

An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials

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Abstract

A framework for the evaluation of inorganic constituent leaching from wastes and secondary materials is presented. The framework is based on the measurement of intrinsic leaching properties of the material in conjunction with mathematical modeling to estimate release under field management scenarios. Site specific and default scenarios are considered, which may be selected based on the evaluation context. A tiered approach is provided to allow the end-user to balance between the specificity of the release estimate, the amount of testing knowledge required, *a priori* knowledge, and resources required to complete an evaluation. Detailed test methodologies are provided for a suite of laboratory leaching tests.

Key Words: leaching, metals, waste, soil, utilization, beneficial use, secondary materials, disposal, landfill, risk assessment, test methods

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INTRODUCTION

Leaching tests are used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including during recycling or reuse, for assessing the efficacy of waste treatment processes, and after disposal. They may also be used to develop endpoints for remediation of contaminated soils and the source term¹ for environmental risk characterization. The Resource Conservation and Recovery Act (RCRA) requires the USEPA to classify wastes as either hazardous or non-hazardous. In implementing this portion of RCRA, the USEPA asks, “Would this waste pose unacceptable environmental hazards if disposed under a plausible, regulatorily defined, mismanagement scenario?” This scenario typically represents “worst case” management (i.e., the estimated highest risk, plausible, legal management option) and wastes posing such unacceptable environmental hazards warrant classification and regulation as hazardous wastes. In developing the Toxicity Characteristic regulation (40 CFR 261.24), the USEPA defined the plausible, worst-case mismanagement scenario for evaluating industrial waste as co-disposal in a municipal solid waste (MSW) landfill. The assumption of this mismanagement scenario, in turn, resulted in the development of the Extraction Procedure Toxicity test and its successor, the Toxicity Characteristic Leaching Procedure (TCLP; see 45 FR 33084, May 19, 1980, and 55 FR 11798, March 29, 1990), which attempts to replicate some key leaching factors typical of MSW landfills.

The TCLP has come under criticism because of overbroad application of the test (and underlying assumption of MSW co-disposal) in evaluating and regulating wastes, and some technical specifications of the methodology. The Science Advisory Board of USEPA reviewed the leaching evaluation framework being employed by the agency in 1991 and 1999 (USEPA, 1991; USEPA, 1999). In the 1999 review, the Science Advisory Board stated:

The current state of the science supports, even encourages, the development and use of different leach tests for different applications. To be most scientifically supportable, a leaching protocol should be both accurate and reasonably related to conditions governing leachability under actual waste disposal conditions.

And

¹ In this context, ‘source term’ refers to representation of constituent release from a waste or contaminated soil that is used in subsequent fate and transport modeling for exposure evaluation in risk assessment.

The multiple uses of TCLP may require the development of multiple leaching tests. The result may be a more flexible, case-specific, tiered testing scheme or a suite of related tests incorporating the most important parameters affecting leaching. Applying the improved procedure(s) to the worst-case scenario likely to be encountered in the field could ameliorate many problems associated with current procedures. Although the Committee recognizes that these modifications may be more cumbersome to implement, this type of protocol would better predict leachability.

The Science Advisory Board also criticized the TCLP protocol on the basis of several technical considerations, including the test's consideration of leaching kinetics, liquid-to-solid ratio, pH, potential for colloid formation, particle size reduction, aging, volatile losses, and co-mingling of the tested material with other wastes (i.e., co-disposal).

In response, this paper offers an alternative framework for evaluation of waste leaching potential that responds to many of the criticisms of the TCLP. It provides a tiered, flexible framework capable of incorporating a range of site conditions that affect waste leaching and so can estimate leaching potential under conditions more representative of actual waste management. The paper also addresses practical implementation of the framework in different applications, and an example application of this approach for evaluating alternative treatment processes for mercury contaminated soils is presented in a companion paper (Sanchez *et al.*, 2002). The leach testing protocols used in the framework also address technical concerns with the TCLP. The test protocols provided here are designed only for application to inorganic species; however, the concepts presented for the integrated framework are general, with application to both inorganic and organic species. Applicable test methods for organic species are the subject of future development. Complete technical specifications for the protocols are provided in the Appendix.

IS THE RIGHT QUESTION BEING ASKED?

In evaluating the leaching potential of wastes based on a single, plausible worst-case mismanagement scenario via TCLP, the USEPA seeks to provide environmental protection for unregulated wastes. However, wastes are managed in many different settings, and under a range of conditions that affect waste leaching. The reliance of the USEPA on a single, plausible worst-case, management scenario for leach testing may be generally protective, but often at the cost of over regulation. It has also proven to be inadequately protective in some cases (see discussion of spent aluminum potliner regulation at 62 FR 41005, July 31, 1997 and 62 FR 63458, December 1, 1997). While reliance on a single waste management scenario as the basis for leach testing may simplify implementation of RCRA, many of the wastes evaluated using TCLP have little if any possibility of co-disposal with MSW; assessment of the release potential of wastes as actually managed is needed to better understand the hazards posed by waste. Neither the TCLP,

nor any other test performed under a single set of conditions, can provide an accurate assessment of waste hazards for all waste.

From an environmental protection perspective (and setting aside the particular requirements of RCRA), the goal of leaching testing is to answer the question “What is the potential for toxic constituent release from this waste by leaching (and therefore the risk) under the selected management option?” For environmentally sound waste management, the following questions result from different perspectives:

- From the waste generator’s prospective - Which waste management options are acceptable for a waste?
- From the waste management facility’s perspective - Which wastes are suitable for disposal in a specific disposal facility?
- From the potential end-user’s perspective - Is this secondary material acceptable for use in commerce (e.g., as a construction material)?

The framework for answering these questions should be consistent across many applications, ranging from multiple waste disposal scenarios to determination of the environmental acceptability of materials that may be subject to leaching (e.g., construction materials). At the same time, the framework should be flexible enough to consider regional and facility-specific differences in factors affecting leaching (e.g., precipitation, facility design). A methodology guideline (ENV 12920, 1996) developed under European standardization initiatives recommends that the management scenario be a central consideration in the testing and evaluation of waste for disposal and beneficial use of secondary materials. This methodology is an extension of the approach in the Building Materials Decree established in The Netherlands (Building Materials Decree, 1995).

The answers to the questions posed above require several interrelated assessments including (i) the release rate and total amount over a defined time interval of potentially hazardous constituents from the waste, (ii) attenuation of the constituents of concern as they migrate from the waste, through groundwater, to the receptor being considered, (iii) exposure of the receptor, and (iv) the toxicity of each specific constituent. Considerable effort has resulted in accurate assessment techniques and data for evaluating contaminant transport through the environment (and attenuation), and toxicity for a large number of constituents.

In contrast to the detailed research on constituent fate, transport and risk following release, estimation of constituent release by leaching most often assumes (i) the total content present is available for

release, or (ii) the contaminant concentration in the leachate will be equal to that measured during a single batch extraction and is constant with time², or (iii) the fraction of the contaminant extracted during a batch extraction is equal to the fraction that will leach (USEPA, 1986; Goumans *et al.*, 1991). These approaches frequently result in grossly inaccurate estimation of actual release (both over- and under-estimation). Inaccurate release estimation, in turn, forces disposal of materials that are suitable for beneficial use, mandates remediation of soils to levels beyond that necessary for environmental protection, unnecessarily depletes disposal capacity, or results in groundwater contamination (if release is underestimated). In addition, treatment processes, that may be proven to reduce the extracted concentration for a regulatory test (TCLP), have resulted in increased release when compared to management scenarios without treatment (Garrabrants, 1998). Thus, methodologies that result in a more accurate estimate of contaminant leaching may both improve environmental protection through more efficient use of resources and be economically beneficial.

In general, leaching tests can be classified into the following categories (Environment Canada, 1990): (i) tests designed to simulate contaminant release under a specific environmental scenario (e.g., synthetic acid rain leach test or TCLP), (ii) sequential chemical extraction tests, or (iii) tests which assess fundamental leaching parameters.

Tests that are designed to simulate release under specific environmental scenarios are limited because they most often do not provide information on release under environmental scenarios different from the one being simulated. This type of limitation has led to widespread misuse and misinterpretation of TCLP results. Reliance on simulation-based testing also results in treatment processes that are designed to “pass the test” rather than to improve waste characteristics or reduce leaching under actual use or disposal scenarios. For instance, it is common practice to include waste treatment additives to buffer the TCLP leachant at a pH resulting in minimum release of target constituents. However, when the buffered material is landfilled, the landfill leachate pH may be dominated either by the material buffering capacity (monofill scenarios) or by other sources (co-disposal scenarios). In either case, the release scenario may differ significantly from conditions simulated by the testing protocol and unpredicted leaching behavior may occur.

Sequential chemical extraction tests evaluate release based on extraction of the waste with a series of increasingly more aggressive extractants. The sequential extraction approach, originally compiled by

² This assumption is often referred to as the “infinite source” assumption.

Tessier *et al.* (Tessier *et al.*, 1979), has been adapted by others (Frazer and Lum, 1983). These adapted approaches have limitations that require case-by-case evaluation (Khebohian and Bauer, 1987; Nirel and Morel, 1990). In addition, the operationally defined nature of sequential extraction approaches make generalized application in a waste management framework difficult.

In addition, geochemical speciation modeling also can provide useful insights into leaching behavior, as it provides information on possible solubility controlling mineral phases (Meima *et al.*, 1999; van der Sloot, 1999; Crannell *et al.*, 2000), the role of sorption processes with Fe, Mn and Al phases (Meima and Comans, 1998; Meima and Comans, 1999), and complexation with dissolved organic matter (Keizer and van Riemsdijk, 1998; Kinniburgh *et al.*, 1999; van der Sloot, 2002). However, geochemical modeling often requires detailed solid phase identification that is either impractical or not possible for complex materials, and needed solubility and adsorption parameters may be unavailable. Although the information it provides can be used effectively in waste management, geochemical modeling often only provides qualitative or semi-quantitative results and is not a tool for regulatory control.

