pH dependence leaching test data from a standard mortar (ref) prepared from a CEM I portland cement and cured for 28 days prior to testing. Species that are either part of ettringite (i.e., sulfate) or co-precipitated with ettringite (i.e., as part of a solid solution), have relatively low solubility over the pH domain from 10 to 13 where ettringite is sparingly soluble, but have increased solubility when ettringite reacts to form calcite. Thus, progressively increasing solubility of sulfate, Mo and Cr are observed between pH 10 to 13 with increasing extent of carbonation.
4.10.3 Case Summary

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).

Figure 4-96. Chemical speciation modeling of the impacts of carbonation on solubility of Ca, SO₄, Mo and Cr compared to pH dependence leaching test data on portland cement CEM I standard mortar after 28-day cure.
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, including by reducing testing and evaluation costs for well-studied classes of materials.

5.1 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 previously evaluated material or material class; 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 anticipated 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 when warranted based on a screening assessment that includes laboratory characterization, 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 initial material characterization and field demonstration projects:

1. Materials being considered should first be characterized using pH dependent leaching (Method 1313) and either percolation column leaching (Method 1314) or as a minimum, leaching at low liquid-to-solid ratio (Method 1316). Monolith leaching (Method 1315) should also be carried out for scenarios where monolith mass transport is anticipated as a significant factor controlling leaching. A sufficient number of samples based on data quality objectives should be characterized to reflect the inherent variability of the material being evaluated.
2. Field demonstration projects should include careful collection and analysis of runoff, pore water, leachate and other contacting water during the demonstration period. All sampling should be carried out using techniques that avoid atmospheric exchange and oxygenation, carbon dioxide uptake, and/or biogenic acidification during sampling. Within the material and for collected fluids, pH, redox and conductivity should be analyzed to the extent practical. Analysis of collected leachates and other aqueous samples should include analysis of major and trace constituents, as well as DOC, DIC and anions.

3. Core samples from the field demonstration project should be obtained at the end of the demonstration period and be considered to be obtained at intermediate time intervals. Laboratory leaching analysis of the cores can provide useful insights into the chemical speciation and physical-chemical status of the material during field aging processes. The comparison of the leaching behavior as function of pH for different ages of the material in combination with leachate data and batch or percolation test data at the appropriate pH provides valuable insight in the leaching behavior over time.

4. An efficient sampling plan consists of preparing a composite of samples taken from different locations from the pilot, lysimeter or field site for pH dependence and percolation and/or monolith leach tests and testing individual samples at L/S=10 and the natural pH to see the variability based on the location of the sampling.

5. Chemical speciation-based LSP and mass-transport modeling should be used to provide insights into leaching conditions that may evolve in the field and are beyond laboratory test conditions.

5.2 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:

This approach focuses on the release flux of potentially toxic constituents over a defined time interval. Thus, the management scenario is evaluated based on a source term that incorporates consideration of system design, net infiltration and the leaching characteristics of the material. Basing assessment and decisions on estimated release allows consideration of the waste as containing a finite amount of the constituent of interest, the time course of release, and the ability to adapt testing results to a range of management scenarios. The measure of release would be the mass of constituent released per affected area over time (i.e., release flux). Knowledge of the release flux would allow more accurate assessment of impact to water resources (e.g., groundwater or surface water) by defining the mass input of constituent to the receiving body over time. Results of this impact-based approach can provide direct input into subsequent risk assessment for decision making, either based on site-specific analysis or using a generalized set of default assumptions.

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 more realistic and refined, scenario-specific
estimate of constituent leaching that can be used as a source-term for risk assessment. While the result is a bounding estimate of leaching potential, consideration of waste and scenario-specific information allows many conservative assumptions to be replaced with data. 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 (Figure 5-1). Subsequently, the EPA published its *Methodology for Evaluating Encapsulated Beneficial Uses of Coal Combustion Residuals* (2013b; also EPA, 2014) which provides for a tiered approach specifically applied to a more limited set of uses of two secondary materials (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 the more detailed recommendations provided below on the use of LEAF test methods, consistent with the initially proposed methodology (2002) and the EPA methodology (2013). Additional relevant details regarding assessment approaches can be found in Kosson et al (2002), Sanchez et al (2002) and Kosson et al (1996), EN 12920 (1996), Verschoor et al (2008), Carter et al (2009), Postma et al (2009), van der Sloot and van Zomeren (2012), and Hjelmar et al (2013). These methodologies also recognize that decision making typically is based on a water concentration-based comparison to human health or ecologically based standards, or an exposure assessment at a point of compliance. It must be emphasized that these recommendations for use of leach testing data 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 in the vadose zone and groundwater or surface water 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). These evaluations are typically incorporated into a model of constituent fate and transport leading to possible receptor exposure (e.g., groundwater transport to a drinking water well, with water ingestion as the exposure pathway).
5.3 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 answer the following questions:

1. **What is the applicable pH domain?** The applicable pH domain will extend at least from the material’s natural pH to neutral pH (pH 7), and may be further extended based (i) material characteristics that may result in self-acidification through oxidation or biodegradation processes (e.g., materials containing significant amounts of sulfides, other reactive phases or biodegradable organic matter), (ii) commingling with either more alkaline or more acidic materials, (iii) external sources of acid or alkalinity such as from adjacent materials or the chemistry of contacting water. Case studies in this report provide examples of applicable pH domains for several materials and scenarios.

2. **Is the material oxidized as produced and subject to reducing conditions under the proposed use or disposal scenario?** Causes of reducing conditions to form include commingling with other reducing materials such as slags or some mining wastes, presence of significant amounts of biodegradable organic matter and barriers to exchange of atmospheric oxygen.
3. *Is the material chemically reduced and subject to oxidizing conditions?* Causes of oxidizing conditions for initially reduced material include exposure to air and oxygenated water (i.e., infiltration).

4. *Will the primary mode of water contact be through infiltration and percolation through the material or through contact and exchange at the exterior surface of a large mass or monolith (e.g., as would occur for materials compacted to low hydraulic conductivity)?*

### 5.4 Screening Assessment (Tier 1)

Recommendations for use of LEAF testing in screening assessment (Tier 1) and equilibrium-based assessment (Tier 2) are provided in Table 5-1. Leaching assessment for screening purposes (Tier 1) 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) 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. The adjusted (conservative) concentration at the applicable pore water L/S can be achieved by

\[ C_{i,\text{adjusted}} = C_{i,\text{L/S=10}} \times CF \]

Where \( C_{i,\text{adjusted}} \) is the adjusted concentration of constituent \( i \), \( C_{i,\text{L/S=10}} \) is the maximum concentration over the relevant pH domain at L/S=10 mL/g (as from Method 1313), and \( CF \) is the correction factor which is equal to 10 divided by the pore water L/S (which can be approximated as the material porosity).

Cases 5 and 8 demonstrated that an effective pore water L/S of 0.5 L/kg is appropriate for coarse landfilled materials subject to percolation and preferential flow, resulting in a multiplier of 20 to adjust the eluate concentrations measured using Method 1313. This screening approach does not account for the amount of material being evaluated that would be present under the scenario (i.e., it implies an “infinite source” of material or COPCs).

