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Radionuclide Release from Slag and Concrete Waste Materials

Part 3: Testing Protocol

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ABSTRACT

A protocol of simple laboratory tests designed to measure values needed to model the release and transport of contaminants from large piles of waste materials at surface sites for regulatory analyses is presented. In the absence of a specific site or performance model, a conceptual approach for modeling the release of contaminants from a waste pile was developed to identify the key information needed from laboratory testing and provide scientific bases for the recommended test methods. The time-dependent concentration of a contaminant released from the waste pile at the interface with the underlying regolith is expressed as a breakthrough curve (BTC) that depends on the release and transport of the contaminant. Each BTC can be thought of as the source term for a contaminant that is available at the bottom of the pile for transport to the surrounding environment. The system of discrete pieces of waste material forming the pile is modeled as a fractured matrix to express properties that depend on the surface areas of particular phases as average values for a representative volume or mass of the waste material. This allows standard approaches and existing models for contaminant transport to be applied to the waste piles. A probability distribution based on the values measured for many small field samples in laboratory tests can be used to represent the behavior of the entire waste pile. Two terms of primary importance to calculating the BTCs due to the weathering of various waste materials are (1) the effective contaminant release rate due to the dissolution or leaching of the host phases in the waste material that is the source of contaminants and (2) the effective retardation of contaminant transport due to several processes, including sorption onto various phases in the waste material, hold-up in stagnant water within tight fractures and voids, solubility limits and precipitation, etc.

An effective contaminant release rate is derived from test results to represent the release from all phases and an effective sorption term is measured to represent all processes retarding the transport of the contaminant. These are key terms in the advection-dispersion equation (ADE) used to model contaminant transport. Analogous to the distribution coefficient K_d that is used to quantify the overall effect of sorption to multiple phases on the contaminant concentration in solution, a term k_r is used to quantify the steady-state release rate of contaminants from multiple host phases on a fractional mass basis. Most important, values of k_r are expressed in terms of waste material mass rather than the surface area of the host phases. The objectives of the protocol of laboratory tests are provide values for these terms that represent the range of waste materials in a waste pile.

Simple batch tests are recommended for quantifying the effective contaminant release due to the dissolution or leaching of all host phases in the waste and the effective sorption/desorption behaviors of contaminants on the waste material. Simple modifications of standardized ASTM test methods are used to determine a representative pore water composition and range of contaminant concentrations (ASTM C1285), measure the contaminant release kinetics and rates, and the desorption rate (ASTM C1308), and measure the effective sorption properties (ASTM C1733). The variances in these property values throughout the waste pile due to heterogeneities in the waste material are estimated by testing samples collected from many locations in the pile to establish probability distributions of responses for each term that can be used in stochastic calculations.

While these tests provide parameter values for the isolated processes that can be used in reactive transport modeling, the release and sorption processes are coupled with each other and with transport terms in the ADE. An optional column test is recommended to calibrate the measured dissolution and sorption values for use in the ADE under well-controlled transport conditions to take the effects of couplings that are not explicitly represented in the ADE into account.

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EXECUTIVE SUMMARY

A protocol of relatively simple laboratory tests is presented that provides key information regarding the release behavior of contaminants (radionuclides) from piles of slag and concrete waste materials in surface disposal sites that can be used in reactive transport-based performance models. These simple laboratory tests represent the minimum testing effort required to characterize the weathering behavior of waste material to support a meaningful performance assessment. An optional and more complicated test method is recommended to optimize the material properties when coupled with transport properties.

A conceptual approach for modeling the performance of surface disposal sites was developed to identify the key information needed from laboratory testing to support reactive transport modeling. A generic disposal system consisting of a pile of rubble was conceptualized as a highly fractured regolith wherein the variously-sized pieces of the waste material comprise the matrix material and the voids between the rubble are represented as fractures. This system can be modeled mathematically using well-established continuum methods, wherein key values are measured or estimated with laboratory samples to represent the averages of fundamental properties of a representative volume of the waste material. The ensemble of average values measured for samples taken from throughout the system of interest provides a probability distribution that can be used in contaminant transport calculations at the field scale by using geostatistical methods. The conceptual approach provides a logical pathway linking laboratory-measured values to reactive transport modeling of the waste pile that utilizes current modeling methods.

Two parameters of primary importance for reactive transport modeling are (1) the contaminant release rates (source terms) due to the dissolution or leaching of all contaminant-bearing host phases distributed throughout the waste pile and (2) the retardation of contaminant transport due to several processes, including sorption onto various phases in the waste, hold-up in stagnant water in tight fractures and voids, solubility limits, etc. In practice, the retardation of contaminant transport is almost always represented in transport models using a linear distribution (partition) coefficient (K_d) model due to computing limitations and constraints imposed by the analytical or numerical solution of the advection-dispersion equation. The K_d approach transforms the dependence of these processes on the surface areas of individual phases to a dependence on the mass of a representative volume of the waste material based on the assumption that the total surface area of a sorbent is proportional to the mass (or volume) of a representative sample of the waste material. An analogous parameter k_r is used to represent the effective contaminant release rate from a representative volume of the waste material on a mass basis.

Variations in the effective contaminant release rates and effective K_d values occur due to spatial variations in the mineral phase assemblage, matrix porosity, environmental conditions, pore solution chemistry, and contaminant concentration throughout the waste pile. These are taken into account using geostatistical methods. Heterogeneity on the cm-scale is addressed by using test samples that are large relative to the distribution of host phases to provide average values. The heterogeneity of the waste pile on the scale of tens of meters is addressed by conducting laboratory tests with samples of materials taken from several regions throughout the pile to determine parameter values representing each region. That is, the individual laboratory tests are used to represent the behavior of a local environment and the large suite of field

samples is used to represent the system of interest.The pooled results of laboratory tests is used to provide the ranges and frequencies of measured property values and generate the probability distribution functions needed to model the field scale system stochastically.

The recommended test methods were selected because (1) the test response highlights a process or combination of processes of interest and provides an effective value that can be used in a continuum model, (2) the method has been applied to a wide range of materials, including engineered and naturally-occurring materials similar to the slag and concretes of interest, and (3) the test is easy and economical to perform. A testing sequence is recommended for efficiently measuring the release of contaminants from the ensemble of host phases and the sorption/desorption properties of the waste material.

The use of three simple laboratory test methods conducted with crushed and sieved waste materials (e.g., –35 +200 mesh[1]) is recommended: ASTM C1285 Method B, ASTM C1308, and ASTM C1733. These tests are used to measure the total amounts of contaminants released from all contaminant-bearing phases, the effective release kinetics of each contaminant, the effective sorption capacity of the waste material, and the reversibility (desorption) of the adsorption process. They are simple enough to conduct with a large number of samples to determine representative property values for several locations in the disposal system. Eight test samples (referred to as Samples A through H) are prepared from each field sample for use in the series of batch tests. The objectives and recommended sequence for the batch tests are as follows:

B1a Perform complete composition analysis of Sample A.

B1b. Conduct ASTM C1285 leach tests in acidic solution with Sample B to aggressively leach contaminants. Calculate the leachable contaminant concentrations in the initial sample (on mass basis), which may be lower than the total concentrations in the waste. This provides more realistic total release limits for predicting long-term contaminant release than measuring the total concentrations in the material, since not all contamination will necessarily be released by weathering. This provides an upper limit for concentrations used in the sorption tests (see Step B4).

B2. Conduct ASTM C1285 leach tests in demineralized water with Sample C to generate a representative pore water composition. Measure the solution composition and concentrations of released contaminants. Formulate a simplified pore water (SPW) solution representing the pH and chemical nature of the solution after interactions with the waste material (i.e., a brine, carbonate, sulfate, or silicate solution) but without contaminants for use in subsequent tests. The measured contaminant concentrations provide lower limits for other solutions used in the sorption tests (see Step B4).

B3. Conduct ASTM C1308 leach tests with SPW solution with Sample D. Use 1-day replacement intervals to measure contaminant release over at least 10 intervals. Determine contaminant release kinetics (i.e., linear with time for dissolution-controlled release or with the square root of time for diffusion-controlled release by leaching) and release rates for each sample.

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[1] All cited mesh sizes are US Standard mesh size; 35 mesh has 0.5 mm openings and 200 mesh has 0.075 mm openings. The -35 +200 mesh size fraction is comprised of material that passes through a 35 mesh sieve but is retained by a 200 mesh sieve.

B4. Conduct separate ASTM C1733 adsorption tests using Samples E, F, G, and H to measure K_d using each of four solutions made by spiking the SPW solution with the contaminant(s) of interest (16 tests in total). Analyze aliquants taken over several days to track sorption kinetics and measure the equilibrium concentrations. Calculate K_d for each concentration and characterize the sorption isotherm for each sample.

B5. Convert the ASTM C1733 test in Step B4 with Sample H to an ASTM C1308 test with the (nonspiked) SPW solution. Use several 1-day replacement intervals to characterize the desorption kinetics and measure the desorption rates.

The contaminant concentrations and sorption property values measured in tests conducted with various field samples define representative probability distribution functions that can be used for field-scale calculations. It is recommended that the sequential series of ASTM C1308 and ASTM C1733 tests in Steps B3 and B4 be applied to as many waste samples collected from different locations in the waste pile as practical. The number of samples required to adequately represent the waste pile will depend on the heterogeneity of the physical and chemical properties of the waste materials in the pile. The strategy provided in MARSSIM (2000) should be followed as appropriate.

An optional packed column test method is recommended to calibrate the contaminant release and sorption parameter values when coupled with the advective term for reactive transport models. The column test method provides well-controlled transport conditions that can be modeled using the advection-dispersion equation (ADE) to account for the effects of advection, contaminant release by dissolution or leaching, and sorption on contaminant release. Test conditions are selected to minimize dispersive effects and simplify the form of the ADE used to model the test. Inverse modeling methods can be used to refine the parameter values for contaminant release and sorption measured in the batch tests to be consistent with the effects of transport as modeled in reactive transport calculations. In this way, effects that are not explicitly considered in the analytical transport model become lumped with the dissolution and sorption parameter values and provide more realistic field-scale modeling.

The column test is more complicated and more difficult to perform than the batch tests and is recommended for use with a single sample of the waste material. Either material collected from a single location or a mixture of materials collected from several locaions can be used (for example, remaining crushed waste materials prepared for the batch tests). If a mixture of materials is used, a sample of that mixture should be subjected to the suite of batch tests to measure property values for gross contaminant concentrations, dissolution, sorption, and desorption kinetics to properly design and evaluate the column test results. The release and sorption properties measured in the batch tests provide insights that can be used to select the column length and flow rate to minimize dispersive effects, highlight advection or reactions, and provide reasonable breakthrough times. The recommended sequence and objectives for the column test are as follows:

C1. Initiate the column test using the SPW solution as the influent to measure the steady-state release rate of contaminants at a constant flow rate.

C2. Switch to a SPW solution spiked with the contaminants of interest (or a nonradioactive surrogate) and a conservative (non-sorbing) tracer (e.g., NaBr) as the influent and continue the test. Measure the effluent to determine the arrival leg of the breakthrough curve of the contaminant and at least until the conservative species reaches steady-state concentration.

C3. Switch back to the SPW solution without contaminants as the influent and continue the test. Measure elution leg of the breakthrough curve at least until the conservative species reaches the background concentration and the tailing behaviors of contaminants have been characterized.

The breakthrough curve generated in this test column test will reflect the combined effects of contaminant release, sorption, and transport. It is recommended that the column test be repeated at a second flow rate that differs enough to affect the relative effects of advection, contaminant release, and sorption on the breakthrough curve. The use of a low flow rate with the small particle size fraction called for in the test highlights the effects of intraparticle diffusion on the test results, whereas the use of a higher flow rate will highlight advective terms. Conducting tests at low and high flow rates provides insights into the sensitivity of the release behavior to the percolation rate through the pile.

The experimental approach and test methods presented in this report are expected to be suitable for assessing the performance of piles of slag or concrete rubble. The test conditions provided in the test descriptions represent initial guesses for generic slag or concrete waste materials based on available test results for similar materials. It is expected that modifications of some test parameters will provide better analyses of specific systems. For example, reaction intervals longer than 1 day may be required in batch tests (Step B3) with durable waste materials to provide measurable contaminant concentrations, or a larger size fraction may be required in column tests to represent the physical properties of the waste material with better fidelity. The results of initial tests should be evaluated to modify the test conditions as necessary.

Finally, although the test protocol was designed to provide the key information regarding waste material behavior and provide values that can be used for a wide range of possible modeling approaches, the development of a particular model may render some measurements in the protocol unnecessary or require additional tests to be added. Aspects of the system of interest, the conceptual model, and the experimental protocol for measuring model parameter values should all be considered within a coordinated approach when developing the assessment strategy. For example, the overall transport through shallow piles will be more affected by wet/dry cycles within the outermost meter of waste than will deeper piles, and separate tests to characterize the effects of wet/dry cycles on the release and transport of contaminants in an outer regolith may be needed for more reliable assessments. Aspects of the experimental approach supporting analytical modeling using the ADE and the conceptual modeling approach of utilizing geostatistical and continuum modeling techniques should be applied when adding new test methods to modified protocols developed for specific wastes.

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Quality of Data and Analyses

Only data from the literature sources cited in the report were used in these analyses. In many cases, the data presented in this report were generated by reading values from tabulated or plotted data in the literature publications. These were used to analyze trends in the data to evaluate reaction behavior and analyze the effects of testing and modeling parameters, and not to extract results for other uses.

The spreadsheet program Microsoft EXCEL 2010 and the plotting program KaleidaGraph version 3.6 2003(Synergy software) were used to plot data, perform regression fits, and compute modeled values. These are commercial software packages.

ACRONYMS AND ABBREVIATIONS

ADE	advection-dispersion (or diffusion) equation
ANL	Argonne National Laboratory
ANS	American Nuclear Society
ASTM	ASTM-International
CFL	Cumulative fraction leached
CFR	Cumulative fraction released
DOE	U.S. Department of Energy
FCRD	Fuel Cycle Research and Development
IAEA	International Atomic Energy Agency
IFL	Incremental fraction leached
L	generic length unit
M	generic mass unit
NRC	U.S. Nuclear Regulatory Commission
OCRWM	DOE Office of Civilian Radioactive Waste Management
OSTI	DOE Office of Science Technology and International (program)
PCE	perchloroethylene
PCT	Product Consistency Test
PDF	probability distribution function
PFA	polyfluro alkoxy (Teflon)
PV	pore volume (or number of pore volumes)
REV	representative element volume
SEM	scanning electron microscope (or microscopy)
SPW	simplified pore water
T	generic time unit

1 INTRODUCTION

Decommissioning of radioactively contaminanted sites requires a number of steps. Scoping and characterization surveys identify site contaminants, determine relative ratios of contaminants, and establish maximum contaminant levels for the disposal or final remediation conditions. Laboratory analyses such as alpha and gamma spectrometry are generally used to identify potential radionuclide contaminants and the relative abundance and isotopic ratios of contaminants like uranium and thorium. Requirements may be based on the spatial distributions of the contaminants and the result of site-specific pathway modeling. Performance assessment modeling provides estimates of the long-term doses and groundwater concentrations due to waste degradation and contaminant release based on short-term measures of the corrosion behavior of the waste material and limited characterization of the site such that the doses associated with these estimated releases can be compared to requirements in 10 CFR 61.

Argonne National Laboratory (ANL) has performed an NRC-sponsored activity to evaluate laboratory and field tests that have been used to characterize slag and concrete degradation and measure the release of radionuclides and how they interface with models used to predict radiation doses in risk assessment calculations. Two previous reports summarized evaluations of commonly applied test methods (Ebert 2010) and the relationship between laboratory tests and field assessments (Ebert 2011). This report describes a simple protocol of short-term laboratory tests to characterize the weathering behavior of waste materials. These results and available field measurements can be used in model calculations to assess the long-term releases of contaminants from waste piles at NRC-regulated sites and evaluate compliance with regulations prior to decommissioning. Simple tests that can be conducted by licensees to measure key aspects of contaminant release used in model calculations were identified. The testing protocol and the rationale are presented in this report.

Although work done to develop models for contaminant transport in geologic waste disposal systems provides valuable insights, modeling surface waste piles adds the complication of a heterogeneous distribution of contaminant host phases throughout the matrix material. This adds a spatially-dependent contaminant source term to the mass balance that is coupled with the suite of sorption/desorption reactions, all of which must be evaluated experimentally. The conservation of mass requirement for contaminant transport systems is quantified using the advection-dispersion equation (ADE), which provides explicit parameters for advection, dispersion, and various source and sink terms representing pertinent chemical, biological, and radiological reactions (Fetter, 1993, Zheng and Bennett, 1995). A chemical sink or source term can be formulated for each chemical species or component of interest. Terms for reactions and sorption are treated separately. Chemical reactions include dissolution, precipitation, reduction and oxidation (redox), bio-assisted degradation reactions, and radioactive decay. Sorption is used as a general term to include many processes in addition to chemisorption that remove contaminants from solution and retard transport, such as size exclusion, and precipitation. A recent review by the Nuclear Energy Agency concluded that “Sorption in the geosphere is one of the key processes for retarding the transport of radionuclides from the disposal vault to the biosphere. In many cases, sorption in the near field and in the biosphere is also important” (NEA, 1992).

1.1 Technical Approach

The conceptual model and experimental approach described in this report were developed to measure the key parameter values for particular waste materials that can be used to determine appropriate analytical forms for the sorption and reaction terms in the ADE formulations expected to be used in geological models for site assessments. Although most reactive transport modeling is conducted using numerical methods due to the limited number of analytical solutions to the ADE for simple systems, the approach taken here is to use empirical measurements that represent averaged behaviors to quantify the effects of key processes. The detailed physical and chemical characteristics that are needed to perform (and justify) more sophisticated modeling approaches will not be available for the waste materials and piles of interest. More important here is to represent the spatial variations in parameter values that occur throughout the waste pile by using the results of laboratory tests with many samples to support estimates of the overall range of behavior occurring at the field scale. A simple modeling approach and focused laboratory tests are expected to adequately evaluate contaminant transport in waste sites. This approach focuses primarily on the chemical properties of the waste material that impact the ADE. The transport properties are necessarily generic for porous and non-porous materials representing slag and concrete wastes, respectively.

A generalized one-dimensional ADE including terms for advection, dispersion, advection, sorption, and chemical reactions can be written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\left(\frac{\partial C_s}{\partial t}\right)_{\text{sorption}} + \sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{\text{reaction } k} , \tag{1.1}$$

where

C is the solution concentration of the contaminant (M L^{-3})[2]
t is time (T)
D is the longitudinal dispersion (diffusion) (L^2 T^{-1})
x is the direction of fluid flow
v_x is the velocity of fluid flow in the x direction (L T^{-1})
ρ_b is the bulk density of the waste pile (M_{solid} L_{solid}^{-3})
θ is the volumetric water content or porosity of the waste (unitless)
C_s is the amount of contaminant sorbed per unit mass of solid (M M_{solid}^{-1})
sorption is the index for sorption
reaction k is the index for a specific chemical reaction k (other than sorption)
N_c is the number of reactions affecting the solute mass of the contaminant.

This is sometimes referred to as the advection-reaction-dispersion equation to emphasize the inclusion of reactions. This equation is the basis for reactive transport models and defines the processes addressed for contaminant transport in waste piles.

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[2] M, L, T are used to denote generic units of mass, length, and time.

An experimental protocol with simple test methods are presented in this report to derive values for the third and fourth terms on the right-hand side of Equation 1.1, with recommendations addressing the selection of test specimens, aspects of designing the test apparatus, and examples of using the test results in contaminant transport models. The properties to be measured in laboratory tests were selected based on the applicability of existing models for degradation, sorption, and transport processes and the selection of efficient testing and analytical methods. The applicability of the test methods to slag and concrete waste materials was evaluated based on applications to similar materials.

The experimental approach underlying the protocol takes the heterogeneities in the materials throughout the waste pile into account by testing as many different samples as practical to generate a range of measured values. Representative reaction terms (lumped with the contaminant release rates) and sorption terms are estimated from the pooled results of experiments performed with several waste samples to support predictions at the field scale for the waste pile. That is, the batch tests provide the range of parameter values representing the waste material and the relative area of the waste pile represented by each field sample can be used to generate probability distributions relating the range of experimental measurements to the entire waste pile. The advection and dispersion terms in the ADE (the first and second terms on the right-hand side of Equation 1.1) depend on the physical nature of the waste pile. As it is impractical to measure the transport behavior of the waste pile directly, literature values for transport properties of groundwater in an analogous natural system can be used to model contaminant transport through the waste pile at the field scale. Literature values providing representative or bounding transport properties can be used with the distribution functions for contaminant release and sorption determined with the batch tests to model contaminant release.

The reliability of the calculations depends both on how well the experiments represent the average behavior of the waste material at the scale of the test samples and how well the collection of field samples represent the waste pile. In most cases of inverse modeling, using separately measured parameter values in an analytical expression such as the ADE does not match well with the property being modeled. This is because the parameters in the analytical expression are often lumped parameters that represent coupled physical processes that are not taken into account in measurements of the individual processes (e.g. Brusseau et al. 1997). An optional column test is recommended to calibrate the contaminant source term and sorption values measured in the batch tests with their use in the ADE coupled with known and controlled transport properties. The column test provides a controlled transport system in which the mean values of parameters for contaminant release and sorption can be optimized. In this way, the batch tests are used to measure the probability distributions for contaminant release and sorption in the waste pile, and the column test is used to optimize that distribution when coupled with transport phenomena in the ADE applied at the laboratory scale. Literature values providing representative or bounding transport properties for the waste pile can then be used with the optimized distribution functions to model contaminant release at the field scale.

1.2 Organization of the Report

In Section 2, a conceptual model is presented that was developed to provide the logical link between the test results generated by the protocol and contaminant transport through a waste pile by utilizing existing transport theory and geochemical modeling approaches. The scientific approach used to identify appropriate laboratory test methods and develop the testing protocol is presented in Section 3. The suite of batch test methods used in the protocol are described in

Section 4, including supporting evidence addressing the applicability of the test method to slags and concretes to generate the data that are needed. An optional but strongly recommended column test method is described in Section 5 with discussion regarding its applicability to slags and concretes. Literature results that provide examples of how the test results can be used to derive parameter values used in transport models are summarized in Section 6. The recommended testing protocol is presented in a step-by-step format in Section 7 for batch tests and an optional column test. The protocol is generic in the sense that a wide range of waste systems can be addressed by selecting test parameter values appropriate for the particular waste material and contaminants of interest. It is intended to provide a template on which site-specific test plans can be developed to match the envisioned modeling approach to evaluate regulatory compliance. Section 8 provides brief summaries of the approach, testing protocol, and testing uncertainty.

2 CONCEPTUAL MODEL OF WASTE PILE

Existing contaminant transport models address systems in which the contaminant is supplied from a source outside the transport system or released from a point source within the transport system. For piles of waste material, the contaminants are present in host phases that are distributed throughout the system and may occupy a large or small fraction of the waste material volume. Water must first be transported (percolate) through the system and contact a contaminant-bearing host phase, the contaminants must then be released from the host phase by leaching or dissolution of the phase and be transported through the primary system (the waste pile) to its boundary with the environment or a secondary system. The material containing the host contaminant phases is collectively referred to as the primary system and the underlying material not containing the host contaminant phases is referred to as the secondary system. This report addresses the release and transport of contaminants through the primary system to provide source terms for contaminants of interest entering the secondary system. The flux of contaminants through the interface between the pile and the underlying regolith provides the source term for separate calculations addressing transport through the secondary system. Transport through the secondary system can be treated using existing simulation models and is not addressed in this report.

This report discusses the modeling and experimental characterization of three coupled processes: (1) percolation of meteoric water through the waste pile, (2) weathering of contaminant-bearing phases to release contaminants, and (3) transport of contaminants through the waste pile to the accessible environment. The physical system being modelled is illustrated in Figure 2.1. Water supplied as rain or snowmelt percolates through voids between pieces of waste and contaminants are transported through the pile and exit the bottom of the pile over time. This is shown by the physical representation at the top. Contaminants drained from the waste pile (including surface run-off) can be modelled as collecting in a mixing cell at the interface between the pile and the underlying material (i.e, the secondary system), as shown as the output at the bottom of Figure 2.1. The mixing cell serves as a source of contaminants available for transport through the underlying system to the surrounding environment by using an appropriate transport model. Transport of the contaminants into the mixing cell is described mathematically as a breakthrough curve of contaminant concentration in the fluid exiting the pile vs. time. This is illustrated by the plot of radionuclide concentration against time representing the mathematical model in the middle of Figure 2.1. Several issues must be addressed for each process.

Percolation of meteoric water through the waste pile—this requires models for water transport by unsaturated flow as affected primarily by the physical nature of the waste material, including a water source term (e.g., due to rain and snow), advection and diffusion characteristics in the pile, porosity and matric potential characteristics.

Weathering of contaminant-bearing phases to release contaminants—this requires models sensitive to the inventories of contaminants in the waste system, distributions of contaminant-bearing phases in the waste material throughout the pile, release modes of contaminants from host phases, and the degradation kinetics of the host phases.

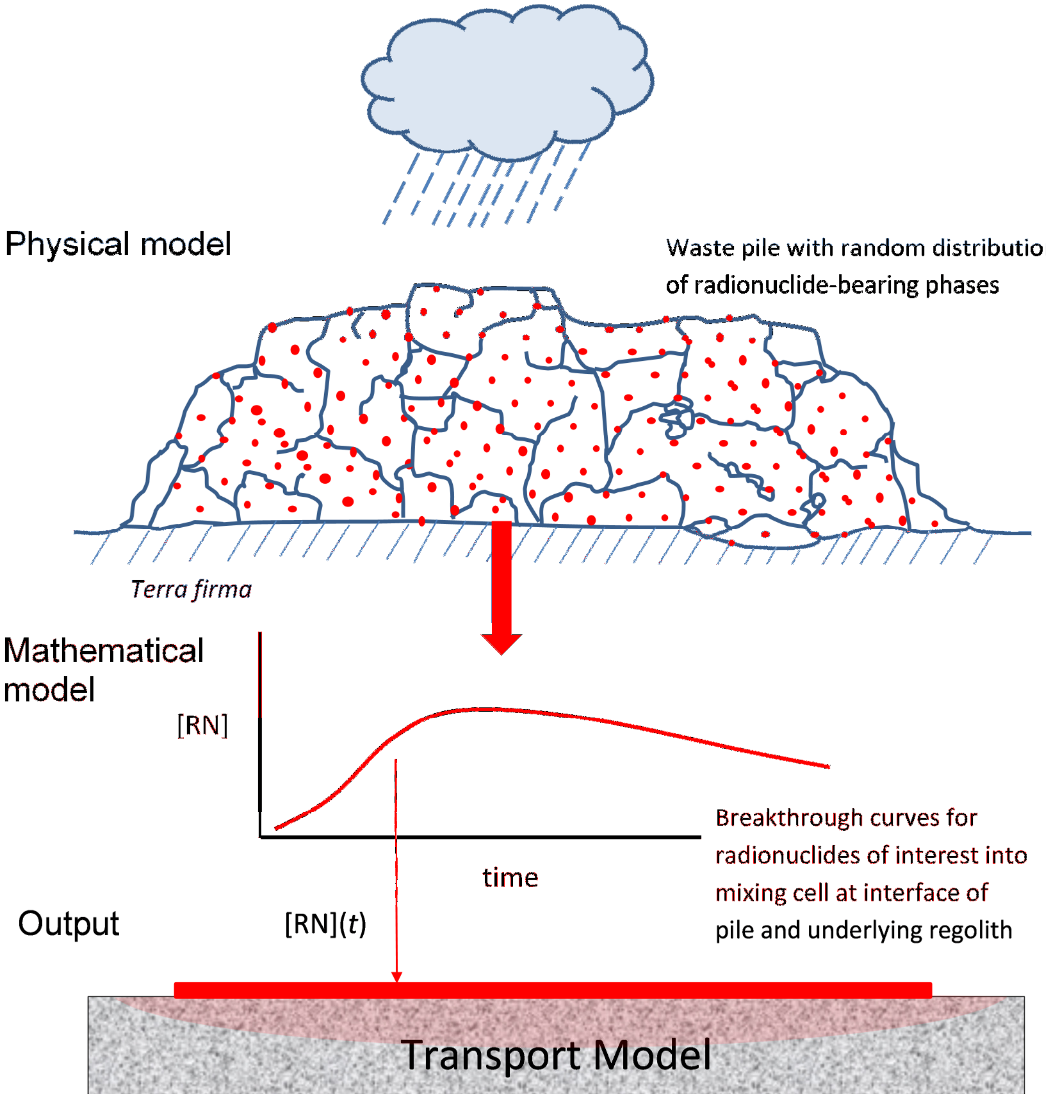

Figure 2.1 Schematic representation of conceptual approach for modeling a surface disposal system. Red regions represent the locations of contaminants.

Transport of contaminants through the waste pile—this requires models for the sorption of contaminants to sorbents in the host material, dissolved concentration limits and phase solubilities, chemical interactions and colloidal transport, and contaminant isotopes to calculate radioactive decay.

2.1 Percolation of Water through a Pile of Rubble

The waste pile can contain matrix materials ranging in size from clay-sized particles to boulders with contaminant-bearing phases distributed throughout the matrices and on the exposed surfaces. Meteoric water can percolate through the pile both by advection through voids between matrix particles and by diffusion through matrix particles. Contaminants can be released from those host phases that are exposed at the surfaces when contacted by advective flow through the voids and from those host phases within the matrix material when they are contacted by diffusing pore water. Contaminated pore water will collect and mix in the void regions between matrix particles. Advective and dispersive transport of contaminants will be affected by physical, chemical, and in the case of radionuclides, radioactive processes. Yeh and Yoon (1981) discussed the various processes and factors affecting contaminant transport, and these are summarized in Table 2.1.

The approach taken in the conceptual model is to utilize information and modeling results addressing physical aspects of transport that are available for naturally-occurring systems as surrogates for the movement of water through the waste pile.Specific laboratory tests are used in the testing protocol to measure the combined effects of the chemical processes in terms of two lumped parameters for each contaminant for the reaction terms. One parameter represents the release of a contaminant from all host phases and the other represents the sorption of the released contaminant onto all sorbent phases in the waste material. Although these processes occur simultaneously, different test conditions are used to highlight each process and measure parameter values.

Table 2.1 Processes affecting contaminant transport

Physical		Chemical	
Process	Factor	Process	Factor
Advection	Topography	Partitioning	Physical properties
Dispersion	Climate	Sorption/Desorption	Chemical properties
Fracture Flow	Precipitation	Ion Exchange	Geology
Diffusion	Soil Type	Volatilization	Microbial environment
Precipitation	Vegetative Cover	Equilibrium Speciation	
Dissolution	Depth to Groundwater	Acid/base	
Erosion	Soil Permeability	Complexation	
	Soil Void Ratio	Hydrolysis	
	Soil Moisture	Oxidation/Reduction	
	Geology	Biodegradation	
	Hydrology		
	Morphology		

2.2 Reactions between Pore Water and Waste Materials

The reaction between a waste material and pore water percolating through the pile is characterized by feedback between the mineral assemblage in the material and the evolving composition of the pore water. The mineral assemblage at any location will change over time due to dissolution and precipitation reactions, which, in turn, will change the solution composition as it moves through the pile. The solution composition will also change due to sorption, radionuclide decay, and biological reactions. These reactions may be coupled with the pore water transport and the rates of other reactions through the saturation state of the pore water composition. In most cases, the reactions are too slow for the pore water to equilibrate with the minerals along the flow path. Thus, the pore water composition and nature of reacting mineral surfaces will evolve along the flow path and over time, and both must be considered when describing the chemical evolution of the pore water, including the contaminant concentrations. This is a well-studied geochemical process with established experimental and modeling approaches that can be brought to bear for modeling waste piles (e.g., Zhu and Lu, 2009). The dissolution rates of contaminant-bearing phases are usually calculated in terms of the saturation state. Dissolution rates are highest under far-from-saturation conditions and lowest near saturation.