The alternative framework described below was designed to assess intrinsic waste leaching parameters, thereby providing a sound basis for estimation of release potential in a range of different potential waste management scenarios. It provides a basis either for choosing acceptable management or disposal from among several possible options or for judging whether a pre-selected management or disposal option is in fact environmentally sound and appropriate.

AN ALTERNATIVE FRAMEWORK FOR EVALUATION OF LEACHING

Waste testing should provide information about potential contaminant release from a waste in the context of the anticipated disposal or utilization conditions. Thus, testing should reflect the range of conditions (e.g., pH, water contact, etc.) that will be present in the waste and at its interface with its surroundings during the long-term, which may be significantly different than the properties of the material immediately following production³.

³ Examples where the material as produced has different constituent release behavior than that during utilization are: (i) concrete pillars immersed in surface water where release reflects the neutral pH of surface water rather than the alkali pH of Portland cement concrete (van der Sloot, 2000), (ii) stabilized coal fly ash exposed to seawater showing surface sealing (Hockley and van der Sloot, 1991), (iii) MSWI bottom ash used in road base application being neutralized with a few years of field exposure (Schreurs *et al.*, 2000), and (iv) use of steel slag in coastal protection applications where V and Cr leaching is reduced by the natural formation of ferric oxide coatings in the utilization environment (Comans *et al.*, 1991).

The goals of a revised framework for evaluation of contaminant leaching should be to: (i) provide conservative⁴ but realistic estimates of contaminant leaching for a broad range of waste types, constituents of concern, environmental conditions, and management options, (ii) utilize testing strategies that can be carried out using standard laboratory practices in reasonable time frames (e.g., several hours to several days, depending on requirements), (iii) provide for release estimates that consider site-specific conditions, (iv) encourage improvements in waste management practices, (v) provide flexibility to allow level of evaluation (and hence degree of over-conservatism⁵) to be based on the user's requirements, (vi) evolve in response to new information and take advantage of prior information, and (vii) be cost effective.

In concert with these goals, evaluation of constituent release can be approached by a series of steps: (i) define management scenarios and mechanisms occurring in the scenarios (e.g., rainfall infiltration) that control constituent release, (ii) measure intrinsic leaching parameters for the waste or material being evaluated (over a range of leaching conditions), (iii) use release models incorporating measured leaching parameters (corresponding to anticipated management conditions) to estimate release fluxes and long-term cumulative release, and (iv) compare release estimates to acceptance criteria. Management scenarios can either be default scenarios that are designed to be conservative or incorporate site-specific information to provide more-accurate estimates of release. In CEN TC 292⁶, such a scenario-based approach has been described as an experimental standard (ENV 12920, 1996). This standard describes steps very similar to those identified above.

The controlling release mechanisms most often can be described in terms of either equilibrium controlled or mass-transfer rate controlled. Equilibrium controlled release occurs for slow percolation through porous or granular materials. Mass transfer rate controlled release occurs when flow is predominantly at the exterior boundary of monolithic materials or percolation is very rapid relative to mass transfer rate of constituent release to the percolating water. Intrinsic leaching parameters that are to be measured using laboratory testing are: constituent availability, constituent partitioning at equilibrium between aqueous and solid phases as a function of pH and liquid-to-solid (LS) ratio, acid and base

⁴ In this paper, "conservative" estimates of release implies that the actual release will be less than or equal to the estimated release during the management scenario considered.

⁵ For most cases, more detailed waste characterization results in more accurate estimates of actual contaminant release, providing safety margins by reducing the degree of over-estimated release. However, more detailed characterization requires additional testing cost and time which may not be justified because of either the limited amount of waste to be managed, time constraints, or other reasons.

⁶ CEN/TC 292 is the European Standardization Organization (CEN) technical committee dealing with characterization of waste (established in 1993). For additional information, see www.cenorm.be on the Internet.

neutralization capacities (ANC and BNC), and constituent mass transfer rates. Definition of management scenarios and application of intrinsic parameters, release models and decision criteria are discussed in later sections of this paper.

To achieve the desired framework goals and series of evaluation steps, a three-tiered testing program is proposed (Figure 1). An analogous, tiered approach, developed with input from the authors of this paper, has been recommended by Eighmy and Chesner for evaluation of secondary materials for use in highway construction (Eighmy and Chesner, 2001). In the framework presented in this paper, each successive tier provides leaching data that is more specific to the material being tested and possible leaching conditions than the previous tier. Individual leaching tests are designed to provide data on intrinsic leaching parameters for a waste or secondary material. Results from multiple tests, used in combination with either default management scenario assumptions (more conservative, but with simpler implementation) or site-specific information, provide more accurate release assessments. However, the results of a single test (e.g., the first tier availability test) can be used as the most conservative approach for management decisions when time or economic considerations do not justify more-detailed evaluations.

Three tiers of assessment can be defined to efficiently address the above waste management questions and criteria:

Tier 1 – Screening based assessment (availability).

Tier 2 – Equilibrium based assessment (over a range of pH and LS conditions).

Tier 3 – Mass transfer based assessment.

Progressing from Tier 1 through Tier 3 provides increasingly more realistic and tailored, and less conservative, estimates of release, but also requires more extensive testing.

Tier 1 is a screening test that provides an assessment of the maximum potential for release under the limits of anticipated environmental conditions, without consideration of the time frame for release to occur. This concept of maximum potential release is often referred to as “availability.” In practical application, availability is operationally defined using a selected test method. Leaching potential is expressed on a mass basis (e.g., mg X leached/kg waste). The basis for this bounding analysis would be testing under extraction conditions that maximize release within practical considerations (see further discussion below). Tier 2 testing is based on defining liquid-solid equilibrium as a function of pH and LS (i.e., chemical retention in the matrix). Tier 3 testing uses information on liquid-solid equilibrium in conjunction with mass transfer rate information (i.e., physical retention of constituents in addition to

chemical retention in the matrix). Both Tier 2 and Tier 3 testing may use either default or site-specific management assumptions (e.g., infiltration rates, fill depth) to estimate release as a function of time. For a scenario, leachate concentrations based on equilibrium will always be greater than or equal to those based on mass transfer rate. Thus, equilibrium release estimates (Tier 2) may be a conservative approximation in the absence of mass transfer rate information (Tier 3)⁷.

For Tier 2 and Tier 3 assessments, three levels of testing (Levels A, B or C) are defined. Each of the three levels of testing may be used depending on the amount of previous knowledge (test data) of the waste, or the degree of site-specific tailoring desired. Level A (in either Tier 2 or 3) uses concise or simplified tests. The basis for Tier 2A would be measurement of the leaching characteristics at conditions that bound the range of anticipated field scenarios for equilibrium (e.g., use of three extractions to define release at acidic, neutral and alkali pH conditions with consideration of the material's natural pH at LS=10 mL/g). The basis for Tier 3A testing would be a coarse estimate of release rates (e.g., a four point, 5 day monolithic leach test). The data from these tests would be used in conjunction with default management scenario bounding conditions, and simplified release models, to provide a conservative assessment in the absence of more detailed knowledge. Example applications of Level A testing (in either Tier 2 or 3) include for routine disposal of wastes that may fail Tier 1 testing, simplified evaluations for disposal or utilization that can be justified based on more conservative assumptions, and verification that a material being tested exhibits characteristics similar to a class of materials that has previously been more extensively characterized (e.g., Level B, see below).

Level B testing provides detailed characterization of the waste or secondary raw material. The basis for Tier 2B testing would be definition of equilibrium over the full range of relevant pH and LS conditions (i.e., pH 2-13, and LS 0.5-10 mL/g). The maximum release observed under these conditions also is functionally equivalent to the availability measured in Tier 1, although the specific values may differ based on the method of determination. The basis for Tier 3B testing would be a more complete definition of mass transfer rates (e.g., 10 data points over 60 days) and verification of material integrity (e.g., strength after leaching). These more detailed data can be used in conjunction with either default or site-specific management scenario assumptions, and either simplified or advanced release models. For example, results from Level B testing in conjunction with default scenarios and simplified release models can provide the basis for comparison of treatment processes. Results from Level B testing used in conjunction with site-

⁷ Extrapolation of laboratory mass transfer test results to field conditions requires careful consideration of

specific information and advanced models provide the most realistic and least conservative assessment. Level B testing would only be carried out initially for a material or class of materials generated in large quantities, and thereafter only if significant changes in material characteristics are indicated by periodic Level A testing. Level B testing provides insight into the critical components for a given material and thus providing the basis for selection of a reduced set of parameters for subsequent testing. After completion of Level B testing, Level A testing can be used to answer the question, “Does the material currently being tested have the same characteristics of the material that was previously characterized in more detail (Level B)?” The frequency of testing can be related to the degree of agreement with the level B testing. Good performance is then rewarded by reduction in test frequency. A deviation then requires initially more frequent testing to verify the deviation, and if necessary a return to the level B testing to evaluate the cause. Additional examples of application of Level B testing include monofill disposal of special wastes and approvals for beneficial use of secondary materials.

Level C provides the most simplified testing for quality control purposes, and relies on measurement of a few key indicators of waste characteristics, as identified in the level B testing. An example of Level C testing would consist of titration of a sample to a designated pH with measurement of the concentration of a limited number of constituents in the resulting single extract. Specific Level C testing requirements would be defined on a case specific basis. Level C should only be used after Level B testing has initially been completed to provide a context for quality control. One application of Level C testing would be the routine (e.g., daily, weekly or monthly) evaluation of incinerator ash prior to disposal.