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

An 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 results in conjunction with Method 1316 at L/S of 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) then measured from Method 1313 at the pH corresponding with the pH measured at L/S of 2 mL/g, then the Method 1313 results are considered to be availability constrained and the maximum concentration from Method 1313 over the applicable pH domain that is adjusted to the pore water L/S is used as the peak source concentration. If the COPC at L/S of 2 mL/g is the same as (within uncertainty) the concentration measured at the corresponding pH from Method 1313, then the COPC is considered solubility constrained and the maximum concentration over the applicable pH domain from Method 1313 is used as the peak source concentration.
Table 5-1. Tier 1 Screening Assessment and Tier 2 Equilibrium-Based Assessment - Summary of recommended test methods and analyses.

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tier 1 – Screening Assessment</strong></td>
<td>Method 1313 (applicable pH range only)</td>
<td>pH, EC, COPCs, DOC</td>
<td>Maximum leachate conc. estimated as 20x or 10x maximum eluate conc. for highly soluble constituents in granular materials and the measured maximum eluate conc. for monolithic materials and solubility controlled constituents (all materials).</td>
</tr>
<tr>
<td><strong>Tier 2 – Equilibrium-based Assessment</strong></td>
<td>Method 1313 (applicable pH range + pH=2, 7, 9 if not included)</td>
<td>pH, EC (natural pH only), COPCs, DOC</td>
<td>Availability estimated as maximum release at measured pH intervals including pH=2 and 9; provides basis for finite source by assuming that availability is maximum cumulative release under field conditions. EC used to estimate ionic strength. Acid/base neutralization capacity to pH=7. Maximum leachate conc. estimated as determined from Tier 2B based on Method 1313 results over applicable pH domain. Method 1316 allows identification of solubility controlled vs highly soluble constituents.</td>
</tr>
<tr>
<td><strong>Tier 2A Compliance</strong></td>
<td>Method 1313 (full set of eluates)</td>
<td>pH, EC &amp; pe (natural pH only), COPCs, DOC</td>
<td>Availability as indicated in Tier 2A. Liquid-solid partitioning as a function of pH used for speciation assessment. Provides baseline understanding of material leaching behavior. Supports chemical speciation simulations to understand effects of changes in L/S, pH, redox, and reactive constituents (e.g., DOC, carbon dioxide, etc.). Maximum leaching concentration as indicated for Tier 1 or based on simulation results at L/S of the material pore solution. Method 1316 provides basis for determination of solubility control and verification of chemical speciation modeling at low L/S.</td>
</tr>
<tr>
<td><strong>Tier 2B Characterization</strong></td>
<td>Method 1313 (full set of eluates)</td>
<td>pH, EC, relevant COPCs (natural pH and for availability) to meet environmental requirements and additional constituents to meet beneficial use requirements</td>
<td>Used to verify leaching over “applicable” pH range, acid/base neutralization capacity to pH=7, and availability of relevant COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Assumes definition after completion of Tier 2B and/or analogous prior information. Chemical analysis only for determination of leaching at natural pH and availability (2 or 3 extracts). Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>
Notes for Table 5-1:

1 For regulatory frameworks based on a source term concentration, the maximum estimated leaching concentration is recommended for use in screening assessment. For regulatory frameworks based on the total mass of constituent potentially leached, availability is recommended for use in screening assessment.

2 The applicable pH range is determined considering the material’s natural pH, changes in pH due to material aging processes, infiltration conditions, and interfaces or comingling with other materials.

3 ”conc.” is used as an abbreviation for concentration or concentrations.

4 Twenty times the maximum eluate concentration is recommended for highly soluble species when the material is homogeneous (e.g., coal fly ash) and ten times the maximum eluate concentration is recommended for heterogeneous materials (e.g., MSW incinerator bottom ash) where significant preferential flow is anticipated. Both multipliers are to account for the increased concentrations expected when estimating pore water concentrations (L/S=0.2 to 0.5 L/kg) from test conditions of L/S=10 mL/g).

5 Highly soluble species are Group IA elements (i.e., Na, K), anions (i.e., bromide, chloride, fluoride, nitrate), and oxyanions (i.e., As, B, Cr, Se, Mo, V).

6 Determination of EC and pe is recommended for natural pH eluate only. The sensitivity and uncertainty of pe measurements are recognized but pe measurement will provide a useful indication of whether or not the material is inherently reducing under abiotic and anoxic conditions.

7 Speciation assessment refers to consideration of the effects of changes in pH, redox conditions, extent of carbonation, complexation with dissolved organic carbon, etc. which may be accomplished heuristically or in combination with geochemical speciation modeling.

8 Relevant COPCs are those constituents that are present in the material and have been found through Tier 2B characterization and/or prior information to leach at concentrations or release values that approach or challenge regulatory or quality control thresholds.

9 Prior information, such as characterization information from similar materials, may reduce or supplant the need for or extent of Tier 2B characterization.
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 (typically pH 2 for cations and pH 9 for oxyanions). 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 (Tier 2B) 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. However, prior knowledge from testing of analogous materials may reduce the need for or extent of characterization testing.

For periodic demonstration of compliance with regulatory thresholds, the extent of Method 1313 testing can be reduced to the applicable pH domain and regulatory COPCs, pH and conductivity23. For quality control purposes, the extent of Method 1313 testing can be further reduced to only the natural pH value and along with the pH 2 and/or 9 as needed to measure availability for the relevant COPCs (those that are present and leach at concentrations that approach thresholds) 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.

5.6 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. Summaries of recommended LEAF testing and evaluation are provided for percolation mass transport-based assessment and monolithic mass transport-based assessment in Table 5-2 and Table 5-3, respectively.

Percolation based regimes can be evaluated through use of the pH dependent test (i.e., Method 1313) in conjunction with the percolation column test (i.e., Method 1314) or batch testing (Method 1316) for initial leachate concentrations. Considering the results of Cases 2, 5 and 8 (Sections 4.2, 4.5 and 4.8) initial eluates from Method 1314 or low L/S results from Method 1316 are good indicators of the anticipated COPC concentrations in initial field leachates and Method 1314 provides 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.

23 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.
### Table 5-2. Tier 3 Percolation Mass Transport-Based Assessment – Summary of recommended test methods and analyses.

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tier 3 – Percolation Mass Transfer Rate-based Assessment</strong></td>
<td></td>
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</tr>
<tr>
<td><strong>Tier 3A Compliance</strong></td>
<td>Method 1313 (pH=2, 9, applicable pH domain) Method 1314 (to L/S=2 mL/g)</td>
<td>pH, EC (natural pH only), COPCs, DOC</td>
<td>Allows verification of liquid-solid partitioning at natural pH and availability (from Method 1313). Maximum leachate conc. estimated as established by Tier 3B as greater of either i) maximum conc. from Method 1314 up to L/S = 2 mL/g, or ii) maximum conc. from Method 1316, or iii) maximum conc. from Method 1313 over applicable pH domain.</td>
</tr>
<tr>
<td><strong>Tier 3B Characterization</strong></td>
<td>Method 1313 (full set of eluates) Method 1314 (full set of eluates) Method 1316 (L/S=2)</td>
<td>pH, EC (natural pH only), COPCs, DOC, DIC, major and minor constituents</td>
<td>Availability and leaching as a function of pH and evaluation of potential changes in conditions as indicated for Tier 2B. Method 1314 provides leachate evolution as a function of L/S for source term based on test elution curve. Supports reactive transport simulations to consider sensitivity to field conditions such as infiltration chemistry, preferential flow and material aging. Provides basis for verification of chemical speciation modeling at low L/S.</td>
</tr>
<tr>
<td><strong>Tier 3C Quality Control</strong></td>
<td>Method 1313 at pH=2, 7 and/or 9 and Method 1316 at L/S = 2</td>
<td>pH, EC, COPCs (1313 for availability and 1314 at L/S of peak release) to meet environmental requirements, additional constituents to meet beneficial use requirements</td>
<td>Method 1313 extractions used to verify acid/base neutralization capacity to pH=7, and availability of selected COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Method 1314 extract at L/S of prior peak concentration to verify maximum leaching conc. Assumes definition after completion of Tier 3B Characterization. Chemical analysis only for determination of leaching at peak release conc. and availability (2 or 3 extracts). Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>
Table 5-3. Tier 3 Monolith Mass Transport-Based Assessment – Summary of recommended test methods and analyses¹.