The release of some contaminants from some waste materials may be better described as leaching than dissolution. This is expected to be the case for soluble phases dispersed in the pore structure of concrete wastes. Leaching is often modeled as a diffusion-controlled process with a square-root time dependence that could be addressed with a separate term in the ADE. Alternatively, the leach rate could be linearized to represent long-term behavior.

2.3 Continuum Approach to Modeling Transport in Fractured Porous Media

No attempt is made to describe the pile of rubble discretely due to the extremely wide range of particle sizes (from sand to boulders) and highly tortuous interparticle pathways for water flow. Instead, the pile is modeled as a highly fractured rock to utilize transport models that have been developed for naturally-occurring systems. The correspondence is shown schematically in Figure 2.2. The illustration on the left represents a cross section of a pile of variously sized sand, gravel, and boulders, and the illustration on the right represents a corresponding fracture network. This transforms the description of the pile from a system of particles having widely ranging volumes, surface areas, void volumes, and tortuous flow paths to a system of matrix blocks with a range of fracture apertures. This allows for the use of existing methods and continuum models that were developed to represent groundwater and contaminant transport through hydrologically unsaturated and saturated media. The fracture aperture and porosity of the matrix blocks can be adjusted to represent the effective transport properties of the complex physical system around and through the waste material.

(a)

(b)

Figure 2.2 Schematic representation of (a) discrete pile of rubble and (b) analogous fractured porous rock matrix.

This transformation is the most innovative aspect of the conceptual approach used to develop the testing protocol. It recasts the impossible problem of modeling the surface area of a pile of rubble into problem of contaminant transport through a fractured matrix. In a study focused on the conceptual models for fluid infiltration in fractured media, the National Research Council provided conclusions regarding the development and testing of conceptual models, flow and transport in the fractured vadose zone, and recommended research included the following (National Research Council, 2001):

- *Development of the conceptual model is the most important part of the modeling process. The conceptual model is the foundation of the quantitative, mathematical representation of the field site (i.e., the mathematical model), which in turn is the basis for the computer code used for simulation.*
- *The context in which a conceptual model is developed constrains the range of its applicability. A conceptual model is by necessity a simplification of the real system, but the degree of simplification must be commensurate with the problem being addressed.*
- *Although not identical, structured soils and fractured rocks exhibit many similarities in flow and transport processes. Macropores and aggregates in structured soils are respectively analogous to fractures and matrix blocks in rock.*
- *The interaction between fracture and matrix exerts a strong control on fluid and solute movement. However, the strength of this interaction in the field is not well known. The simplified representation of this interaction in current models also requires further evaluation.*
- *Solute transport in the fractured vadose zone*[3] *can exhibit complex behavior due to the large variations in fluid velocity and the interplay of advective and diffusive transport between fractures and matrix. Solute transport models are more complex than flow models, and can involve multiple regions to represent the diversity of macropore and micropore sizes.*
- *Research is needed to understand the spatial variability in the vadose zone properties, and to develop upscaling methods. Spatial variability is a key cause of model uncertainty, because the subsurface cannot be exhaustively sampled. Upscaling methods are needed to derive field-scale flow and transport properties from small-scale laboratory measurements.*
- *Current models should be evaluated for their adequacy for simulating flow and transport in the presence of fingering, flow instability, and funneling. Of particular importance is the evaluation of transfer coefficients to represent fluid and solute exchange between fracture and matrix.*

The same conclusions apply to transport through waste piles. Nonlinearities in groundwater flow paths occur at the microscopic (and macroscopic) level due to variabilities in the size and orientation of matrix blocks, heterogeneous distributions of mineral phases, variations in void volumes and inter-block spacings, etc. For modeling large-scale systems, these nonlinearities can be taken into account by using “a stochastic approach, which assumes that local soil properties are realizations of three-dimensional random fields…for derivation of a large-scale model representation…by averaging the local governing flow equation over the ensemble of realizations of the underlying soil property random fields” (Mantoglou and Gelhar 1987). That is, local variabilities of soil and rock in natural systems require a suitable sampling strategy to use properties that are measured on the small scale to model large-scale behavior. The same approach can be applied to waste piles.

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[3] The vadose zone is the hydrologically unsaturated zone above the water table.

Of interest here is a system that includes regions of a porous or nonporous medium and the void space between the regions of media that are occupied by fluid (water or air). In the geological models that are recommended herein as the basis for modeling piles of slag and concrete, the pieces of waste material are analogous to regions of rock matrix and void spaces between the pieces of waste material are analogous to fractures (as discussed in the previous section). The fractures can be modeled to be of various aperture size and roughness and the matrix material can be modeled as being porous or nonporous. The same mathematical models can be used for contaminant transport through the two subsystems (matrix and fractures), which are interconnected networks of voids enclosing blocks of matrix material. The interconnectivity of the system of fractures is an important issue in modeling flow and contaminant transport through fractured rock addressed using percolation theory. This is discussed in Section 2.3.1.

In the continuum approach, the average values of atomistic (microscopic) properties that are too complex to be measured or modeled directly are measured and modeled at the intermediate scale of laboratory samples to develop probability distributions that can be used in calculations at the macroscopic level (e.g., Bear 1993). The continuum approach avoids the need for immeasurable microscopic details that control a behavioral property by using a macroscopic average of that property, which can be measured for a volume of the material known to provide an appropriate average value for the domain size of interest. That volume is referred to as the representative elementary volume (REV) for the property of interest. In this protocol, each test sample is used as the REV for a region of the pile. Every extensive property of the material within the entire domain (i.e., the test sample) can be modeled using a continuum to provide an average value. The volume over which properties are averaged must be large enough to be independent of the heterogeneities of the system on the microscopic scale, but small enough to describe the heterogeneities present on the macroscopic scale of the test samples. The collection of field samples provides a set of test samples (REVs) used to represent the ranges of average property values throughout the waste pile.

Applying the continuum approach to waste piles allows the dependencies of properties on the surface areas of contaminant source and sorbent phases to be represented as dependencies on the mass (or volume) of waste material used in a test. That is, the test specimens represent the REVs for contaminant sorption and release. Variations in the amounts and surface areas of host phases in the pile are represented by the range of release rates and K_d values measured for the set of field samples. For example, the mass (or Ci) of a contaminant that is released from the pile per year is based on the values measured for the set of REVs on a mass contaminant per mass test sample scaled by the mass of the waste pile. The probability distribution derived from the set of field samples can be used directly in stochastic calculations or to determine a single probability-weighted average value.

2.3.1 Conceptual Flow Models

Bear (1993) defined a fractured porous medium as “a portion of space in which the void space is composed of two parts: an interconnected network of fractures, and blocks of a porous medium. The entire void space is occupied by one or more fluids. Such a domain can be treated as a *single continuum*, provided an appropriate REV can be found for it.” He goes on to say “in defining the REV, we require that macroscopic coefficients of the porous medium be independent of the volume of the REV.”

It is convenient to model the fluid in the fractures and the fluid in the pores as separate but exchangeable fluid phases (both of which occupy the entire domain). The characteristics of the fractures (location, shape, length, aperture, etc.) are treated statistically rather than deterministically. In this basic approach, the network of fractures is modeled as one subsystem and the network of porous blocks is modeled as another subsystem. These are referred to as dual-porosity systems, which are a subset of the dual-permeability classification in which the permeability of the fractures is typically more than 100-times the permeability of the matrix. In dual-porosity systems, advective flow through the matrix is taken to be negligible relative to advective flow through the fractures in transport calculations. Each subsystem can be represented in more detail by using subsystems with distinguishable properties, for example, by modeling fractures having narrow or wide apertures as separate continua. Figure 2.3 illustrates the representation of the physical system presented in Figure 2.1 as separate continua of fractures and matrix material having flow paths F_F and F_M. Fluid in the fracture is often referred to as mobile and fluid within the matrix pores as immobile. Contaminants in the fracture fluid are transported by advection and diffusion, whereas contaminants in the pore fluid are transported by diffusion alone. The fluid in one continuum (fracture or matrix) can be transported to the other continuum (matrix or fracture) by a separate diffusion process. This can be modeled using an exchange mixing cell.

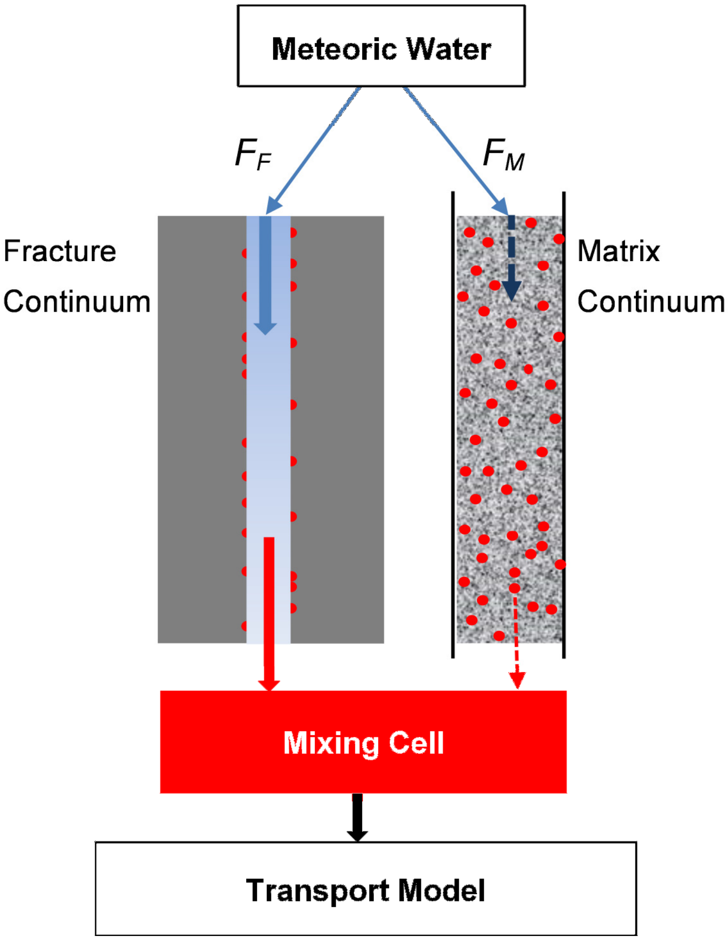

Figure 2.3 Schematic representation of alternative conceptual flow models. The red dots represent host phases with contaminants.

For particular media, the flow in either the fracture or the matix may be negligible (or can be treated as such) to provide a simpler model in which only one of the flow paths is considered. Single continuum models may be appropriate for piles of slag and concrete, wherein transport through the fractures will dominate for non-porous slags and transport through the matrix will dominate for unsaturated concretes with high matric potentials. A single set of parameter values would be adequate for modeling the system in that case. However, significant amounts of water can be stored in the dead-end fractures and voids that do not form a continuous percolation channel of even low-permeability materials. The exchange of solutes between the water flowing in fractures and this stagnant water can retard the transport of contaminants the same as diffusion in the matrix retards transport in more porous materials. The testing protocol provides insights into the overall behavior of the waste material that can inform the modeling approach and assumptions based on the average values of the properties that are measured.

The numerical methods and models applied to water flow, contaminant transport, and solid mechanics in the natural system depend on the simplifications that are used. Five conceptual models for fluid flow are listed below in order of increasing complexity:

> Equivalent porous medium—all processes and material properties treated as a porous medium in a single continuum. Material properties are based on the effective characteristics of the medium alone. $F_F = 0$ in Figure 2.3 (negligible fracture flow).
>
> Composite porous medium— all processes and material properties treated as a porous medium in a single continuum. Relative permeability-capillary pressure relationships are modified to represent effects of fractures. $F_F = 0$ in Figure 2.3 (negligible fracture flow).
>
> Equivalent fracture medium—porous medium treated as a single fracture continuum. Material properties are based on the effective characteristics of the fractures alone. $F_M = 0$ in Figure 2.3 (negligible matrix flow).
>
> Dual porosity—Medium treated as separated co-located fracture continuum and matrix continuum. Flow occurs only in the fracture continuum and diffusion occurs only in the matrix continuum. Solute exchange occurs between fracture and matrix continua. $F_M = 0$ in Figure 2.3 (negligible matrix flow).
>
> Dual permeability—Medium treated as separated co-located fracture continuum and matrix continuum. Flow occurs in both continua at different velocities. Solute exchange occurs between fracture and matrix continua. $F_M \neq 0$ and $F_F \neq 0$ in Figure 2.3.

Several aspects of continuum modeling pertinent to modeling waste piles and the testing protocol are discussed below.

Different conceptual models may be appropriate for different waste systems or even for different regions within a waste system (Neuman, 2005). The equivalent porous medium model can be used to represent granular media and low-permeability clay, whereas the dual porosity approach is usually more appropriate for densely fractured rock, though it may be possible to model some fractured systems as a single porous medium (e.g., Berkowitz et al., 1988). The spatial scale of the waste system will also influence the appropriateness of continuum models. Transport paths that are short relative to the REV may require use of a discrete fracture network model (e.g., Dverstorp et al., 1992; Murphy and Thomson, 1993; Therrien and Sudicky, 1996; Painter and Cvetkovic, 2005; Chambon et al., 2010; Chambon et al. 2011). Although this could be the case for a relatively thin layer of waste material (e.g., less than 1 m), the contribution of such a region to the total contaminant release is expected to be small and adequately represented by the continuum approach.

2.3.2 Dual Porosity Model

The dual porosity method was developed for modeling non-equilibrium transport in soil, wherein the water is assumed to be comprised of a mobile phase and an immobile phase. The mobile phase occupies the center of saturated pores and the immobile water consists of thin coatings on soil particles, dead-end pores, and water trapped in small unsaturated pores (Coats and Smith, 1964). Solutes become distributed between the mobile and immobile phases and can exchange between these phases by diffusion; solutes in either the mobile or immobile phases can participate in adsorption-desorption reactions. The dual porosity model is now widely used for modeling transport through fractured materials. Fractures serve as the primary pathway for pore water flow and the water in the saturated matrix is considered to be almost immobile. Pore water and solutes can react with minerals in the matrix and both can move through the matrix and between the matrix and the fractures by matrix diffusion. Diffusion from fractures into the matrix and sorption within the matrix retard the transport of solutes.

Dual porosity (dual region) models are often used to describe solute transport through fractured geologic media wherein the flow domain is divided into two regions that have a large contrast in permeability such that flow is negligible in one of the regions (e.g., Gerke et al., 1993a, 1993b; Zimmerman et al., 1993; Finsterle, 2000). There are two main variants of the model that differ in how contaminants are transferred between the two regions (Berkowitz et al., 1988; Dykhuizen, 1990). In one, the diffusive mass transfer of solutes between flowing and non-flowing regions (fractures and matrix) is described explicitly using diffusion equations within the non-flowing matrix material (Tang, 1981; Callahan et al., 2000; Reimus et al., 2003a, 2003b). In the other, solute transfer is approximated using reversible first-order rate expressions to account for mass transfer between the flowing and non-flowing regions (Bajracharya and Barry, 1997; Maraqa et al., 1999). Parameters that affect the matrix dissolution rates (matrix diffusion coefficients, matrix porosity, and effective fracture apertures) can be distinguished from parameters that affect the diffusion length scales (matrix block size and shape, flowing fracture spacing). The variability in the matrix dissolution parameter values observed in laboratory tests cannot account for the much slower field-scale behavior that is controlled by the diffusion length scale. Reimus and Callahan (2007) stated that “unless extremely long experiments or observations or highly detailed hydrogeologic characterizations are performed, matrix diffusion length scales in fractured rock aquifers are probably best addressed in risk assessment models through sensitivity analyses using alternative conceptual model geometries”. Accordingly, the testing protocol is focused on measuring parameters for contaminant release (regardless of the mechanism). Models must rely on information from surrogate systems for field-scale diffusion length characteristics.

2.3.3 Boundary Conditions

Defining the boundary conditions for any model of the waste system is an important component of developing the conceptual model because the overall behavior of the model is largely determined by those boundary conditions. Site-specific information and inferences about water flow systems are used to define the boundary conditions. Reasonable assumptions about the boundary conditions for a waste pile can be made on the basis of “typical” natural system characteristics. For example, flow will typically be driven by distributed recharge of meteoric water (rain and snow) on the topographic surface and water discharge at the bottom of the flow system, which results in a relatively low average horizontal hydraulic gradient. Such a flow system corresponds to an area with limited topographic relief and lack of large-scale regional driving forces. The surface boundary condition can be defined as constant concentration or a constant flux. The permeability of the regolith underlying the waste pile will determine the boundary condition for contaminants in the effluent exiting the pile. It is expected that modeling the pile as being semi-infinite will be mathematically convenient while adequately representing the behavior of the system. The testing protocol does not restrict the boundary conditions that may be used for assessment models and the derived values are not affected by them.

2.3.4 Scale

Bear (1993) introduced four zones that are related to the scale of the system being modeled and the REV:

- The *very near field* is a single fracture and surface of a matrix block that is treated deterministically.
- The *near field* includes a small number of well-defined fractures of known size and shape, which can be treated deterministically or statistically.
- The *far field* represents transport in two overlapping continua and exchange of fluids between the continua.
- The *very far field* is such that the entire domain can be treated as a single continuum, that is, the behavior of water in fractures and pores can be modeled as a single continuum.

Modeling at the very near field and near field scales requires information on every fracture regarding aperture, length, spacing, orientation, etc. that is only possible for very small domains and simple geometries. The far field and very far field scales require the continuum approach to take into account the contributions of thousands of fractures and detailed information needed to calculate transport behavior. The application of continuum models to large-scale systems (on the far field scale) often utilizes multiple overlapping continua to model subsystems having common properties, such as grouping fractures with common aperture sizes providing a multimodal distribution of hydraulic conductivities. Even very large systems (on the very far field scale) can often be modeled as a single porous material represented using a single continuum.

Many problems require descriptions of the system on the microscopic, very near field, and mesoscopic near field scales to determine average values for the continua used in far field scale modeling. This is accomplished by a process referred to as upscaling that is performed using geostatistics. The effects of scale on transport properties have been studied using continuous time random walk (Berkowitz and Scher, 1998; Cvetkovic et al., 2004; Frampton and Cvetkovic, 2007) and the dual porosity model with mass transfer coefficients (Huang and Hu, 2000, 2001; Hu et al., 2002; Reimus et al., 2003a, 2003b). The spatial variability of reactive minerals will determine the effect of scale on the matrix sorption coefficients and other properties. This is because, in geostatistics terms, the spatial distributions determine correlation lengths, composite means, and variances of tortuosity and sorption coefficient that can result in different covariance functions. The spatial distributions of reactive minerals in sediments often show a nested hierarchical structure of subunits of similar reactive mineral distributions (Cushman et al., 2002). Hierarchical structure can be characterized using indicator geostatistics combined with transition probability models (Dai and Sampler, 2004; Dai et al., 2005; Ritzi et al., 2004). Specifically, when a rock is made up of several minerals each having different sorption coefficients for a species of interest, that rock can be characterized using a multimodal statistical distribution representing the sorption coefficients for individual minerals. Because the transport parameters are spatially heterogeneous at the different scales, the spatial distributions of the minerals and the physical and chemical heterogeneities that control sorption processes must be characterized at different scales. The approach used in this protocol is to collect a large set of field samples to represent the scale of the waste pile and conduct tests with subsamples that are sufficiently large to provide average property values representing the near field. Enough samples are used to characterize the heterogeneity of the waste pile and the ranges of values measured for the set of field samples are used to represent the overall behavior of the waste pile.

2.3.5 Geostatistics

Like soils and fractured rock, the physical nature of the waste pile is much too complicated to be modeled deterministically and must instead be modeled statistically. Geostatistical techniques utilize random function (random variable) theory to model the uncertainties in parameter values that are associated with location in the system by using correlated random variables. Geostatistics can be thought of as an extension of interpolation, wherein an unknown value of the variable of interest $\boldsymbol{x}$, such as the presence or absence of a contaminant-bearing phase, at a particular location is represented mathematically as $\mathbf{Z}(\boldsymbol{x})$. Geostatistics treats $\mathbf{Z}(\boldsymbol{x})$ as a random variable that may or may not be bounded by a cumulative distribution function based on what is known about $\mathbf{Z}(\boldsymbol{x})$. The geostatistical method used to estimate the value at one location based on known values at other nearby locations is kriging. Known information can limit the randomness of $\mathbf{Z}(\boldsymbol{x})$ for many properties. The known mean and covariance of a random process is used to minimize the variance of the error in the estimation (e.g., Yeh et al., 1983).

In a natural medium, the hydraulic conductivity in the mobile zone, sorption coefficients in the mobile and immobile zones, and the mass diffusion rate between the two zones are all spatial random variables that contribute to the spatial variability of the physical and chemical properties. The spatial continuity of a variable is described by a variogram. If the same statistical properties are applicable over the entire domain of interest, a single spatial model can be applied to the system. It is expected that most waste piles will be restricted to being modeled as homogenous with regard to contaminant and transport characteristics due to a paucity of measured field characteristics; this is not a restriction of the conceptual model.

The probability distribution function (pdf) describes the probability that a continuous random variable $\boldsymbol{Z}$ has a particular value at a particular location. The pdf can be sampled repeatedly during modeling to create a set of alternative mappings of $\boldsymbol{Z}$ that consider the possible values for successive locations across the system. The ensemble of realizations is used as a probabalisitic prediction. Many applications of geostatistics involve solving geological problems by using inverse modeling, wherein the parameter values for a complex combination of processes having many variables are adjusted to match a measured overall response (see Yeh, 1986; Dai and Sampler, 2006; Dai et al., 2006). The measured response provides a constraint to the model. For example, groundwater flow models are constrained by comparisons with field data including water saturation and moisture tension measured in boreholes, perched water data, etc. Realizations far outside the measured response can be neglected as physically unrealistic. In most cases, contaminant transport models cannot be constrained owing to both the lack of field data and the complexity of the models. However, contaminant distributions in some waste piles may be constrained based on similarities in waste materials from a common waste generation campaign, processing method, source material, age, or other characteristic that affects the contaminant release or retardation properties that are measured in the protocol.

2.3.6 Upscaling and Volume Averaging

Several studies have addressed the scaling of transport parameters in fractured rock (Berkowitz and Scher, 1998; Reimus et al., 2003a, 2003b; Cvetkovic et al., 2004; Dai et al., 2007; Liu et al., 2007). Key parameters that depend on the scale of the system being evaluated include diffusion coefficients (Liu et al., 2007; Zhou et al., 2007; Dai et al., 2007), sorption coefficients (Liu et al., 2008; Dai et al., 2009), reaction rates (Lichtner, 1993), and retardation factors (Rajaram, 1997; Dai et al., 2009). These processes are affected by various factors, including fracture aperture, fracture volume fraction, matrix porosity and tortuosity, and the type and accessibility of surface areas of minerals within the matrix. For the waste materials of interest in this report, the combined release of contaminants from all contaminant-bearing phases is another key parameter that is sensitive to scale.

Reactions between groundwater, contaminants, and minerals depend not only on the physical and chemical conditions in the system, but also on the spatial distribution of the minerals in fractured rocks. The spatial distribution of reactive minerals will affect the impact of dissolution reactions on contaminant release and the impact of sorption reactions on contaminant transport. Because different minerals will contain, release, and sorb different amounts of contaminants, their distributions on different scales will affect the reactive transport model. The key parameters affecting the transport of contaminants are primarily sorption, permeability, porosity, tortuosity, and the mass transfer coefficient for the movement of contaminants between fractures and matrix continua.

The objective of upscaling is to identify a homogenous domain that approximates the response of the heterogeneous domain under the same boundary conditions. Upscaling uses the averages of parameter values that are measured at the small scale to model the average behavior of the system at a larger scale. The spatial distributions of the minerals in a rock and the physical and chemical heterogeneities that control transport and sorption processes (and mineral dissolution) must be characterized at different scales. The distributions of minerals that release contaminants into the solution (the host phases) and minerals that sorb contaminants from solution must be scaled from the microscopic or mesoscopic scale at which they are characterized in laboratory studies to the field scale. Likewise, the sorption coefficients and dissolution rates must be scaled to account for heterogeneities in the system.

The scaling of the retardation factor of a chemical species is strongly related to the variability of the sorption coefficients for the minerals in the rock (e.g., Allen-King et al., 2006; Zavarin et al., 2004). In the absence of an applicable upscaling rule, the parameters controlling sorption under field conditions are usually approximated using values derived from column experiments. Characterization of the physical and chemical heterogeneities that control sorption processes is required because key parameter values are spatially heterogeneous at various scales.

Volume averaging is used to homogenize spatially variable properties into a single model parameter value. The method of volume averaging allows the macroscopic governing equations needed to model large-scale systems to be established from microscopic equations and boundary conditions that can be solved to describe behavior based on natural laws and theory. Volume-averaged properties are often used to represent the direction of groundwater flow, net infiltration rates, pore velocities, fracture permeability, water saturation, etc. Volume averaging is used in the testing protocol to scale the contaminant release rates and sorption properties of the waste materials collected in field samples to the overall waste pile.

The distributions of contaminants on the scale of the volumes that are sampled for use in laboratory tests will influence the representativeness of each test sample and how well the set of test samples represent the wastes being evaluated. Although it is not uncommon for modelers to use laboratory-measured values of tortuosity and sorption coefficient for field-scale calculations directly and without upscaling, this may lead to inaccurate simulation of physical and chemical processes using stochastic methods if the set of samples is not representative of the waste system. This emphasizes the importance of subjecting a large number of field samples to the testing protocol and utilizing all available information regarding known characteristics of waste materials distributed throughout the pile.

2.3.7 Experimental Approach to Scaling

The three scales of interest are the microscopic scale of the process models for contaminant release and transport, the mesoscale of the laboratory tests, and large scale of the waste pile to be modeled. The locations for five field samples taken from a waste pile and variations in the sampled materials are shown schematically in Figure 2.4. The contaminant-bearing phases are shown by small red dots and the sorbing phases are shown by large black dots. The microscale is defined by the individual phases. The distributions of both define the homogeneous system represented by each field sample.

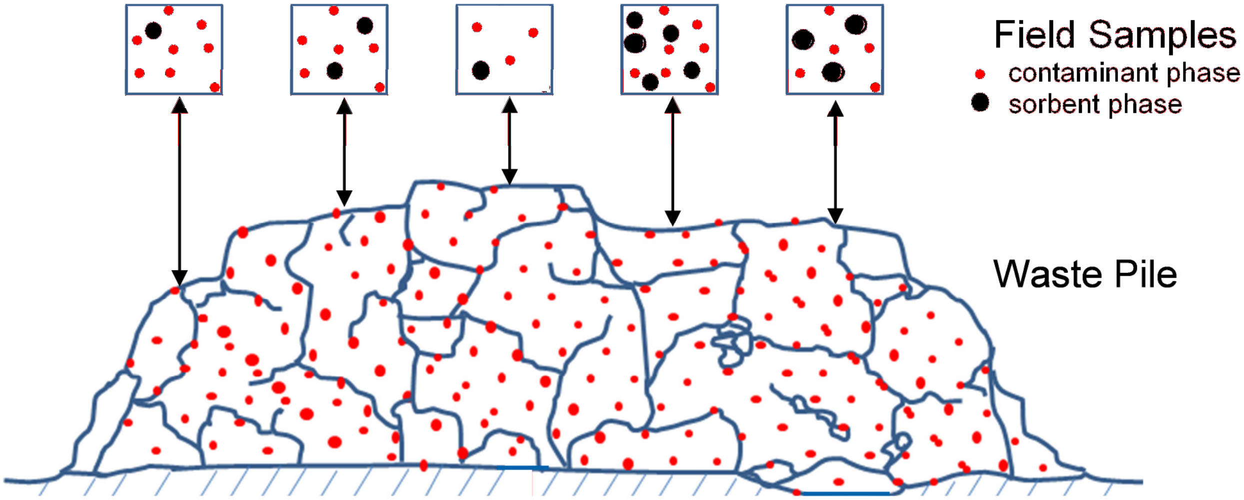

Figure 2.4 Schematic representation of field samples and sampled locations on the waste pile.

The volume of the field sample is defined to be a REV for both the contaminant release and sorption values representing a fraction of the waste pile. The differences in the distributions of those phases between the various field samples represent the heterogeneity of the waste pile. The number of field samples establishes the sensitivity that can be achieved in performance assessment models. Whereas five field samples are shown in Figure 2.4 for illustration, analyzing a much larger number of field samples would be appropriate for waste piles covering several hectares (MARSSIM 2000).

The testing protocol provides property values for the field samples that can be utilized in field-scale models of the waste pile as either a probability distribution for stochastic models or as a weighted mean value for deterministic calculations for either single or dual porosity representations.

2.4 Summary of Conceptual Modeling Approach

Just as it is impossible to describe the microstructure of a soil or the fracture structure of a mountain, it is impossible to characterize the void spaces and surface areas of a large pile of rubble for deterministic calculations. The continuum approach is the only practicable means of modeling contaminant release from a large and poorly characterized pile of rubble with a limited testing effort. In this chapter, it was shown how the macroscopic-continuum approach can be used to model contaminant release in piles of variously sized rubble of slag or concrete by modeling the pile as fractured rock. The waste pieces are analogous to the matrix material and the voids between the waste pieces are analogous to the fractures. In this way, the need to estimate the surface area of a waste pile contacted by water is replaced by a need to estimate the fracture and pore properties of the pile. This allows existing continuum models of groundwater flow and contaminant migration in fractured rock to be applied to the system of meteoric water percolating through and reacted with waste piles. Several well-established modeling methods and techniques used in continuum models are pertinent to waste piles and are used to identify the information to be provided by the laboratory testing protocol.

The flow and transport components in each continuum are described by sets of governing equations that conserve mass, energy, and momentum in the system while quantifying the system response to external mass inputs and the interrelationships between the various processes that are involved. Models have been developed to quantify the physical and chemical processes and interrelationships that control the transport of contaminants, upscale properties measured at the microscale and mesoscale to large field systems, and predict long-term behaviors and sensitivities. The governing equations underlying the reactive transport models were evaluated regarding possible application to modeling surface disposal sites. The analytical advection-dispersion equation (ADE) used to calculate contaminant transport can be applied to the fracture and matrix systems separately using different parameters and parameter values. The ADE includes separate terms for the contributions of processes affecting the transport: advection, dispersion, and various contaminant sources and sinks (host phase dissolution, precipitation, sorption, radioactive decay, oxidation/reduction, etc.). That analysis has lead to the formulation of a suite of laboratory tests that provide enough site-specific information to model contaminant release using approaches similar to that outlined in this section for site assessment. In essence, the laboratory tests provide values required to generate probability distributions for contaminant release and retardation that can be used in continuum models for transport through a waste pile. This is described in the following sections.