A feedback loop is provided between Tier 2C and Tier 2A within the framework (Figure 1). This loop is provided to indicate that Tier 2A testing can be used on a random basis to provide further assurance of attainment of regulatory objectives when much more simplified testing is allowed on a routine basis (Tier 2C). In this case, the Tier 2A testing is compared with the more complete Tier 2B characterization testing to verify that the batch of material being tested has not deviated significantly from the material that was originally characterized and serves as the baseline assessment. A similar approach may be used when quality control testing is based on mass transfer rate testing (Tier 3C) rather than equilibrium testing (Tier 2C).

While the above framework provides the specific basis only for evaluation of inorganic constituents, an analogous set of test conditions can be described for evaluation of organic constituents.

the external surface area for water contact and the potential for external stresses.

Additional considerations for organic constituents would include (i) the potential for mobility of a non-aqueous phase liquid, (ii) the fact that pH dependence of aqueous partitioning is usually limited to the indirect (although important) effect of pH on dissolved organic carbon levels from humic or similar substances, and (iii) availability for many organic constituents is limited and may require a more complex modeling approach.

DECISION MAKING BASED ON THE EVALUATION FRAMEWORK

Application of laboratory testing results to environmental decision-making requires linking the laboratory data to environmental endpoints of concern (protection of human health and environment). This is done through data or models that represent environmental processes, including groundwater transport of released constituents, exposure to humans or animals via drinking water, and the toxicity of the released constituents of concern.

This linkage was established for the TCLP based on assuming the test results yielded a leachate constituent concentration that reflected anticipated field leachate that would be produced during disposal in the bounding scenario. This leachate constituent concentration in turn would be reduced through natural groundwater attenuation processes as it moved through the groundwater (e.g., dilution and adsorption) before reaching a drinking water well. This “concentration-based approach” implicitly assumes an infinite source of the constituents of concern and does not account for either the anticipated changes in release over time (including exhaustion of the source) or the potential for cumulative effects of release over time. Furthermore, this approach considers only the leaching behavior of the material; it does not consider the management context (e.g., disposal vs. utilization, design of the management scenario, geographic location). Thus, the concentration-based approach establishes a leachate concentration (as measured in the TCLP) below which no significant impact to drinking water is anticipated. This approach also can be misleading if the test conditions do not reasonably reflect the field conditions (e.g., with respect to pH and LS ratio).

The proposed alternative is a performance or “impact-based approach.” 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.

Management scenarios

Waste management or utilization scenarios must be used to link laboratory assessment results to impact assessment. Defining scenarios for this purpose requires the leaching mode controlling release (equilibrium or mass transfer), the site-specific LS ratio, the field pH, and a time frame for assessment. Values describing a specific waste management facility or a hypothetical default scenario could be used. Using these site conditions with laboratory measures of constituent solubility as a function of pH and LS ratio, a simple release model can be used to estimate the cumulative mass of the constituent released over the time frame for a percolation/equilibrium scenario. Including laboratory measurement mass transfer rates allows application of simple release models for mass transfer rate controlled management scenarios (e.g., monolithic materials).

For a hypothetical default landfill disposal scenario, parameter values may be based on national data for different landfill types, or defined as a policy matter. Values for field pH and LS ratio may be either measured at an actual site or estimated for the site. Measuring field pH requires collecting landfill leachate or landfill pore water and measuring the pH before contact with the air begins to alter the pH. LS ratio serves as the surrogate parameter for time. Good agreement has been obtained between laboratory test data and landfill leachate based on LS (van der Sloot, 2001). Measuring field LS ratio involves measuring the volume of leachate collected (annually) from the landfill, and comparing it with the estimated waste volume in the landfill, or the landfill design capacity. As an alternative to measuring the LS ratio, it may be estimated, based on defining the geometry for the management scenario and local environmental conditions. Parameters for defining the management scenario include fill geometry (relating waste mass to impacted area), net infiltration rates (defining amount of water contact), and time frame. For example, a default disposal scenario may be a fill height of 10 m, 20 cm infiltration per year and 100 years (alternatively, the total mass of waste and footprint area may be specified). The selection of the default

management scenario is ultimately a consideration of typical waste management practices and of societal value judgments reflected in the regulatory development process.

For discussion purposes, a 100-year interval is suggested as a hypothetical assessment period, although other time frames could be used⁸. For comparison of treated wastes, a cube one meter on edge is assumed. Laboratory test results are presented primarily as release per unit mass of waste tested (e.g., mg X/kg waste), but also are presented and used on a concentration basis for Tier 2 testing.

Environmental Considerations

Release estimates for most cases assume that conditions influencing release are controlled by the waste material and associated design conditions; however, properties of surrounding materials may dominate the release conditions in some scenarios. These external stresses (e.g., pH or redox gradients, carbonation, co-mingling effects) can lead to substantial deviation from material-driven leaching behavior. For instance, caution must be used if large pH or redox gradients exist between the waste and the surrounding environment or within the waste matrix. The solubility of many inorganic species may be strongly a function of pH (e.g., Pb, Cd, Ba) or significantly altered by redox conditions (e.g., Cr, Se, As). Large gradients in pH or redox potential can result in precipitation or rapid dissolution phenomena for some elements as concentration gradients within the material or at the material boundary redistribute over long time intervals (van der Sloot *et al.*, 1994; Sanchez, 1996). The release of highly soluble species (e.g., Na, K, Cl) is not considered a strong function of leachate conditions.

Redox gradients and reducing conditions may result from material characteristics, biological activity or external inputs. Materials with inherent reducing properties include several types of industrial slag, fresh sediment and degrading organic matter. Testing of these materials under air-exposed conditions may lead to unrepresentative answers for the situation to be evaluated. For an appropriate assessment of reducing materials, testing and release modeling that considers conditions imposed by external factors, rather than by the waste itself, will be necessary. This is still an underdeveloped area of research.

For most alkaline wastes, the most prevalent interface reaction is absorption of carbon dioxide. Carbonation of waste materials results in the formation of carbonate species and neutralization of alkaline buffering capacity. For Portland cement-based matrices, the conversion of calcium hydroxide to calcium carbonate has been noted to reduce pore water pH towards 8 (Sanchez, 2001; Garrabrants, 2001). Thus, if

pH-dependent species are a concern, carbonation of the matrix can play a significant role in predicting long-term release.

Currently, the proposed approach does not consider the impact of co-mingling different types of wastes during disposal other than the impact of resulting changes in pH. In cases where a pH gradient appears to be the most significant factor, release estimates can be accomplished using advanced modeling approaches in conjunction with characterization data interpolated from the concentration as a function of pH as defined under Tier 2. Test methods and release models to assess the impact of material aging under carbonation and reducing conditions are under development (NVN 7438, 2000; Garrabrants, 2001; Sanchez *et al.*, 2001a). Experimental work is in progress to evaluate waste-waste interaction by quantifying buffering of pH, dissolved organic carbon, and leaching from waste mixtures (van der Sloot *et al.*, 2001a; van der Sloot *et al.*, 2001b).

TEST METHODS FOR USE IN THE FRAMEWORK

CRITERIA FOR EQUILIBRIUM TEST METHODS

Important considerations for the design of equilibrium test methods are (i) the relationships between particle size, sample size and contact time, (ii) definition of an appropriate LS ratio, (ii) selection of the acid or alkali for pH modification, and (iii) practical mechanical limits. Experimental observations with several wastes have indicated that use of a maximum particle size of 2 mm and contact time of 48 hours results in a reasonable measurement of equilibrium (Garrabrants, 1998). If diffusion is assumed to be the rate controlling mechanism, the relationships between particle size and contact time required to approach equilibrium can be approximated as diffusion from a sphere into a finite bath (Crank, 1975). Critical parameters are the fraction of constituent released at equilibrium, observed diffusivity, particle diameter and contact time. The ratio between the fraction of constituent released at a given time and the fraction of the constituent released at equilibrium can be considered an index of the approach to equilibrium. Results of simulations using this modeling approach are consistent with approaching equilibrium after 48 hours for observed diffusivities less than 10^{-14} m²/s (Garrabrants, 1998).

⁸ The authors have found 100 years to be a useful period for release estimates. This period is typically longer than a lifetime but short enough to be comprehensible. In addition, for many cases, a major fraction of the long-term release is anticipated to occur during a period less than this interval.

Equilibration times for different particle size systems, assuming all other properties remain constant (e.g., observed diffusivity, liquid-solid ratio, fractional release at equilibrium), can be evaluated using a dimensionless time parameter:

$$\tau = \frac{D^{obs} \cdot t}{r^2} \quad (\text{Equation 1})$$

where τ is the dimensionless time parameter [-];

t is the contact time [s];

r is the particle radius [m]; and,

D^{obs} is the observed diffusivity [m²/s].

Based on this approach, achieving a condition equivalent to the 2 mm/48 hr case, a particle size of 5 mm would require extraction for 12.5 days; for a particle size of 9 mm, 40.5 days would be required. However, most materials undergoing testing would be sized reduced or naturally have a particle size distribution with the maximum particle size specified. Thus, a maximum particle size of 2 mm with a 48 hr minimum contact time is specified as a base case, with alternative conditions suggested considering both equivalent approaches to equilibrium and practical limitations (Table 1). Demonstration of approximating equilibrium conditions for the material being tested is recommended before using alternative contact times.