<table>
<thead>
<tr>
<th>Assessment Type</th>
<th>Leaching Methods</th>
<th>Eluate Analyses</th>
<th>Assessment Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 3A</td>
<td>Method 1313 (pH=2, 9, applicable pH domain) Method 1315 (to 7 days)</td>
<td>pH, EC (natural pH for Method 1313 and all Method 1315 eluates), COPCs, DOC</td>
<td>Allows verification of liquid-solid partitioning at natural pH and availability (from Method 1313). Maximum leachate conc. estimated as established by Tier 3B as greater of either i) maximum conc. from Method 1314 up to L/S =2 mL/g, or ii) maximum conc. from Method 1316, or iii) maximum conc. from Method 1313 over applicable pH domain.</td>
</tr>
<tr>
<td>Tier 3B</td>
<td>Method 1313 (full set of eluates) Method 1314 (full set of eluates) Method 1315 (to 64 days)</td>
<td>pH, EC (natural pH only for Method 1313 and all Method 1314, and 1315 eluates), COPCs, DOC, DIC, major and minor constituents</td>
<td>Availability and leaching as a function of pH as indicated for Tier 2B. Method 1314 (crushed material) up to L/S=2 provides estimate of initial pore water composition. Method 1315 provides cumulative release as a function of leaching time for saturated and intermittent wetting conditions. Also provides basis for estimating reactive transport parameters (e.g., tortuosity) for simulation of evolving conditions (e.g., low liquid to surface area, external solution chemistry, carbonation, oxidation, intermittent wetting, etc.). Provides basis for Tier 3C quality control.</td>
</tr>
<tr>
<td>Tier 3C</td>
<td>Method 1313 at pH=2, 7 and/or 9 and Method 1315 (to 7 days)</td>
<td>pH, EC, COPCs (1313 for availability and 1314 at L/S of peak release) to meet environmental requirements, additional constituents to meet beneficial use requirements</td>
<td>Method 1313 extractions used to verify acid/base neutralization capacity to pH=7, and availability of selected COPCs and other (if applicable) constituents central to beneficial use application (e.g., Ca, sulfate, etc.). Method 1315 cumulative release to 7 days to verify consistency with characterization results (Tier 2B). Assumes definition after completion of Tier 3B Characterization. Further simplification may be possible based on additional available information.</td>
</tr>
</tbody>
</table>

¹The cure time prior to testing of monolithic materials is an important consideration because for many cementitious materials, hydration and microstructure development continues for more than a one year; with initial cure times of 90 days recommended prior to Method 1315 testing.
Initial percolation characterization testing should include analysis of both major and trace constituents in all leaching test eluates (Methods 1313 and 1314 or 1316) because knowledge of the major constituents (such as Ca, Fe, DOC or SO₄) 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 can be used as described above (Equilibrium Based Assessment) and Method 1314 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 reduced to only the pH values that result in peak concentrations over the applicable pH domain and the relevant COPCs or Method 1314 testing as described for compliance testing can be used.

Monolith regimes can be evaluated based on use of Method 1315 in conjunction with Method 1313 (Table 5-3). 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). An example approach for use of empirical data from Method 1313 (i.e., for availability) and Method 1315 (i.e., for estimated effective diffusivity) is provided for MSWI bottom ash scenarios in Kosson et al (1996). These approaches can also be used in conjunction with chemical speciation based mass transfer models (see Section 3) 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 and 1315) 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 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 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 can be reduced to only analysis of pH and conductivity and composited eluates up to 7 days for COPCs to determine cumulative release.
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 during field disposal and beneficial use conditions. 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 small changes in leaching relative to freshly prepared material after initial curing periods (i.e., 90 days). 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 accurate estimates within defined uncertainty bounds of maximum field leachate concentrations, extent of leaching and expected leaching responses over time and to changes in environmental conditions 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 plausible, 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.

a. For elements and species that are highly soluble, solubility is not a function of pH and a saturated solution is not expected to occur (e.g., Cl, K, Na). The initial eluates from a column leaching test (i.e., Method 1314) are a reasonable estimate of the expected peak concentration from field leaching and are representative of porewater solutions. Constituent concentrations obtained from the pH-dependent leaching test (i.e., Method 1313) at the material natural pH at L/S=10 mL/g can be multiplied by the ratio of L/S at batch testing conditions to the L/S at porewater conditions based on field porosity (i.e., L/S=0.2-0.5 mL/g with resulting factors of 20-50) to estimate anticipated concentrations under porewater conditions. Similarly, results from an L/S dependence leaching test (i.e., Method 1316) at L/S=0.5 mL/g can provide a reasonable estimate of the expected peak concentration from field leaching. However, for many conditions, because of either solubility constraints or preferential flow, the estimated value under pore water conditions may be overly conservative and not realized in field leachate. Considering these factors, an adjustment factor of 20 has been shown to be a reasonable basis for estimating peak concentrations from LSP data obtained at L/S=10 mL/g. For monolithic materials, peak concentrations are indicative of a “first flush” phenomenon occurring during initial surface wetting after a period without leaching, whereby internal concentration gradients have relaxed. Peak concentrations will decline rapidly during a prolonged wetting event because of diffusion and dissolution limitations on leaching at the external surface. Higher concentrations will return after a non-flow period because of relaxation of internal concentration gradients and re-equilibration of porewater.

b. For elements and species where solubility is pH-dependent and a saturated solution is found to occur based on pH-dependence and column or batch L/S leaching tests, the pH-dependent leaching test (i.e., Method 1313) provides a reasonable estimate of the expected field leachate concentrations over the anticipated pH domain with solubility control, which in turn may be diluted by flow channeling that bypasses contact with the solid material (such as often happens with collection systems or large spatial integration). For monolithic materials, local equilibrium between the porewater and monolith surface can be anticipated as a result of intermittent
infiltration and wetting, followed by diffusion controlled leaching and gradient relaxation.

c. For field percolation scenarios and for elements and species that are highly soluble over a limited portion of the anticipated pH domain (e.g., oxyanions of Cr, As, V), laboratory column test results may be indicative of leaching under initial conditions and as long as oxidized field conditions are anticipated. Peak barium concentrations under oxidized field conditions may be much lower than indicated by laboratory testing because of precipitation with sulfate present at higher concentrations in pore water and leachate. Under field reducing conditions, several oxyanions (e.g., As, Cr, Mo, Se) along with phosphorus and barium exhibit leaching behavior as highly soluble species, a result, in part, of loss of iron oxide sorptive surfaces during iron reduction and mobilization, and therefore high concentrations of iron in leachate should be considered as indicative of reducing conditions. The resulting peak field leachate concentrations are greater than measured during laboratory column testing because the laboratory column test methods typically do not achieve the strongly reduced conditions. As a result, the peak leachate concentration for these constituents under reducing conditions (if anticipated) is best conservatively estimated based on the mass of the constituent available for leaching based on the pH-dependent leaching test multiplied by the correction factor from L/S=10 L/kg to the L/S based on field porosity.