3 PURPOSE OF TESTING

3.1 Testing Objectives and Approach

The protocol of recommended tests is intended to provide data from which model parameter values can be derived for use in reactive transport calculations simulating contaminant mobilization. Reactive transport models are based on a formulation of the ADE representing the processes contributing to each term. Equation 1.1 is reproduced in Equation 3.1 for convenience, except the sorption term is labeled “sink” and the reaction term is labeled “source” to emphasize each of those parameters may represent several processes.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\left(\frac{\partial C_s}{\partial t}\right)_{\mathrm{sink}} + \sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{source} \tag{3.1}$$

Laboratory tests are conducted to provide waste material-specific and contaminant-specific values for (1) overall contaminant release rates from the host phases for use as the source term and (2) contaminant sorption to the waste material for use in reactive transport calculations without regard to which phases contribute to the release or sorption. These are key parameter values for modeling contaminant transport. The tests also provide measures of (3) a representative pore water solution composition, including contaminant concentrations, which is used in test design and data interpretations, and (4) the total releaseable concentration of the contaminant in the waste material, which is important to long-term predictions.

3.1.1 Contaminant Source Term

Contaminant release is addressed by the reaction term in the ADE, which may include the effects of several processes that release contaminants from the waste material to the pore solution. Key aspects related to the release of each contaminant from the waste material are:

- Contaminant concentration in the waste material—The total concentration of each contaminant of interest is measured, without regard to the identity of the host phase from which it is released.
- Contaminant release mode—This refers to the apparent process by which a contaminant is released from all the phases containing it, typically by dissolution or degradation of the host phase or by leaching from the host phase. The measured kinetics may represent the overall result of several distinct processes, such as dissolution and leaching, and coupled processes, such as oxidation of the contaminant to a soluble oxide followed by the dissolution of that oxide.
- Contaminant release rate—This refers to the time dependence of the contaminant becoming transportable and the effects of environmental variables. The objective is to measure an effective rate for the combined release from all host phases due to reaction with a typical pore water. For the purpose of reactive transport modeling, the release rate is expressed on a fractional basis as mass contaminant per mass waste material, which does not require quantitation of the surface areas of the host phases. The use of test samples large enough to provide representative specific surface areas of contaminant-bearing phases within the sample mass supports scaling on a mass-of-waste material basis.

- Composition and chemistry of pore water—The objective is to generate a solution that is representative of the pore water by reacting either demineralized water or a simple solution representing rain water (if desired for locations with acidic rain water) with the waste material. The composition of water percolating through the waste pile will be determined by reactions with all phases within the waste, including phases that do not host radionuclides, and will vary with the flow rate. A single solution representing the pore water composition after significant weathering of the waste material is used in tests to measure contaminant release and sorption in the laboratory tests. That solution is referred to as the simplified pore water (SPW) solution. A simplified composition is used because large volumes are required to conduct the laboratory tests.
- The contaminant release rate will vary over time due to changes in the environmental conditions, such as the pore water composition, and changes in the waste material, such as the development of surface depletion layers. The release kinetics of each contaminant is characterized as linear or non-linear to determine a representative rate for use in modeling.

3.1.2 Contaminant Sorption Term

The sorption of a contaminant on the waste material is addressed in the sorption term in the ADE, which is a lumped parameter including many processes that withdraw contaminants from the solution and retain them on the solid. The partition coefficient is defined as

$$K_d = \frac{\text{mass of contaminant retained on solid per unit mass solid}}{\text{mass of contaminant dissolved per unit volume solution}} \qquad (3.2)$$

Direct measurement of K_d values is considered to be essential for site-specific calculations (Triay et al., 1997; EPA 1999). The combined effects of all sink terms are measured using method ASTM C1733 to determine effective K_d values over a range of contaminant concentrations for use in modeling. That range is based on the concentrations measured in batch tests:

- Contaminant concentrations in pore water—The lowest contaminant concentration(s) used in sorption tests to determine the concentration dependence of K_d is based on those measured in the tests to determine the SPW composition. Several higher contaminant concentrations are used up to the highest releasable contaminant concentration for the set of field samples.
- Dependence on contaminant concentration—The objective is to measure K_d by using SPW solutions that have been spiked with a range of contaminant concentrations to establish the sorption isotherm. Most reactive transport calculations assume a linear isotherm, but models can accommodate more complicated isotherms. Separate values of K_d can be used to differentiate specific zones of different waste materials in the pile comprised of specific weathering conditions, such as materials at the surface and in the interior of the pile. This can be incorporated into the model by using a bimodal probability distribution function for the sorption term.

3.1.3 Contaminant Transport Terms

Contaminant transport by advective and dispersive forces (including diffusion) addressed by the first two terms on the right-hand side of Equation 3.1 are properties of the waste pile system and not measured as part of the testing protocol. It is likely that parameter values for these terms must be estimated from a natural system having characteristics similar to those determined or estimated for the waste pile.

An optional column test is recommended to calibrate (condition) the source term and sorption parameter values measured in the batch tests for their use when coupled with the transport terms. Application of the ADE to the results of column tests conducted under carefully controlled flow and flow path conditions can be used to validate the model and calibrate the model parameter values. Details of the batch and column tests are presented in Sections 4 and 5 of this report, and a brief discussion of optimization is included in Section 6. The rest of this section summarizes the roles of the tests in supporting contaminant transport models.

3.2 Recommended Test Methods and Materials

A sequential series of tests and analyses is recommended for characterizing the release of contaminants from the host phases and the sorption of contaminants onto the waste material. These provide measures of the contaminant release and sorption properties of the waste material at a scale that represents the local composition. Heterogeneity at the field-scale requires the analysis of samples taken from many locations to measure the range and probabilities of property values needed to upscale the laboratory measurements using geostatistical methods. The accuracy of that process depends strongly on the probability distribution functions for contaminant release and sorption that are determined from tests conducted with the collected specimens. In effect, the volume of the waste pile represented by each field sample is defined by the number and locations of those samples.

The Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM, 2000) and the companion Multi-Agency Radiological Laboratory Analytical Protocols manual (MARLAP, 2004) are consensus documents developed by the US Environmental Protection Agency, the Nucear Regulatory Commission, and the Departments of Energy and Defense that provide information on planning and conducting radiological surveys of contaminated sites for demonstrating compliance with regulations and for planning and conducting radioanalytical laboratory work. The reader is encouraged to apply the approaches for conducting surveys, radioanalytical laboratory work, and data-handeling that are recommended in those documents to plan and execute the collection of field specimens for use as test samples (some examples are cited in the following sections). For the purpose of this report, it is assumed that basic characterization of the waste material was done as part of the survey used to determine that further evaluation of the site was required and are not repeated here. Significantly different waste materials present in the same waste site (or waste pile) should be modeled using separate parameter values measured in separate sets of tests. (See Section 3.2.3.)

3.2.1 Batch Tests

Batch tests are conducted to measure dissolution and sorption/desorption parameter values. It is important that these tests be conducted with multiple samples of waste material collected from different areas to generate a statistical distribution of parameter values that represent the heterogeneity of the mineral distribution. These simple tests can be applied to a large number of samples with reasonable effort and cost, and the results can be used directly to support scaling the dissolution and sorption behaviors measured at the laboratory scale to the field scale. It should be emphasized that the objective of the batch tests is to characterize the collective contaminant release and sorption behaviors of the host and sorbent phases present on the surface or in the bulk of the waste material, not to determine the behaviors of individual phases. Neither are the tests intended to simulate the waste pile system. Rather, crushed material is used to expose phases in the interior of the piece of waste material to include them in the measured responses, with the intent being to expose surface areas of the constituent phases in proportion to their volume fraction in the material. A lower bound to the size fraction is used in the tests to exclude fine material that could be completely dissolved during the test or removed from the test vessel when solutions are removed during replacement steps. The use of bounding sieve sizes also improves the precision of the specific (and total) surface areas of different samples. Batch test methods are discussed in detail in Section 4 of this report.

3.2.2 Column Tests

Column tests are conducted at a constant flow rate to optimize the dissolution and sorption parameters determined from batch tests for use in modeling dynamic conditions. Tests at two flow rates are recommended to measure the effect of residence time on the transport parameters. The column tests are not intended to represent the flow paths of the real system. The flow paths in a waste pile are more complicated than can be replicated in any laboratory experiment, and the relationship between the laboratory system and the real system cannot be evaluated in the absence of detailed characterization of the real system. At most, it is expected that a range of percolation rates will be assumed in transport calculations for the waste pile based on surrogate natural systems and the climate at the waste site. The column test provides a controlled environment that can be used to modify the contaminant release and sorption parameter values measured in the batch tests to better represent the effective values in a dynamic system modeled with the advection-dispersion equation. This so-called optimization provides improved source term and sorption parameter values for use in those calculations.

The objective of the column test is to determine differences between the source term and sorption values measured in the batch tests and the values that provide ADE-modelled rates that are consistent with the rates measured in the column test. Column tests are too expensive, difficult, and time consuming to perform with the large number of samples needed to represent the waste pile. Instead, it is recommended that tests be conducted with a single test sample of the crushed waste material at two flow rates. The probability distribution functions for contaminant release and sorption that are determined from the batch tests can be calibrated by simply shifting uniformly to higher or lower values based on the results of the column test. For this reason, it is recommended that the column test be conducted with a sample of the waste material having parameter values near the center of the distribution measured with the batch tests. Column test methods are discussed in detail in Section 5 of this report.

3.2.3 Waste Material Samples

Chapter 7 of the MARSSIM document addresses sampling and preparation of materials for laboratory measurements: Sampling is defined as the process of collecting a representative portion of an environmental medium. Key aspects of the collected sample are its physical characteristics and how well it represents the contaminant content and distribution in local material. Each sampled location is referred to as a survey point. Several survey points are typically selected to represent regions within the site having distinguishable characteristics or exposure pathways. A sufficient number of survey points should be utilized to ensure complete characterization of the site without bias. The physical characteristics of the sample and the sampling method should be consistent with the dose or risk pathway model and supporting laboratory tests that are to be used. Sufficient material must be collected to be representative of contaminants at the survey point, to provide measurable contaminant concentrations, and to provide specimens for tests and analyses. The collection of subsurface samples is most important for the modeling approach and tests recommended in this report. It is recommended that samples be collected for use in the batch tests from as many survey locations as practical to measure representative ranges of effective contaminant release rates and sorption properties (see Section 7) for scaling the laboratory results to model the entire waste pile.

From MARLAP (p. 10-1), "a field sampling plan should provide comprehensive guidance for collecting, preparing, preserving, shipping, and tracking field samples and recording field data. The principal objective of a well-designed sampling plan is to provide representative samples of the proper size for analysis." These measurements are used to determine the probability distribution functions (pdf) for the contaminant release rate (source term) and K_d for each contaminant. The laboratory test specimens serve as REV on the mesoscale for the chemical reactions occurring in the system, including the contaminant release rates, concentrations, and sorption onto other constituent phases. Therefore, it is important that the sub-samples of crushed material that are prepared from the field samples taken from the waste pile be representative. Methods developed to produce representative sub-samples should be utilized or simulated, such as riffle splitter. For example, the entire field sample should be crushed enough to separate a representative one-fourth of the material for further crushing, with one-quarter of the resulting pieces used in the next step, and so forth until an adequate amount of sized material is available for testing. The field sample must provide sufficient material to produce test specimens in this manner. The test samples represent a homogeneous field sample.

The column tests can be conducted with a sample of the most abundant waste material, if the waste pile is found to be fairly homogeneous based on the batch tests, or a mixture of materials taken from various locations. As discussed above, it is recommended that the material used in the column test represent the center of the parameter value distributions and that the distribution be shifted based on the results of the column test. Therefore, a sample of the mixture using in the column test should be subjected to the suit of batch tests to measure the release kinetics and sorption properties to properly analyze and apply the results of the column test to the probability distribution.

The waste material is crushed and sieved to isolate a particular size fraction for use in the tests. This is done to maintain a constant specific (geometric) surface area for the test samples and support scaling laboratory measurements to the much larger waste pile based on the mass (or volume) of waste material rather than the surface area. Although the geometric approximation used to estimate the specific surface area of small particles[4] is inexact with respect to the actual reactive surface area, it provides a reasonable and practical scaling factor to relate the measured processes (contamininant release and sorption) to full-sized pieces of waste on a mass or volume basis. The recommended size fraction represents a compromise between the various batch tests and column tests that highlight different processes. Small particles are expected to represent reactions of the constituent phases for the contaminant release rate and sorption measurements better than large particles because a greater fraction of the mass is

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[4] Using a specific size fraction allows the geometric specific surface area to be estimated based on the density of the material (ρ) by defining the diameter of an assumed spherical particle (d) as the average sieve opening. The geometric specific surface area of a sphere is

$$S_{geometric} = \frac{6}{\rho d}\,.$$

exposed to water. Larger particles are expected to better represent the role of matrix diffusion and hold-up in column tests. Column tests require column diameters that are about 30-times the particle diameter to avoid forming preferential flow paths. In general, larger columns, larger sample masses, and larger volumes of solution are needed to conduct tests with larger particles. Therefore, particles within the –35 +200 mesh size fraction (opening size range between 0.075 and 0.50 mm) are recommended for the samples used in batch and column tests. This will provide enough high-specific-surface-area material for dissolution and sorption measurements, be suitable for a column having 1.5-cm diameter[5], and be large enough to adequately represent the porosity of the bulk waste material, including concretes. (The effects of microporosity of the concretes on the measured properties are more important than the effects of the macroporosity, which is adequately represented by the free surfaces.) The overall high surface-to-solution volume ratio achieved in batch tests with this size fraction will accelerate the approach to equilibrium in the batch tests and steady state in the column tests.

3.2.4 Pore Water Solution

Many of the tests recommended in this report are conducted with a solution formulated to simulate pore water. The composition of that solution must be determined before those tests can be conducted. In systems with high material surface area-to-volume ratios, the pore water composition and pH are expected to be controlled by interactions with the materials in the pile. This is because the rainwater sources have low dissolved solids contents and are not expected to provide significant pH buffering capacity. The Eh in the rainwater is expected to be controlled by dissolved oxygen from air contact; air occupying unsaturated pore spaces in the waste piles may provide a continuing source of dissolved oxygen that will serve to buffer the Eh of water percolating through the pile, although other redox couples imposed as water interacts with the waste materials may also influence the Eh.

It is recommended that the interaction between meteoric water and the waste be measured using demineralized water, and that the resulting solution be used to represent key properties of the pore water, including pH, major solute concentrations, and contaminant concentrations. It is expected that components released from the waste material during the test will dominate the composition of solutions generated during the test, such as a local groundwater having little buffering capacity, and that the presence of minor constituents in the leachant will be insignificant in the final solution. Using demineralized water simplifies testing and ensures consistency in tests with different waste samples. Tests should be conducted with several waste samples to measure the ranges of solution compositions and contaminant concentrations that are generated.

While the dissolution rates of most phases and the sorption behaviors of most species are sensitive to the solution chemistry, including the pH, Eh, and key solute concentrations, it is usually not practical to track and quantify all of these effects in reactive transport calculations. Likewise, sorption typically depends on the pH value of the solution and the concentrations of solutes competing for sorption sites. It is not expected that the range of pore water compositions at different percolation distances or in voids, fractures, of the waste pile will be known or measured. The approach taken in developing the protocol is to use a simulated pore water solution that results from contact with weathered waste material.

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[5] The barrel of a 10 mL syringe has an i.d. of about 1.5 cm and makes an acceptable test column.

It is expected that phases near the surface of a waste pile will be contacted by meteoric water and that dissolved waste material components will become more concentrated in the pore water as it percolates through the pile. Slow transport through the material by matrix diffusion will likely lead to higher dissolved concentrations than will be attained in water transported rapidly through fractures (inter-particle voids). The dissolution rates of the host phases are expected to vary between maximum values in very dilute pore waters to near-zero rates in highly concentrated pore waters. The selection of any leachant composition for use in the tests to measure the contaminant release and sorption behavior represents a point in the evolution of the pore water that is somewhat arbitrary. The approach followed in the testing protocol is to react the waste with demineralized water to represent chemical properties of the pore water generated after extensive interactions with the waste material that affect contaminant release and concentrations.

The conditions of ASTM C1285 method A (see Section 4.1) are used to generate a representative pore waste solution. The temperature (90 ºC), size fraction (–100 + 200 mesh), material mass-to-volume ratio (1 g:10 mL), and test duration (7 days) called for in ASTM C1285 are aggressive relative to ambient conditions and will promote the dissolution and leaching of most phases in the waste material. The test is conducted in an air environment, which provides oxidizing conditions in the test vessel and represents the surface of the waste pile. The pH is measured after the solution cools to room temperature, which represents the pH of the pore water solution. The other important result to be represented is the “chemical nature” of the solution, i.e., if it is a brine, carbonate, sulfate, or silicate solution, that will affect the solubilities of contaminants. The solution generated within the short test duration and aggressive conditions in the static ASTM C1285-A method is used to represent (qualitatively) the solution generated during a much longer reaction time under less aggressive conditions.

It is recommended that a simplified simulated solution composition be used to represent key aspects of the solution generated with the ASTM C1285 test for use in the other tests. These include the pH and chemical nature of the solution. Contaminants are excluded from the simplified solution and added separately to prepare specific solutions for the adsorption tests. This will simplify preparation of solutions spiked with contaminants (or surrogates) for use in the sorption tests and the large amounts of solution needed for the column tests (see Section 7), and also facilitate analyses by eliminating the need to measure background concentrations.

4 BATCH TEST METHODS

Modifications of three simple laboratory test methods standardized by ASTM-International (ASTM, 2014a) are recommended to measure specific model parameter values:

- ASTM C1285 *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)*,
- ASTM C1308 *Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms*, and
- ASTM C1733 *Standard Test Method for Distribution Coefficients of Inorganic Species by the Batch Method*.

These tests are used to measure the effective dissolution rate of the combined contaminant-bearing phases, the effective kinetics of contaminant release (dissolution or leaching), the effective sorption capacity of the collective phases in the waste material (and the desorption behavior), and the releasable amounts of contaminants in the waste material. Test methods ASTM C1285 and ASTM C1733 are designed to be conducted with crushed and sieved materials, but ASTM C1308 is designed to be conducted with a monolithic specimen. For this application, ASTM C1308 is modified in that crushed material (-35 +200 mesh) is used instead of a monolithic specimen to expose more of the waste material to water. These tests are simple enough to conduct with multiple samples of the waste material collected from different locations in the waste pile to determine the ranges of property values and probability distributions. Several subsamples are produced from each field specimen of the waste material for use in testing and analysis.

This section discusses the appropriateness of the standardized test methods and modifications made for this application. The testing protocol in which the methods are used is presented with additional step-by-step details in Section 7. It is recommended that the test protocol be applied to multiple samples of the waste material to determine spatial distributions of contaminant concentrations and sorption properties that can be used in the field scale models. Because the heterogeneity of contaminant concentrations in the waste pile is expected to exceed the uncertainty in the values measured for each subsample subjected to the test protocol, simplified operations can be used to expedite the testing. For example, removing solution during exchanges by decanting or pipetting is adequate (rather than by centrifugation), even though a small amount of solution will be retained with the crushed solids and added to the solution in the next interval. The error in the values determined for each test sample will be negligible compared with the effects of heterogeneity in the waste pile.

4.1 Method ASTM C1285

Static corrosion leach tests are commonly used to measure the dissolution behaviors of glasses[6] and minerals. The ASTM C1285 Product Consistency Test (PCT) methods were developed to study and compare the dissolution behaviors of glass waste forms (ASTM 2014a);

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[6] Although glass is metastable and does not have a solubility limit in the thermodynamic sense, it is convenient to assign glass a pseudo-solubility for modeling purposes based on the very slow dissolution kinetics that occur in solutions with high concentrations of dissolved glass.

these are static tests conducted with crushed and sized glass. The purposes of conducting the ASTM C1285 test with samples of the waste pile materials are (1) to generate a solution to represent pore water in the waste pile and (2) to provide concentrations of released contaminant to establish the range of concentrations used in sorption tests.

The ASTM C1285 test method was developed to assess the relative dissolution kinetics of various borosilicate waste glasses for comparison with standard and reference glasses: Method A tests are conducted under specific conditions to support direct comparisons and Method B tests are conducted to study the effects of the test duration and test parameters, including temperature, glass/water mass ratios, and glass particle size fraction. Both PCT Method A and Method B are static tests in which the dissolved glass components accumulate in the test solution over the test duration. The build-up of dissolved components has a significant effect on the dissolution rate, primarily through the dissolved silicon concentration and evolving pH. The effect of solution feed-back on the continued dissolution rate is modeled using a reaction affinity model. The dissolution of many minerals occurs by the same mechanism and is affected by similar feed-back effects. The test conditions called for in Method A result in solutions with relatively high amounts of dissolved glass components within 7 days, even for durable materials. The solution generated in an ASTM C1285 Method A test conducted at 90 ºC is expected to provide a bounding composition of pore water generated by the interaction of meteoric water with the waste material over a long residence time. Assuming that the dissolution rates double for every 10 ºC increase in temperature as a rough approximation, dissolution for 7 days at 90 ºC is equivalent to dissolution for 896 days at 20 ºC.

A modification of the ASTM C1285 test is recommended to measure the releasable concentration of contaminants in the waste material in addition to performing a complete compositional analysis. An aggressive solution (0.1 M HNO_3) is used to extract contaminants from the crushed waste material. This is not intended to completely dissolve the waste material; rather, it is used as a simple method to estimate the maximum amount of contaminants that can be removed by weathering under ambient conditions during the performance period. Reagents other than nitric acid can be used based on knowledge of the waste material.

4.2 Method ASTM C1308

Solution replacement leach tests are conducted by immersing a monolithic sample of known geometric surface area in a large volume of leachant solution and then replacing *the entire test solution* with fresh leachant after a prescribed duration. The test method is semi-dynamic in the sense that dissolved components are removed from the reaction volume during the test. This mitigates the accumulation of dissolved components over long test duration and allows the effects of solution feed-back to be distinguished from effects due to alteration of the specimen surface. The concentrations of the contaminant of interest in the solutions recovered at each exchange are monitored to determine the release kinetics. Solution replacement test methods are designed to study diffusion-controlled releases but the results can be used to distinguish other release mechanisms. Since the same test specimen is used in each interval, the cumulative concentrations of soluble constituents are expected to increase linearly with time if the release is due to an affinity-controlled mechanism and to increase linearly with the square root of time if by a diffusion-controlled mechanism. Note that constant exchange intervals are required to differentiate these time dependencies because the concentrations depend on the reaction time for both mechanisms.

A test method utilizing solution replacement was developed to determine the diffusion coefficient for contaminants leached from host matrices such as portland cements and has been standardized by ASTM-International as Standard Test Method C1308 (ASTM 2014a). The method provides guidance for generating data that can be analyzed using the diffusion equation for release from either a semi-infinite solid or a finite cylinder. Although the method calls for the use of a cylindrical test specimen to facilitate calculation of the diffusion coefficient of the contaminant using a finite cylinder model when extensive depletion occurs, the same test procedure has also been conducted with rectangular wafers or parallelepipeds. These are modeled as semi-infinite solids for the purpose of extracting diffusion model parameters (i.e., neglecting edge effects), which is adequate for the small extent of reaction that occurs during the test. Derivation of the diffusion equation utilizes a zero concentration boundary, so the method calls for replacing the test solution frequently to avoid solution feed-back effects. The first three replacements are called for in the C1308 method after intervals of 2, 5 and 17 hours (cumulative duration of 2, 7, and 24 hours). Subsequent exchanges are made daily.

The concentration of a contaminant that is measured during a test interval (a_n) is usually normalized to the total amount of that contaminant in the test sample (A_o) to provide the incremental fraction leached (IFL) during that interval. The cumulative amount of a contaminant released over consecutive intervals is the sum of the IFL values, which is referred to as the cumulative fraction leached (CFL)[7]:

$$IFL_n = \frac{a_n}{A_o} \quad \text{and} \quad CFL = \frac{\sum a_n}{A_o} \quad . \tag{4.1}$$

Variations in the IFL and the resulting time dependence of the CFL (CFR) provide information regarding the release kinetics. Note that the measured value a_n may represent the combined release of a contaminant from multiple phases at different rates, and that the value of A_o may represent the concentrations in several phase. Because a contaminant might not be released from a phase under the testing (or weathering) conditions, the effective value of A_o that is appropriate for modeling long-term behavior may be less than the total content of the contaminant. It is recommended that both the total contents and total leachable contents be determined as part of the testing data base available for use in performance modeling.

The ASTM C1308 method is essentially the same as the ANS16.1 test method (ANS 2009), except the replacement schedule for the ANSI/ANS16.1 method is after intervals of 2, 5, 17, 24, 24, 24, and 24 hours, 14, 28, and 43 days with a cumulative test duration of 90 days. An abbreviated ANS16.1 test omits the final three samplings. The ASTM C1308 method expands the ANSI/ANS16.1 method to include tests at elevated temperatures, addresses use of the test results to determine the effective diffusion coefficient, and provides guidance for extrapolations in time and scale. The ASTM C1308 method also provides guidance and models for deriving an effective diffusion coefficient from the test results.

Although short exchange intervals are expected to provide the best measure of the diffusion behavior and are the most consistent with the boundary conditions used to derive the diffusion equation, longer exchange intervals provide added insights to the dissolution behavior with

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[7] The term cumulative fraction released (CFR) is used to include the release of contaminants by mechanisms other than leaching.

regard to (1) feed-back effects from dissolved components that accumulate in the solution and (2) the effects of alteration layers that may form on the surface as the test material corrodes. As discussed in a recent review (Ebert, 2011), these effects can slow the weathering rates of minerals by several orders of magnitude.

The use of non-constant exchange intervals has been shown to affect the cumulative test response and kinetics and complicate modeling (Ebert, 2010). Therefore, it is recommended that daily exchanges be used to characterize and quantify the contaminant release behavior. Longer exchange intervals (which may be non-periodic) may be used to *qualitatively* study the possible effects on contaminant release of solution feedback, depletion of the contaminant, and alteration of the material. Examples of the application of the ANSI/ANS16.1 and C1308 test methods (following various exchange schedules) to cement-based materials, slags, and glass are presented and discussed below.

4.2.1 Application to Portland Cement-Based Concretes

The responses of materials made with portland cement and added contaminants, ion exchange resins, fly ash, etc. provide insights to the likely responses of contaminated concretes in ASTM C1308 tests. Figures 4.1a and 4.1b show results for tests with cast specimens of four such materials plotted against the square root of the cumulative time. The data from samplings having common replacement intervals (the average intervals are shown on the plots) are evaluated as sub-sets to emphasize the effect of the interval on the test response. Figure 4.1a shows the release of Cs from ion exchange resin encapsulated in portland cement (grout) made without and with added vermiculite. The results in Figure 4.1b show different linear behavior for 1-day and 7-day intervals, with single data points for samplings after 3-day and 49-day intervals falling at lower CFL values than predicted by extrapolating the fits at shorter intervals. The slopes of the linear fits (in a root-time plot) are important because they are proportional to the effective diffusion coefficient for releases controlled by transport out of the waste material. Because the diffusion coefficient depends on the properties of the solid and contaminant but only weakly on the solution composition, it is expected to be independent of the exchange interval. The observed dependence on the exchange interval may be an artifact of using linear average releases (i.e., the measured initial and final solution concentrations) to represent a non-linear process. Even a minor difference in the test interval (e.g., the 1.3-day interval between the second and third sampling in Figure 4.1a) affects the cumulative results. The shortest constant exchange interval provides the most accurate measure of the diffusion coefficient. The 1-day interval called for in ASTM C1308 is expected to be sufficient for most materials, although longer immersion times may be required for the bulk water to equilibrate with water in small pores.

4.2.2 Application to Slag Materials

Figures 4.2a - 4.2c show the results of tests with monolithic specimens of three different slags from Cabot-Reading and Molycorp-Washington sites (Pickett et al., 1998), and an unnamed site E-1 (Fuhrmann and Schoonen, 1997). The results show the same effect of the exchange interval that was seen in tests with portland cement, except the kinetics is linear with the cumulative reaction time rather than with the square root of the reaction time. Figure 4.2a shows linear releases of Ca and Al occur for the 1-day intervals shown in the inset) and for the longer-term sampling intervals (at a lower rate), but not for the initial samplings taken at different intervals. Likewise, Figures 4.2b and 4.2c show linear releases for the 1-day intervals but not for the initial samplings taken at different intervals.

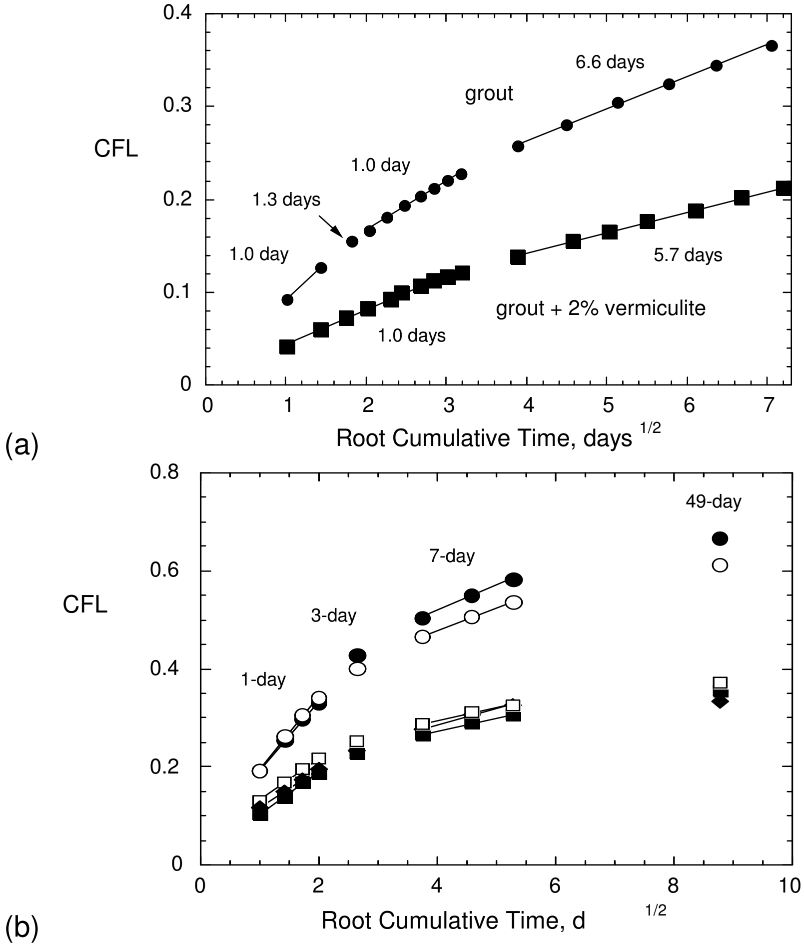

Figure 4.1 Release of Cs from portland cements encapsulating various resins measured in tests by (a) Christensen (1982) and (b) Habayeb (1985).

These slags are comprised of several minerals and glass phases. The linear kinetics suggests that only the phases exposed at the surface are dissolving and water is not diffusing into the slag. In most cases, the release rates decrease with the exchange interval. This is attributed to decreasing reaction affinities as released elements accumulate in the solution and saturation conditions are approached. A few exceptions are seen, for example, the release of Si in Figure 4.2c occurs faster at longer intervals. This could be an effect of increasing solution pH. Over long test durations, some minor phases at the surface could completely dissolve, in which case the cumulative mass loss would reach a maximum value.