Selection of sample sizes assumes testing of representative aliquots of the material being evaluated. For the base case with a maximum particle size of 2 mm, a sample size of 40 g (equivalent dry weight) is recommended when carrying out an extraction at an LS ratio of 10 mL/g. Heterogeneous materials and materials with a larger particle size will require either testing of larger aliquots or homogenization and particle size reduction prior to sub-sampling for testing. A discussion and example of sampling of heterogeneous materials and particle size reduction followed sub-sampling for leaching tests is provided elsewhere (IAWG, 1997).

For many test methods, an LS ratio of 10 mL/g has been selected to provide adequate extract volumes for subsequent filtration and analysis while using standard size extraction containers (i.e., 500 mL). This liquid-to-solid ratio also provides for reasonable approach to equilibrium based on theoretical considerations. Typically, use of an LS ratio of 10 mL/g provides solubility-controlled equilibrium over the range of pH relevant for extrapolation to the field. The resulting solution concentration is generally only

weakly dependent on LS ratio between LS ratio of 10 and 2 mL/g. LS ratio dependence may be verified using an extraction at lower LS (see methods below).

In the experimental methods, pH adjustments are made using aliquots of nitric acid or potassium hydroxide. Nitric acid was chosen to minimize the potential for precipitation (e.g., such as occurring with sulfuric acid), complexation (e.g., with organic acids or hydrochloric acid) or analytical interferences. It is also recognized that nitric acid is oxidizing which is a conservative selection due to the solubility behavior of metal hydroxyl species (e.g., $\text{Pb}(\text{OH})_3^-$, $\text{Cd}(\text{OH})_3^-$) and the potential for oxidizing conditions during management. However, oxyanions (e.g., chromate) exhibit maximum release at near neutral to slightly alkaline conditions that typically are achievable without significant acid additions. Testing for release under reducing conditions requires the development of additional test methods because consideration must be given to acid selection, sample handling and establishment of reproducible reducing conditions. Potassium hydroxide was selected to avoid interference with the use of sodium ion as an inert tracer in some applications; however, sodium hydroxide may be substituted for cases in which potassium characterization is a concern.

During extraction, complete mixing should be insured by end-over-end mixing. In all cases, it is desired to test the material with the minimum amount of manipulation or modification needed prior to extraction. Thus, it is preferable to avoid sample drying before testing, although this can be acceptable when non-volatile constituents are of primary interest and it is necessary to achieve particle size reduction.

RECOMMENDED TEST METHODS

The following test methods are recommended for use in the proposed tiered leaching framework. The general purpose, approach and application of these test methods are shown in Table 2. Detailed protocols for these test methods are presented as Appendix A.

Tier 1 – Screening Tests

An ideal screening test would result in a conservative estimate of release over the broad range of anticipated environmental conditions. In addition, this screening test would require only a single extraction that could be completed in less than 24 hours. However, this ideal scenario is impossible to achieve. Several approaches to measuring “availability” or maximum leaching potential have been developed or considered. One approach is a two step sequential extraction procedure with particle size $<300 \mu\text{m}$, $\text{LS}=100 \text{ mL/g}$ and

control at pH 8 and 4 (NEN 7341, 1994). Another approach uses EDTA to chelate metals of interest in solution at near neutral pH during a single extraction (Garrabrants and Kosson, 2000). Either of these approaches can be used as a screening test, but both approaches have practical limitations relative to implementation. The NEN 7341⁹ requires a small particle size, two extractions and pH control. The approach of Garrabrants and Kosson (2000) requires a pre-titration and can have some difficulties in controlling the pH. This approach also has been criticized as providing a release estimate that may be too conservative.

Tier 2 - Solubility and Release as a Function of pH

The objectives of this testing is to determine the acid/base titration buffering capacity of the tested material and the liquid-solid partitioning equilibrium of the “constituents of potential concern” (COPCs). For wastes with high levels of COPCs, the liquid-solid partitioning equilibrium is determined by aqueous solubility as a function of pH. For low levels of COPCs, equilibrium may be dominated by adsorption processes. However, the concurrent release of other constituents (e.g., dissolved organic carbon, other ions) will also impact the results by modifying the solution characteristics of the aqueous phase¹⁰. The two approaches that have been considered for achieving the objective of measuring solubility and release as a function of pH are (i) static (controlled) pH testing at multiple pH values through use of a pH controller at desired set points (van der Sloot *et al.*, 1997), and (ii) a series of parallel extractions of multiple sample aliquots using a range of additions of acid or alkali to achieve the desired range of endpoint pH values (Environment Canada and Alberta Environmental Center, 1986; Kosson *et al.*, 1996; Kosson and van der Sloot, 1997; prEN14429, 2001). Both testing approaches have been shown to provide similar results (van der Sloot and Hoede, 1997), including determination of both the acid/base titration buffering capacities of the tested material and the characteristic behavior of the constituents of potential concern. The static pH approach has the advantage of being able to achieve desired pH endpoints with a high degree of accuracy. The parallel extraction approach has the advantage of mechanical simplicity. The range of pH examined should include the extreme values of pH anticipated under field conditions and the pH when controlled by the tested material (i.e., “natural” or “own” pH). Thus, while the recommended method below provides a

⁹ NEN is the national Dutch standardization organization, where a standardization committee has been addressing the development of leaching tests for construction materials and waste materials since 1983. For additional information, see www.nen.nl on the Internet.

¹⁰ For example, the dissolution of organic carbon from a waste has been shown to increase the solubility of copper in municipal solid waste incinerator (MSWI) bottom ash and several metals in matrices containing organic matter (van der Sloot, 2002).

full characteristic behavior curve (i.e., for Tier 2, level B testing), an abbreviated version based on three analysis points may be used for simplified testing (i.e., for Tier 2A). The recommended method below is also analogous to CEN TC 292 Characterization of Waste – Leaching Behavior Test – pH Dependence Test with Initial Acid/Base Addition (prEN14429, 2001).

SR002.1 (Alkalinity, Solubility and Release as a Function of pH)

This protocol consists of 11 parallel extractions of particle size reduced material at a liquid-to-solid ratio of 10 mL extractant/g dry sample. An acid or base addition schedule is formulated for eleven extracts with final solution pH values between 3 and 12, through addition of aliquots of HNO₃ or KOH as needed. The exact schedule is adjusted based on the nature of the material; however, the range of pH values includes the natural pH of the matrix that may extend the pH domain (e.g., for very alkaline or acidic materials). Using the schedule, the equivalents of acid or base are added to a combination of deionized (DI) water and the particle size reduced material. The final liquid-solid (LS) ratio is 10 mL extractant/g dry sample which includes DI water, the added acid or base, and the amount of moisture that is inherent to the waste matrix as determined by moisture content analysis. The eleven extractions are tumbled in an end-over-end fashion at 28±2 rpm. Contact time is a function of the selected maximum particle size, with an extraction period of 48 hr for the base case of 2 mm maximum particle size. Following gross separation of the solid and liquid phases by centrifugation or settling, leachate pH measurements are taken and the phases are separated by vacuum filtration through 0.45-µm polypropylene filtration membranes. Analytical samples of the leachates are collected and preserved as appropriate for chemical analysis. The acid and base neutralization behavior of the materials is evaluated by plotting the pH of each extract as a function of equivalents of acid or base added per gram of dry solid. Equivalents of base are presented as opposite sign of acid equivalents. Concentration of constituents of interest for each extract is plotted as a function of extract final pH to provide liquid-solid partitioning equilibrium as a function of pH. Figure 2 (a-b) shows conceptual output from the recommended SR002.1 protocol with the recognition that a broad range of behaviors is possible. In Figure 3a, the output data of the SR002.1 protocol for a cementitious synthetic waste matrix (Garrabrants, 2001) is compared to the total elemental content and constituent availability (Tier 1 value).

The abbreviated version of the SR002.1-A (Alkalinity, Solubility and Release as a Function of pH) protocol consists of three parallel extractions of particle size reduced material at a liquid-to-solid ratio of 10 mL extractant/g dry sample. The selection of the target pH values is dependent on the natural pH of the

material. If the natural pH is <5 , then natural pH, 7 and 9 are selected as the target pH values. If the natural pH ranges between 5 and 9, then 5, 7 and 9 are selected as the target pH values, and if the natural pH is >9 , then 5, 7 and natural pH are selected as the target pH values.

Tier 2 - Solubility and Release as a Function of LS Ratio

The objective of this test is to determine the effect of low liquid-to-solid ratio on liquid-solid partitioning equilibrium when the solution phase is controlled by the tested material. This is used to approximate initial pore-water conditions and initial leachate compositions in many percolation scenarios (e.g., monofills). This objective is accomplished by a series of parallel extractions using multiple aliquots of the tested material at different LS ratio with deionized water to achieve the desired range of conditions. When necessary, results can be extrapolated to lower LS ratio than readily achieved under typical laboratory conditions. The range of LS ratio examined should include the condition used for solubility and release as a function of pH testing (i.e., LS=10 mL/g) and the lowest LS practically achievable that approaches typical pore water solutions (i.e., LS=0.5 mL/g). Thus, while the recommended method below provides a full characteristic behavior curve (i.e., for Tier 2, level B testing), an abbreviated version based on two analysis points may be used for simplified testing (i.e., for Tier 2A)¹¹.

For some materials, LS <2 mL/g may be difficult to achieve with sufficient quantity of eluate for analysis due to limitations of solid-liquid separation. In addition, the formation of leachate colloids can result in overestimation of release for some metals and organic contaminants. Use of a column test is an alternative to use of batch testing for measuring release as function of LS. A column test (prEN14405, 2001), similar to the Dutch standard column test (NEN 7343, 1995), has been developed within the European Standardization Organization CEN.