d. Highly alkaline materials (e.g., cement stabilized wastes, alkaline fly ashes, etc.) are likely to exhibit highly alkaline natural pH during laboratory testing (11 < pH < 13), but will react with atmospheric carbon dioxide under field conditions, resulting in field leachates and runoff with pH trending from highly alkaline (observed laboratory pH) to near neutral (pH ≥ 7.0) conditions. Carbonation will result in lower solubility of Group II elements of the periodic table (i.e., calcium, strontium, etc.) due to formation of carbonate minerals, and loss of ettringite can result in increased leaching of co-precipitated oxyanions (e.g., chromate, molybdate, arsenate). Leaching of solubility controlled constituents will reflect the liquid-solid partitioning as indicated by the pH-dependent test results at the resultant pH. Thus, leaching for these constituents should be evaluated based on the pH domain from the initial natural pH of the material to a near neutral pH or the anticipated pH domain anticipated for mixed materials.

e. Dissolved organic carbon (DOC), often in the form of substances analogous to humic substances or volatile fatty acids, can result in complexation of several elements (e.g., copper, chromium), and thereby increase measured aqueous phase concentrations of these elements during laboratory testing and under field conditions. Reducing conditions in the field along with high organic matter content in materials being managed can result in elevated concentrations of DOC in the leachate not observed in results from laboratory test methods.

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 modeling 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. The resulting estimates of COPC release reduce the use of conservative assumptions in favor of more complete data and refined speciation models, and consequently expands alternatives and provides a sound scientific basis for making decisions about appropriate disposal or use of secondary materials on the ground.
REFERENCES


Carter C.M., H.A. van der Sloot and D. Cooling (2009) “pH dependent extraction of soils and soil amendments to understand the factors controlling element mobility - new approach to assess soil


Lundgren T and J. Hartlén; "Slagg från avfallsförbränning Teknik och Miljö" (In Swedish), REFORSK rapport FoU nr 61, REFORSK, Malmö, 1991


van der Sloot H.A., K.-U. Heyer, K. Hupe, R. Stegmann, and P. Buurman (2000a) Milieueigenschappen en potentiële toepassingsmogelijkheden van het eindproduct van een mechanisch gescheiden organische fractie na stabilisatie in een bioreactor; ECN-C-00-54, Netherlands Energy Research Foundation, Petten, the Netherlands.


APPENDIX A. CHEMICAL SPECIATION MODELS FOR EXAMPLE CASES

TABLE OF CONTENTS

<table>
<thead>
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<th>Waste Type</th>
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<td>Coal Fly Ash</td>
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<tr>
<td>MSWI Bottom Ash</td>
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<tr>
<td>Inorganic Industrial Waste (Nauerna Landfill)</td>
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<td>MSW</td>
<td>A-16</td>
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<td>Stabilized Waste</td>
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Table A-1. Chemical Speciation Fingerprint for Coal Combustion Fly Ash

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<td>Solved fraction DOC</td>
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<td></td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L/S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percolation material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg L/S first perc. fract.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactant concentrations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selected Minerals</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A-1. Chemical speciation model for constituents in coal combustion fly ash.
Figure A-2. Chemical speciation model for constituents in coal combustion fly ash.
Figure A-3. Chemical speciation model for constituents in coal combustion fly ash.
Figure A-4. Chemical speciation model for constituents in coal combustion fly ash.
Table A.2. Chemical Speciation Fingerprint for MSWI Bottom Ash

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<tr>
<td>Speciation session</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSWI BA Austria + kolom AA</td>
<td></td>
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</tr>
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<td>[DOC] (kg/l)</td>
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<td>1.00</td>
<td>6.711E-05</td>
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<th>LeachXS</th>
<th>2012</th>
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<tr>
<td>Speciation session</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSWI BA Austria + kolom AA</td>
<td></td>
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</table>

<table>
<thead>
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<th>URL</th>
<th>CODE</th>
<th>MESS</th>
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</thead>
<tbody>
<tr>
<td>DOC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DHA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[DOC] (kg/l)</td>
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<td>[DHA] (kg/l)</td>
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<th>CODE</th>
<th>MESS</th>
<th>REACTION</th>
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<td>L/S</td>
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<td></td>
</tr>
<tr>
<td>I/kg</td>
<td></td>
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<tr>
<td>Clay</td>
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<td>4.880E-05</td>
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<td>HFO</td>
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<td>SHA</td>
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<tr>
<td>Percolation material</td>
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<tr>
<td>MSWI BA A A (C,1,1)</td>
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<td></td>
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<td>Avg L/S first perc. fractions</td>
<td>0.2195</td>
<td>I/kg</td>
<td>11.86</td>
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<td>0.14</td>
<td>8.026E-05</td>
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<td>Ag+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al+3</td>
<td>3.614E+03</td>
<td>1.674E+02</td>
<td>1.139E+02</td>
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<tr>
<td>H3AsO4</td>
<td>1.837E-01</td>
<td>5.000E+01</td>
<td>6.727E-01</td>
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<td>H3BO3</td>
<td>2.180E+01</td>
<td>2.079E+03</td>
<td>3.669E+03</td>
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<td>Ba+2</td>
<td>1.463E+01</td>
<td>3.800E+04</td>
<td>1.000E+01</td>
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<tr>
<td>Br-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca+2</td>
<td>5.178E+04</td>
<td>1.373E+03</td>
<td>5.717E+02</td>
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<tr>
<td>Cd+2</td>
<td>4.110E+00</td>
<td>1.408E+02</td>
<td>6.088E+02</td>
</tr>
<tr>
<td>Cl-</td>
<td>2.000E+04</td>
<td>2.760E+00</td>
<td>1.408E+02</td>
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<table>
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<th>URL</th>
<th>CODE</th>
<th>MESS</th>
<th>REACTION</th>
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</thead>
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<td>AA_3CaO_A12O3_6H2O[s]</td>
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<td></td>
<td></td>
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<tr>
<td>AA_3CaO_Fe2O3_6H2O[s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AA_Ai[OH]3[am]</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>AA_Brutite</td>
<td>BaSrSO4[50%Ba]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AA_Calcite</td>
<td>Ca2Cd[PO4]2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AA_Fe[OH]3[microcr]</td>
<td>Ca4Cd[PO4]3OH</td>
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<td></td>
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<th>MESS</th>
<th>REACTION</th>
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<tr>
<td>AA_Magnesite</td>
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<td></td>
</tr>
<tr>
<td>AA_Portlandite</td>
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<td></td>
<td></td>
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<tr>
<td>AA_Calcite</td>
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<td></td>
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<tr>
<td>AA_Fe[OH]3[microcr]</td>
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</table>
Figure A-5. Chemical speciation model for constituents in municipal solid waste incinerator bottom ash.
Figure A-6. Chemical speciation model for constituents in municipal solid waste incinerator bottom ash.
Figure A-7. Chemical speciation model for constituents in municipal solid waste incinerator bottom ash.
Figure A-8. Chemical speciation model for constituents in municipal solid waste incinerator bottom ash.
Table A-3. Chemical Speciation Fingerprint for Inorganic Waste Landfill at Nauerna (The Netherlands).