4.2.3 Application to Glass

The applicability to glass is important because (1) glassy phases will be important constituents in many waste materials and (2) the dissolution behavior of silicate glasses is the same as that of many silicate (and other) minerals. Recent studies in which the ASTM C1308 method was applied to borosilicate glasses provide insights into the likely responses of glassy phases and minerals present in slags. Figure 4.3a shows the results of ASTM C1308 tests conducted with a

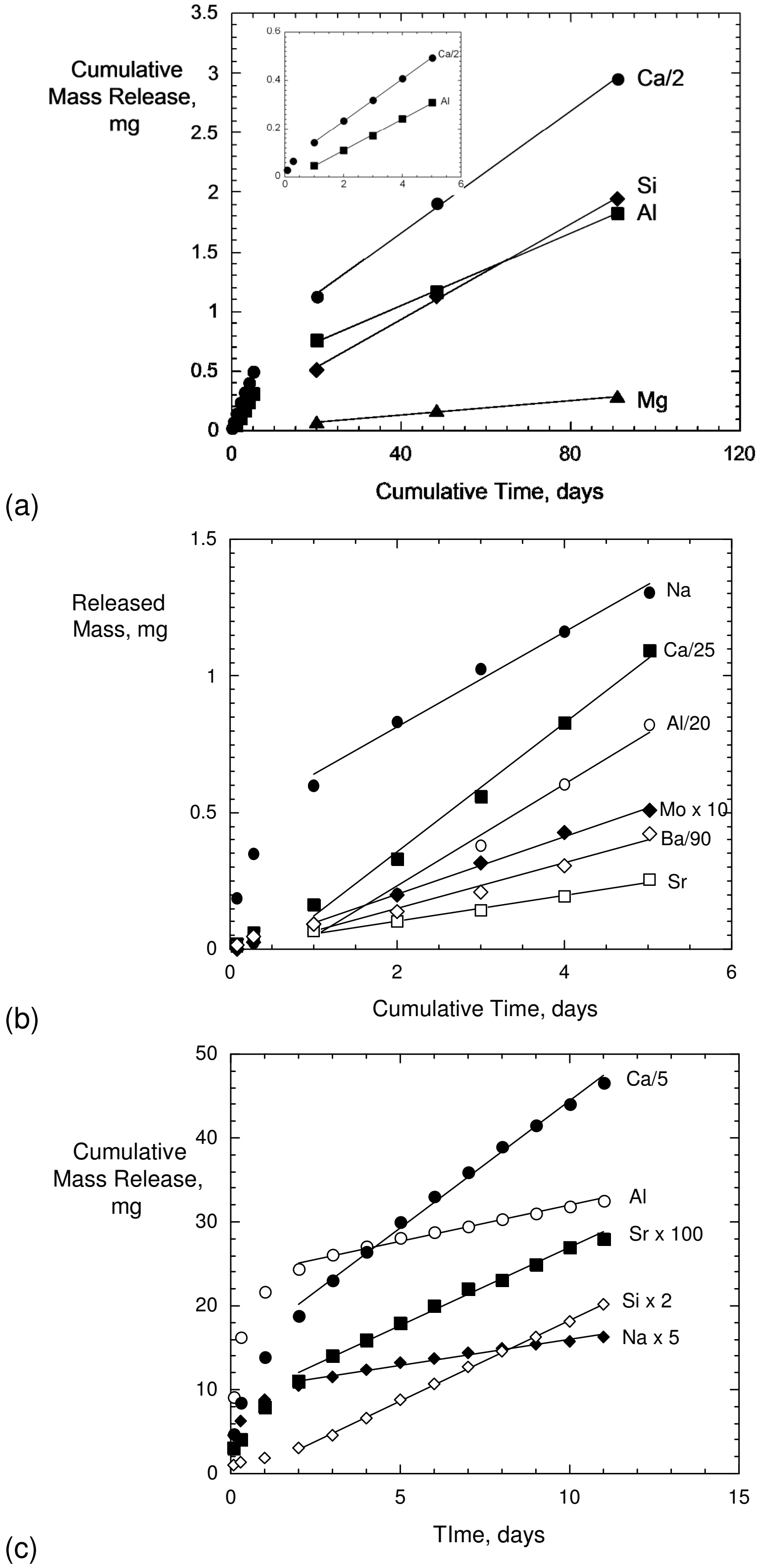

Figure 4.2 Results of ASTM C1308 tests with monolithic specimens of slags (a) from Cabot-Reading, (b) from Molycorp-Washington site, and (c) from site E-1. The inset in (a) shows the linearity of the initial Al and Ca releases.

glass referred to here as AFCI glass in a pH 8.5 buffer solution at 90 ºC and glass surface area-to-solution volume ratios of 1, 3, 10, and 50 m^{-1} (Ebert 2012). The solution replacement interval was 1 day in all tests. These tests were conducted with specimens prepared as wafers polished to a 600-grit finish. The results are shown as the cumulative normalized mass loss based on the measured boron concentrations:

$$NL(B) = \frac{C_B V}{S f_B} \tag{4.2}$$

where

$NL(B)$ is the normalized mass loss based on boron (M L^{-2})
C_B is the boron concentration (M L^{-3})
S is the surface area of the glass specimen (L^2)
V is the system volume (L^3)
f_B is the mass fraction of B in the glass.

The values of $NL(B)$ are directly proportional to the cumulative mass of boron released. The results are fit well with linear regressions to the cumulative test duration and show linear kinetics. The dissolution rates (which are given by the slopes) are seen to decrease with increasing S/V ratios. The effect of the S/V ratio is attributed to the higher solution concentrations that are generated during the test interval.

Figure 4.3b shows the results of tests with AFCI glass conducted in the same pH 8.5 buffer solution at 90 ºC at an S/V ratio of 1 m^{-1} at exchange intervals of 1, 3.5, and 7 days. Increasing the exchange interval leads to a change in the release kinetics as well as a decreasing rate. Note that the effect is different than that seen on the dissolution of slag in Figure 4.2a, where the rates were linear for exchange frequencies of 1 day and longer. Although slightly higher concentrations are generated during the longer test intervals, the similarity of the rates observed through about 500 hours indicates that this does not have a significant effect on the glass dissolution rate. Instead, the results suggest an increasing contribution of mass transport limit that adds root-time character to the release kinetics as the exchange interval increases. This is attributed to the effects of a surface layer that forms due to nonstoichiometric dissolution. The formation rate of the layer and the extent of root-time character are affected by the solution composition, as indicated by the differences in the behaviors with 1-day, 3.5-day, and 7-day exchange intervals. More frequent exchanges maintain more dilute solutions and slow the formation of the layer and diffusion barrier.

4.3 Modified ASTM C1308

Solution replacement tests are most often conducted with a monolithic sample having a known geometric surface area to study the role of mass transfer in the release of contaminants to solution. The ASTM C1308 method provides recommended size, shape, and aspect ratios for test samples to support data analyses. This is because the depletion depth (due to dissolution or diffusion) can become deep enough that edge effects influence the test results and quantification of the diffusion coefficient. Those effects can become significant over long test

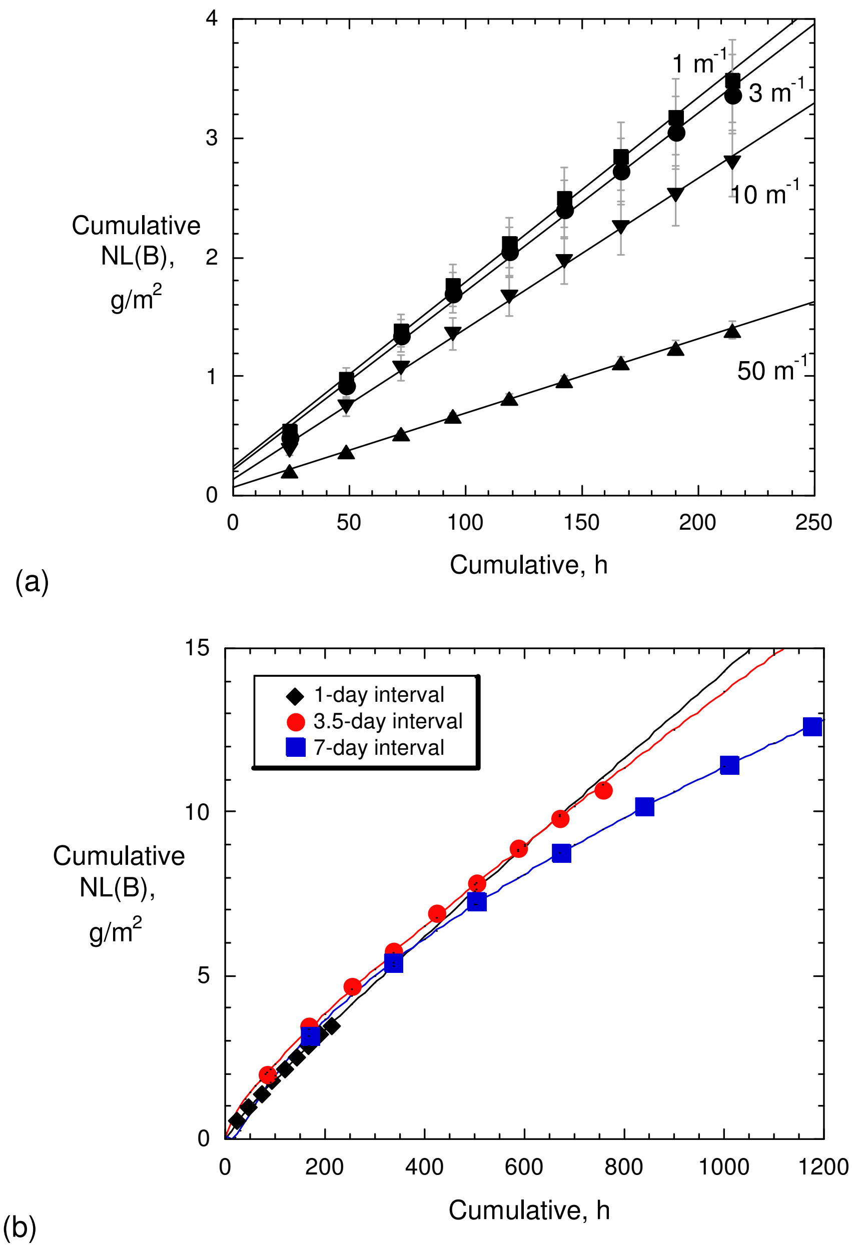

Figure 4.3 **Results of ASTM C1308 tests with monolithic specimens of AFCI glass: (a) at 1, 3, 10, and 50 m^{-1} with a 1-day exchange interval and (b) at 1 m^{-1} with exchange intervals of 1, 3.5, and 7 days.**

durations called for in ANSI/ANS16.1, but are expected to remain negligible over the short test durations that are called for in the recommended protocol. Although few tests have been conducted with crushed material under the test conditions in ASTM C1308, one directly relevant test was conducted by Fuhrmann and Schoonen (1997) with powdered Ameristeel slag (AS). Based on comparing the results of C1308 tests conducted with powdered samples contained in a dialysis membrane and monolithic samples, the authors conclude the following

"Samples in Membranes versus Monoliths

> *The AS samples were used as a reference to compare leaching of powders in membranes versus leaching of monoliths. Results are presented for both forms. Figure 6 illustrates leach rates for the* [powdered] *AS samples contained in membranes and AS samples that were monoliths. It illustrates that no significant differences between releases from the monolith and the membrane samples were apparent. Leach rates of Si and Ca tended to be tightly clustered for both types of samples. In contrast, rates of Sr, Al, and Na were more spread out, but in no systematic way. This means that leaching from the two types of samples is equivalent, allowing direct comparison of the data from the two."* Fuhrmann and Schoonen (1997) page 20.

Figure 4.4 shows the results from Figure 6 of Fuhrmann and Schoonen (1997) replotted with additional results taken from Table 9 of that report. The fractional release rate is simply the cumulative fraction leached divided by the test duration. Note that this is the mass of the contaminant (or matrix element) released divided by the mass of the contaminant (or matrix element) in the test sample, not divided by the mass of the test sample.

Fuhrmann and Schoonen (1997) provided the results for tests ASTM C1308 tests conducted with three powdered samples of Ameristeel slag. The results of ASTM C1308 tests with these powders conducted at 20 ºC (from Appendix A of Fuhrmann and Schoonen 1997) are plotted in Figures 4.5a – 4.5c. The cumulative fractional releases (CFR) of Al, Ca, Si, and Sr are linear for samplings at 1-day intervals in tests with AS001 and AS002, while the release of Na is not. The difference is probably due to depletion of Na from the dissolving minerals, with the increase in the last samples either reflecting analytical uncertainty or the exposure of a Na-bearing phase. The low Na contents in the slag samples and the nonlinear release behaviors suggest the distributions of the Na-bearing phases are less uniform than those of the other phases. The gross compositions are given in Table 4.1. Those analyses show the samples have similar overall compositions. Differences in the elemental releases are likely due to differences in the phase assemblages contributing to the overall corrosion behavior.

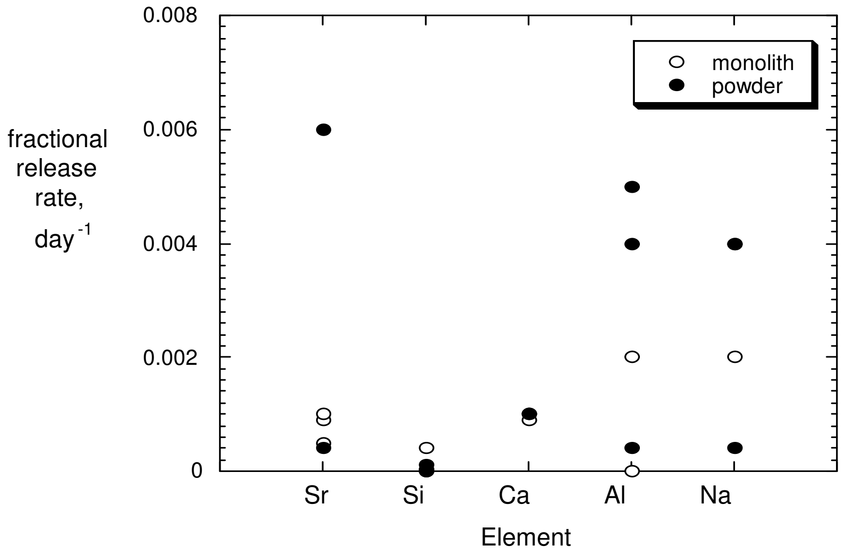

Figure 4.4 Reproduction of Figure 6 in Fuhrmann and Schoonen (1997).

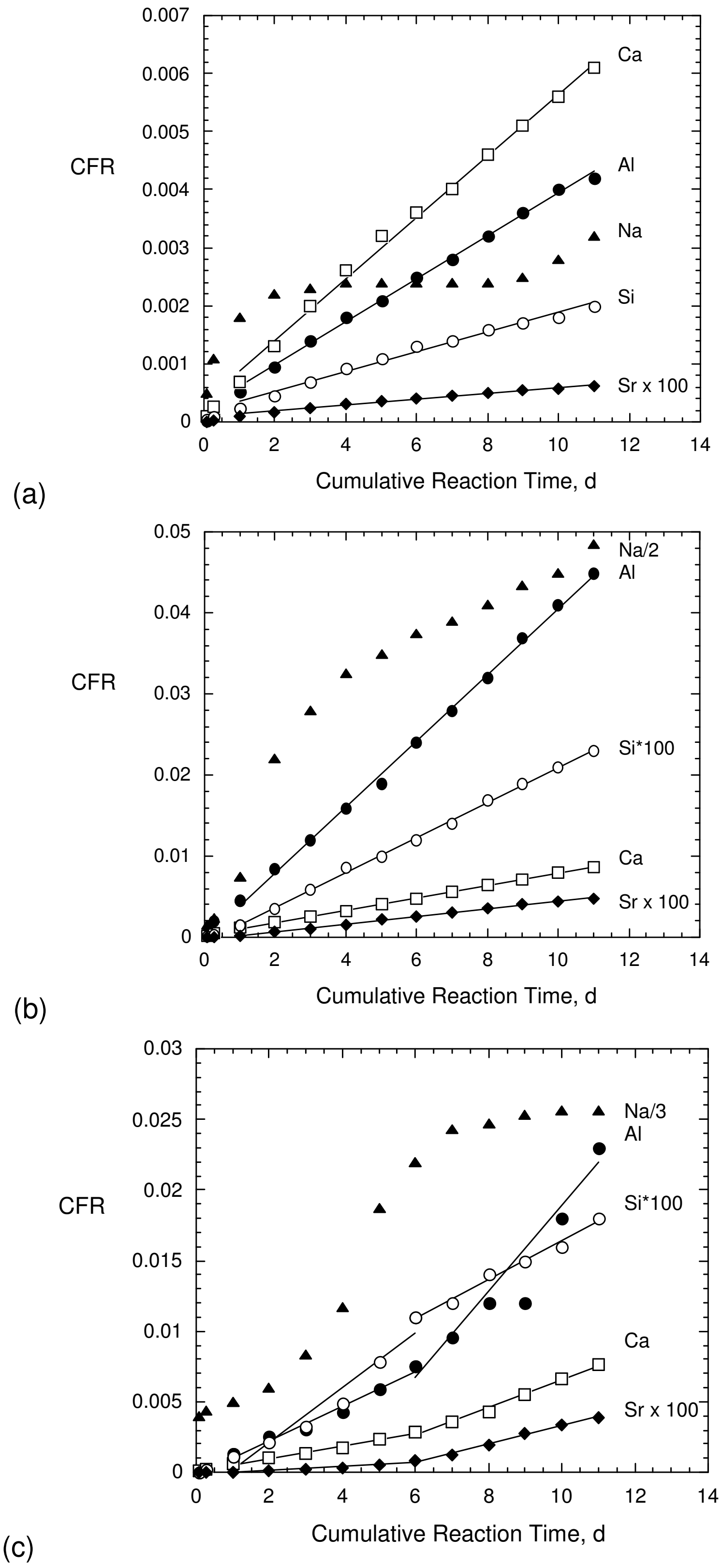

Figure 4.5 Results of ASTM C1308 tests conducted with powdered samples of slags (a) AS001, (b) AS002, and (c) AS003.

Table 4.1 Major constituents of non-radioactive Ameristeel slags, as mass percent

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	P_2O_5	TiO_2	SrO
AS001	19.07	10.49	19.99	6.77	5.24	34.88	0.08	0.36	0.44	0.0308
AS002	16.34	8.63	17.75	4.18	11.11	37.84	0.06	0.50	0.38	0.0248
AS003	17.67	8.88	15.57	4.58	10.97	39.19	0.04	0.35	0.44	0.0300

The results of the test with AS003 suggest changes in the amounts of all dissolving phases occur after about 7 days. The releases of Al, Ca, and Sr are linear between 1 and 6 days and between 7 and 11 days (the Al result at 9 days is excluded), and the release of Si is linear between 6 and 11 days. The Na release indicates the surface is depleted of Na after about 7 days. This coincides with increases in the release rates of other Al, Ca, and Sr, but a decrease in the release of Si, which suggests Na and Si are being released from the same phase(s). This shows the importance of measuring contaminant behavior directly and for an extended duration.

4.4 Method ASTM C1733

The ASTM C1733 *Standard Test Method for Distribution Coefficients of Inorganic Species by the Batch Method* is a static method that can be used to measure the distribution coefficient (K_{d}) value of a particular system (ASTM 2014a). In current practice, bounding values of K_{d} are often used to provide conservative estimates to evaluate remediation needs. Conservatively low values of K_{d} are used when groundwater contamination is of concern (as it is for this protocol) and conservatively high values are used when soil contamination is of concern. Measurements made under site-specific conditions are considered to be essential for defensible assessments. While the test method itself is simple to perform, the sensitivity of test response to condition of the solid and the chemistry of the groundwater calls for the utmost care during sample collection, handling, transport, and storage for representative results.

An important issue regarding the measurement of K_{d} values with tests excluding pieces larger than about 2 mm is the so-called gravel issue. Excluding pieces larger than 2 mm from measurements is usually viewed as a negligible error due to the much higher specific surface areas of small particles relative to large particles. The ASTM C1733 method recommends either scaling the K_{d} value measured with the <2 mm fraction by the mass fraction of gravel, as in Equation 4.3a, or measuring K_{d} for a sample of particles > 2 mm and calculating a weighted average value, as in Equation 4.3b

$$K_d = (1-f)K_{d<2mm} \tag{4.3a}$$

$$K_d = (1-f)K_{d<2mm} + (f)K_{d>2mm} \tag{4.3b}$$

where

$K_{d<2mm}$ is the K_d value for the <2mm fraction
$K_{d>2mm}$ is the K_d value for the >2mm fraction
f is mass fraction of the >2 mm material in the mixture.

Um et al. (2009) measured the sorption of ^{99}Tc, ^{237}Np, and ^{238}U onto two samples of sediment material taken from Hanford near the site being prepared for low-activity waste disposal, referred to as Pit 30. A solution spiked with the radionuclides was sorbed onto various mixtures of sediments sized to <2 mm and 2 mm < X < 9.5 mm for 7 days. The test results for the two materials 30-2 and 30-3, which have slightly different phase ratios, are shown in Figure 4.6. (Note that the K_d values for Tc have been multiplied by 10 to show on the same scale as values for U and Np.) Application of Equation 4.3a is shown by the dashed lines and application of Equation 4.3b is shown by the solid lines, with the exception that the outlying value for Np measured in the gravel is excluded and the line is drawn through the result of the measurement with 80% gravel. Although Equation 4.3b is more consistent with the data, the use of $K_{d<2mm}$ for all mixtures results in only a small error for the sparingly sorbed species and about a factor of 2 error in the strongly sorbed species.

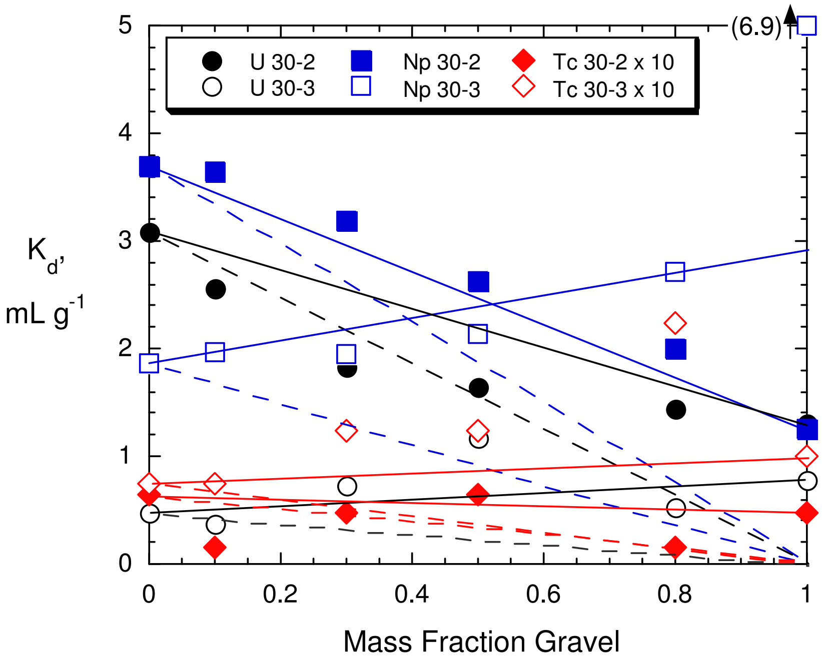

Figure 4.6 Sorption measurements of Tc, U, and Np on Hanford sediments.

Measurement of material larger than the size fraction called for in the testing protocol recommended in this report (–35 +200 mesh) is considered to be unnecessary, since that size fraction (< 0.5 mm) is already biased low relative to the 2 mm threshold commonly used for batch tests.

At waste sites, the composition of meteoric water that percolates through the waste pile and diffuses into pores and voids is expected to become dominated by the dissolution of material at the near surface. Regional variations in the composition of rain water may be important initially, such as acid rain, but these have little buffering capacity. The ASTM C1733 method recommends that tests be conducted at reference pH and temperature values to facilitate comparisons of test results with those for other contaminants and other soils. For the present application to a disposal site, the pH and chemical composition of the SPW solution reflect pore water that has interacted with the waste material for an extended period.

The usefulness of the measured values is greatly increased if dependencies of the K_d value on key environmental variables can be quantified. Probably most important is the dependence on the contaminant concentration in the groundwater. For example, the method recommends that measurements be made for a range of contamination concentrations that can be used to develop an analytical relationship between the contaminant concentration and the K_d value. This is usually quantified in the form of an adsorption isotherm. While the dependence on the contaminant concentration is probably the most important relationship for remediation analyses, additional relationships can be determined between K_d values and other environmental factors, such as pH, T, and Eh (groundwater redox), the presence of complexants and competing species, ionic strength, etc. ASTM C1733 does not address these other dependencies directly, but stresses the importance of collecting groundwater from the source and simulating the natural conditions to the extent possible. As discussed in Section 3.2 on pore water, the latter recommendation to simulate the natural conditions is essentially the strategy used in this protocol.

Since K_d is usually considered to be an equilibrium value, the method calls for the use of scoping tests to determine the duration required to reach a constant solution concentration indicating the system has reached equilibrium (or steady state). The required time to reach equilibrium will vary with the system being evaluated, and it is left to the user to determine the appropriate test duration. This can be done using separate batch tests conducted for different durations or by periodically sampling the test solution until a constant contaminant concentration is measured. The latter approach requires aliquants small enough that the water-to-soil ratio does not change significantly over the cumulative test duration. Conducting tests with larger amounts of the solid is expected to provide a more representative average value of the heterogeneous material than tests with smaller amounts.

An issue in determining the effective K_d value for waste material is that the contaminants of interest will be released by dissolution of the host phases during the K_d measurement. This was observed in a recent study using ASTM C1733 to measure the sorption of Cs and Sr on soil (Ebert and Petri, 2012). The contaminant concentrations measured in the ASTM C1285 test are expected to be significantly higher than those generated in ASTM C1733 tests, which are conducted at a lower temperature and typically for shorter durations. This is expected to be verified in the ASTM C1308 dissolution experiments conducted in the test protocol prior to the ASTM C1733 tests. It is recommended that the isotherm be determined for concentrations ranging from a low value near that measured in the ASTM C1285 test to higher concentrations based on the maximum leachable concentrations. The results of sorption experiments with low contaminant concentrations can be adjusted to account for the masses released in previously run ASTM C1308 dissolution experiments.

4.5 Desorption with ASTM C1308

The parameter K_d measured in the batch sorption tests is a thermodynamic term representing sorption as a system in dynamic equilibrium. More rigorous models treat sorption as a kinetic system with distinct sorption and desorption rates (note that K_d is the ratio of the sorption and desorption rates: $\text{rate}_{\text{sorption}}/\text{rate}_{\text{desorption}}$.) Separate sorption and desorption rates will be needed to apply such a kinetic model to evaluate the column test results. An example of that approach is discussed in Section 6.2.

The ASTM C1733 test used to measure K_d provides a crude measure of the sorption rate based on the reaction time required to attain a constant solution concentration. Useful information regarding the desorption kinetics and reversibility of contaminant uptake can be measured with little additional effort by applying the ASTM C1308 procedure to the waste material recovered from the ASTM C1733 test after it has been equilibrated with the highest contaminant concentration. That solution is decanted and replaced by a contaminant-free leachant that is sampled and replaced in a subsequent series of 1-day exchanges. The semi-dynamic nature of the test method is utilized to measure the desorption kinetics. How strongly a contaminant is bound to the sorbent will impact the role of sorption in contaminant transport in an advective system. This is expected to be observed in the column tests.

4.6 Units

The data in the figures provided in this section are presented in units of contaminant mass normalized variously to: the total amount of contaminant in the test specimen, the total amount of contaminant in the test solution, the mass of the waste form sample, or the combination of the area of the waste form and mass fraction of contaminant in the waste form. The contaminant source term used in reactive-transport calculations is in units of mass contaminant released per mass waste form per day. The results of contaminant release rate measurements in this testing protocol can be represented as mass contaminant released to solution per mass test sample per day. This can be scaled to the waste pile by the estimated mass of the pile.

5 COLUMN TEST METHOD

A column test is recommended to measure the coupled chemical and transport properties of the waste material. A procedure for conducting up-flow percolation tests has been standardized by the European community as CEN/TS 14405 (CEN, 2004) and a variation of that method is being developed by the US EPA as method 1314 (see Garrabrants et al. 2012). Although the experimental apparatus described in those methods is appropriate for the measurements recommended here, the solution collection procedure recommended in the protocol is modified from those procedures to measure incremental releases rather than cumulative releases. This is because the objective of the column test with waste materials is to measure steady-state contaminant concentrations in a dynamic system for modeling, whereas the objective in the standardized method is to measure the accumulated released concentrations to evaluate compliance with regulations. The general methodology used by several researchers (Fuhrmann and Schoonen 1997, Taylor et al. 2000a, Dean 2011) is also appropriate. The steps are listed below[8]:

C1. Conduct column test with crushed waste material and SPW solution to attain steady state concentrations of a contaminant or host phase component in the column eluate. Collect samples of eluate periodically throughout experiment. [NOTE: the first few column pore volumes of eluate will reflect the rapid dissolution of fines and fracture edges and should be excluded from the steady state determination.] Measure total collection time and mass for each eluate sample to calculate the volumetric flow rate at each sampling. Measure pH and concentrations of contaminants and major host phase components. Calculate the effective contaminant release rate based on characteristics of the column (some of which will be determined in Step C2), flow rate, and solution concentration results. Continue until the system reaches steady state.

C2. Switch to a SPW solution spiked with contaminant(s) of interest or tracer(s) and a conservative tracer (e.g., NaBr) of known concentrations as input solution and continue test for at least 5 column volumes at the same flow rate. Continue to collect samples of eluent throughout the experiment. Measure total reaction time and volumetric flow rate for each collection interval. Measure pH and concentrations of contaminants,tracer, and host phase components. These results are used to characterize the front end of the breakthrough curve and column characteristic (from the conservative tracer).

C3. Switch back to non-spiked SPW solution as leachant. Continue test at same flow rate. Collect samples of eluent throughout experiment. Measure total reaction time and volumetric flow rate for each collection. Measure pH and concentrations of contaminants, tracer, and host phase components. These results are used to characterize the back end of the breakthrough curves showing delayed release (tailing) due to sorption and matrix transport.

Repeat Steps C2 and C3 at a different flow rate using the same material.

Step C1 is used to measure the release of contaminants from the waste material, whereas Steps C2 and C3 generate the leading and trailing legs of a square pulse of contaminant that is used to measure the sorption behavior. Evaluate the initial breakthrough and final

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[8] The letter C preceding the step number indicates the step is a part of the column test series.

tailing behaviors of the conservative tracer and contaminant(s) or tracer(s) based on cumulative masses measured in eluent samplings. Use the breakthrough data for the conservative tracer to determine column transport characteristics (see discussion in Section 6). Use the breakthrough curves and inverse modeling (e.g., by using PEST, Doherty et al. 2010) to evaluate and refine parameter values for the contaminant release and sorption behaviors.

5.1 Reaction in a Column Test

In a packed column, the solution composition will not remain uniform throughout the length of the column under dynamic conditions if solutes interact with the solid. Dissolution or leaching of the solid will result in increasing concentrations, while sorption of a contaminant from the solution onto the solid will result in decreasing concentrations. The extent to which sorption occurs will depend on the relative kinetics of the sorption/desorption process and flow rate. In the simplest case of plug flow, a concentration gradient will develop along the length of the column, but be uniform laterally. Although steady-state conditions can be attained in the column, the steady-state concentration will vary continuously along the length of the column. The steady-state concentration measured in the eluate exiting the column will depend on the flow rate and the column length, as well as on the effective release rate from the host phases and the sorption rate. That concentration is used to determine the coupled reaction-transport rate.