SR003.1 (Solubility and Release as a Function of LS Ratio)

This protocol consists of five parallel batch extractions over a range of LS ratios (i.e., 10, 5, 2, 1, and 0.5 mL/g dry material), using deionized (DI) water as the extractant with aliquots of material that has been particle size reduced. The mass of material used for the test varies with the particle size of the material. All extractions are conducted at room temperature ($20\pm 2^\circ\text{C}$) in leak-proof vessels that are tumbled in an end-over-end fashion at 28 ± 2 rpm. Contact time is a function of the selected maximum particle size, with an extraction period of 48 hr for the base case of 2 mm maximum particle size. Following gross

separation of the solid and liquid phases by centrifugation or settling, leachate pH and conductivity measurements are taken and the phases are separated by a combination of pressure and vacuum filtration using 0.45- μm polypropylene filter membrane. The five leachates are collected, and preserved as appropriate for chemical analysis. Figure 2 (c-d) shows conceptual output from the recommended SR003.1 protocol with the recognition that a broad range of behaviors is possible. In Figure 3b, the output data of equilibrium-based protocols (SR002.1 and SR003.1) are compared for a cementitious synthetic waste matrix (Garrabrants, 2001).

The abbreviated version, SR003.1-A (Solubility and Release as a Function of LS Ratio) protocol consists of two parallel extractions of particle size reduced material using DI water at liquid-to-solid ratio of 10 and 0.5 mL extractant /g dry sample, respectively. The extraction at an LS ratio of 10 mL/g may be the same sample as used in SR002.1-A to reduce the required number of analyses.

Tier 3 - Mass Transfer Rate (Monolithic and Compacted Granular Materials)

The objective of mass transfer rate tests is to measure the rate of COPC release from a monolithic material (e.g., solidified waste form or concrete matrix) or a compacted granular material. Results of these tests are to estimate intrinsic mass transfer parameters (e.g., observed diffusivities for COPCs) that are then used in conjunction with other testing results and assessment models to estimate release. Results of these tests reflect both physical and chemical interactions within the tested matrix, thus requiring additional test results for integrated assessment. While the recommended methods are derivatives of ANS 16.1 (ANS, 1986), a leachability index is not assumed nor used as a decision criterion. The recommended methods below are also analogous to NEN 7345 (NEN 7345, 1994) and methods under development by CEN/TC 292.

MT001.0 (Mass Transfer Rates in Monolithic Materials)

This protocol consists of tank leaching of continuously water-saturated monolithic material with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen so that the sample is fully immersed in the leaching solution. Cylinders of 2 cm minimum diameter and 4-cm minimum height or 4-cm minimum cubes are contacted with DI water using a liquid to surface area ratio of 10 mL of DI water for every cm^2 of exposed solid surface area. Larger cylinder sizes are recommended for treated materials that have a particle size greater than 2 mm prior to solidification. Typically, the cylinder diameter

¹¹ The abbreviated methods for testing solubility as a function of pH (three points) and solubility as a function of LS (two points) include one common point in both tests. Thus, for integrated testing under Tier

and height or cube dimension should be at least ten times the maximum particle size of the material contained therein. Leaching solution is exchanged with fresh DI water at pre-determined cumulative times of 2, 5 and 8 hours, 1, 2, 4 and 8 days¹². This schedule results in seven leachates with leaching intervals of 2, 3, 3, 16 hours, 1, 2 and 4 days. At the completion of each contact period, the mass of the monolithic sample after being freely drained is recorded to monitor the amount of leachant absorbed into the solid matrix. The solution pH and conductivity for each leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45- μm pore size polypropylene filtration membrane and preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 at the extract pH for quality control to insure that release was not limited by saturation of the leachate. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity). Figure 4 shows sample output data from the MT001.1 test for a solidified waste matrix (van der Sloot, 1999). The solubility data shown in the figure corresponds to data derived from SR002.1.

MT002.0 (Mass Transfer Rates in Compacted Granular Materials)

This protocol consists of tank leaching of continuously water-saturated compacted granular material with intermittent renewal of the leaching solution. This test is used when a granular material is expected to behave as a monolith because of compaction during field placement. An unconsolidated or granular material is compacted into molds at optimum moisture content using a modified Proctor compactive effort (NEN 7347, 1997). A 10-cm diameter cylindrical mold is used and the sample is packed to a depth of 7 cm. The mold and sample are immersed in deionized water such that only the surface area of the top face of the sample contacted the leaching medium, without mixing. The leachant is refreshed with an equal volume of deionized water using a liquid to surface area ratio of 10 mL/cm² (i.e., LS ratio of 10 cm) at cumulative times of 2, 5 and 8 hours, 1, 2, 4 and 8 days (see footnote 12). This schedule results in seven leachates with leaching intervals of 2, 3, 3, 16 hours, 1, 2 and 4 days. The solution pH and conductivity for each leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45- μm pore size polypropylene filtration membrane and

2, four analysis points are recommended.

¹² This schedule may be extended for additional extractions to provide more information about longer-term release. The recommended schedule extension would be additional cumulative times 14 days, 21 days, 28 days, and every four weeks thereafter as desired. Alternately, the duration of the test may be shortened (e.g., cumulative time of 4 days) for compliance testing.

preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 at the extract pH for quality control. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity).

RELEASE ASSESSMENT ESTIMATES

Release estimates may be obtained for site-specific and management scenario-specific cases when appropriate environmental data (e.g., precipitation frequency and amounts) and design information (e.g., placement geometry, infiltration rates) are available. For many situations, site-specific information either may not be readily available or may not be necessary (e.g., as in the case when the intent of testing is only to provide uniform side-by-side comparisons of treatment processes). For these situations, default scenarios may be defined; an application of this approach is provided in the companion paper (Sanchez *et al.*, 2002). These default scenarios are for illustrative purposes only, and other parameter values may be more appropriate for different management scenarios and geographic locations.

Percolation-controlled scenario

Percolation-controlled release occurs when water flows through a permeable fill with low infiltration rate and low liquid-to-solid ratio (Figure 5). In this case, local equilibrium at field pH is assumed to be limiting release. The information required to estimate constituent release during this scenario is the (i) field geometry, (ii) field density, (iii) anticipated infiltration rate, (iv) anticipated field pH, (v) anticipated site-specific liquid-to-solid ratio, and (vi) constituent solubility at the anticipated field pH. The anticipated site-specific liquid-to-solid (LS_{site}) ratio represents the cumulative liquid-to-solid ratio that can be expected to contact the fill over the estimated time period. It is based on the infiltration rate, the contact time, the fill density and the fill geometry and can be determined according to (Hjelmar, 1990; Kosson *et al.*, 1996):

$$LS_{site} = 10 \frac{inf \cdot t_{year}}{\rho \cdot H_{fill}} \quad (\text{Equation 2})$$

where, LS_{site} is the anticipated site-specific liquid-to-solid ratio [L/kg];

inf is the anticipated infiltration rate [cm/year];

t_{year} the estimated time period [year];

ρ is the fill density [kg/m^3];

H_{fill} is the fill depth [m]; and,

10 is a conversion factor [10 L/cm-m²].

Over an interval of 100 years or longer, LS_{site} values greater than 10 mL/g may be obtained for cases that have relatively high rates of infiltration or limited placement depth (Kosson *et al.*, 1996; Schreurs *et al.*, 2000). However, for many disposal scenarios, the observed LS_{site} has been less than 2 L/kg over a period of *ca.* 10 years and for an isolated landfill site with reduced infiltration, it may take 1000 years to reach LS_{site} of 1 L/kg (Johnson *et al.*, 1998; Johnson *et al.*, 1999; Hjelmar *et al.*, 2001).

An estimate of the cumulative mass release per unit mass of material can then be obtained using the anticipated site-specific LS ratio and the constituent solubility at the anticipated field pH ($S_{field\ pH}$) according to:

$$M_{mass}^{t_{year}} = (LS_{site}) (S_{field\ pH}) \quad \text{(Equation 3)}$$

where, $M_{mass}^{t_{year}}$ is the cumulative mass of the constituent released (mass basis) at time t_{year} [mg/kg]; and,

$S_{field\ pH}$ is the constituent solubility [mg/L] at the pH value corresponding to field pH.

Mass transfer-controlled scenario

Mass transfer-controlled scenario occurs when infiltrating water is diverted around a low permeability fill or prevented from percolating through the fill due to an impermeable overlay (Figure 6) or adjacent high permeability channels. In this case, mass transport within the solid matrix is rate limiting. The information required to estimate constituent release during such scenario are the (i) field geometry, (ii) field density, (iii) initial leachable content and (iv) observed diffusivity of the species of concern.

The mechanisms of release under mass transfer control can be quite complex and constituent-specific. The rate of COPC diffusion through the material can be retarded by surface reactions or precipitation of insoluble compounds. Alternately, mass transport may be enhanced by species complexation or mineral phase dissolution. Numerical techniques often are required to fully describe release under complex mechanistic conditions. Sophisticated models have been developed, or are under development, to dissolution/precipitation phenomena (Batchelor, 1990; Cheng and Bishop, 1990; Batchelor, 1992; Hinsenveld, 1992; Batchelor and Wu, 1993; Hinsenveld and Bishop, 1996; Moszkowicz *et al.*, 1996; Sanchez, 1996; Baker and Bishop, 1997; Moszkowicz *et al.*, 1997; Batchelor, 1998; Moszkowicz *et al.*, 1998), sorption/desorption phenomena, and material heterogeneity (Sanchez *et al.*, 2001b).