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<th>LeachXS</th>
<th>2012</th>
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<td><strong>Prediction case</strong></td>
<td><strong>EPA LtoF Predominantly Inorganic Waste Landfill</strong></td>
<td><strong>DOC</strong></td>
<td><strong>[DOC] (kg/l)</strong></td>
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<td><strong>LtoF Nauerna_pilot</strong></td>
<td><strong>pH</strong></td>
<td><strong>DHA</strong></td>
</tr>
<tr>
<td><strong>Material</strong></td>
<td><strong>Pred Inorg Wastemix NL(P,1,1)</strong></td>
<td>1.00</td>
<td>2.914E-05</td>
</tr>
<tr>
<td><strong>Solved fraction DOC</strong></td>
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<td>3.02</td>
<td>1.500E-05</td>
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<td><strong>Sum of pH and pe</strong></td>
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<td>4.00</td>
<td>1.840E-06</td>
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<td><strong>L/S</strong></td>
<td>10.00</td>
<td>5.27</td>
<td>3.800E-06</td>
</tr>
<tr>
<td><strong>Clay</strong></td>
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<td>2.580E-06</td>
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<td>6.81</td>
<td>3.560E-06</td>
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<td><strong>SHA</strong></td>
<td>1.900E-02</td>
<td>9.51</td>
<td>7.800E-06</td>
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<td><strong>Percolation material</strong></td>
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<td></td>
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<td>14.00</td>
<td>1.408E-04</td>
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<td><strong>Reactant concentrations</strong></td>
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<tr>
<td><strong>Reactant</strong></td>
<td><strong>mg/kg</strong></td>
<td><strong>Reactant</strong></td>
<td><strong>mg/kg</strong></td>
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<td>Ferrihydrite</td>
<td>Ni[OH]2[s]</td>
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<td>Ca2Cd[PO4]2</td>
<td>Fluorite</td>
<td>NiCO3[s]</td>
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<td>alpha-TCP</td>
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<td>OCP</td>
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<td>Anhydrite</td>
<td>Calcite</td>
<td>Hausmannite</td>
<td>Otavite</td>
</tr>
<tr>
<td>BaSrSO4[50%Ba]</td>
<td>Cd[OH]2[C]</td>
<td>Hydromagnesite</td>
<td>Pb2V2O7</td>
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<tr>
<td>Boehmite</td>
<td>Cr[OH]3[A]</td>
<td>Leucite</td>
<td>PbCrO4</td>
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Figure A-9. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-10. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-11. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-12. Chemical speciation model for constituents in inorganic waste landfill material.
Table A-4. Chemical Speciation Fingerprint for Municipal Solid Waste (The Netherlands).

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<th>Chemical Speciation Fingerprint - Municipal Solid Waste Landfill</th>
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</tr>
<tr>
<td>HFO</td>
<td>1.000E-02</td>
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<tr>
<td>SHA</td>
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<td>Percolation material</td>
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</tr>
<tr>
<td>Ca+2</td>
<td>2.272E-04</td>
</tr>
<tr>
<td>Cd+2</td>
<td>1.695E+01</td>
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<tr>
<td>Cl-</td>
<td>2.330E+03</td>
</tr>
<tr>
<td>Selected Minerals</td>
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<tr>
<td>AI[OH]3[a]</td>
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</tr>
<tr>
<td>alpha-TCP</td>
<td>Brucite</td>
</tr>
<tr>
<td>Analbite</td>
<td>Ca2Zn[PO4]2</td>
</tr>
<tr>
<td>Anglesite</td>
<td>CaCu2[PO4]2</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Calcite</td>
</tr>
<tr>
<td>Ba[Sc]O4[96%SO4]</td>
<td>Cerrusite</td>
</tr>
<tr>
<td>BaSrSO4[50%Ba]</td>
<td></td>
</tr>
</tbody>
</table>
Figure A-13. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-14. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-15. Chemical speciation model for constituents in inorganic waste landfill material.
Figure A-16. Chemical speciation model for constituents in inorganic waste landfill material.
### Table A-5. Chemical Speciation Fingerprint for Stabilized Waste Landfill Material (The Netherlands).

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<td>Stabilised waste</td>
</tr>
<tr>
<td>Material</td>
<td>Stabilised waste NL (P,6,1)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Solved fraction DOC</td>
<td>0.2</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
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</tr>
<tr>
<td>L/S</td>
<td>10.000</td>
</tr>
<tr>
<td>Clay</td>
<td>0.000E+00 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>0.000E+00 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>0.000E+00 kg/kg</td>
</tr>
<tr>
<td>Percolation material</td>
<td>Stabilised waste NL (C,15,1)</td>
</tr>
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<td>Avg L/S first perc. fractions</td>
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<table>
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<th>Reactant</th>
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<th>Reactant</th>
<th>mg/kg</th>
<th>Reactant</th>
<th>mg/kg</th>
<th>Reactant</th>
<th>mg/kg</th>
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<td>9.690E+00</td>
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<td>SO4-2</td>
<td>1.066E+04</td>
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<td>Cu+2</td>
<td>3.650E+02</td>
<td>Mn+2</td>
<td>1.750E+02</td>
<td>Sb[OH]6-</td>
<td>4.920E+00</td>
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<td>1.450E-01</td>
<td>F-</td>
<td>1.904E+03</td>
<td>MoO4-2</td>
<td>7.700E+00</td>
<td>SeO4-2</td>
<td>4.600E-01</td>
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<td>H3BO3</td>
<td>5.947E+01</td>
<td>Fe+3</td>
<td>7.393E+01</td>
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<td>2.563E+04</td>
<td>H4SiO4</td>
<td>3.556E+03</td>
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<tr>
<td>Ba+2</td>
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<td>H2CO3</td>
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<td>NH4+</td>
<td>not measured</td>
<td>Sr+2</td>
<td>2.060E+02</td>
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<td>Br-</td>
<td>8.338E+02</td>
<td>Hg+2</td>
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<td>Ni+2</td>
<td>9.290E+00</td>
<td>Th+4</td>
<td>not measured</td>
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<tr>
<td>Ca+2</td>
<td>8.362E+04</td>
<td>I-</td>
<td>not measured</td>
<td>NO3-</td>
<td>not measured</td>
<td>UO2+</td>
<td>not measured</td>
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<tr>
<td>Cd+2</td>
<td>1.782E+02</td>
<td>K+</td>
<td>3.381E+04</td>
<td>PO4-3</td>
<td>4.740E+00</td>
<td>VO2+</td>
<td>5.800E-01</td>
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<tr>
<td>Cl-</td>
<td>5.350E+04</td>
<td>Li+</td>
<td>2.452E+01</td>
<td>Pb+2</td>
<td>9.551E+02</td>
<td>Zn+2</td>
<td>8.015E+03</td>
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**Selected Minerals**