5.1.1 Contaminant Release Rate

Consider the simple case of a non-sorbing contaminant A that is distributed uniformly throughout the column and released at the rate measured in the batch tests, which is the sum of the rates of all reactions involving contaminant A

$$\sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{source} = \dot{Q}_A \, . \tag{5.1}$$

Under test conditions in which the dispersion and sorption terms are negligible, the ADE in Equation 3.1 can be written as

$$\frac{\partial C_A}{\partial t} = -v_x \frac{\partial C_A}{\partial x} + \dot{Q}_A \; . \tag{5.2}$$

Futhermore, under steady state conditions, the contaminant concentration is invariant with time and the concentration at any location in the column is

$$\frac{\partial C_A}{\partial x} = \frac{\dot{Q}_A}{v_x} \; . \tag{5.3}$$

Rearranging Equation 5.3 and integrating over the input and output concentrations of A and over the length of the column gives

$$\int_{input}^{output} \frac{\partial C_A}{\dot{Q}_A} = \frac{L}{v_x}. \quad (5.4)$$

The dissolution rates of many minerals and glasses are proportional to the surface area S and volume V of solution in contact with the solid (which is the column pore volume) as

$$\dot{Q}_A = k_A \frac{S}{V} fn(\Delta G), \quad (5.5)$$

where k_A is the kinetic rate constant for the dissolution reaction and $fn(\Delta G)$ represents the thermodynamic reaction affinity (see Taylor et al. 2000a). For a system that is far from equilibrium such that $fn(\Delta G) = 1$, Equation 5.4 can be written in the simple form

$$\frac{\partial C_A}{\partial x} = \frac{k_A S}{V v_x} \quad (5.6)$$

and integrated as

$$\int_{input}^{output} \partial C_A = \int_0^L \frac{k_A}{V v_x} S \, dx. \quad (5.7)$$

The solution at any particular point x in a packed column will have only contacted the surface area of the material in the column up to that point, $S(x)$, and will reflect those interactions. In the analysis of the column tests, an average surface area per unit of column lengh $\tilde{S}$ can be defined as (Mogollon et al. 1996; Taylor et al. 2000a, 2000b)

$$\tilde{S} = \frac{1}{L} \int_0^L S(x) \, dx \quad (5.8)$$

for points x through a column of length L. The average surface area is simply the total surface area of material in the column divided by the column length. The total surface area can also be calculated as the product of the specific surface area and mass of material in the column, such that

$$\tilde{S} L = S_{sp} m. \quad (5.9)$$

The volume of eluate solution that is collected for analysis will have contacted all the surface area, but each unit $\tilde{S}$ is contacted for only a fraction of the residence time in the column.

For a column system far from equilibrium and at steady state, the contaminant concentration in the eluate (with no contaminant in the input solution) is related to the release rate as

$$C_{eluate} = \frac{k_A \tilde{S}}{V} \frac{L}{v_x}. \tag{5.10}$$

This shows the relative effects of the column characteristics L, V, and v_x, and waste characteristics k_A and $\tilde{S}$ on the measured contaminant concentration in the eluate. For reaction conditions that are not far from equilibrium, the reaction affinity will attenuate the release rate. The dissolution rates of many minerals and glasses can be represented as a first-order decay reaction (Bear 1979)

$$\dot{Q}_A = \frac{S k_A C}{V}, \tag{5.11}$$

or using a linear affinity term (Steefel and MacQuarrie 1996)

$$\dot{Q}_A = \frac{S k_A}{V}\left(1 - \frac{C}{C_{eq}}\right), \tag{5.12}$$

where C_{eq} is the solubility limit. The contaminant concentration in the eluate will be affected by the concentration dependence of the release rate, including under steady state conditions. The form of the affinity term can be derived by inverse modeling the results of column tests conducted at a range of flow rates (e.g., Taylor et al. 2000b), but that is beyond the scope of the testing protocol and expected modeling effort. Instead, the batch tests and column tests measure the rate under conditions in which the effects of the reaction affinity are small and the product $k_A C$ can be considered constant.

For the purpose of modeling the material behavior as a continuum, only the combined release from all phases bearing the contaminant is of interest and the material can be treated as if it were homogeneous. For a uniformly heterogeneous material, the fraction of the surface area that is occupied by a constituent phase is equal to the volume fraction of that constituent phase in the material. Therefore, the volume fractions and k_A for all A-bearing phases in the waste are represented by single terms. The average surface area is estimated from the geometric specific surface area of the crushed and sized waste. The column pore volume can be estimated from the volume occupied by a known mass of dry waste material, the length and cross sectional area of the column are measured.

The linear flow rate is calculated by dividing the volumetric flow rate (which is calculated as the mass of each eluent sample divided by the collection time) by the cross sectional area of the column. At any particular constant flow rate, the dissolution of a suite of component phases at constant rates will yield constant steady-state solution concentrations. The dissolution rates will depend on the flow rate through the dependence on the steady-state concentrations. That is, the value of k_A will depend on the environmental conditions. Other tests must be conducted at several different flow rates to determine that dependence, but it is not needed for the current application.

In the column test Step C1 conducted with the pore water solution, the value of the affinity term is expected to remain near one throughout the column, meaning the reaction is far from equilibrium. In that case, the response will be dominated by the reactions releasing A from the host phases and the effects of the sorption term in the ADE will be small. The release rate in the simulated pore water solution derived from the steady state concentration measured in Step C1 can be compared with the release rate measured in the batch test.

5.1.2 Contaminant Sorption and Desorption

When the input solution is changed in Step C2 to a spiked solution having a very high contaminant content, the contribution of release from host phases to the contaminant source term in the ADE becomes negligible and the contaminant concentration in the eluent reflects the degree of sorption and other processes that retard transport of contaminants provided by the influent solution. Steady state will not be attained until the sorption capacity of the column is reached, and might not be attained if other retarding processes are significant. When the input solution is changed back to the SPW solution in Step C3, desorption reactions are expected to be the dominate source of the contaminant concentrations measured in the eluent. Steady state will not be attained until the desorbable fraction has been released and the source is dominated again by contaminant release reactions.

The analysis of breakthrough curves to determine reactive transport parameters is well-established (e.g., van Genuchten, 1981; Parker and van Genuchten, 1984). The techniques developed for soils and fractured rocks are expected to be directly applicable to column test results with waste materials including slags and concretes. For example, breakthrough curves provide insights regarding various rate-limited and nonlinear processes (primarily sorption) that occur between contaminants and the solid. Breakthrough curves represent the response of the system to a sudden change in the input concentration of a contaminant due to transport and sorption effects. Figure 5.1 shows breakthrough curves calculated by Brusseau et al. (1997) for

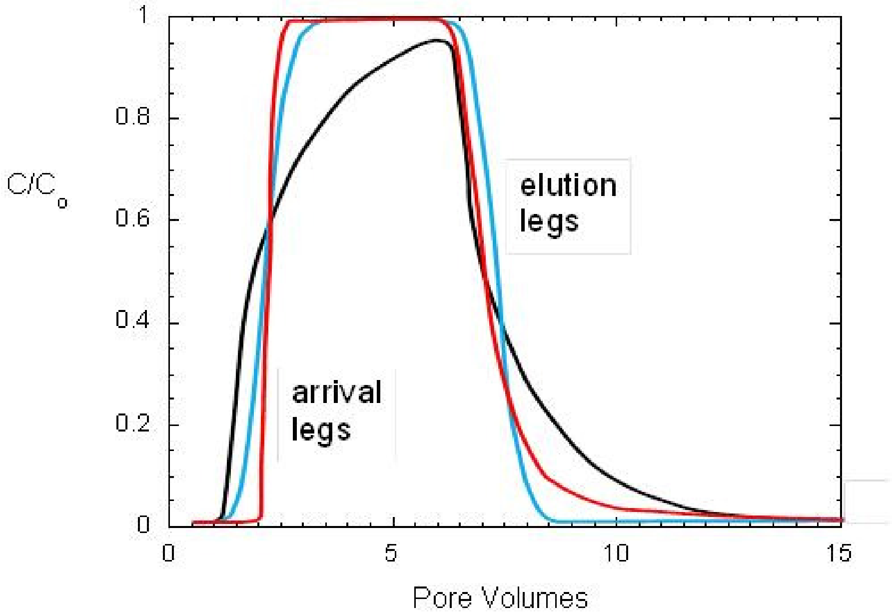


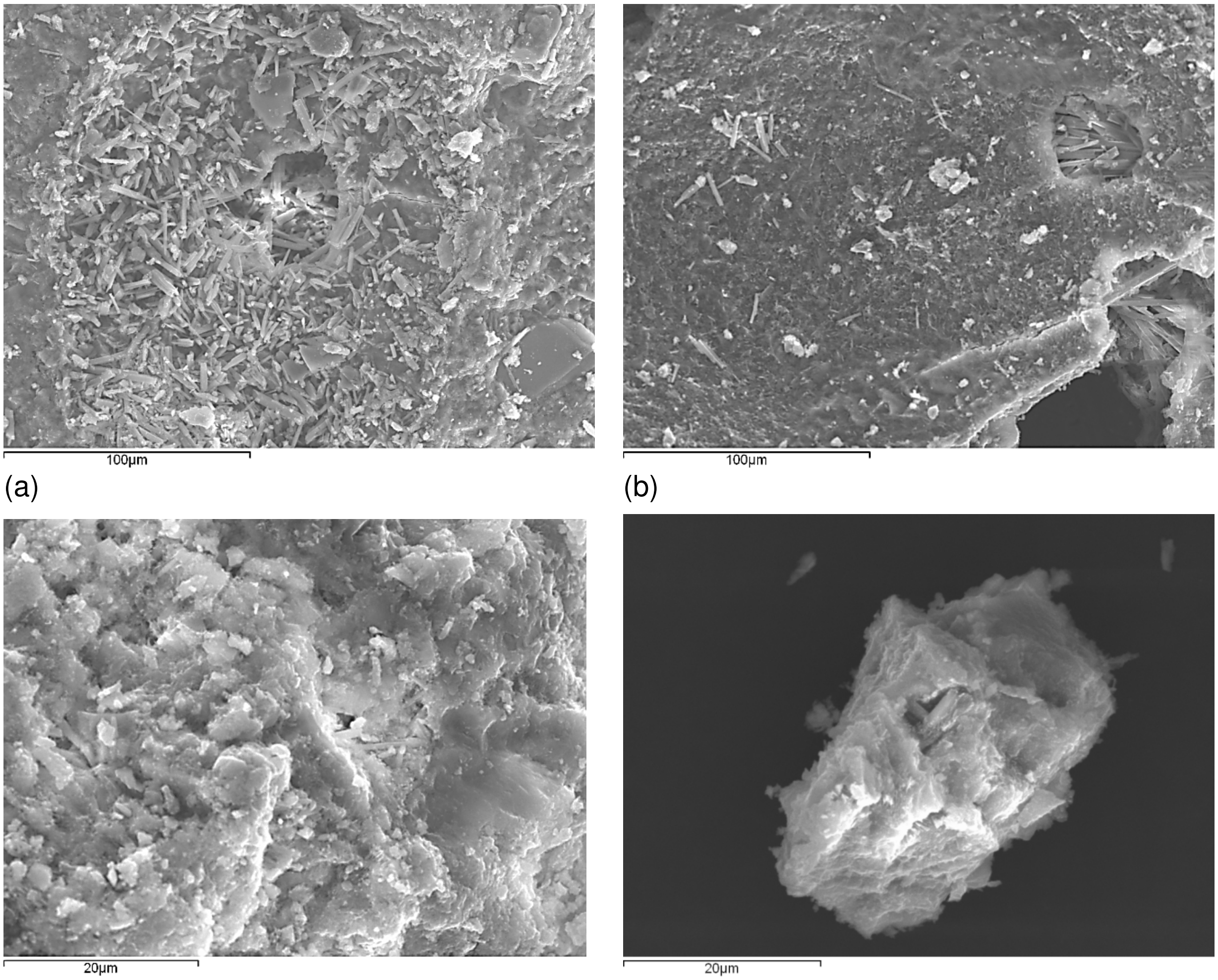
Figure 5.1 Representative breakthrough curves for contaminants with different sorption properties.

three contaminants having different sorption properties: the blue curve represents linear and instantaneous sorption, the red curve represents nonlinear and instantaneous sorption, and the black curve represents linear and rate-limited sorption. The influence of rate-limited sorption leads to tailing of both the arrival and elution legs of the breakthrough curves. Nonlinear sorption leads to asymmetric breakthrough curves where tailing occurs in the elution leg but not in the arrival leg. In Figure 5.1, the arrival legs for the linear and nonlinear cases of instantaneous sorption (blue and red curves) are very similar, but the processes are distinguished by the greater tailing in the elution curve for nonlinear sorption (red curve). The case of rate-limited sorption (black curve) leads to an asymmetric breakthrough curve for the contaminant—the slow buildup of the arrival curve is reproduced by the extended decrease of the elution curve. Brusseau et al. (1997) point out that these differences require sufficient pulse duration (i.e., a long enough interval between arrival and elution legs) to be distinguished and may not be apparent for small contaminant volumes. The sorption term in the ADE is usually evaluated by inverse modeling.

5.2 Application of Column Tests to Waste Materials

The use of various column and flow tests to study the dissolution kinetics of minerals, silicate glasses, and slags has been discussed in detail elsewhere (Ebert 2010; Ebert 2011) and will not be repeated here. Publications by Taylor et al. (2000a; 2000b), Mogollon et al. (1996), and citations therein provide excellent descriptions of the test execution and data analysis methods for determining dissolution kinetics. The sorptive behaviors of naturally-occurring minerals and silicate glasses have been studied extensively with column tests; three examples are presented in Section 6. The proposed use of the column test to study the coupled dissolution and sorption behaviors does not alter the procedure, but data analyses will likely be more complicated than analyses of the separate dissolution and sorption processes.

The high porosity of concretes is expected to (1) slow the approach to steady state in the dissolution tests in Step C1, (2) retard both the conservative tracer and contaminants in Step C2, and (3) generate long tails on the breakthrough curves measured in Step C3. It may be necessary to use a coarser size fraction of concrete and shorter column lengths to generate quantitative breakthrough results within practical test durations. An important question regarding concrete test samples is the impact of crushing on the pore structure and how well the crushed material represents the rubble in the waste pile. A walnut-sized piece of ordinary concrete was crushed to compare the pores that can be seen with a scanning electron microscope (SEM) for different particle sizes. Figure 5.2 shows the surfaces of several particles of ordinary concrete that were generated by crushing a larger piece and removing large aggregate (pebbles). Similar pores and crystalline phases are seen on the large (about 2 mm) piece in Figure 5.2a, the moderate size (about 0.2 mm) piece shown in Figure 5.2b, the small (about 0.2 mm) piece shown in Figure 5.2c, and the very small (about 0.1 mm) piece shown in Figure 5.2d. These photos show the small pore structure in concrete rubble are retained in the crushed materials. The larger pores that are lost during crushing would behave as free surfaces in the laboratory tests due to free access to water, so that the size fraction used in the batch tests adequately represent the behavior of the larger pieces. It also appears that the areal density of pores is not affected by crushing.



(a) (b) (c) (d)

Figure 5-2. SEM photomicrographs showing pore structures of (a) relatively large, (b) moderate, (c) small, and (d) very small pieces of crushed ordinary concrete.

5.3 Recommended Column Test Apparatus and Design

Figure 5.3 provides a schematic diagram of the recommended column test apparatus. Solution is pumped from a reservoir using a peristaltic pump upward through a packed column of crushed and sized waste material. Small amounts of the eluent are collected after several test intervals. It is recommended that the eluate be sampled at nearly constant intervals with the objective of detecting steady state conditions. Contaminant releases that are not transport-limited due to diffusion out of the matrix are expected to attain steady state concentrations, which are determined by the flow rate and the kinetics of the release reactions and sorption/desorption processes. Insights into the expected responses in column tests will be provided by the contaminant release and sorption behaviors measured in the batch tests. These can be utilized to determine the column test parameters, including column length and solution flow rate.

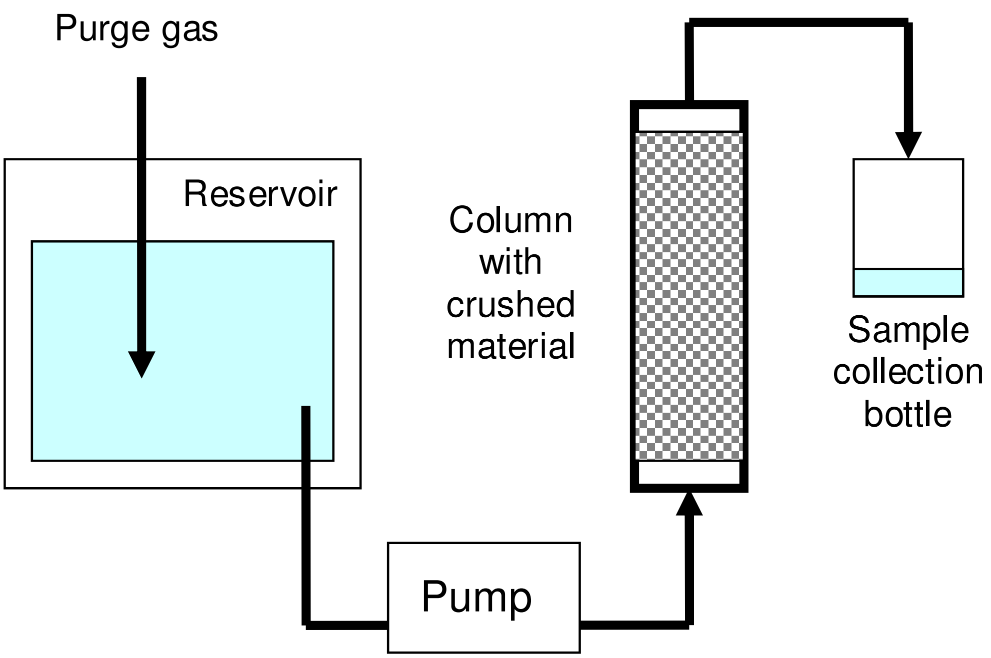


Figure 5-3. Schematic diagram of a column test apparatus.

The solutions in the reservoirs can be stirred and deaerated during the test. Only small amounts of eluate are collected during the test with the solution otherwise being directed to a waste bottle. This provides a “real time” measure of the solution composition at the time of sampling reflecting the composition of solution at the top of the column. Samples are collected by simply moving the tubing from the waste collection bottle to the eluate collection bottle and measuring the time over which the sample is collected. The flow rate is calculated as the mass collected divided by the collection time. (The density of the solution can be measured to convert mass to volume.) The long collection times called for in the CEN/TS 14405 (CEN 2004) and related EPA Method 1314 (see Garrabrants et al. 2012) methods are avoided to better reflect the kinetics of the reactions.

The design of column reactors and interpretation of test results must take into account the relative effects of the flow rate, diffusion, and reaction rates on the response. It is important to characterize the column behavior using engineering parameters to relate these factors to the test response to identify which process will dominate the test response under particular conditions. Key design parameters for laboratory tests include grain size, column diameter, column length, and leachant flow rate. For column tests used to measure K_d, Relyea (1982) recommended the column diameter be at least 30 times the maximum particle size to avoid local velocity and dispersion effects such as channeling and preferential flow at the column edge. The same requirement is recommended for column tests to measure the coupled dissolution, flow, and sorption behavior. For example, use of a 1.5-cm diameter column is adequate for particles that are smaller than 0.5 mm (–35 mesh). Note that the CEN 14405 procedure recommends the column diameter be 10 times the particle size and EPA Method 1314 calls for a 6-cm diameter column regardless of particle size. The length of the column that is filled with material will also affect the response. Using a short column length will minimize the duration required to measure breakthrough behavior, but also decrease the resolution of the breakthrough profiles relative to longer columns. Dean (2011) used a 50-cm long column with an estimated 1.5-cm diameter for tests with –35 +200 mesh material (see Section 6.3). This, and scoping tests conducted with crushed glass by the author, provides confidence that the small particles used in the batch tests can also be used in the column tests.

The flow rates used in the column tests are not intended to represent percolation rates through a waste pile or other natural system. Experimental flow rates are used to highlight (or minimize) the contributions of particular terms in the ADE. Details regarding column design provided by chemical engineering concepts are discussed in Appendix A.

6 DERIVING PARAMETER VALUES

The objective of the laboratory tests is to provide values representing waste materials and the waste pile that can be used in the advection-dispersion equation to model contaminant transport. The general form of the ADE as represented in Equation 3.1 is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\left(\frac{\partial C_s}{\partial t}\right)_{\mathrm{sink}} + \sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{source} \quad . \tag{3.1}$$

Analytical forms of the terms are assigned to reflect the contributing processes. For example, the sorption term is usually expressed in terms of the linear sorption model to yield

$$R\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) - v_x\frac{\partial C}{\partial x} + \sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{source} \quad , \tag{6.1}$$

with

$$R = 1 + \frac{\rho_b}{\theta}\frac{\partial C_s}{\partial C} \quad \text{and} \quad \frac{\partial C_s}{\partial C} = K_d \quad . \tag{6.2}$$

Non-linear sorption results in different definitions of R depending on the isotherm. The terms D and v_x are transport properties of the waste pile or a surrogate natural system, and the term K_d, R, and the source term reactions are properties of the waste material measured in the batch tests. Evaluation of dissolution kinetics using batch and column tests have been discussed in detail elsewhere (Ebert 2010). The same approach used to evaluate the sorption term in the ADE can be used to evaluate the contaminant source term, which is derived as a lumped parameter value representing all contributing reactions by inverse modeling. Contaminant transport in the absence of the reaction source term is calculated using a simplified ADE as

$$R\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) - v_x\frac{\partial C}{\partial x} \quad . \tag{6.3}$$

Three examples of applying inverse modeling techniques to modeling the retardation (sorption) terms are discussed in detail. The first example demonstrates the use of parameter values determined in batch tests in combination with values determined from field data to model contaminant transport at the field scale. The second example compares the results of batch sorption measurements with those derived from column experiments (sometimes referred to as optimized or conditioned values). The final example addresses the consistency of values determined from batch tests and column experiments similar to those recommended in the protocol for characterizing waste materials that also include sorption/desorption processes. Although most inverse modeling is done to minimize the error in the model output (relative to the measured outputs) by optimizing the parameter values, the analytical form of governing equation can be optimized instead. The number of parameters that can be identified for inverse modeling is typically limited by the quantity and quality of the data. An important issue that must be addressed is whether the parameter values have physical meaning (e.g., Brusseau et al. 1994). That is, the derived (optimized) values may represent lumped parameters that include the effects of processes not explicitly represented in the analytical model. Comparing the values measured in batch tests with those derived by inverse modeling can provide a valuable verification of both the analytical model and the optimized parameter values.

Knowledge of the sorption properties of the reactive minerals and the volumetric proportions of the reactive and non-reactive phases in the rock allows for calculation of the overall distribution of K_d values for that assemblage. It is common in definitions of continuum values to cast random variables in terms of a mean value and variance about the mean that is symmetric on the linear or log scale, depending on the property (Gelhar and Axness, 1983). Of course, if only one reactive mineral is present in the assemblage or if all reactive minerals have about the same sorption properties, the sorption coefficients will fall into a single mode.

It is recommended that the range (and number of modes) of effective K_d values be determined at the small scale of laboratory tests based on analysis of a large number of samples rather than from microscopic examinations of a few test specimens to characterize the individual host phases. Simply summing of the sorption properties of the individual minerals cannot be assumed to represent the retardation behavior of the material. This is because minerals that do not sorb the contaminant of interest may nevertheless affect the overall behavior of the rock because they occupy space and affect the volumetric proportions of sorbing minerals in the rock. The impact of the volume (surface area) occupied by nonsorbing phases on the effective value of K_d must be taken into account. This is because the value of K_d is on a per-mass basis, and the entire mass of the waste material is of interest and used to scale the laboratory results to field calculations, not just the mass of the sorbing phase.

As an example, Allen-King et al. (2006) measured the K_d values for perchloroethylene (PCE) on soil samples from the Borden aquifer in a study of the spatial geostatistics of sorption and permeability. A total of 380 test samples were taken from 11 core samples at about 1-m intervals to represent variance due to depth and lateral distance. Batch sorption tests were conducted with 7 g of pulverized sediment from each sample and 3.35 µg PCE in 4 mL of synthetic groundwater (0.838 µg mL^{-1}) for 72 hour durations. The average of the PCE concentrations in the test solutions was 0.466 µg mL^{-1}, giving an averge value of K_d = 0.57 mL $^{-1}$g ($\ln K_\mathrm{d}$ = -0.56). Figure 6.1a indicates the spread in $\ln K_\mathrm{d}$ values for the 380 measurements with a normal distribution curve shown for comparison. (The curves shown in Figures 6.1a and 6.1b were not regressed to the data and are only intended to show the general shape of the data set.) Allen-King et al. (2006) fit the results using a slightly skewed normal distribution having a mean $\ln K_\mathrm{d}$ = -1.05 for the range of -2.55 to 1.72, a variance of 0.37, and skewness coefficient of 1.16. The statistical mean value is K_d = 0.35 mL g^{-1} (ln K_d = -1.04).

Figure 6.1b shows the distribution of 857 measurements of permeability made using materials from the core samples and a normal distribution curve drawn with the mean value reported by Allen-King et al. (2006) of $\ln k$ = -14.90, but with a slightly higher variance than the reported value (0.6 compared to 0.37) and with a normal distribution rather than the reported skewness of 0.04 (for simplicity). Although the hydraulic conductivity is not measured in the testing protocol, these results show how physical property values of the material (such as those affecting the column tests) can be treated in the same manner. The pooled results define

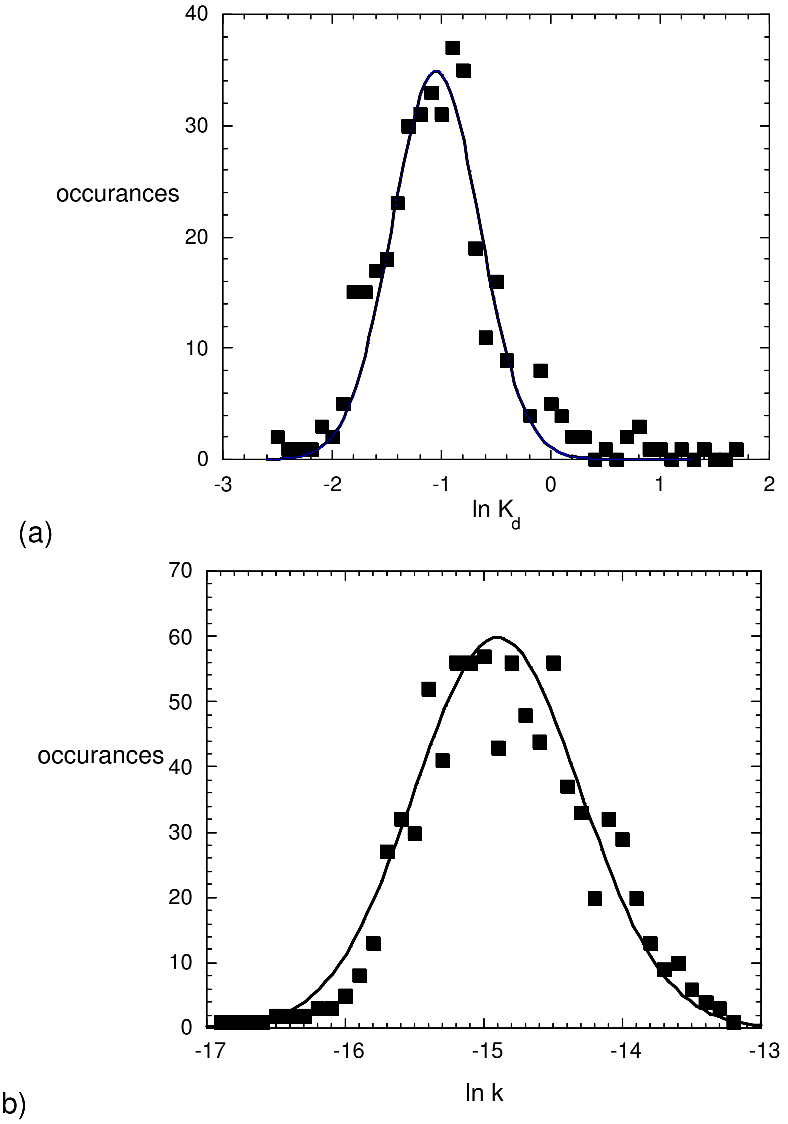


Figure 6.1 Spatial variance of (a) ln K_d for the the sorption of PCE and (b) hydraulic conductivity, as measured ln k, on samples of Borden soil.

probability distributions that can be used to model the system at a scale that is much larger than the test samples. In the case of these K_d measurements, each 7-g sample of sediment provided the total sorption capacity of the minerals exposed within that volume.

Although the ranges of results of Allen-King et al. (2006) for K_d and hydraulic conductivity are adequately represented as single modes (albeit slightly skewed), they represent a relatively small area of the natural system (i.e., that area represented by the 11 core samples). Each of the individual samples provides a value reflecting the response of the mineral assemblage at a particular location and depth. The pooled results estimate the behavior of the larger spatial region that was sampled by the 11 cores.

6.1 Combining Batch Test Results and Field Data

Batch tests provide the quickest and most economical methods for determining chemical parameter values. However, their use has for many years been criticized due to neglect of groundwater flow conditions, with some researchers preferring to use dynamic column tests (e.g., Huggenberger et al., 1972; Hill and Lake, 1978). Nevertheless, the combination of chemical information measured in batch tests with transport information obtained from field measurements has proved to be successful (Wood, 1978; Grove and Wood, 1979; Valocchi et al., 1981a, 1981b; Miller and Benson, 1983). The work of Valocchi is provided as an example.

Valocchi (1980) applied chromatographic theory to model the effect of ion exchange on contaminant transport using an effective K_d value. This approach can be applied to systems in which the reactions can be represented as equilibrium reactions. Chemical parameter values determined from batch laboratory tests were combined with hydrogeological parameter values determined from analyses of site data in transport simulations at the field scale (Valocchi et al. 1981a, 1981b, 1984). Field data were available for the test site near Palo Alto, California, for a solution containing Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+} that was injected in a well at an average rate of 21 m^3 h^{-1}. Water compositions were measured in neighboring wells. The compositions of the the injected water and the native groundwaters in the injection well and collection Well 23 are given in Table 6.1. The injected concentrations are much lower than the concentrations in the native groundwaters. The injected solution has a lower Mg/Na ratio and higher Ca/Na ratio than the native groundwaters. The selectivity of the ion exchange reactions affects the sorption and transport behaviors of Mg and Ca.

Breakthrough curves for the conservative (nonsorbing) Cl^- ion were used to determine hydrological parameters and the breakthrough results for the other ions (which participated in ion exchange reactions during transport) were compared with the modeling results. The breakthrough results for Cl^- were well-modeled using a longitudinal dispersivity factor of 1.0 m and a transverse dispersivity factor of 0.1 m, which resulted in the fit shown in Figure 6.2a (Valocchi et al., 1981a). Figure 6.2b shows the measured and modeled breakthrough curves for Mg^{2+} (filled circles and solid curve) and Ca^{2+} (open circles and dashed curve); these results were fit with the selectivity coefficients $K_{Mg/Na}$ = 1.7 eq L^{-1} and $K_{Ca/Na}$ = 3.0 eq L^{-1} that were measured in batch tests (Valocchi et al., 1981a). Details regarding the modeling approach and the effects of binary and ternary homovalent and heterovalent exchange are provided in Valocchi (1980), Valocchi et al. (1981a), and references therein.