Fickian Diffusion model

The Fickian diffusion model, based on Fick's second law, assumes that the species of interest is initially present throughout the homogeneous porous medium at uniform concentration and considers that mass transfer takes place in response to concentration gradients in the pore water solution of the porous medium. The assumptions and release estimation approach shown here is most appropriate for release scenarios for which only highly soluble species are a concern or for which external stresses (e.g., pH gradients, carbonation, redox changes) are not significant.

In the classical representation of the diffusion model, two coupled parameters characterize the magnitude and rate of the release: C_0 , the initial leachable content (e.g., available release potential, total elemental content)¹³ and D^{obs} , the observed diffusivity of the species in the porous medium. When the species of concern is not depleted over the time period of interest, the cumulative mass release can be described by a one-dimensional semi-infinite geometry. Depletion is considered to occur when more than 20% of the total leachable content has been released (de Groot, 1993).

For a one-dimensional geometry, an analytical solution for Fickian diffusion is provided by Crank (1975) with the simplifying assumption of zero concentration at the solid-liquid interface (i.e., case of a sufficient water renewal; infinite bath assumption):

$$M_{area}^t = 2 \cdot \rho \cdot C_0 \left(\frac{D^{obs} \cdot t}{\pi} \right)^{1/2} \quad \text{(Equation 4)}$$

where M_{area}^t is the cumulative mass of the constituent released (surface area basis) at time t [mg/m²];

C_0 is the initial leachable content (i.e., available or total elemental content) [mg/kg];

ρ is the sample density [kg/m³];

t is the time interval [s]; and,

D^{obs} is the observed diffusivity of the species of concern [m²/s].

The test conditions for the MT series protocols (i.e., MT001.1 and MT002.1) are designed to ensure a non-depleting matrix and approximate the zero-concentration boundary, although field conditions may not satisfy these simplifications for many cases and the resulting release estimate may overestimate release. Therefore, other modeling approaches may be required to more accurately extrapolate to field conditions.

In release scenarios for which COPC depletion does not occur and Fickian diffusion is considered the dominant release mechanism, the mass release is proportional to release time by a $t^{1/2}$ relationship. After a log transform, Equation 4 becomes:

$$\log M_{area}^t = \log \left[2 \cdot \rho \cdot C_o \left(\frac{D^{obs}}{\pi} \right)^{1/2} \right] + \frac{1}{2} \log t \quad (\text{Equation 5})$$

Thus, the logarithm of the cumulative release plotted versus the logarithm of time is expected to be a straight line with a slope of 0.5. Often, initial release as observed from laboratory testing reflects wash off or dissolution of surface-associated constituents. The apparent constituent release then may be followed by diffusion-controlled release. Mass release over this initial time when surface phenomena are observed would result in a line with a slope greater than 0.5. In these cases, only the data points reflecting diffusion-controlled release are used to estimate observed diffusivity. The initial release should be verified to be insignificant in relation to the long-term field estimate of release (see Sanchez et al, 2002 for an illustration of this phenomena).

Estimation of observed diffusivity

Under the assumptions of the Fickian diffusion model, an observed diffusivity can be determined for each leaching interval where the slope is 0.5 ± 0.15 by (de Groot and van der Sloot, 1992):

$$D_i^{obs} = \pi \left(\frac{M_{area}^{t_i}}{2 \cdot \rho \cdot C_o (\sqrt{t_i} - \sqrt{t_{i-1}})} \right)^2 \quad (\text{Equation 6})$$

where D_i^{obs} is the observed diffusivity of the species of concern for leaching interval i [m^2/s];

$M_{area}^{t_i}$ is the mass released (surface area basis) during leaching interval i [mg/m^2];

t_i is the contact time after leaching interval i [s]; and,

t_{i-1} is the contact time after leaching interval $i-1$ [s].

The overall observed diffusivity is then determined by taking the average of the interval observed diffusivities.

Release estimates

¹³ The value used for the initial leachable content and the determined observed diffusivity are coupled parameters such that the same set of parameters obtained from experimental data must be used in determining long-term release estimates.

An estimate of the cumulative mass release for the management scenario can then be obtained using the analytical solution (Equation 4) over the anticipated assessment interval. When COPC release per unit mass of material is desired, conversion based on material field geometry can be applied to Equation 4.

$$M_{mass}^t = 2 \cdot C_0 \cdot \frac{S}{V} \cdot \left(\frac{D^{obs} \cdot t}{\pi} \right)^{1/2} \quad (\text{Equation 7})$$

where, M_{mass}^t is the cumulative mass of the constituent released (mass basis) at time t [mg/kg];

S is the fill surface area [m²]; and,

V is the fill volume [m³].

In the case where initial surface wash-off is considered to provide significant contribution to the release prediction (i.e., >5% of cumulative release), release from initial surface wash-off is added to release estimate from diffusion-controlled phenomena. An estimate of the cumulative mass release can then be obtained using:

$$M_{mass}^t = M_{area}^{wash-off} \cdot S + 2 \cdot C_0 \cdot \frac{S}{V} \cdot \left(\frac{D^{obs} \cdot t}{\pi} \right)^{1/2} \quad (\text{Equation 8})$$

where, $M_{area}^{wash-off}$ is the mass of constituent released (surface area basis) from surface wash-off [mg/m²].

When depletion of the COPC is anticipated to occur over the release interval, three-dimensional analysis using finite body models may be required to estimate cumulative release. Analytical solutions may be found for different geometries in mass transport literature (Crank, 1975) or simplifying assumptions may be applied to validate the above 1-D approach (Kosson *et al.*, 1996). Alternately, numerical methods may be used to solve the Fickian diffusion equation in three dimensions (Barna, 1994).

The above estimates represent a conservative approach for most mass transfer-controlled release scenarios where significant external stresses are not present. A zero surface concentration assumes a maximum gradient, or driving force, for mass transport (infinite bath assumption). In the case of slow water flow past the surface or small liquid-to-surface area ratios, accumulation of the COPC concentration in the leachate reduces the concentration gradient and limits leachate concentration to the mass of COPC in equilibrium with the solid phase. Thus, the upper bound (or maximum concentration) for mass transfer-controlled release should be estimated using release estimates obtained from equilibrium assumptions (e.g., Tier 2 testing in conjunction with percolation controlled release).

Other modeling considerations

Mass transport modeling approaches (Garrabrants, 2001; Garrabrants *et al.*, 2001; Sanchez *et al.*, 2001a; Tiruta-Barna *et al.*, 2001) are under development to address environmental conditions that are more likely to be encountered in the field such as intermittent wetting under varied environmental conditions (i.e., relative humidity and CO₂ content). Additional modeling also has been done to relate column test results to field leaching through application of geochemical speciation (Dijkstra *et al.*, 2001). These models can provide more accurate release estimates, but typically require additional information (experimental and field) and greater expertise for use. The simple modeling approach provided here is intended to be a conservative, first-order approximation that will result in overestimation of actual release for most cases.

EXAMPLE APPLICATIONS OF THE FRAMEWORK

Important potential applications of the leaching framework defined here include (i) the comparative assessment of waste treatment processes, such as for determinations of equivalent treatment under RCRA, (ii) estimating environmental impacts from utilization of secondary materials in construction applications, or (iii) estimating releases from large scale waste monofills. For these cases, Tier 2B and Tier 3B testing is recommended for initial evaluation. An example of this application is provided in the accompanying paper (Sanchez *et al.*, 2002). Subsequently, Tier 2A testing can be used to establish consistency between the materials initially tested and other similar materials.

ECONOMIC CONSIDERATIONS

The more extensive testing recommended in the proposed framework will obviously increase initial testing costs. However, these initial costs should be offset by several factors. First, detailed characterization of a material is only necessary initially to define its characteristic leaching properties, and only for materials that are produced in relatively large quantities. Subsequently, much less testing is needed to verify that new samples conform to the previously established properties. Second, cost savings should be realized through the framework by enabling alternative management strategies that are not possible under the current rigid system. Treatment processes evaluated under this system will be better targeted to reducing leaching under field scenarios. Reduced treatment costs may be achieved in many cases (however,

treatment costs may increase in cases where treatment processes were only effective at meeting TCLP, but were ineffective at reducing leaching in the field to levels consistent with risk-based endpoints). In addition, the potential for environmental damage and future liability will be reduced because of the closer relationship between testing and field performance. Costs for Tier 1 and Tier 2A testing should be of the same order-of-magnitude as current TCLP testing. Reductions in costs are anticipated as the methods become commercialized and data interpretation is automated.

CONCLUSIONS

The proposed framework presents an approach to evaluate the leaching potential of wastes over a range of values for parameters that have a significant impact on constituent leaching (e.g., pH, LS, and waste form) and considering the management scenario. This approach presents the potential to estimate leaching much more accurately (than many currently used leach tests), relative to field leaching, when conditions for leach test data are matched with field conditions. The greater accuracy of the proposed approach makes it a useful tool for examining waste and assessing the environmental soundness of a range of waste management options as well as for assessing the effectiveness of proposed waste treatment methods. In addition, the proposed framework provides flexibility to the end user to select the extent of testing based on the level of information needed and readily permits the incorporation of new testing methods and release models as they are developed for specific applications. Appropriately used in waste regulatory programs, this approach could make those programs substantially more cost-effective and protective of the environment. The flexibility of the proposed approach allows for development of the framework to provide a greater degree of tailoring to site conditions, to account for the effects of other waste leaching parameters critical to a particular site. Reliance on a tiered approach to testing can also make this approach more economical for smaller waste volumes and therefore more broadly feasible.