- AA_2CaO_Ai2O3_8H2O[s]
- AA_2CaO_Ai2O3_SiO2_8H2O[s]
- AA_2CaO_Fe2O3_SiO2_8H2O[s]
- AA_3CaO_Ai2O3[Ca(OH)2][0.5_[CaCO3]0.5_11_5H2O[s]
- AA_3CaO_Ai2O3_CaCO3_11H2O[s]
- AA_3CaO_Ai2O3_CaSO4_12H2O[s]
- AA_3CaO_Fe2O3_CaCO3_11H2O[s]
- AA_4CaO_Ai2O3_13H2O[s]
- AA_Ai[OH]3[am]
- AA_Brucite
- AA_Calcite
- AA_CaCO3-hydrotalcite
- AA_CCO3-hydroglaucite
- AA_Gibbsite
- AA_Gypsum
- AA_Jennite
- AA_Magnesite
- AA_Portlandite
- AA_Syngenite
- AA_Trinarboaluminate
- AA_A2CaO_Ai2O3_10H2O[s]
- AA_CO3-hydroglaucite
- AA_Fe[OH]3[microcr]
- AA_Gypsum
- AA_Gypsum
- AA_Gypsum
- AA_Jennite
- AA_Magnesite
- AA_Magnesite
- AA_Portlandite
- AA_Syngenite
- AA_Syngenite
- AA_Trinarboaluminate
- BaSrSO4[50%Ba]
- BaSO4[50%Sr]
- CaSO4[50%Ca]
- Cr[OH]3[C]
- Cu[OH]2[Ca]
- Cu[OH]2[Ca]
- Cu[OH]2[Ca]
- Cu[OH]2[Ca]
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- Cu[OH]2[Ca]
Figure A-17. Chemical speciation model for constituents in stabilized waste landfill material.
Figure A-18. Chemical speciation model for constituents in stabilized waste landfill material.
Figure A-19. Chemical speciation model for constituents in stabilized waste landfill material.
Figure A-20. Chemical speciation model for constituents in stabilized waste landfill material.
Table A-6.  Chemical Speciation Fingerprint for Concrete.

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<th>Chemical Speciation Fingerprint - Cement Mortar</th>
<th>LeachXS</th>
<th>2012</th>
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<tr>
<td>Prediction case</td>
<td>DOC/DHA data</td>
<td>pH</td>
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<td>LTF Cement Mortar CEM</td>
<td>Cement Mortar CEM</td>
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<td>Speciation session</td>
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<tr>
<td>Material</td>
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<td>0.20</td>
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<tr>
<td>Solved fraction DOC</td>
<td>Cement Mortar CEM_SCCC</td>
<td>5.10</td>
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<td>Sum of pH and pe</td>
<td>Cement Mortar CEM_SCCC</td>
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<td>Clay</td>
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</tr>
<tr>
<td>HFO</td>
<td>Cement Mortar CEM_SCCC</td>
<td>2.00E-04</td>
</tr>
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<td>SHA</td>
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<td>2.00E-05</td>
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<td>Percolation material</td>
<td>Cement Mortar CEM_SCCC</td>
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<th>Reactant</th>
<th>mg/kg</th>
<th>Reactant</th>
<th>mg/kg</th>
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</thead>
<tbody>
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<td>H⁺</td>
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<td>Na⁺</td>
<td>4.28E+03</td>
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<td>Mo⁴⁺</td>
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<td>1.95E+03</td>
<td></td>
<td>Mg⁺</td>
<td>1.83E+03</td>
</tr>
<tr>
<td>H⁺</td>
<td>2.00E+05</td>
<td></td>
<td>Sr⁺</td>
<td>6.66E+01</td>
<td></td>
<td>Mg⁺</td>
<td>1.95E+03</td>
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<td>Sb[OH]₆⁻</td>
<td>1.79E+01</td>
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<td>Ba²⁺</td>
<td>6.66E+01</td>
<td></td>
<td>Mg⁺</td>
<td>1.95E+03</td>
<td></td>
<td>Sb[OH]₆⁻</td>
<td>1.79E+01</td>
</tr>
<tr>
<td>H⁺</td>
<td>2.00E+05</td>
<td></td>
<td>Sr⁺</td>
<td>6.66E+01</td>
<td></td>
<td>Mg⁺</td>
<td>1.95E+03</td>
<td></td>
<td>Sb[OH]₆⁻</td>
<td>1.79E+01</td>
</tr>
<tr>
<td>H⁺</td>
<td>2.00E+04</td>
<td></td>
<td>Sr⁺</td>
<td>6.66E+01</td>
<td></td>
<td>Mg⁺</td>
<td>1.95E+03</td>
<td></td>
<td>Sb[OH]₆⁻</td>
<td>1.79E+01</td>
</tr>
<tr>
<td>H⁺</td>
<td>2.00E+05</td>
<td></td>
<td>Sr⁺</td>
<td>6.66E+01</td>
<td></td>
<td>Mg⁺</td>
<td>1.95E+03</td>
<td></td>
<td>Sb[OH]₆⁻</td>
<td>1.79E+01</td>
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Selected Minerals

| AA_2CaO\_Al₂O₃\_SiO₂\_8H₂O[s] | AA_Calcite | AA_Tobermorite-I | Magnesite | PbMoO₄[C] |
| AA_2CaO\_Fe₂O₃\_8H₂O[s] | AA_CO₃-hydrotralcite | Analbite | Manganite | Tenorite |
| AA_3CaO\_Al₂O₃\_6H₂O[s] | AA_Gypsum | Ca₄Cd[PO₄]₃OH | Pb[OH]₂[C] | |
| AA_3CaO\_Fe₂O₃\_6H₂O[s] | AA_Jennite | Cd[OH]₂[C] | Pb₂V₂O₇ | |
| AA_Brucite | AA_Portlandite | Fe_Vanadate | PbCrO₄ | |
Figure A-21. Chemical speciation model for constituents in concrete.
Figure A-22. Chemical speciation model for constituents in concrete.
Figure A-23. Chemical speciation model for constituents in concrete.
Figure A-24. Chemical speciation model for constituents in concrete.
APPENDIX B. COAL COMBUSTION FLY ASH LANDFILL LEACHATE (U.S.)
Figure B-1. Comparison of laboratory and field concentration results for coal combustion fly ash landfill (United States).
Figure B-2. Comparison of laboratory and field concentration results for coal combustion fly ash landfill (United States).
Figure B-3. Comparison of laboratory and field concentration results for coal combustion fly ash landfill (United States).
Figure B-4. Comparison of laboratory and field concentration results for coal combustion fly ash landfill (United States).
Figure B-5. Comparison of laboratory and field concentration results for coal combustion fly ash landfill (United States).
APPENDIX C.  LANDFILL OF COAL COMBUSTION FIXATED SCRUBBER SLUDGE WITH LIME (UNITED STATES)

Table C-1.  Data Sources for Laboratory-to-Field Comparisons for Coal Combustion Fixated Scrubber Sludge with Lime.