Table 6.1 Water compositions used by Valocchi, in mg L^{-1}

Species	Injection Solution	Injection Well	Well 23
Cl^-	320 ± 54	3200	5700
Na^+	216 ± 30	1200	1990
Mg^{2+}	12 ± 5.6	310	436
Ca^{2+}	85 ± 12	262	444

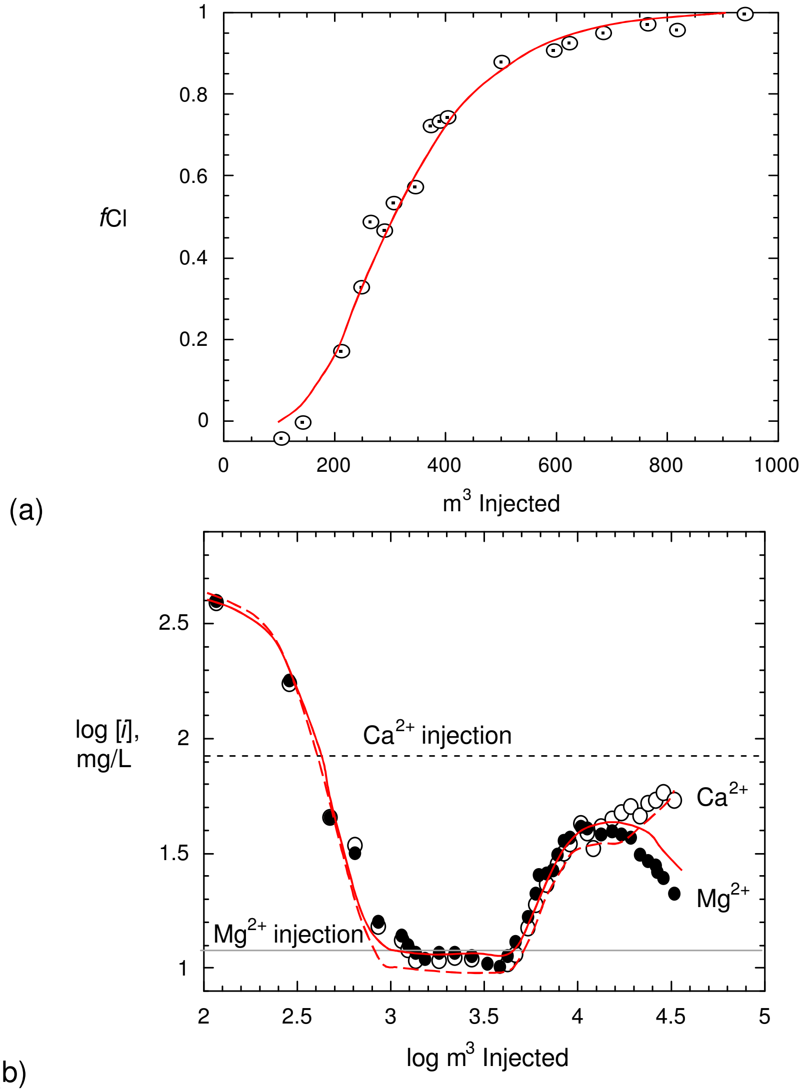


Figure 6.2 Measured and modeled breakthrough of (a) Cl^- and (b) Ca^{2+} (open circles and dashed curve) and Mg^{2+} (filled circles and solid curve).

The authors concluded that the

> "*close agreement between the simulated and actual breakthrough curves…indicates that laboratory-determined chemical parameter values can be utilized in field-scale transport simulations, if the hydrogeologic and hydrodynamic parameters are chosen to simulate reliably the movement of a conservative tracer*." They also noted that "*In applying the simulation model to a field transport problem it is anticipated that the most troublesome and expensive effort will be devoted to estimating values of velocity and dispersivity*."

This example represents the utilization of properties measured in batch laboratory tests combined with transport properties obtained separately to predict contaminant transport. In this example, the known transport properties for the non-sorbing Cl^- ion were used to derive advection and dispersion values. In the case of waste piles, the transport properties must be assumed based on other analyzed systems used as surrogates for the waste pile. The column tests recommended in the protocol provide information regarding transport properties under controlled conditions and their effects on the contaminant release and sorption properties relative to the parameter values measured in the batch tests. An example of how column test results are used to optimize the sorption parameters is discussed in the next section. This also justifies the recommended method for conducting the column tests.

6.2 Comparing Batch Test Values with Optimized Values from Column Tests

Pang and Close (1999) studied the transport of cadmium through alluvial gravel from New Zealand using both batch and column tests. Batch tests were used to characterize the sorption kinetics and isotherm, while column tests were used to study retardation and transport. The batch sorption results were fit with Freundlich isotherms of the form

$$C_s = K\,C^n\,, \tag{6.4}$$

$$\frac{\partial C_s}{\partial C} = K\,n\,C^{n-1}\,, \tag{6.5}$$

where

C_s is the amount of solute sorbed at equilibrium ($M_{contaminant}\ M_{solid}^{-1}$).
C is the dissolved concentration of the solute at equilibrium ($M_{contaminant}\ L_{solution}^{-3}$)
K and n are Freundlich coefficients.

Figure 6.3 shows the batch test results fit with a Freundlich isotherm having the parameters K = 21.9 and n = 0.337 shown by the curve. (Note that this is a subset of the data evaluated by Pang and Close.) The Freundlich parameter values were determined by a linear fit to a plot of log (C_s) vs. log (C_{aq}) for the range of concentrations.

6.2.1 Linearizing Non-Linear Isotherms

As discussed earlier and addressed by Pang and Close (1999), non-linear isotherms can be linearized to determine appropriate values of K_d for use in transport models. Two methods were given by van Genuchten (1981) for linearizing Freundlich isotherms based on the assumption that the total amount sorbed over the concentration range of interest is equal for the linear and non-linear isotherms. Considering that the isotherms cover the range starting at zero concentration (for simplicity), the areas calculated by integrating the sorbed concentrations as expressed by the linear and Freundlich isotherm equations from zero to the concentration of interest are

$$\int_0^{C_m} K_{d1}\,C\,dC = \int_0^{C_m} K\,C^n\,dC\,. \tag{6.6}$$

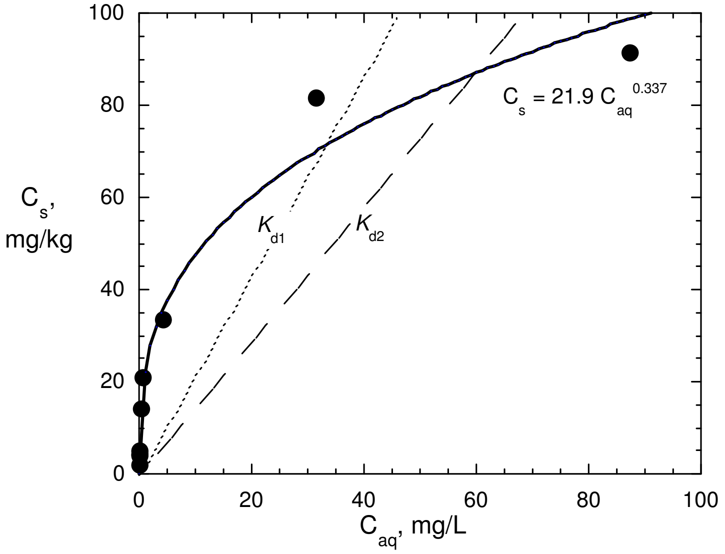


Figure 6.3 Sorption isotherm for Cd on alluvium. Dashed lines show two linearizations of the Freundlich isotherm at 60 mg/L.

Integration gives

$$\frac{K_{d1}\,C_m^2}{2} = \frac{K\,C_m^{(n+1)}}{(n+1)} \tag{6.7}$$

and rearrangement gives

$$K_{d1} = \frac{2K\,C_m^{(n-1)}}{(n+1)}\,, \tag{6.8}$$

where

C_m is the amount of solute sorbed per unit mass of solid (M M^{-1})
C is the solution concentration of the solute (M L^{-3})
K and n are Freundlich parameters
K_{d1} is the partition coefficient.

In the second approach, K_d is assumed to equal the average slope of the non-linear isotherm, which for the Freundlich isotherm can be written

$$K_{d2} = \frac{1}{C_m}\int_0^{C_m} \frac{\partial C_s}{\partial C}\,dC\,. \tag{6.9}$$

Substituting the Freundlich isotherm expression from Equation 6.5 gives

$$K_{d2} = \frac{1}{C_m} \int_0^{C_m} \frac{\partial K C^n}{\partial C} dC \,, \tag{6.10}$$

and integrating yields

$$K_{d2} = K C_m^{(n-1)} \,. \tag{6.11}$$

The two forms differ by a factor $2/(n+1)$ and are identical for $n=1$, which is the linear isotherm. For an aqueous concentration of 60 mg L^{-1} and Freundlich parameter values K = 21.9 mL g^{-1}, and n = 0.337, Equation 6.8 gives K_{d1} = 2.17 and Equation 6.11 gives K_{d2} = 1.45. Lines showing these linearized fits are drawn on Figure 6.3. The linear approximation given by K_{d2} provides a more accurate representation of sorption behavior at the high end of the concentration range, whereas the approximation given by K_{d1} is more accurate at the low end. Which parameter value is preferable for modeling depends on the range of concentrations expected to be important to the modelled system. Both can be compared with parameter values derived from inverse modeling of column tests, as discussed below.

6.2.2 Measuring System Characteristics with Nonsorbing Species

Pang and Close (1999) conducted column tests using a large column (200 cm long, 19 cm id) at flow rates of 20 and 61 m d^{-1} and using a small column (18 cm long, 10 cm id) at 18 m d^{-1} and 58 m d^{-1}. Figure 6.4a shows the breakthrough curves for Cd and Br in a low velocity test in the large column. The solution concentrations (C) of each are normalized to the concentrations in the injected solutions (C_o) to facilitate comparisons. Dissolved Br was introduced for 21 days (205 pore volumes) and dissolved Cd was introduced for 41 days (401 pore volumes). After 58.5 pore volumes, the flow was interrupted for 2 hours to study the response of the system. Flow interruption is an experimental method for identifying non-equilibrium conditions in flow tests (Brusseau et al. 1989; Brusseau et al. 1997). No effect is seen in the Br curve, which indicates an equilibrium condition expected for a nonsorbing species, but a clear decrease is seen in the Cd curve, which indicates a non-equilibrium condition expected for a quickly sorbing species.

The Br concentration in the eluate becomes equal to the the injected concentration after about two pore volumes, which indicates negligible retardation. The Cd concentration in the eluate reaches about 94% the injected concentration in pore volumes 350 through 405, which indicates significant retardataion. The rate of increase slows after the flow was interrupted (after 58.5 pore volumes), which may indicate greater hydrodynamic dispersion due to diffusion in the absence of flow.

The Br content in the eluate drops to nearly zero in the 216th pore volume, which is about 10 pore volumes after the injection of Br was stopped. Long tails for conservative species generally indicates solute exchange between mobile and immobile phases is delaying equilibrium. The Cd content in the eluate decreases much more slowly after the Cd injection was stopped after 401 pore volumes. The Cd concentration (relative to the injected concentration) dropped from about C/C_o = 0.96 immediately after the injection was stopped to C/C_o = 0.21 after the column was eluted with an additional 95 pore volumes.

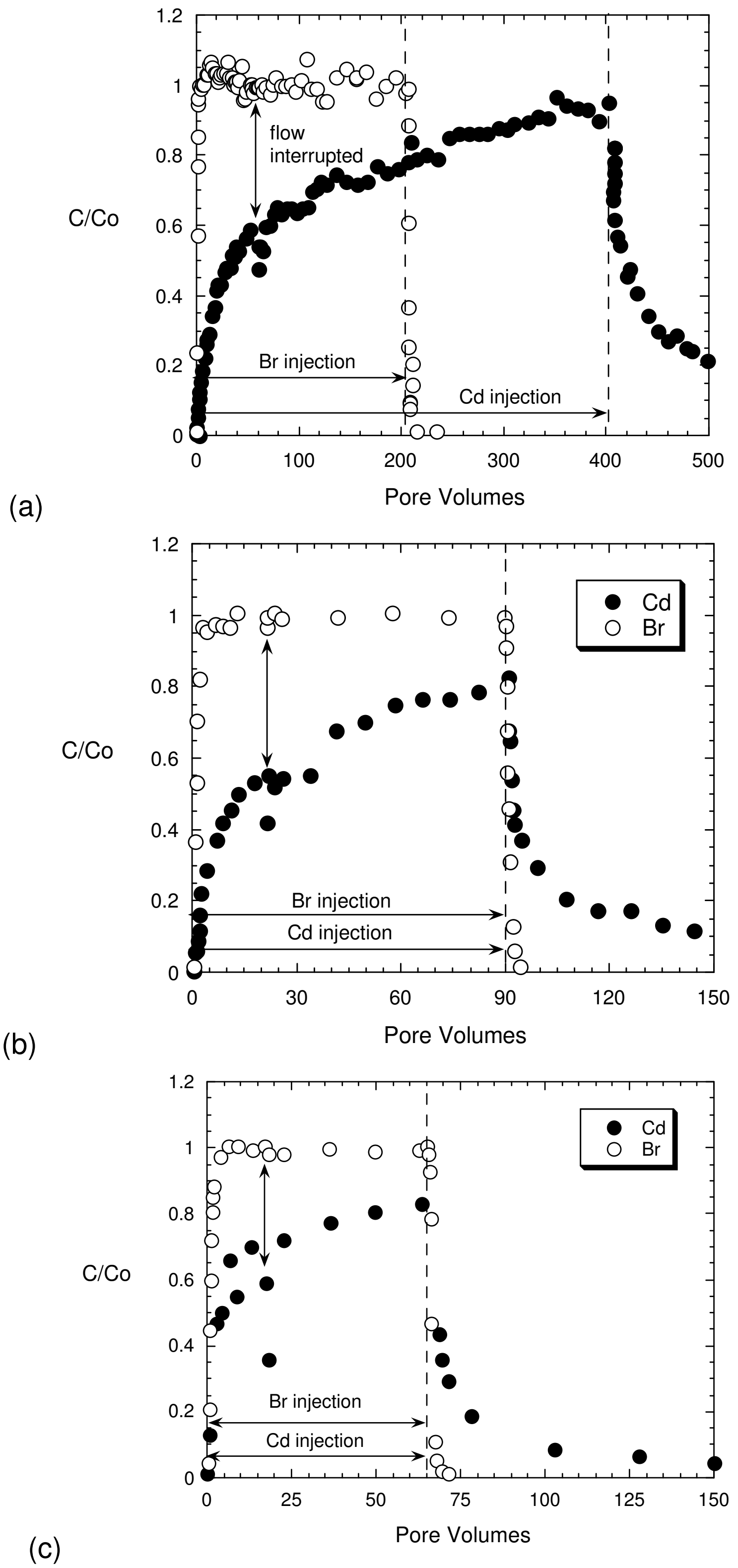


Figure 6.4 Breakthrough curves for Br and Cd in column tests with alluvial gravel: (a) low flow through a long column, (b) low flow through a short column, and (b) high flow through the short column. Ordinant gives relative concentrations.

The asymmetry between the leading and trailing edges of a long pulse provides insight into the coupling of reaction rates and flow, but that can also be affected by the relative importance of advection and dispersion. Systems with low Péclet numbers have significant dispersive spreading that leads to asymmetry. The results of tests conducted in the short column at low and high flows are shown in Figures 6.4b and 6.4c. The vertical arrows indicate when the flow was interrupted and show the same effect on Cd and lack of effect on Br that was seen at the low rate in the long column in Figure 6.4a. The same behavior is seen in the long and short columns and at the two flow rates. Pang and Close (1999) determined Péclet numbers of 2.45 for the long column and 12.1 for the short column at the low flow, and 2.45 and 15.6 for the long and short columns at high flows based on breakthrough of the conservative species. The Péclet number indicates the relative importance of advection and dispersion in the flow system (see Appendix A), and the reported values greater than 1 indicate the contributions of dispersion were negligible in all systems. Of course, the flow interruption perturbs the system such that only diffusion occurs and dispersion becomes important during those periods.

The effects of flow rate in the short column are shown in Figure 6.5. Figure 6.5a highlights the initial Cd breakthrough and saturation of the column. The initial breakthrough is seen to occur after fewer pore volumes at the high flow than at the low flow. Figure 6.5b highlights the long-term elution and shows the tailing to be more severe at the low flow for the same elution volume. Note that the breakthrough curve for the high flow shown in Figure 6.5b has been shifted by +24.3 pore volumes in the plot so that the points on the curves at which the injections were stopped coincide to allow for direct comparisons of the elution tails. The elution tails reflect the effect of the retardation factor.

Analytical methods for relating breakthrough curves to reactive transport models using the ADE are well estabilished for natural media and directly applicable to waste materials (see van Genuchten, 1981; Kool et al., 1987; Pang and Close, 1999; and references therein). Pang and Close (1999) analyzed the measured breakthrough curves to derive optimized values for contaminant transport parameters including the retardation factor (R), dispersion coefficient (D), Péclet number (Pe), partitioning coefficient (β), and mass transfer coefficient (ω). Table 6.2 summarizes the results for the retardation factor. Linearization method 1 gave a slightly better fit to the Cd releases measured in the column tests (i.e., were closer to the optimized values) under 3 of the 4 test conditions. The tests conducted with short columns at high velocities generated lower solution concentrations, which were seen in Figure 6.3 to be better represented by K_{d1}. However, the differences are small (less than a factor of 3). R values derived from column tests are typically lower than those measured in batch tests because of the shorter residence time (Bouchard et al. 1988), but retardation in the batch tests and column tests are affected by different processes. For example, batch tests may be affected by

Table 6.2. Sorption behavior of Cd from column and batch tests

Column size	Velocity, m d^{-1}	Pe	Optimized R	R from K_{d1}	R from K_{d2}
Long	61	2.45	65.8	48.9	37.4
Long	20	2.45	133	72.0	54.9
Short	58	15.6	22.2	67.9	34.5
Short	18	12.1	54.0	47.4	36.3

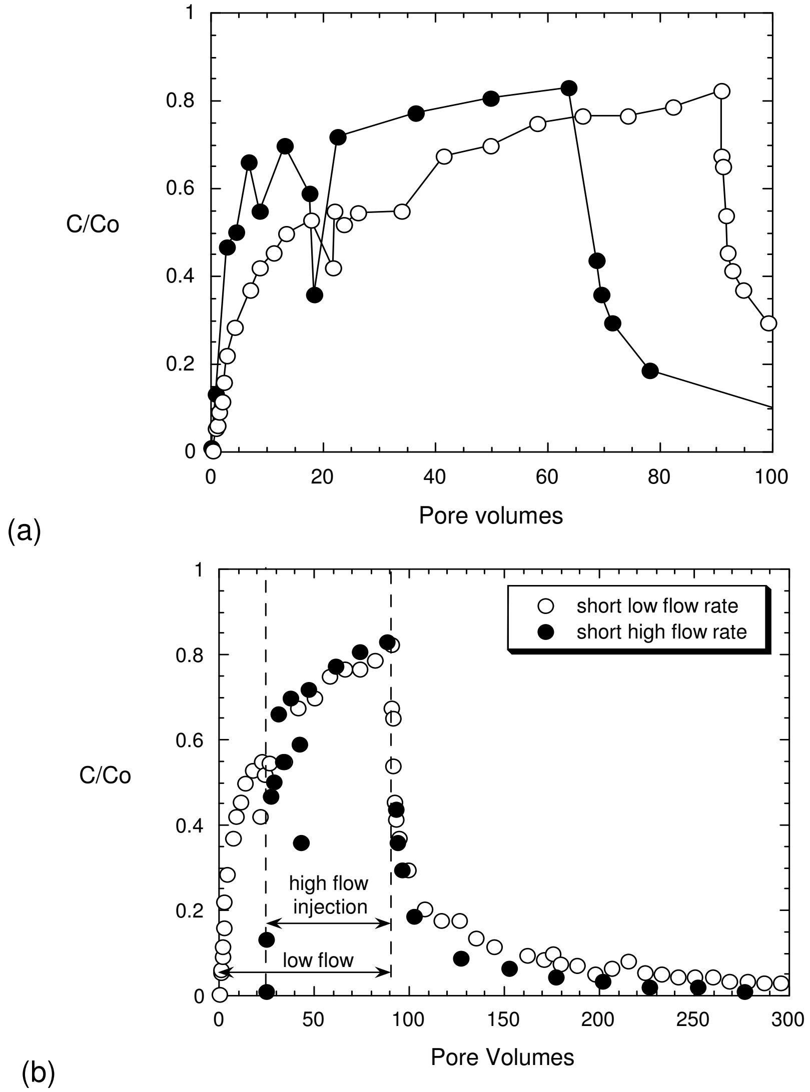


Figure 6.5 Breakthrough curves for Cd in a short column at low and high flow rates: (a) showing initial breakthrough and (b) comparing tailing after injections ceased. Note that the values for the high flow rate test is shifted in (b) to align the desorption tails.

precipitation and usually represent a near-equilibrium condition, whereas column tests may be affected by dispersion, preferential channeling, and slow sorption kinetics, and are further from equilibrium. These results demonstrate the variance in the parameter values for sorption with the transport conditions in the column tests: the optimized values varied by a factor of about 6 and the values from the batch tests varyied by less than a factor of 2. The averages also differed by less than a factor of 2.

6.3 Derivation of Sorption Term by Inverse Modeling

Three series of experiments were conducted by Dean (2011) to measure the sorption and desorption of ^{233}U(VI) present in tuff groundwater onto various samples of tuff rock under static and flowing conditions. This research was sponsored by DOE “with the goal of demonstrating that additional natural system performance could be realized for the Yucca Mountain repository system by taking credit for slow radionuclide desorption processes that are not accounted for in transport models implementing simple partition coefficients to describe radionuclide interactions with rock surfaces” (Arnold et at. 2011 p. 27). The results were evaluated within the current Fuel Cycle Research & Development (FCRD) Project as representing an experimental and interpretive methodology that could be utilized for other geologic media. Because a very similar approach is recommended herein for characterizing surface piles of slag and concrete rubble, the approach and results of Dean (2011) are described and evaluated in detail. However, it should be emphasized that these tests did not include analysis of the contaminant source term, which is an important issue for analyzing waste piles. This is because contaminant release in the repository was modelled to occur from a point source (the waste package) rather than from the tuff itself.

The approach couples a simplified geochemical description of the system including sorption and transport with laboratory experiments. It was hypothesized that adsorption and desorption rate constants could be extracted from laboratory experiments and then upscaled to take into account the effects of heterogeneous mineral distributions on reactive transport modeling at the field scale. Experiments were designed to represent the natural mineralogy and geochemistry of the system, and different methods were used to determine adsorption and desorption rates to evaluate the use of the measured values in ADE calculations modeling the dynamic system. With regard to waste materials of interest for this protocol, this work provides insights into the effects of treating all sorbing phases separately or as a single effective phase. It is also used as an example comparing parameter values derived from batch and column tests.

6.3.1 Test Method and Analysis

Core samples of tuff rock were crushed and sieved to isolate the -35 +200 mesh size fraction (500 µm to 75 µm) for use in the sorption and desorption experiments. Samples of tuff rock that were enriched in analcime, mordenite, smectite, or illite were evaluated. The smectite-rich material that was tested most extensively was comprised of about 26.2 mass% quartz, 29.1 mass% K-feldspar, 31.1 mass% plagioclase, 11.2 mass% illite/mica, and 2.2 mass% smectite based on X-ray diffraction analysis. In the first test series, static batch sorption tests were conducted using ~1×10^{-6} $\underline{M}$ $^{233}UO_2(NO_3)_3$ and the solution was sampled over a 14-day period to measure the overall sorption of ^{233}U. In the second series, ^{233}U was desorbed from the fully-loaded solids generated in the batch sorption tests into flowing groundwater to measure the desorption kinetics. The sorption and desorption kinetics were modeled as the combined actions of up to four sorbing phases on the U solution concentration as

$$\frac{dC}{dt} = \frac{1}{V}\left\{ Q\left(C_{\text{influent}} - C\right) - \left[\sum_{j=1}^{n} k_{f,j}\left(1 - \frac{C_{s,j}}{C_{s,j}^{\max}}\right)\right] \bullet C + \sum_{j=1}^{n} k_{r,j} C_{s,j} \right\} \tag{6.12}$$

and

$$\frac{dC_{s,j}}{dt} = \frac{1}{M}\left[k_{f,j}\left(1 - \frac{C_{s,j}}{C_{s,j}^{\max}}\right) \bullet C - k_{r,j}\, C_{s,j} \right], \tag{6.13}$$

where

C is the contaminant concentration in the effluent (M L^{-3})
$C_{s,j}$ is the contaminant concentration sorbed to the j-th sorbing site-type (M M^{-1})
$C_{s,j}^{\max}$ is the maximum contaminant concentration that can sorb to the j-th sorbing site-type (M M^{-1})
C_{influent} is the contaminant concentration in the influent (M L^{-3})
Q is the flow rate (L^3 T^{-1})
V is the volume of the reaction cell (L^3)
M is the mass of solid (M)
$k_{f,j}$ is the sorption rate on the j-th sorbing site-type (T^{-1})
$k_{r,j}$ is the desorption rate on the j-th sorbing site-type (T^{-1})
n is the number of sorbing site types considered ($n \leq 4$).

The third series of tests included column break-through experiments conducted at flow rates of about 7 mL h^{-1} and 28 mL h^{-1}. The breakthough behavior was modeled by inserting the sorption kinetics into the advection-dispersion equation (see Equation 1.1). Using the expression for multiple sites to model the sorption term and ignoring decay and chemical reactions, the ADE can be written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\left\{ \sum_{j=1}^{n} k_{f,j}\left(1 - \frac{C_{s,j}}{C_{s,j}^{\max}}\right) \bullet C - \sum_{j=1}^{n} k_{r,j} C_{s,j} \right\}, \tag{6.14}$$

where

D is the dispersion coefficient (L^2 T^{-1})
v is the mean pore velocity (L T^{-1})
x is the distance along the column (L)
t is time (T)
ρ is the bulk density of the tuff (M L^{-3})
θ is the porosity (unitless).

Preliminary experiments were conducted with tritiated water (^{3}HHO) as a nonsorbing species to measure the characteristics of each column, which include the Pêclet number (Pe), mean water residence time (τ), bulk density (ρ), and porosity (θ). Pe and τ are related to the mean pore velocity (v) and the solute dispersion coefficient (D) as $Pe = vL/D$, where L is the length of the column and $\tau = L/v$.

Equations 6.12 and 6.13 were fit (Dean, 2011) to the results of the sorption/desorption experiments to determine parameter values for the rate constants, number of sorption sites, and site densities. These values were then used in Equation 6.14 to predict the uranium transport behavior for comparison with the column experiments. She also predicted the uranium transport with Equation 6.14 using the equilibrium K_d value measured by the batch tests to represent the sorption term in place of the term in braces. The transport behavior observed in the column experiments was used to derive optimized K_d values or sorption and desorption parameter values by inverse modeling with Equation 6.14. This provides an example how the results of tests recommended in the protocol can be used for modeling contaminant transport in waste piles.

6.3.2 Testing and Modeling Results

The results for experiments with smectite-rich tuff are shown by the diamond symbols in Figure 6.6 (Arnold et al. 2011). The red dashed curve shows the regression fit of the multi-site model in Equations 6.12 and 6.13 to the first and second series of experiments with the smectite rich Sample 3. The K_d value determined in the batch sorption test represents sorption on all sites and is 6.48 mL g^{-1}. The multisite model sums the contributions of each site weighted by the mass fraction of that site. The weighting factors X_j (mass fraction of phase j) and the individual and combined K_d values determined by regression of Equation 6.12 to the desorption test results for a 3-site model are given in Table 6.3 (Dean 2011). Note that Dean (2011) reported the value 911.9 mL g^{-1}, which is the sum of the K_d values for the individual phases without the weighting factors. The weighted sum is 111.7 mL g^{-1}. The fit shown by the red solid curve is based on the optimized parameter values determined from the breakthrough curve of a column experiment in the third series of experiments. Dean (2011) noted that the contributions of slow sorption and desorption from phases 2 and 3 to the responses in the short-term batch measurements were negligible, but dominated the long- term desorption

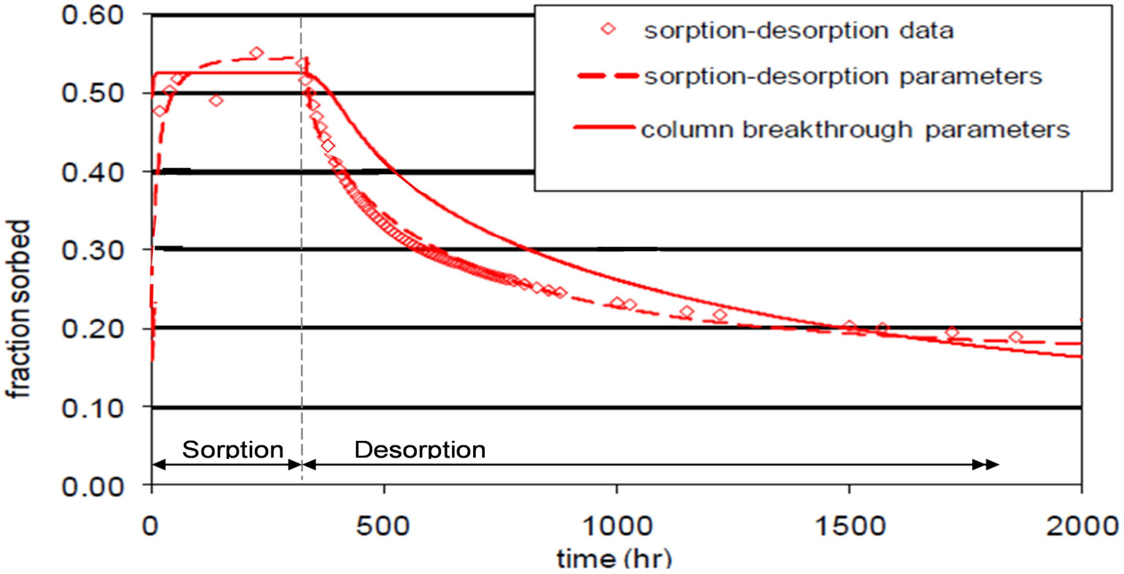


Figure 6.6 Data for sorption and desorption experiments with smectite-rich tuff Sample 3 and model results.

Table 6.3 Parameter values derived from desorption tests with smectite-rich tuff

Sorbing phase *j*	k_f	k_r	$\overline{C}_j^{\max}$	X_j^a	K_d	K_d^{total}
1	0.50	0.1	10,500	0.50	2.5	911.9[b]
2	0.50	0.0052	5000	0.39	37.2	
3	0.08	0.00001	4000	0.11	872.2	

[a]Mass fraction of phase *j* in Sample 3.
[b]Value reported by Dean (2011).

measurements. Although Dean assumed equilibrium was reached after 100 hours, inspection of Figure 6.6 suggests the system may not have reached equilibrium during the sorption tests, which means the K_d value may be too low.