ACKNOWLEDGEMENT AND DISCLAIMER

Primary support for this research was provided by the USEPA Northeast Hazardous Substances Research Center and the USEPA Office of Solid Waste. Limited support also was provided by (i) The Consortium for Risk Evaluation with Stakeholder Involvement (CRESP) through U.S. Department of Energy grants DE-FG26-00NT 40938 and DE-FG02-00ER63022.A000 and (ii) EU DG Research funded projects. The authors

gratefully acknowledge the thoughtful feedback from Mr. Greg Helms (USEPA), and Dr. Charles W. Powers (Institute for Responsible Management) during the development of this manuscript and the technical support of Ms. Teresa Kosson during the development of the test methods. The authors also gratefully acknowledge the thoughtful comments and feedback of the anonymous reviewers and the assistance of the Editor, Dr. D. Grasso, lead author of the USEPA Science Advisory Board Review (1999) for which this paper is primarily in response. The viewpoints expressed in this paper are solely the responsibility of the authors and do not necessarily reflect the view or endorsement of the USEPA.

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Table 1. Specifications for the base case and suggested alternative conditions for equilibrium extractions.

| | Maximum Particle Size [mm] | | |
|---------------------------|----------------------------|----------------------|--------------|
| | Base case | Suggested alternates | |
| | 2 | 0.3 | 5 |
| Minimum sample size [g] | 40 | 20 | 80 |
| Minimum contact time [hr] | 48 | 18 | 168 (7 days) |
| Container size [mL] | 250 | 500 | 1000 |

Table 2. Comparison of recommended leaching protocols and applications.

| Tier | Test Name | Purpose | Methodology | Output | Application |
|------|-----------|--|---|--|--|
| 1 | AV001.1 | To determine the potentially extractable content of constituents under environmental conditions. | Parallel extractions at pH 4 and 8 in DI water; Liquid-to-solid (LS) ratio of 100 mL/g; contact time dependent on particle size. | Availability at pH 4 Availability at pH 8 | Screening: conservative release estimate. Characterization: realistic source term for modeling mass transport-controlled release. |
| 1 | AV002.1 | To determine the potentially extractable content of constituents under environmental conditions. | Single extraction using 50 mM EDTA; LS ratio of 100 mL/g; contact time dependent on particle size | Availability in EDTA | Screening: conservative release estimate. Characterization: realistic source term for modeling mass transport-controlled release. |
| 2 | SR002.1 | To obtain solubility and release data as a function of leachate pH | Multiple parallel extractions using DI water and HNO ₃ or KOH; LS ratio of 10 mL/g; contact time dependent on particle size. | Material-specific acid/base titration curve. Solubility and release as a function of pH | Characterization: detailed behavior of COPC as a function of pH. Compliance: abbreviated protocol to indicate consistency with previous characterization. |
| 2 | SR003.1 | To estimate pore water conditions by obtaining solubility and release data as a function of LS ratio. | Multiple parallel extractions using DI water; LS ratios of 0.5 to 10 mL/g; contact time dependent on particle size. | Solubility and release as a function of LS ratio. | Characterization: detailed behavior of COPC as a function of LS ratio. Compliance: abbreviated protocol to indicate consistency with previous characterization. |
| 3 | MT001.1 | To determine mass transfer parameters. To estimate rate of release under continuously saturated conditions. | Semi-dynamic tank leaching of monolithic material; Liquid-to-surface-area ratio of 10 [mL/cm ²] | Observed constituent diffusivity. Rate and cumulative release of constituent release under continuously saturated conditions. | Characterization: detailed leaching mechanisms and rate of release under mass-controlled leaching scenario. Compliance: abbreviated to indicate consistency with previous characterization. |
| 3 | MT002.1 | To determine mass transfer parameters. To estimate rate of release under continuously saturated conditions. | Semi-dynamic tank leaching of compacted granular material; Liquid-to-surface-area ratio of 10 [mL/cm ²] | Observed constituent diffusivity. Rate and cumulative release of constituent release under continuously saturated conditions. | Characterization: detailed leaching mechanisms and rate of release under mass-controlled leaching scenario. Compliance: abbreviated to indicate consistency with previous characterization. |

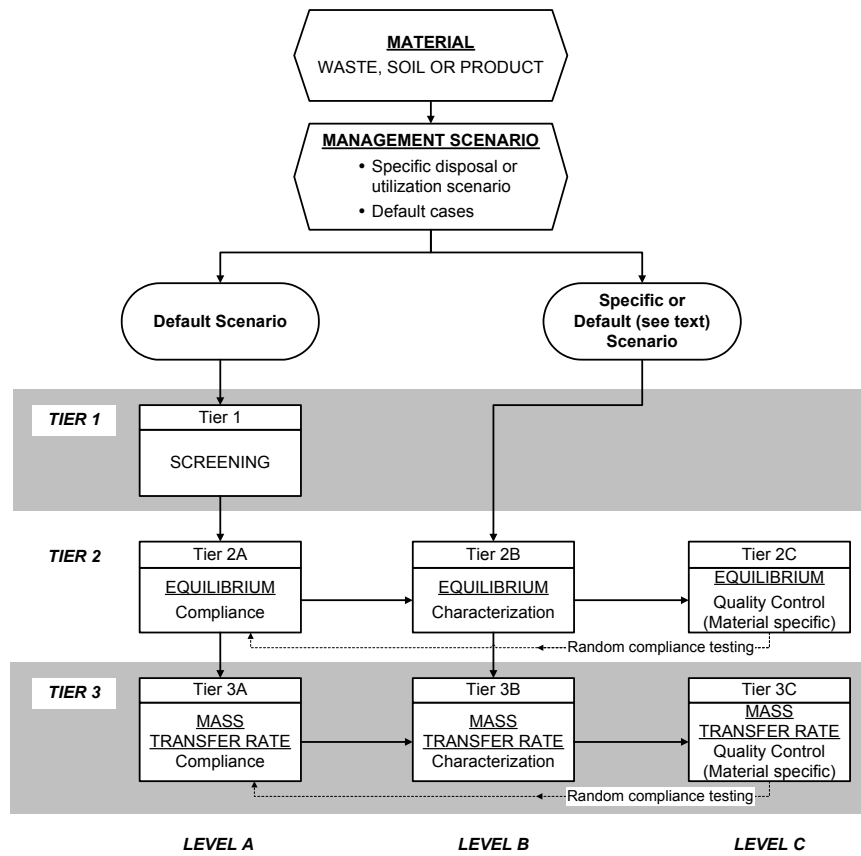


Figure 1. Alternative Framework for evaluation of leaching

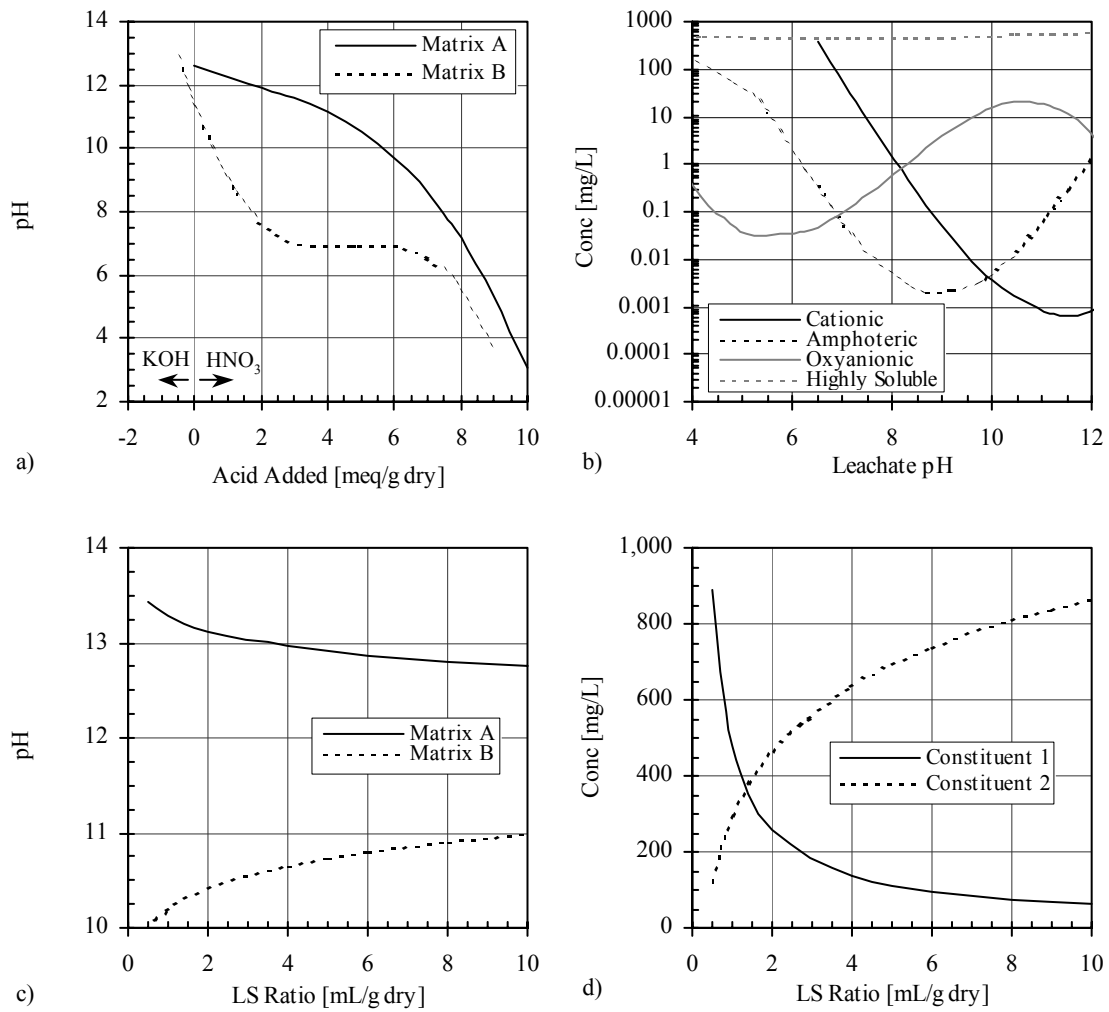


Figure 2. Conceptual data obtained using equilibrium-based testing protocols: a) titration curve (SR002.1), b) constituent release as a function of pH (SR002.1), c) pH as a function of LS ratio (SR003.1), and d) constituent concentration as a function of LS ratio (SR003.1).