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSSL – “as produced” (MAD)</td>
<td>Pub Mill (fresh 4 hr composite)</td>
<td>Fixated Scrubber Sludge with Lime</td>
<td>pH-dependence (SR002)</td>
<td>Sanchez et al., 2008</td>
</tr>
<tr>
<td>FSSL – Field Core (FCM)</td>
<td>FSSL Landfill</td>
<td>Core at depth (3-5 m)</td>
<td>pH-dependence (SR002)</td>
<td>EPRI, 2012 (draft)</td>
</tr>
<tr>
<td>Landfill Porewater</td>
<td>FSSL Landfill</td>
<td>Leachate</td>
<td>-</td>
<td>EPRI, 2012 (draft)</td>
</tr>
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</table>
Figure C-1. Comparison of laboratory and field concentration results for a coal combustion fixated scrubber sludge with lime (FSSL) landfill (United States).
Figure C-2. Comparison of laboratory and field concentration results for a coal combustion fixed scrubber sludge with lime (FSSL) landfill (United States).
Figure C-3. Comparison of laboratory and field concentration results for a coal combustion fixated scrubber sludge with lime (FSSL) landfill (United States).
Figure C-4. Comparison of laboratory and field concentration results for a coal combustion fixated scrubber sludge with lime (FSSL) landfill (United States).
Figure C-5. Comparison of laboratory and field concentration results for a coal combustion fixed scrubber sludge with lime (FSSL) landfill (United States).
**APPENDIX D.  MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH LANDFILL (DENMARK)**

Table D-1.  Data Sources for Laboratory-to-Field Comparisons for MSWI Bottom Ash Landfill

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSWI BA (AT)</td>
<td>Austria, MSW Incinerator</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence</td>
<td>van der Sloot et al., 2000b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Percolation</td>
<td></td>
</tr>
<tr>
<td>MSWI BA (DE)</td>
<td>Germany, MSW Incinerator 1</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence</td>
<td>Berger et al., 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Percolation</td>
<td></td>
</tr>
<tr>
<td>Landfill Leachate (DK)</td>
<td>Denmark</td>
<td>Field Leachate</td>
<td>-</td>
<td>Hjelmar et al., 1991</td>
</tr>
<tr>
<td>Landfill Core (DK)</td>
<td>Denmark</td>
<td>Landfill Core</td>
<td>Batch L/S</td>
<td>Meima, 1997</td>
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<tr>
<td>MSWI BA (NL)</td>
<td>The Netherlands</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence</td>
<td>ECN ongoing studies on MSWI BA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Percolation</td>
<td></td>
</tr>
<tr>
<td>MSWI BA (IT)</td>
<td>Italy</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence</td>
<td>ECN ongoing studies on MSWI BA (Italian client)</td>
</tr>
<tr>
<td></td>
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<td>Percolation</td>
<td></td>
</tr>
<tr>
<td>MSWI BA (UK)</td>
<td>UK, MSW Incinerator</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence</td>
<td>ECN studies on UK MSWI BA</td>
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<tr>
<td></td>
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<td>Percolation</td>
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</table>
Figure D-1. Eluate pH from leachates from the Vestkoven monofill (red circles) compared to the percolation column pH for comparable bottom ash samples (solid symbols).
Figure D-2. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D.3. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-4. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-5. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-6. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-7. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-8. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-9. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-10. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-11. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
Figure D-12. Comparison of laboratory and field concentration results for a MSWI bottom ash landfill (Denmark).
## APPENDIX E. MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH USE IN ROADBASE (SWEDEN)

### Table E-1. Data Sources for Laboratory-to-Field Comparisons for MSWI Bottom Ash used in Roadbase (Sweden).

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
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<tbody>
<tr>
<td>Vändöra – Core 1</td>
<td>Sweden</td>
<td>Core composite from roadbase based on level of carbonation</td>
<td>pH-dependence Percolation</td>
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</tr>
<tr>
<td>Vändöra – Core 2</td>
<td>Sweden</td>
<td>Core composite from roadbase based on level of carbonation</td>
<td>pH-dependence Percolation</td>
<td></td>
</tr>
<tr>
<td>Vändöra – Core 3</td>
<td>Sweden</td>
<td>Core composite from roadbase based on level of carbonation</td>
<td>pH-dependence Percolation</td>
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</tr>
<tr>
<td>Vändöra – Core 4</td>
<td>Sweden</td>
<td>Core composite from roadbase based on level of carbonation</td>
<td>pH-dependence Percolation</td>
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<tr>
<td>Vändöra – Individual Cores (L/S 10 16 yrs)</td>
<td>Sweden</td>
<td>Cores from roadbase</td>
<td>Batch L/S (EN 12457-2)</td>
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<tr>
<td>MSWI BA (NL)</td>
<td>The Netherlands</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>ECN ongoing studies on MSWI BA</td>
</tr>
<tr>
<td>MSWI BA 2 (NL)</td>
<td>The Netherlands</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>ECN ongoing studies on MSWI BA</td>
</tr>
<tr>
<td>MSWI BA (DE)</td>
<td>SIWAP, Germany</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>Berger et al., 2005</td>
</tr>
<tr>
<td>MSWI BA (AT)</td>
<td>Austria, MSW Incinerator</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>van der Sloot et al., 2000b</td>
</tr>
<tr>
<td>MSWI BA (UK)</td>
<td>UK, MSW Incinerator</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>ECN studies on UK MSWI BA</td>
</tr>
<tr>
<td>MSWI BA (DE)</td>
<td>Germany, MSW Incinerator 1</td>
<td>MSWI Bottom Ash</td>
<td>pH-dependence Percolation</td>
<td>Berger et al., 2005</td>
</tr>
</tbody>
</table>
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Figure E-3. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-4. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-5. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-6. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-7.  Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-8  Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-9. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-10. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-11. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
Figure E-12. Comparison of laboratory and field concentration results for MSWI bottom ash used in roadbase (Sweden).
APPENDIX F. INORGANIC INDUSTRIAL WASTE LANDFILL (THE NETHERLANDS)

Table F-1. Data Sources for Laboratory-to-Field Comparisons for Inorganic Waste Landfill.

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
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<tr>
<td>Inorganic Waste Mix</td>
<td>Nauerna Landfill, the Netherlands</td>
<td>Mixed Waste (predominantly inorganic – input to landfill)</td>
<td>pH-dependence (CEN/TS 14429) Percolation (CEN/TS 14405)</td>
<td>van der Sloot et al., 2003 van Zomeren and van der Sloot, 2006b</td>
</tr>
<tr>
<td>NAU-Lysimeter 13AA</td>
<td>Nauerna Landfill, the Netherlands</td>
<td>Leachate</td>
<td>-</td>
<td>van der Sloot et al., 2003 van Zomeren and van der Sloot, 2006b</td>
</tr>
<tr>
<td>NAU-Lysimeter 1</td>
<td>Nauerna Landfill, the Netherlands</td>
<td>Leachate</td>
<td>-</td>
<td>van der Sloot et al., 2003 van Zomeren and van der Sloot, 2006b</td>
</tr>
</tbody>
</table>
Figure F-1. Comparison of laboratory and field pH results for an inorganic industrial waste landfill (The Netherlands).
Figure F-2. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
Figure F-3. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
Figure F-4. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
Figure F-5. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
Figure F-6. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
Figure F-7. Comparison of laboratory and field concentration results for an inorganic industrial waste landfill (The Netherlands).
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APPENDIX G. MUNICIPAL SOLID WASTE LANDFILL (THE NETHERLANDS)

Table G-1. Data Sources for Laboratory-to-Field Comparisons for MSW Landfill

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW Organic Waste (initial)</td>
<td>Landgraaf, The Netherlands</td>
<td>Mixture of MSW organic waste</td>
<td>pH-dependence (CEN/TS 14429) Percolation (CEN/TS 14405)</td>
<td>Luning et al., 2006 van der Sloot et al., 2008a</td>
</tr>
<tr>
<td>MSW Landfill – Core Composite (8 yr)</td>
<td>Pilot-scale landfill, Landgraaf, The Netherlands</td>
<td>Composite of landfill cores after 8 years in landfill</td>
<td>pH-dependence (CEN/TS 14429) Percolation (CEN/TS 14405)</td>
<td>Luning et al., 2006 van der Sloot et al., 2008a</td>
</tr>
<tr>
<td>MSW Landfill – Individual Cores (L/S 10; 8 yr)</td>
<td>Pilot-scale landfill, Landgraaf, The Netherlands</td>
<td>Cored material after 8 years in landfill</td>
<td>Batch L/S (EN 12457-2)</td>
<td>Luning et al., 2006 van der Sloot et al., 2008a</td>
</tr>
<tr>
<td>MSW Landfill – Leachate (recirculation)</td>
<td>Pilot-scale landfill, Landgraaf, The Netherlands</td>
<td>Landfill Leachate</td>
<td>-</td>
<td>Luning et al., 2006 van der Sloot et al., 2008a</td>
</tr>
</tbody>
</table>
Figure G-1. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-2. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-3. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-4. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-5. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-6. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-7. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
Figure G-8. Comparison of laboratory and field concentration results for a municipal solid waste landfill (The Netherlands).
### Table H-1. Data Sources for Laboratory-to-Field Comparisons for Stabilized Waste (The Netherlands).