Dean (2011) referred to the column experiments as being upscaled in the sense that the impact of multiple sorption sites will be greater over longer transport distances than indicated in batch tests. She compared the behaviors predicted by using the K_d value measured by the separate sorption tests and the K_d^{total} value determined from the desorption tests with the behavior that was observed in column tests. The attenuation of solute transport velocity relative to the groundwater is modeled using the retardation factor, which is related to the K_d and K_d^{total} values as

$$R = \frac{v_\text{groundwater}}{v_\text{contaminant}} = 1 + \frac{\rho_b K_d}{\theta}, \tag{6.15a}$$

and

$$R = \frac{v_\text{groundwater}}{v_\text{contaminant}} = 1 + \frac{\rho_b}{\theta}\sum_{j=1}^{n} K_{d,j} X_j = 1 + \frac{\rho_b K_d^{total}}{\theta}, \tag{6.15b}$$

where X_j represents the relative mass fractions of the sorbing phase(s). The retardation factor can be calculated using the equilibrium K_d value from the batch test or the K_d^{total} value determined from the desorption tests. Conversely, an optimized K_d value can be derived from the column test results. For the column experiments conducted by Dean (2011), the dry bulk density (ρ_b) and porosity (θ) were 1.19 g cm^{-3} and 0.59 for the tuff used in the column of the 7 mL h^{-1} experiment and 1.32 g cm^{-3} and 0.57 for the tuff used in the column of the 28 mL h^{-1} experiment. The pore volumes were 52.13 mL and 50.36 mL, and the mean residence times were 7.4 h and 1.7 h, respectively.

Figure 6.7 shows the solution results for column tests with the smectite-rich tuff (symbols) conducted at two flow rates and the model calculations using the sorption/desorption parameters (dashed curves) (from Arnold et al. 2011). The U breakthrough is observed to occur after about 100 and 110 pore volumes at the lower and higher flow rates; breakthrough of the conservative species (tritiated water) occurred after about one pore volume at both flow

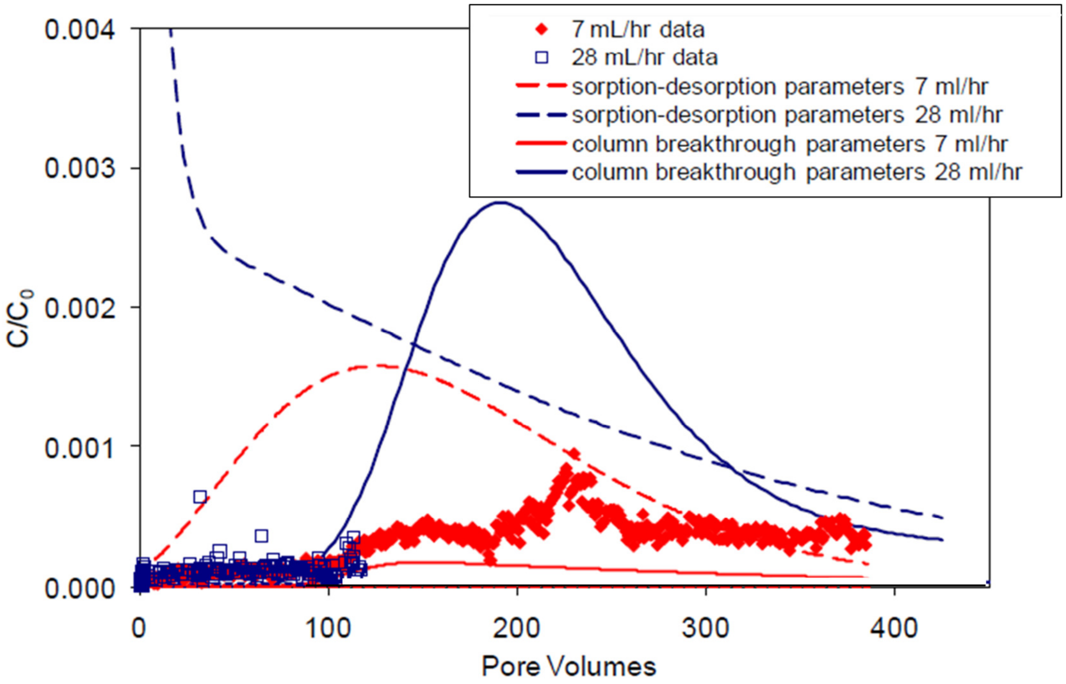


Figure 6.7 Solution breakthrough data for column experiments with UO_2^{2+} solution and smectite-rich tuff with model results. Results for experiments at flow rates of 7 mL h^{-1} (red) and 28 mL h^{-1} (blue) with parameter values determined from breakthrough measurements (solid curves) and from batch tests (dashed curves).

rates (Dean 2011). Breakthroughs are predicted to occur after 14 and 15 pore volumes at the two flow rates by using the K_d values from batch sorption experiments in Equation 6.14 (dashed curves). Almost all of the U is predicted to pass through the column after 100 pore volumes in the high flow experiment based on the K_d value from the static tests. Conversely, using the effective K_d^{total} value predicts breakthroughs after about 1600 and 1750 pore volumes (Dean 2011). It is likely that these extremely high breakthrough values are due in large part to the too-high effective K_d^{total} values that were calculated (911.9 mL g^{-1} rather than 111.7 mL g^{-1}) and by not taking the mass fraction corresponding to the nonsorbing part of the tuff into account. The solid curves show the regressions to the measured breakthrough concentrations using the multi-site model. The optimized K_d values were calculated from the retardation factor as expressed in terms of the transport velocities of uranium and tritiated water and using Equation 6.15a. The optimized model parameters for the 3-site and single-site models are summarized in Table 6.4. The optimized values from the column tests using the the single-site model are about 8-times higher than the K_d value determined from the sorption tests, about 20-times lower than the effective K_d^{total} value of 911.9 mL g^{-1} determined from the desorption tests by Dean (2011), and about a factor of 8 lower than an effective K_d^{total} value of 111.7 mL g^{-1}

Table 6.4. Optimized sorption parameter values from column tests

	7 mL h^{-1}			28 mL h^{-1}		
Sorbing phase j	k_f, mL g^{-1} h^{-1}	k_r, mL g^{-1} h^{-1}	K_d , mL g^{-1}	k_f, mL g^{-1} h^{-1}	k_r, mL g^{-1} h^{-1}	K_d , mL g^{-1}
1	13.5	0.1	49.1	13.5	0.1	43.2
2	0.125	0.002		0.125	0.002	
3	0.25	0.00001		0.25	0.00001	

6.4 Summary of Using Test Results in Models

The works of Valocchi, Pang and Close, and Dean summarized in this section provide detailed examples of key aspects of the assessments to be supported by this testing protocol. The first two examples show the application of test results to systems that can be modelled relatively simply, whereas the work of Dean (2011) demonstrates the added complication of speciation when modeling just the sorption process in even an experimental system that is well-constrained. A situation in which the various sources of radioactive contaminants are distributed throughout the system and intermingled with sorption sites will further complicate the contaminant transport behavior through the system and our capacity to model it. The tests by Dean (2011) and additional analyses of her data by several experts in the field of groundwater and contaminant transport (Arnold et al. 2011) show the necessity of the geostatistical approach underlying this testing protocol to measure volume-averaged parameter values rather than approaching the problem deterministically. Of particular importance to the testing protocol, the empirical K_d values representing the combined effects of several sorbent materials that were measured by Dean (2011) in batch tests were shown to represent the sorption behavior better than the weighted sum of the individual phases. This shows there is (at this time) no advantage to taking the compositions or abundances of contaminant-sorbing phases present in the waste materials into account for performance calculations. Instead, the overall behavior measured for a set of samples of the waste material (i.e., a REV) provides a more representative parameter value for modeling contaminant retardation than individual analyses of the constituent phases. However, modeling those results may require using a multi-site and multi-component reaction model.

Whereas empirical observations from column tests provide the best available method to determine the importance of sorption kinetics, qualitative insights can be gained by monitoring the approach to equilibrium when conducting static tests such as ASTM C1733 and subsequent desorption. The parameter value can be adjusted empirically to represent the effects of the sorption and desorption kinetics.

Measuring the desorption rate as part of the test protocol indicates the reversibility of the sorption processes and its importance to transport. Precipitation of contaminant-bearing phases can occur during batch sorption tests conducted for long times or with high contaminant concentrations that render the measured K_d meaningless. Measuring the desorbed fraction is a simple way to detect the occurrence of such processes and make appropriate corrections, such as excluding the high concentration results from the isotherm determination. Correcting measured sorption values for precipitation and similar effects will decrease the values of the retardation factor used in ADE calculations. The transport behaviors of contaminants that are strongly or weakly sorbed will differ significantly and lead to differences between sorption parameter values measured in batch tests and those derived from column tests. The optimized values determined from column tests will provide more reliable predictions of the behavior in a waste pile than will parameter values from batch tests, albeit only for flow rates near that used in the column test.

7 TESTING PROTOCOL

This section presents the logical progression of the testing protocol in a step-by-step format for the batch and column test methods that were described in Sections 4 and 5. The protocols for batch and column tests are also provided as flow diagrams. It is recommended that specific test plans are developed for application of the protocol to specific systems. Such a test plan would specify the number of field specimens to be collected and subjected to each test method, contaminants of interest, testing parameters based characteristics of the waste material, and data needs of the model in which the test results are to be used.

7.1 Collection and Preparation of Test Materials

Collect samples of waste material from multiple locations in the waste pile. The number of samples should be determined from the estimated heterogeneity of the waste pile based on records, process knowledge, and survey results. A MARSSIM-like sampling protocol should be considered. Collect at least 300 g of material from each location for use in batch tests and an additional 200 g of material if the optional column tests will be performed. A series of boxes is used to represent tests to be performed with some or all subsamples produced from each field sample of the waste material, as shown in Figure 7.1.

Waste Material 1	Waste Material 2	Waste Material 3	Waste Material 4	Waste Material 5	. . .	Waste Material *n*

Figure 7.1. Matrix of field samples used for testing.

Crush each material and sieve to isolate the material that passes a 35 mesh sieve (0.5 mm opening) but is retained by a 200 mesh sieve (0.075 mm opening), that is, the -35 +200 mesh size fraction. Note that the recovery of crushed material in the desired size fraction is typically on the order of 40%. Since about 100 g of crushed and sized material is required for batch tests and about 150 g is needed for two column tests, 500-g field samples are expected to provide enough material for testing.

Follow an analytical fractioning method such as ASTM C702 (ASTM 2014b) to produce representative test samples from the field samples of waste material. Rinse each retained fraction with absolute ethanol (99%) repeatedly to remove fines following ASTM C1285 methodology for solids preparation. Do not rinse with water to avoid dissolving soluble phases during sample preparation.

About 80 g of crushed and sized material from each field sample is required to conduct the full suite of batch tests:

10 g for “total” elemental analysis of major elements and contaminants of concern in Step B1a (Sample A)
10 g for ASTM C1285 acid rinse contaminant release tests in Step B1b (Sample B)
10 g for ASTM C1285 pore water characterization test in Step B2 (Sample C)
10 g for ASTM C1308 leach test in Step B3 (Sample D)
40 g for ASTM C1733 4 samples for sorption tests at four concentrations of contaminant in Step B4 (Samples E, F, G, and H)

At least 100 g of crushed and sized material should be prepared from each field sample to avoid bias in generating subsamples for testing. It is strongly recommended that enough sized material be prepared to repeat a test if necessary.

About 60 g of crushed and sized material (depending on density of waste material) is required for running a column test using a 30 cm x 1 cm id column. Either a single sample of the waste material or a mixture of material samples can be used in the column test.

Containers for conducting batch tests at an elevated temperature should be made from PFA Teflon, such as digestion vessels available from Savillex (Part 30-120-03). Other containers for room temperature tests may be PFA Teflon or HDPE bottles. The amounts of solids and solutions can be scaled for other vessel sizes and altered for practical or safety reasons. It is recommended that at least 5 g of solids be used to represent the sampled region.

7.2 Batch Tests

B1. Contaminant Source Concentrations. Objective: Determine the total concentrations of contaminants in the waste material and the fractions of each contaminant that are leachable in an acidic solution.

B1a. Total contaminant content. Measure the total concentrations of contaminants of interest in test Sample A for each field sample of the waste material. Analysis of major elemental constituents of the waste should be considered. Methods standardized by ASTM-International or other organizations are recommended. Samples can be sent to an outside analytical chemistry lab for analysis. The sample matrix is summarized in Figure 7.2.

Waste Material 1 Sample A	Waste Material 2 Sample A	Waste Material 3 Sample A	Waste Material 4 Sample A	Waste Material 5 Sample A	. . .	Waste Material *n* Sample A

Figure 7.2. Matrix of test samples used to measure total contaminant content.

B1b. Leachable contaminant content. Conduct ASTM C1285 test with test Sample B for each field sample of the waste material using 0.1 M HNO$_3$ instead of water. The sample matrix is summarized in Figure 7.3.

Waste Material 1 Sample B in 0.1 M HNO$_3$	Waste Material 2 Sample B in 0.1 M HNO$_3$	Waste Material 3 Sample B in 0.1 M HNO$_3$	Waste Material 4 Sample B in 0.1 M HNO$_3$	Waste Material 5 Sample B in 0.1 M HNO$_3$	. . .	Waste Material *n* Sample B in 0.1 M HNO$_3$

Figure 7.3. Matrix of test samples used to measure leachable contaminant content.

- 10 g crushed solids + 100 g nitric acid solution; pass test solutions through 450 nm cellulose filter to remove suspended solids
- Measure releasable contaminant concentrations in all solutions.
- Calculate the mass fractions of releasable contaminants present in each waste material specimen.

B2. **Pore Water Characterization**. Objective: Determine representative pore water composition, including contaminant concentrations, for use in testing. Conduct ASTM C1285 tests with test Sample C in demineralized water (DIW) or synthetic rain water. Select samples representing predominant areas of the waste pile, for example, consider that materials 1, 2, and 4 were taken from the bottoms catchment areas and represent the primary water flow paths and generate the most representative pore water composition. The sample matrix is summarized in Figure 7.4.

Waste Material 1 Sample C in DIW	Waste Material 2 Sample C in DIW	Waste Material 4 Sample C in DIW

Figure 7.4. Matrix of test samples used to measure pore water composition.

- React 10 g of solid in 100 g of demineralized water or synthetic rain water.
- Compare solution compositions generated in Steps B1a and B1b with different waste material samples; identify contaminants and concentrations of major solutes and pH.
- Formulate a simplified surrogate pore water (SPW) solution composition having similar pH and major solute species concentrations to represent the measured compositions, excluding the contaminants.

Table 7.1 provides an example of a SPW solution representing the average of 3 solutions generated in ASTM C1285 tests conducted with DIW to represent the pore water. A method to formulate simplified surrogate solutions using Geochemist's Workbench is provided in Appendix B, using U and Cs as examples of contaminants. The U and Cs contaminants are excluded from the SPW composition, but are used to determine the amounts of U and Cs added to the spiked solutions made for use in protocol Steps B4 and C2.

Prepare surrogate solution (excluding contaminants) for use in testing:

Approximately 2 L SPW solution will be required for each material that is subjected to full suite of batch tests (e.g., testing 20 waste specimens will require 400 L):
11*100 mL for ASTM C1308 contaminant release tests in Step B3,
4*100 mL for preparing each Solution SPW-A, -B, -C, and -D for use in Step B4,
4*100 mL for ASTM C1308 desorption tests in Step B5.

Approximately 10 L of SPW will be required for conducting a column test (see Section 7.3.2).

Table 7.1 Example of measured C1285 test solution compositions and formulated SPW solution, in mg L^{-1}

	Measured Test 1	Measured Test 2	Measured Test 4	SPW
Al	0.63	0.43	<0.1	—
Ca	9.08	7.10	11.9	8
Li	0.04	0.04	0.05	—
K	0.02	0.01	0	—
Mg	0.96	0.25	0.95	—
Na	46.5	49.3	45.4	50
Si	34.4	35.7	30.6	36
HCO_3^-	118	120	121	120
F^-	2.4	2.8	2.5	—
Cl^-	7.2	8.4	7.7	—
NO_3^-	7.6	7.2	8.4	—
U	0.05	0.25	0.11	(0.3)[a]
Cs	0.62	0.05	0.11	(0.5)[a]
pH	8.10	8.23	7.61	8.23

[a] Reference contaminant concentrations in spiked solution used in Step B4.

B3. **Contaminant leach tests**. Objective: Determine the effective release rates of contaminants from crushed waste material. Conduct ASTM C1308 tests with test Sample D for all field samples of the waste material in SPW solution to measure contaminant release rates; exchange solutions daily for 11 consecutive days. Use of dialysis bags to contain the crushed waste material is recommended. The sample matrix is summarized in Figure 7.5.

Waste Material 1 Sample D in SPW	Waste Material 2 Sample D in SPW	Waste Material 3 Sample D in SPW	Waste Material 4 Sample D in SPW	Waste Material 5 Sample D in SPW	…	Waste Material *n* Sample D in SPW

Figure 7.5 Matrix of test samples used to contaminant release rates.

- React 10 g crushed solids in 100 g SPW solution.
- Replace solution daily.
- Pass each 2-mL aliquant of test solution through 450 nm cellulose filter (SFCA) to remove any suspended solids prior to analysis.
- Dilute filtrate with demineralized water to provide enough test solution for the required analysis.
- Measure contaminant concentrations in all solutions.
- Determine contaminant release rates for all samples.

B4. **Sorption Tests.** Objective: Measure effective sorption of contaminants on the waste material. Conduct ASTM C1733 tests with selected waste material samples and contaminant-doped SPW solutions. ASTM C1733 calls for a preliminary test to determine the time needed to establish steady-state concentrations. It is recommended that small aliquants of the test solution be analyzed at three test durations to confirm system is close to equilibrium (do not replace the solution). Note that the contaminant-loaded Samples H will be retained after the final sorption interval and used in Step B5.

Prepare surrogate solutions doped with various amounts of contaminants for use in Step B4. Span range of concentrations from a minimum value that is lower than the concentration measured in Step B2 to a maximum value similar to the concentration measured in Step B1b. For example:

Solution A: 0.2 mg L^{-1} U + 0.4 mg L^{-1}Cs
Solution B: 0.5 mg L^{-1} U+ 1 mg L^{-1} Cs
Solution C: 1 mg L^{-1} U + 2 mg L^{-1} Cs
Solution D: 3 mg L^{-1} U+ 5 mg L^{-1} Cs (or maximum concentration measured in Step B1b).

Prepare 100 mL of each solution for use in C1733 tests to be conducted with each material. The sample matrix is summarized in Figure 7.6.

Waste Material 1 Sample E in SPW-A	Waste Material 2 Sample E in SPW-A	Waste Material 3 Sample E in SPW-A	Waste Material 4 Sample E in SPW-A	Waste Material 5 Sample E in SPW-A	…	Waste Material *n* Sample E in SPW-A
Waste Material 1 Sample F in SPW-B	Waste Material 2 Sample F in SPW-B	Waste Material 3 Sample F in SPW-B	Waste Material 4 Sample F in SPW-B	Waste Material 5 Sample F in SPW-B	…	Waste Material *n* Sample F in SPW-B
Waste Material 1 Sample G in SPW-C	Waste Material 2 Sample G in SPW-C	Waste Material 3 Sample G in SPW-C	Waste Material 4 Sample G in SPW-C	Waste Material 5 Sample G in SPW-C	…	Waste Material *n* Sample G in SPW-C
Waste Material 1 Sample H in SPW-D	Waste Material 2 Sample H in SPW-D	Waste Material 3 Sample H in SPW-D	Waste Material 4 Sample H in SPW-D	Waste Material 5 Sample H in SPW-D	…	Waste Material *n* Sample H in SPW-D

Figure 7.6 Matrix of test samples used to contaminant sorption isotherms.

- React 10 g of crushed solids + 100 g of doped SPW solution.
- Pass solution taken for analysis through 450-nm cellulose filter to remove suspended solids.
- If needed, quantitatively dilute[9] aliquant with demineralized water and acidify with conc. HNO_3 to stabilize for analysis.
- Determine total amount of each contaminant sorbed.
- Determine individual K_d values and isotherms for each contaminant for each sample.
- Determine range of K_d values for the materials tested and the probability distribution functions.

B5. **Measure desorption**. Objective: Measure extent and rate of contaminant desorption from waste material. Conduct ASTM C1308 tests by adding contaminant-free SPW solution to the test vessel with the contaminant-loaded Sample H immediately after the last test interval in Step B4. Replace the SPW solution daily for a total of four samplings. The sample matrix is summarized in Figure 7.7.

Waste Material 1 Sample H in SPW	Waste Material 2 Sample H in SPW	Waste Material 3 Sample H in SPW	Waste Material 4 Sample H in SPW	Waste Material 5 Sample H in SPW	…	Waste Material *n* Sample H in SPW

Figure 7.7 Matrix of test samples used to measure contaminant desorption.

- React 10 g crushed solids from C1733 test + 100 g fresh SPW solution.
- Filter aliquant of each decanted solution through a 450 nm pore size cellulose filter to remove any suspended solids.
- If needed, quantitatively dilute with demineralized water and acidify with conc. HNO_3 to stabilize for analysis.
- Determine amounts of contaminant desorbed daily and cumulatively.
- Compare total amounts of contaminant sorbed in Step B4 and desorbed in Step B5.
- Determine effective desorption rate for each contaminant for each material.

The testing protocol is shown in the form of an activity flow diagram in Figure 7.8, where the rectangular boxes indicate experimental activities, the rounded boxes indicate analyses, and the text in bold font indicates calculations to be made using experimental results.

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[9] Determine mass of solution aliquant in solution bottle, add known mass of demineralized water to provide sufficient volume for analysis, and add known mass of conc. nitric acid (about 2 drops per 10 mL solution) to prevent precipitation or interactions with solution bottle.

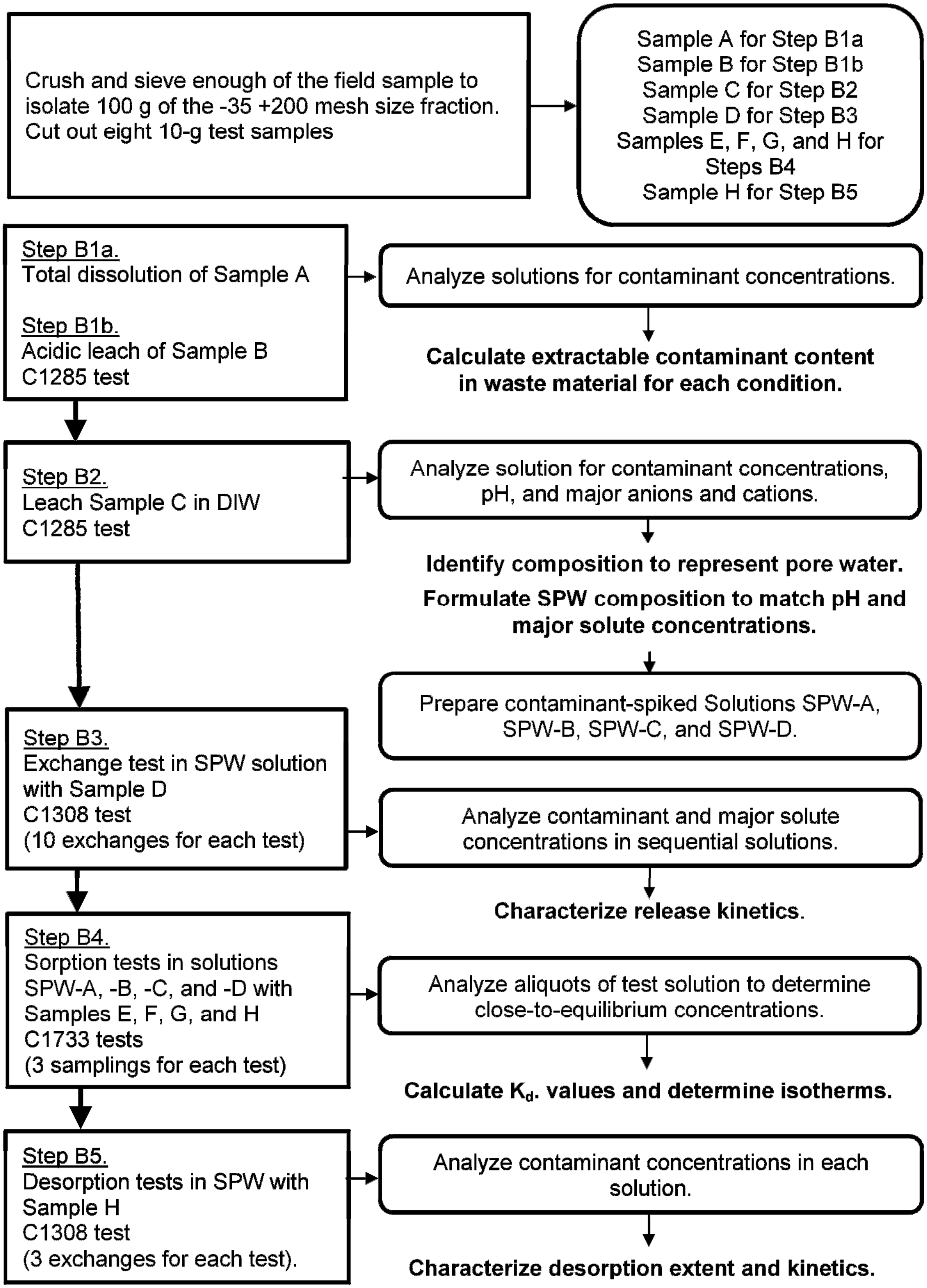

Figure 7.8 Series of batch tests represented as a procedural flow diagram.

7.3 Column Tests

7.3.1 Collection and Preparation of Test Materials

Tests may be conducted with material from a single field sample of the waste material or with a mixture of the excess crushed and sized materials prepared from several field samples for use in the batch tests. If a mixture is used, document the mass of material from each field sample in the mixture.

The column design and test conditions should be selected based on the behavior of the waste material measured in the batch tests. The cross-sectional area and length of the column will affect the relative influences of advection and dispersion and the flow rate will effect the efficiency of the reactions (e.g., through the Péclet and Damköhler numbers as described in Appendix A). In general, low flow rates (e.g., 5 mL h^{-1}) and long columns should be used for waste materials having low contaminant release and sorption rates, and high flow rates (e.g., 20 mL h^{-1}) should be used for waste materials having high contaminant releases and sorption rates.

7.3.2 Loading the Column

Knowledge of the void volume in the column is not used in data analysis, but will facilitate selecting the collection schedule of samples during the initial breakthrough of the conservative species in Step C2. It may also be useful for comparisons with literature data for surrogate natural systems. The void volume includes the volume between particles and porosity in the particles accessible to advective flow. An inert frit or wad of polyethylene or quartz wool should be placed at the bottom of the column to retain the crushed waste material during loading. A known mass of the crushed and sized material should be poured into the column and covered with an inert frit or quartz wool to ensure the crushed waste material is contained while water is passed through the column.

Estimate the void volume in the loaded column, for example, from the mass of crushed waste material that was added (see Section 5.4). The porosity of the material itself (pore volume) and the void volume between the particles of waste material in the column (void volume) must be measured to relate the batch and column test results. The dry density and effective porosity are used to relate the partition function for sorption determined from the batch tests to the retardation factor measured in the column test through Equation 6.15. This can be done most readily before the material is loaded into the column using the following procedure.

Calibrate the graduated cylinder:

- Measure the volume of a graduated cylinder similar in size to the column used in the test apparatus based on the mass of water required to fill to a predetermined height H1 (e.g., to the 25 mL mark in a 25- mL graduated cylinder). Record as V1.
- Empty and dry the graduated cylinder.

Measure the inter-particle void volume representing a packed column:

- Fill the graduated cylinder with dry crushed test material to H1.
- Determine the mass of test material required to fill the graduated cylinder. This is most easily done by weighing the source container before and after transferring the material to fill the graduated cylinder. Record as M1.

Calculate volumes occupied by material and residual void volume.

- From the known density of the test material, calculate the volume occupied by the known mass of material as M1/density. Record as V2.
- Subtract the volume occupied by material from the volume of the graduated cylinder to determine the void volume. Record as V3. (V1-V2 = V3)
- Calculate the void volume per mass of material as V3/M1.

The void volume per mass of crushed material can be used to calculate the void volume of the column based on the mass of material used in the column.

Measure the intra-particle void volume of the waste material:

- Measure mass of weighing pan; record as mp.
- Disperse wet material recovered from a batch or column test in the weighing pan. Weigh the drained (but still wet) material to determine the sum of the pan, material, water on the surface, and water in the void volume. m1
- Measure mass of material occasionally (e.g., twice daily) as surface water evaporates at room temperature to a constant mass in about 3 days; record constant mass as m1 and wet material mass as m2 = m1-mp.

Measure wet density of the crushed waste material with immersion method:

- Weigh a volumetric flask or graduated cylinder having graduation volume vf; record flask mass as mf.
- Quantitatively transfer crushed material into pre-weighed volumetric flask or graduated cylinder and fill with water to graduation mark.
- Weigh total mass flask+wet material+water; record as total mass m3. Calculate volume of wet material as v1 = vf-(m3-m2-mf)/(1 g/cc); record wet volume as v1.
- Quantitatively recover material from volumetric flask or graduated cylinder and place in same glass petri dish.
- Place petri dish with material in oven at 50-90 ºC to dry to a constant mass. Record constant mass as m4 and stable dry material mass as m5 = m4-mp.

Determine pore water mass in the material as m6 = m2-m5; record pore water mass as m6.
Determine pore water volume as v2 = m6/(1 g/cc); record pore water volume as v2.
Determine waste material volume as v3 = v1 –v2; record waste material volume as v3.
Determine the dry density of the waste material as ρ = m5/v3.
Determine effective porosity of waste material as θ = v2/v3.

For example, using the procedure described above, 31.22 g of dry -60 +100 mesh glass (density of 2.52 g cm^{-3} and non-porous) filled a calibrated 25.0-mL graduated cylinder. The volume occupied by this mass of glass is calculated from the glass density to be 12.4 cm^{3}, leaving a void volume of 12.6 cm^{3} (50.4% of the occupied volume) to be filled with water. The pore volume is 12.6 mL. A second measurement with the same glass yielded a void volume of 12.2 cm^{3} (48.7%). Two measurements with -35+60 mesh size fraction glass indicated void volumes of 47.6% and 49.1%. The range of particle sizes in both size fractions was large enough to result in the same packing densities within experimental uncertainty, although the reactive surface areas are different. The average of the ratios void volume/mass glass is 38.1 ± 1.8%, which is useful when the mass of glass in the column is known but not the column volume. A volumetric flow rate of 10 mL h^{-1} through this amount of glass corresponds to 0.82 pore volumes h^{-1} and 19.6 pore volumes day^{-1}, and 137 pore volumes week^{-1}. Running a column test at this rate for one week would consume 1.68 L of SPW solution. Although waste materials are expected to be less dense and more porous than glass, this provides a representative estimate of the amounts of test materials required for the column test.

The amount of SPW solution required to conduct a column test will depend on the flow rate used and test duration. Following the test method recommended in Section 7.3.3, a test conducted for three weeks at a flow rate of 10 mL h^{-1} will require about 5 L of SPW solution; about 1.5 L of that solution is spiked with contaminants.

7.3.3 Three-Step Column Test

The column test is optional but strongly recommended. It is conducted in three steps to monitor the transport of a square pulse of contaminant through the column. The initial part (Step C1) is designed to attain steady-state flow conditions prior to the pulse and measure the subsequent release of contaminants into the SPW solution under dynamic conditions. The second part (Step C2) introduces high concentrations of the contaminant(s) and a conservative species to measure the initial breakthrough curves of the conservative species at the beginning of the pulse and the new steady-state behavior of the contaminant that may be attained (depending on the sorption kinetics). The third part (Step C3) returns to the low contaminant concentrations in the SPW solution to measure the decreasing contaminant concentrations and tailing leg at the end of the pulse.