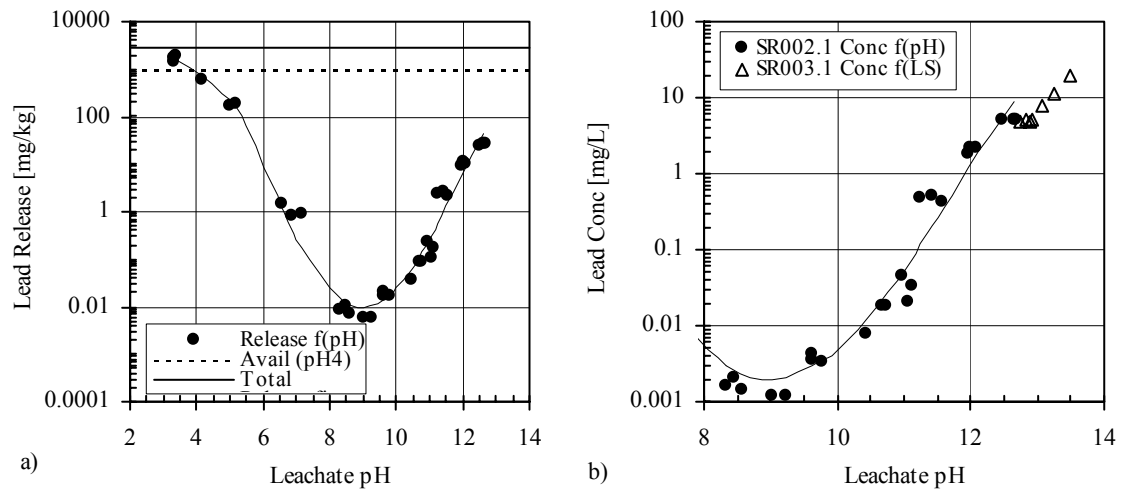


Figure 3. Actual data obtained using equilibrium-based testing protocols from a cementitious synthetic waste: a) lead release as a function of pH compared to lead availability and total lead content and b) comparison of SR002.1 and SR003.1 concentration data.

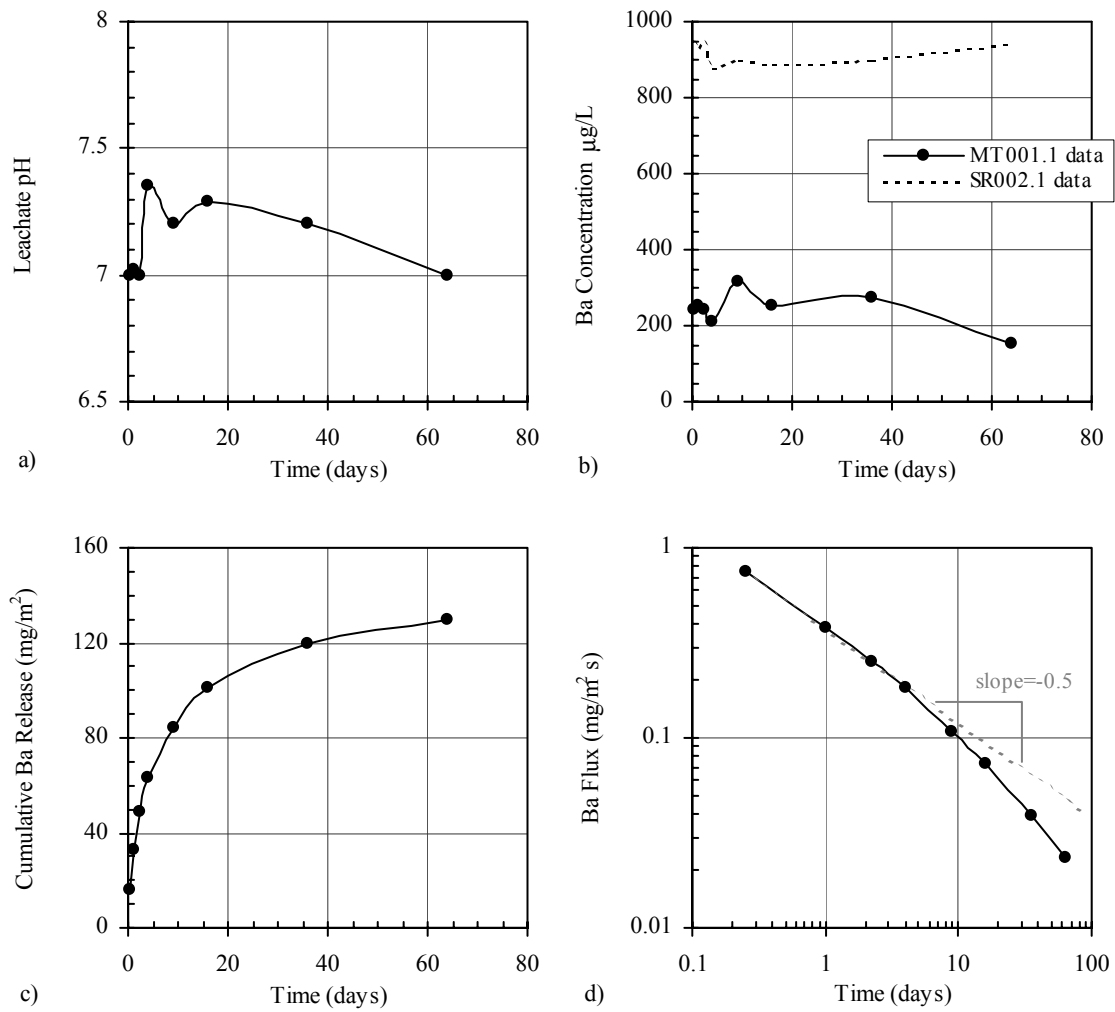


Figure 4. Actual data obtained using MT001.1 protocol from a stabilized waste (van der Sloot, 1999): a) leachate pH as a function of cumulative time, b) comparison of leachate barium concentration (MT001.1) and barium solubility as a function of pH (SR002.1), c) cumulative release of barium as a function of cumulative time, and d) barium flux as a function of mean cumulative time.

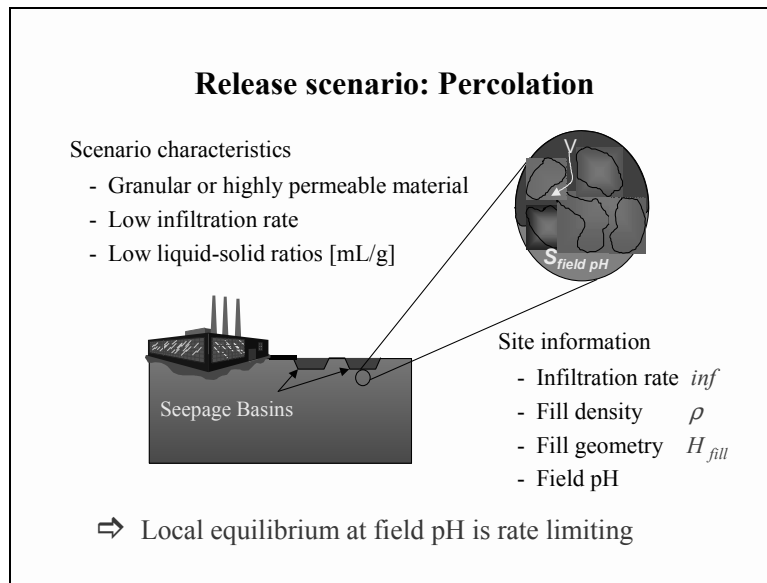


Figure 5. Release scenario: percolation.

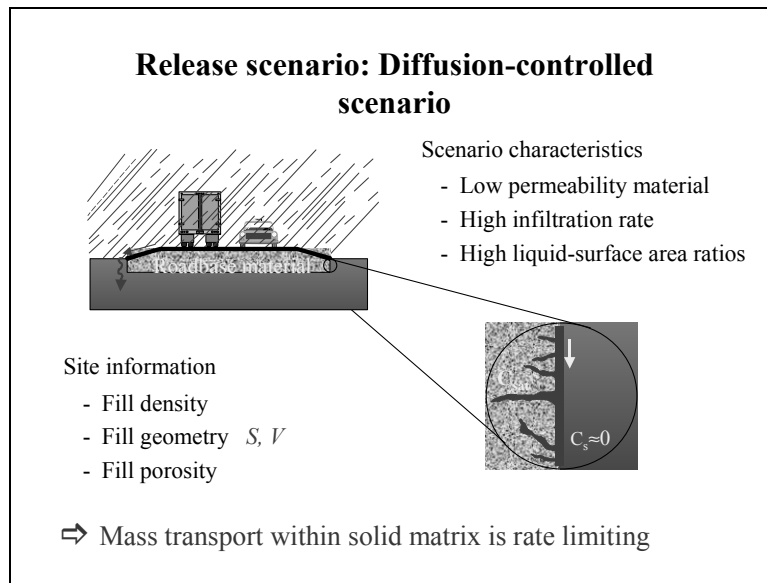


Figure 6. Release scenario: diffusion-controlled scenario.