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
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<tr>
<td>Fresh Stabilized Waste</td>
<td>S/S MSWI FA</td>
<td>pH-dependence</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<tr>
<td></td>
<td></td>
<td>(CEN/TS 14429)</td>
<td>Keulen, 2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Percolation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CEN/TS 14405)</td>
<td></td>
<td></td>
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<tr>
<td>Monofill – Individual Cores (10 yr)</td>
<td>Full-scale monofill,</td>
<td>Individual cores at depth &gt; 12 m</td>
<td>van Zomeren and van der Sloot, 2006b</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Keulen, 2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Batch L/S (EN 12457-2)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td>Percolation</td>
<td></td>
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<tr>
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<td></td>
<td>(CEN/TS 14405)</td>
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<tr>
<td>Monofill Leachate</td>
<td>Full-scale monofill,</td>
<td>Field Leachate (bottom of drain)</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Keulen, 2010</td>
<td></td>
</tr>
<tr>
<td>Cell B – Core Composite (4 yr)</td>
<td>Pilot Cell B</td>
<td>Composite – top layer uncovered cell</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<tr>
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<td>(MSWI FA, 5x8x2.4m)</td>
<td></td>
<td>Keulen, 2010</td>
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<tr>
<td></td>
<td></td>
<td>pH-dependence</td>
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<td></td>
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<td>(CEN/TS 14429)</td>
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<tr>
<td>Cell B – Individual Cores (L/S 10; 4 yr)</td>
<td>Pilot Cell B</td>
<td>Individual cores at depth</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<td></td>
<td>Keulen, 2010</td>
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<tr>
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<td></td>
<td>Batch L/S (EN 12457-2)</td>
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<tr>
<td></td>
<td></td>
<td>Percolation</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(CEN/TS 14405)</td>
<td></td>
<td></td>
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<tr>
<td>Cell B Leachate</td>
<td>Pilot Cell B</td>
<td>Field Leachate (bottom of drain)</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<td>Keulen, 2010</td>
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<tr>
<td>Cell C – Composite (covered; 4 yr)</td>
<td>Pilot Cell C</td>
<td>Composite – top layer covered cell</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<td>(MSWI FA, 5x8x2.4m)</td>
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<td>Keulen, 2010</td>
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<td>pH-dependence</td>
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<td>(CEN/TS 14429)</td>
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<td>Cell C – Individual Cores (L/S 10; 4 yr)</td>
<td>Pilot Cell C</td>
<td>Individual cores at depth</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<td>Keulen, 2010</td>
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<tr>
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<td>Batch L/S (EN 12457-2)</td>
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</tr>
<tr>
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<td></td>
<td>Percolation</td>
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</tr>
<tr>
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<td></td>
<td>(CEN/TS 14405)</td>
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<tr>
<td>Cell C Leachate</td>
<td>Pilot Cell C</td>
<td>Field Leachate (bottom of drain)</td>
<td>van Zomeren and van der Sloot, 2006b</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Keulen, 2010</td>
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</tr>
<tr>
<td>Cell D – Individual Cores (4 yr)</td>
<td>Pilot Cell D</td>
<td>Composite – top layer uncovered cell</td>
<td>van Zomeren and van der Sloot, 2006b</td>
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<tr>
<td></td>
<td>(MSWI FA, 5x8x2.4m)</td>
<td></td>
<td>Keulen, 2010</td>
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</tr>
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<td></td>
<td></td>
<td>pH-dependence</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(CEN/TS 14429)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell D Leachate</td>
<td>Pilot Cell D</td>
<td>Field Leachate (bottom of drain)</td>
<td>van Zomeren and van der Sloot, 2006b</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Keulen, 2010</td>
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</table>
Figure H-1. Comparison of laboratory and field pH for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-2. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-3. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-4. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-5. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-6. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-7. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
Figure H-8. Comparison of laboratory and field concentration results for stabilized MSWI fly ash disposal (The Netherlands).
### APPENDIX I: PORTLAND CEMENT MORTARS AND CONCRETE

#### Table I-1. Data Sources for Laboratory-to-Field Comparisons for Portland Cement Mortars and Concrete

<table>
<thead>
<tr>
<th>Legend ID</th>
<th>Source</th>
<th>Material Type</th>
<th>Data Type</th>
<th>Citation</th>
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<tr>
<td>Cement Mortar CEM I (DE)</td>
<td>Germany</td>
<td>CEM I type cement mortar</td>
<td>pH-dependence</td>
<td>Schießl, 2003</td>
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<td>Concrete – Core (40 yr; rain exposed, DE)</td>
<td>Germany</td>
<td>pH-dependence</td>
<td>Schießl, 2003</td>
<td></td>
</tr>
<tr>
<td>Concrete – Core (40 yr; immersed, DE)</td>
<td>Germany</td>
<td>pH-dependence</td>
<td>Schießl, 2003</td>
<td></td>
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<tr>
<td>Roman Aqueduct – Core (2,000 yr; DE)</td>
<td>Germany</td>
<td>Core from Roman Aqueduct</td>
<td>pH-dependence</td>
<td>van der Sloot et al., 2011</td>
</tr>
<tr>
<td>Cement Mortar CEM I (NO)</td>
<td>Norway</td>
<td>CEM I type cement mortar</td>
<td>pH-dependence</td>
<td>Engelsen et al., 2009; 2010</td>
</tr>
<tr>
<td>RCA (fresh, NO)</td>
<td>Norway</td>
<td>Recycled Concrete Aggregate</td>
<td>pH-dependence</td>
<td>Engelsen et al., 2009; 2010</td>
</tr>
<tr>
<td>RCA – Roadbase (4 yr; &lt;10 mm, NO)</td>
<td>Norway</td>
<td>Recycled Concrete Aggregate, recovered from roadbase (depth &lt; 10 mm</td>
<td>pH-dependence</td>
<td>Engelsen et al., 2009; 2010</td>
</tr>
<tr>
<td>RCA – Roadbase (4 yr; 20-120 mm, NO)</td>
<td>Norway</td>
<td>Recycled Concrete Aggregate, recovered from roadbase</td>
<td>pH-dependence</td>
<td>Engelsen et al., 2009; 2010</td>
</tr>
</tbody>
</table>
Figure I-1. Comparison of portland cement mortars, concretes and recycled aggregates.
Figure 1-2. Comparison of portland cement mortars, concretes and recycled aggregates.
Figure I-3. Comparison of portland cement mortars, concretes and recycled aggregates.
Figure I-4. Comparison of portland cement mortars, concretes and recycled aggregates.
Figure I-5. Comparison of portland cement mortars, concretes and recycled aggregates.