C1. Measure the contaminant release behavior at a constant flow rate of the SPW solution. Collect samples of the eluate twice daily for about two weeks to track the concentrations of contaminants and major solutes representing the dissolution of constituent phases. Measure the mass and duration of each eluate sample that was collected to calculate volumetric flow rate. Adjust the pump speed if necessary. Record the overall test duration (i.e., from when the column was initially filled with SPW solution) at the time each sample is collected. A schematic diagram of the C1 test is shown in Figure 7.9.

Figure 7.9 Schematic flow diagram for column test Step C1.

C2. Measure the transport of conservative solute (NaBr) and contaminants at a constant flow rate of the spiked SPW solution (e.g., SPW-C). Switch the input line to the spiked SPW-C solution reservoir and note the overall test duration when the switch was made. Samples should be collected frequently (e.g., every 12 hours) during the first two column volumes to better track the breakthrough of the conservative species. Continue to collect samples of the eluate twice daily for about three weeks to track the concentrations of contaminants and major solutes representing the dissolution of constituent phases. Measure the mass and duration each eluate sample to calculate volumetric flow rate. Adjust the pump speed if necessary to maintain a nearly constant flow rate. Record the overall test duration at the time each sample is collected (i.e., from when the column was initially filled). A schematic diagram of the C2 test is shown in Figure 7.10.

Figure 7.10 Schematic flow diagram for column test Step C2.

C3. Measure the tail of the breakthrough curves for contaminants at a constant flow rate of the SPW solution. Switch the input line from the spiked SPW solution reservoir back to the SPW solution reservoir and note the overall test duration the switch was made. Continue to collect samples of the eluate twice daily for about three weeks to track the concentrations of contaminants and major solutes representing the dissolution of constituent phases. Measure the mass and duration of each eluate sample collected to calculate volumetric flow rate. Adjust the pump speed if necessary. Record the overall test duration (i.e., from the time the column was initially filled) when each sample is collected. A schematic diagram of the C3 test is shown in Figure 7.11.

Figure 7.11 Schematic flow diagram for column test Step C3.

It is recommended that the column continue to be flushed until the contaminant concentration decreases to near the steady-state concentration measured at the end of Step C1 before starting another experiment at a different flow rate.

The column test protocol is provided in the form of an activity flow diagram in Figure 7.12.

7.4 Expected Test Results

Figure 7.13 illustrates the input solution concentrations and output solution results expected during the three steps of the column test experiment for a waste material of low porosity and high K_d. During Step C1, the contaminant concentration in the effluent increases slightly as SPW solution is passed through the column and a small amount of contaminant is released from the waste material. To facilitate discussion, consider Step C1 to pass two pore volumes. The influent is changed to a solution of SPW that is spiked with a high contaminant concentration (e.g., SPW-C) and a conservative species (such as Br^-) at the beginning of Step C2. Transport of the conservative species without retardation due to sorption and minor retardation due to the porosity of the waste material is rapid, whereas transport of the contaminant is slowed due to both sorption and porosity. After about two pore volumes have passed, the concentration of the conservative species in the eluent is the same as in the influent. The concentration of the contaminant increases throughout Step C2 until the sorption

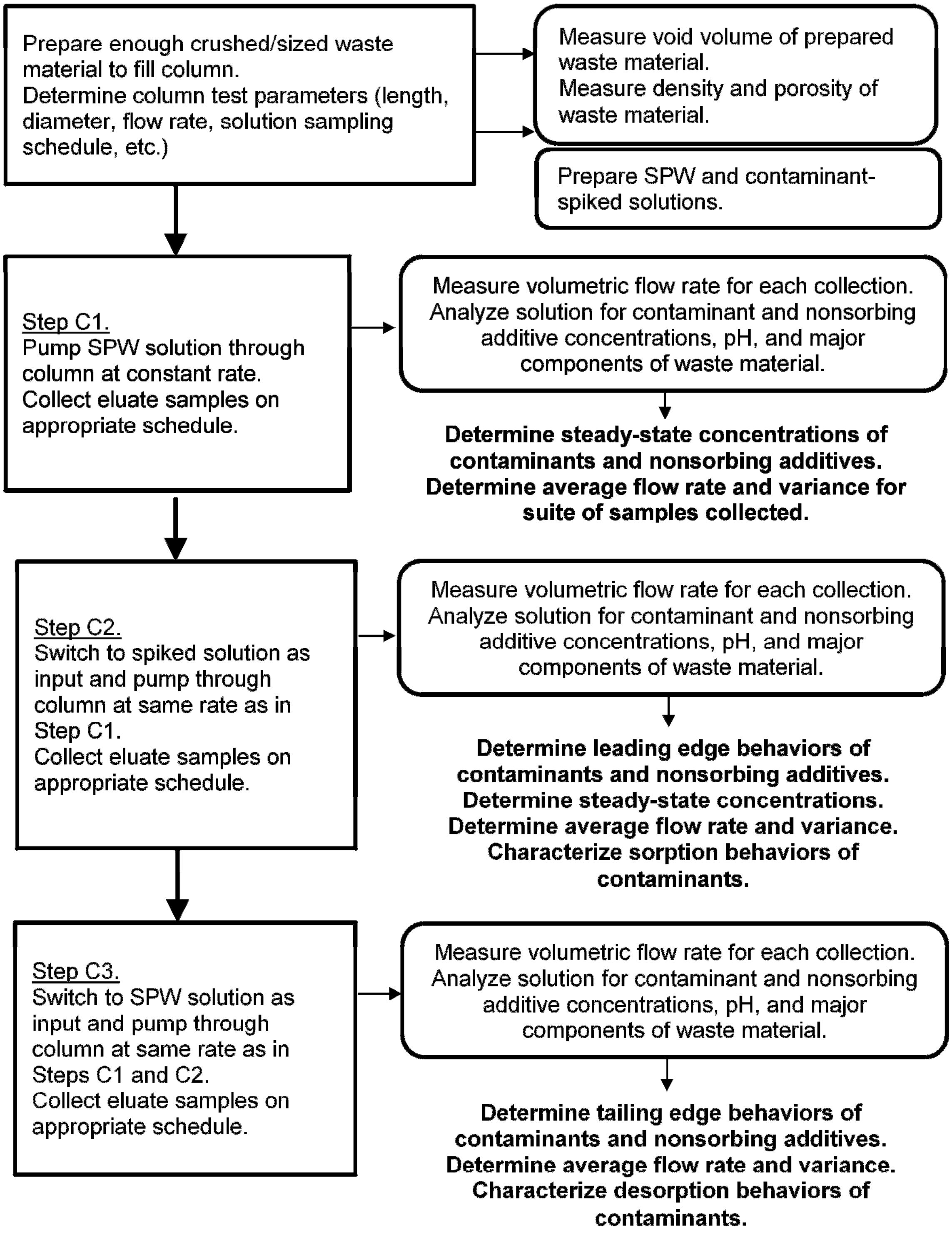

Figure 7.12 Series of column tests represented as a procedural flow diagram.

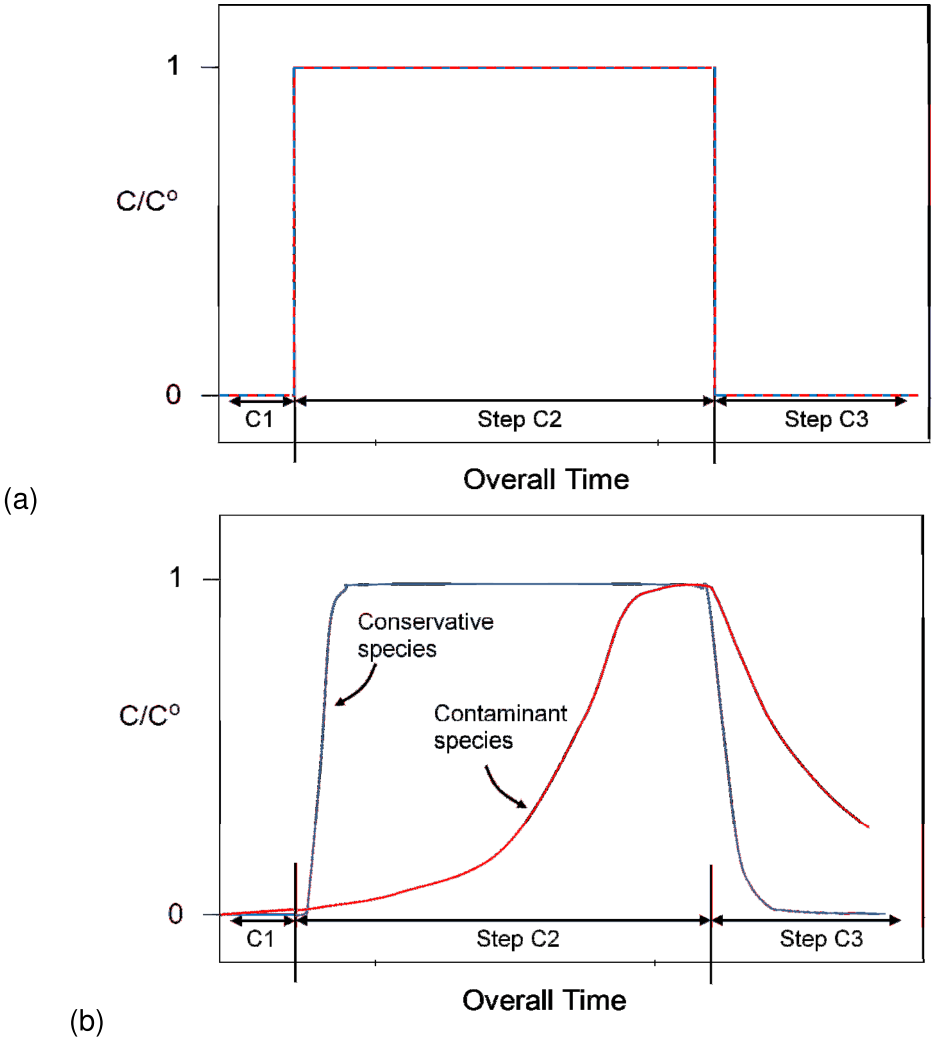

Figure 7.13 Illustration of anticipated column test results (a) input solution concentrations and (b) effluent solution concentrations.

sites are saturated and the concentration of the contaminant is the same in the influent and effluent. In Step C3, the influent is changed back to the SPW solution and the conservative species is flushed out of the column within two pore volumes. The contaminant species is desorbed slowly over many pore volumes.

The contaminant concentration decreases at a rate that depends on the desorption kinetics. Strongly sorbed contaminants might not be completely eluted during practicable experimental durations. The slow sorption and desorption behavior would have been observed in the batch tests (Steps B4 and B5) and indicated the benefit of using a short column to expedite the saturation and elution steps or long test duration to track desorption.

Figure 7.14 shows schematically how the values measured in the batch tests can be used to determine probability distributions for parameter values that can be used in field-scale modeling. While it is not expected that enough field samples will be tested to generate an occurrence plot similar to that shown in Figure 6.1, the experimental results can be weighted by the relative

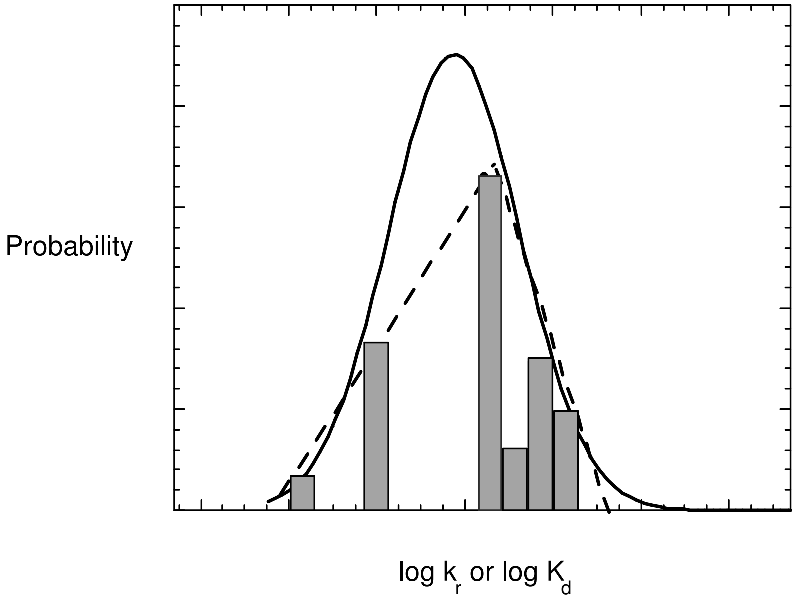

Figure 7.14 Illustration of using parameter values measured in laboratory experiments (bars) to generate a probability distribution for modeling at the field scale (dashed lines and solid curve).

abundance of waste material represented by each field sample. The heights of the bars in Figure 7.14 indicate the weights assigned to values measured in tests with individual samples of the waste material based on characterization of the waste pile. For the example in Figure 7.14, the measured values plotted from left to right are weighted to represent 4%, 20%, 40%, 8%, 16%, and 12% of the waste pile volume. The probability distribution for the parameter values used in field-scale calculations could be represented by the normal distribution shown by the solid curve or the skewed triangular distribution shown by the dashed lines to weight the distribution according to abundance. Other statistical weightings could be used to represent preferential pathways, regions with higher contaminant concentrations, etc. This shows the value of collecting many field samples (e.g., 60 samples instead of 6) to define the probability distribution of parameter values.

7.5 Comments on Section 7

The recommended testing protocol is consistent with approaches used to model contaminant transport in soils and fractured porous media. Characterization of the sorption effects and flow effects matches issues important to those systems. Tests for modeling waste piles must include characterization of contaminant sources that are distributed throughout the matrix and surfaces of waste pieces. The approach is designed to obtain effective values of two key parameters needed for reactive transport modeling using the advection-dispersion equation: contaminant release rates and retardation factors. The release rate accounts for dissolution of the host phases or leaching of contaminants, and effective retardation factors account for sorption and other processes that slow contaminant transport. The test methods also provide insights into the contaminant release mechanisms (leaching or dissolution of the host phases) and matrix properties (porosity, matrix diffusivity of contaminants, and suction pressure) that will inform the selection of an appropriate surrogate geology to represent the waste pile for modeling transport through the fractures. While the testing approach is based on expected responses of slag and concrete wastes, some modifications will likely be required for particular materials. For example, crushing concrete to the small particle size that is called for may change the characteristics of the pore structures to the point that important mass transport limits are eliminated. Other measurements with specimens in a larger size fraction may be required to provide some of the necessary information. Application of the measured properties to model calculations may also require some modifications of the parameter definitions, such as for lumping oxidation and dissolution processes for multivalent contaminants. The approaches discussed in Section 6 provide general examples, but some details will likely need to be modified to better suit application to particular slag or concrete materials.

The execution and analysis of the batch tests are straight-forward and routine and provide direct (or nearly direct) measurements of parameter values. The column test is much more experimental in nature and requires more analyses to extract model parameter values than is required for the batch tests. The test responses in column tests will be sensitive to the material, the test conditions, and the column design. Several key aspects are discussed, but no specific guidance is provided on the design. This is because some of the parameters affecting the design will not be known until preliminary tests (or batch tests) are conducted, particularly the contaminant release rates. Previously used designs available in the literature should be used as a starting point. Aspects typically considered in column design are summarized in Appendix A.

8 SUMMARY AND COMMENTS

The primary objective of the analyses described in this report was to recommend a laboratory testing protocol that can be used to support and inform assessments of surface waste disposal sites . A conceptual model for a generic waste pile comprised of slag or concrete rubble was developed with the sole purpose of identifying the characteristics of contaminant release and transport that should be quantified to support evaluations of regulatory compliance. That conceptual model is not proposed for use in actual site analyses. The characteristic values measured in the laboratory tests provide values for parameters in the advection-dispersion equation, which is the mathematical foundation of all reactive transport models. Various formulations of the ADE include terms for advection, dispersion, and various sources and sinks that exist in the system. The testing protocol provides data that can be used to determine the appropriate analytical forms for the contaminant source terms due to host phase degradation (e.g., corresponding to dissolution and leaching rate laws) and to the retardation of transport due to sorption (e.g., in the form of sorption isotherms).

The recommended testing protocol includes test methods that can be conducted without sophisticated equipment or instrumentation to provide meaningful measures of the waste material resistance to weathering and releases of contaminants. Based on evaluation of current reactive transport approaches, it is expected that these data can be utilized in computer simulations to estimate long-term weathering behavior and contaminant release. Whereas it is possible to characterize the weathering behavior of a particular sample of the waste material very precisely and in detail, such an effort is unwarranted due to both the uncertainties associated with the heterogeneities in the properties of the waste at the scale of the system and the current limitations on taking that detailed information into account in contaminant transport models. Instead, the overall behavior of several 10-g samples of the waste material is measured empirically and treated statistically to represent the overall behavior of the waste pile.

The waste pile is modeled conceptually as a highly fractured medium in which the pieces of waste material are represented by the matrix blocks and the voids between the pieces are represented by the fractures. Continuum models developed for soils and fractured rock can be applied to the separate (or combined) matrix and fracture systems, and geostatistics can be used to account for the heterogeneities in the material and distributions of contaminants. This eliminates the need to estimate separately the surface area of the waste material and the volume of voids between the pieces (which is impossible) and transforms the scaling of laboratory-measured values to field systems from a surface area-based approximation to either a mass-based or volume-based approximation of the entire waste pile. Just as the continuum approach is used to upscale heterogeneities present at the atomistic scale using volume averaging, heterogeneities on the mesoscale of laboratory measurements and waste pieces can be upscaled to the large scale of a waste pile using geostatistics. However, that requires subjecting many samples to the testing protocol to capture the heterogeneities of the waste pile within the probability distribution functions to support the upscaling. This approach allows well-established reactive transport and geostastical modeling techniques to be applied when modeling the waste pile, which provides several benefits:

- It allows characteristics measured for natural systems to be used as surrogates for transport behavior in waste systems.

- It provides analytical solutions to reactive transport equations that include terms for contaminant release, sorption, and radionuclide decay that directly link laboratory measurements to assessment calculations.
- It provides the flexibility to model porous and nonporous waste materials by using different parameter values and the dual porosity (or dual permeability) technique.

The dual porosity model is a continuum technique in which the matrix blocks (waste pieces) and fractures (voids between the waste pieces) are treated as separate systems with distinct property values, but are coupled to allow material to exchange between them. Pore water and contaminant transport occurs by advection through the fractures and by diffusion through the matrix blocks. The recommended approach is to relate the laboratory experiments to characterization of the bulk and surface properties of the matrix blocks (pieces of waste) to provide parameter values for the contaminant source and sink terms that are used in the matrix and the fracture transport calculations. Different forms of the ADE and different parameter values can be used for the matrix and fracture models. For example, sorption at fractures and in the matrix material could be represented by different isotherms highlighting sorption measured for low and high contaminant concentrations, respectively. Likewise, different contaminant inventories can be assigned to fractures and the matrix material based on the amounts of contaminants released readily in Step B1 or requiring the aggressive conditions in Step B2.

Reactive transport models typically provide breakthrough concentrations for injected contaminants exiting the layer of interest. These can result in peak or steady-state release values depending on the input profile of water and the relative importance of matrix and fracture transport to the overall release of contaminants. In the case of contaminant transport in waste piles, the contaminant sources are distributed throughout the pile and are expected to show steady state releases from fractures and matrix material that depend on water percolation rates. The breakthrough from fractures is expected to dominate systems with nonporous waste materials as a relatively early peak, whereas the breakthrough for porous waste materials is expected to occur later with a very broad profile. The water percolation volume and rate must be inferred from regional meteorological data and measurements for similar geologies that can be considered analogues for groundwater transport properties.

8.1 Comments Regarding Laboratory Test Protocol

A challenge in recommending a testing protocol was achieving the proper balance between the use of simple and routine laboratory tests and the more sophisticated experiments supporting reactive transport modeling that require greater expertise. The approach taken was to recommend simple tests that can be used to derive parameter values and also provide insights into the waste behavior regarding the release of contaminants as the host phases are weathered and the effective retardation of contaminant transport due to the combined effects of sorption, solution concentration limits (solubility), size filtration, etc.

One of the important issues first considered when developing the testing protocol was scaling the laboratory results for use in field-scale calculations. In terms of the continuum modeling discussed in Section 2, the laboratory test specimens serve as REV on the mesoscale for the chemical reactions occurring in the system, including the contaminant release rates, concentrations, and sorption onto other constituent phases. Therefore, it is important that the sub-samples of crushed material that are prepared from the field samples represent the vicinity of the waste pile from which they are taken. Methods developed to produce representative sub-samples for testing should be utilized or simulated, such as using a riffle splitter. For example, the entire field sample should be crushed enough to separate a representative one-fourth of the material for further crushing, with one-quarter of the resulting pieces used in the next step, and so forth until an adequate amount of sized material is prepared for testing. The results of laboratory measurements for samples taken from many locations provide probability distributions for reaction parameters that can be used in field-scale calculations following the example discussed in Section 7.4.

Geostatistical methods developed to account for the heterogeneity of natural systems can be utilized for modeling waste systems. These methods relate observations and measurements made on the small scale of laboratory experiments to the larger field scale of the systems of interest. Heterogeneities in the wastes produced during an industrial operation are equivalent to large-scale heterogeneities that occur in geologic systems due to variations in the formation conditions. The analysis of samples collected from many locations of a waste pile or geologic formation is necessary to determine the range of property values for the system and establish the probability distributions of parameter values needed for reliable modeling at the field system. This was discussed in Section 2.

Similar sensitivity studies are recommended for modeling waste piles to assess the relative importance of both the model parameter values and the uncertainty in each parameter to contaminant release. These sensitivity calculations can prioritize laboratory testing, such as the number of samples to subject to batch tests to determine the distribution of values representing the dissolution rate or K_d, the range of pore water flow rates to be evaluated, and relevant column characteristics necessary to decrease the influence of dispersion on the test result and highlight the kinetics of contaminant release and sorption.

The key information provided by the laboratory tests includes

- The relative importance of release from the surface and interior of the pieces of waste material.
- Representative pore water compositions.
- The effective mode of contaminant release (surface dissolution or leaching).
- The effective release rates of contaminants.
- The characteristics of the sorption isotherm (linear or non-linear).
- Effective K_d values for contaminants of interest.
- The relative importance of desorption.

The approach recommend for waste materials does not measure or model the behaviors of individual host phases (or other constituent phases). Rather, the effective behavior of the collection of phases is measured in the batch and column tests for both contaminant release and contaminant sorption properties.

Tests conducted with samples collected from various locations of the waste pile are used primarily as a measure of the spatial variance and range of parameter values to quantify the heterogeneity of the waste pile, but are also used to formulate a surrogate pore water solution for use in the tests to characterize the contaminant release and concentration. It is recommended that a reasonable number of samples be collected for use in ASTM C1285 tests to produce representative pore water solutions and that judgment be used to select one solution as the surrogate pore water solution. As many samples as practical should then be tested to determine a range of responses and the variance of the effective dissolution rate in that solution and K_d values for a range of contaminant concentrations. Measuring the range of values for materials distributed throughout the pile, both across the surface and at various depths, is more important than the precision of measuring a single value. This information is used to provide the probability distributions that can be used in field-scale calculations.

In addition to the basic parameter values for contaminant release and sorption, the tests provide information relevant to the mechanisms to support more detailed modeling. The behavior of crushed waste materials measured in ASTM C1308 solution exchange tests can be used to represent the matrix behavior of the material, including the relative importance of matrix diffusion. The initial sampling of the ASTM C1308 test to measure contaminant release can be used as a measure of the release due to surface run-off. This also provides a value for dissolution at the fracture walls. Subsequent samplings are used to determine parameter values for matrix diffusion and dissolution of the host phases (e.g., by application of the Dankwerts-Godbee-Joy equation; see Ebert 2010). The effective diffusion coefficient determined from the ASTM C1308 test results for contaminants released by leaching can be used to inform the selection of the matrix diffusion coefficient used in the transport model. If the diffusion coefficient is high, contaminant transport will likely be dominated by matrix transport, whereas a negligibly low value of the diffusion coefficient indicates transport will likely be dominated by surface reactions and fracture flow. This information can be used to select a representative natural system for modeling transport through the pile. The measured diffusion coefficient can be compared with the range of matrix diffusion parameter values that have been measured for tuff, granite, clay, and other systems.

Optional column tests provide additional insights into the behavior of the waste material in a dynamic reacting system. This includes calibrating (optimizing) the parameter values for contaminant release and sorption measured in the batch tests by inverse modeling, evaluating the effect of the flow rate on the “efficiency” of host phase dissolution and sorption, and characterizing alteration of the waste material as it weathers.

8.2 Comments Regarding Uncertainty

How well current models represent release behavior in waste piles is affected by how well the reactive transport model represents the weathering behavior of the system, uncertainties in the analytical expressions used to represent the contributing processes and their couplings through terms used in the underlying ADE, how well experimentally measured values represent the model parameters, and the experimental uncertainties associated with measuring those values. Some uncertainties related to test execution and specific derived parameter values are quantifiable, but other uncertainties are essentially unmeasurable. The inability to quantify discrete uncertainties on the field scale relevant to waste piles is addressed statistically. In this way, uncertainties in the measured values for model parameters and the efficacy of the analytical parameters to represent the contributing process are transformed to probabilities and ranges of input values and modeled responses. The modeled responses can only be compared with measured field responses to evaluate the consistency of the analytical model and measured parameter values. This is done by inverse modeling, the accuracy of which is limited by the data set.

Application of the ADE to modeling waste piles will be characterized by many degrees of freedom and few data for calibration by inverse modeling. Calibration (optimization) is a process in which input parameters are adjusted until the model outputs match experimental or field observations. The model input parameters include all properties required to run the model and the output values may include flow rates, contaminant arrival times, concentrations, or masses, etc. The input parameters are uncertain regardless of how well a site has been characterized, perhaps due to deficiencies in the conceptual model and inadequate estimates of parameter values. Because initially assigned parameter values seldom lead to an acceptable output, calibration is used to optimize the parameter values, the analytical form of the model, and the regions to which the model applies. Model calibration is an inverse modeling process. It is assumed here that the suite of field observations made for a waste pile, if any, will be inadequate to calibrate the parameters measured for the waste materials in laboratory tests with field data. Instead, the use of a controlled experimental system (i.e., the column tests) is recommended to generate data that can be evaluated with inverse modeling using the ADE to support (verify) the parameter values measured for contaminant release and sorption. The focus of the calibration effort is on key properties associated with the waste material (namely, the chemical contaminant release and sorption properties and physical transport of contaminants within the waste material itself) rather than those associated with transport through the waste pile. This provides the best support to evaluations of the regulatory compliance of various waste materials.

Model verification is based on the successful application of the calibrated model to reproduce an independent observation (i.e., data that were not used to calibrate the model). This could be as simple as predicting the test response of a field sample based on the pooled results of other field samples (i.e., the pdf based on the range of dissolution and sorption properties measured for different samples of the waste material). Model validation is based on the capacity of the model to predict future observations under particular conditions. The IAEA (2003) defines validation as

> “**validation, model.** In *radioactive waste management*, the process of building confidence that a *model* adequately represents a real system for a specific purpose.”

Sensitivity is a measure of the effect of changing one parameter (usually an input parameter) on the value of another (usually an output parameter). Sensitivity analyses are used for (1) evaluating the overall response to changes in specific model parameters, (2) relating the uncertainty in the model results to uncertainty in the model parameters, and (3) determining how well parameter values will likely be estimated by inverse modeling. Varying the flow rate or column dimensions in column tests provides a measure of the overall sensitivities of reaction and transport processes, but may change the relative importance of processes such that it no longer represents the natural system of interest. Likewise, the composition of the pore water used in the batch or column tests can be varied, the exchange intervals or mass ratio used in the ASTM C1308 tests can be varied, etc. Sensitivity analyses are more efficiently conducted by first modeling the impact, and then confirming that prediction by testing.

8.3 Final Comments

In the absence of a specific assessment model for waste piles, a conceptual model was defined that utilizes recent advances in modeling contaminant transport in geological media. In particular, the continuum approaches developed for groundwater transport through soils recently applied to fractured porous media, such as tuff at Yucca Mountain, can be further extended to model piles of contaminated slag and concrete. Likewise, the underlying mathematics used for reactive transport in geological media, including the percolation of groundwater through porous fractured rock, can be applied for modeling percolation of pore water through surface waste piles. Key advantages of modeling the pile as a fractured porous dual continuum are (1) defining the surface area of the waste material is not required, (2) effective values of important material parameters, including the release rates of contaminants from host phases and sorption of dissolved contaminant species, can be used to represent the complex phase composition and heterogeneous phase distributions, and (3) transport properties can be estimated by comparisons with previously evaluated regoliths having similar characteristics.

Confidence in the suitability of the recommended testing approach was provided by a brief review of groundwater transport work by hydrologists and soil scientists. That literature provides a large number of studies that can be used as templates for developing models and supporting testing programs to address specific waste piles. Enough of the literature was reviewed to evaluate the applicability of key aspects of reactive transport and continuum modeling contaminant transport through a waste pile to provide confidence the recommended tests will to provide parameter values necessary for modeling the weathering of slag and concrete waste materials.

Standardized test methods that are simple and economical to conduct are recommended for characterizing large numbers of waste material samples to provide statistical distributions of the source term and sorption values used in reactive transport modeling relevant to the scale of the surface disposal system. The objective of the recommended protocol was to provide the key information needed to conduct meaningful assessments of surface disposal systems with the minimum amount of laboratory testing that could be performed by licensees and most commercial laboratories. This protocol provides a useful simple initial approach to addressing a complex problem. Additional column tests that can be conducted to study the coupling of the source terms and sorption terms with the transport parameters were recommended as the next step to establish the scientific basis for performance models.

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APPENDIX A

DIMENSIONLESS NUMBERS

Dimensionless Numbers

Dimensionless numbers are used in modeling breakthrough curves from column and field measurements. Dimensionless numbers represent parameter values that have been normalized to characteristic values for the system being studied to be scale-independent. Converting the partial differential form of the ADE to its dimensionless form describes the relative importance of contributing dynamic processes (e.g., Pang and Close 1999; Steefel and Maher 2009). This is valuable for column design and upscaling experimental results to field scale.

A.1 Fundamental Dimensions

Fundamental dimensions of length and time are represented by the characteristic dimensions of the system. These could be the column length for experiments or the depth of the waste pile for modeling used for the length variable, and characteristic rates for diffusion, advection, or reaction for the time variable. Comparing characteristic advection and diffusion length and time scales for the system being modeled provides an indication of when approximations apply. Characteristic length and time scales for advection are

$$L = v\,t \tag{A.1}$$

and

$$t_A = \frac{L}{v}. \tag{A.2}$$

The scales for diffusion are

$$L = (D\,t)^{0.5} \tag{A.3}$$

and

$$t_D = \frac{L^2}{D}. \tag{A.4}$$

A characteristic time for the general reaction

$$rate = A\,k\left(1 - \frac{C}{C_{eq}}\right) \tag{A.5}$$

is

$$t_R = \frac{C_{eq}}{A\,k}. \tag{A.6}$$

These characteristic scales provide a rough solution to transport problems that can aid in the design or assessment of the test system. Note that radionuclides add another time scale based on the half-life.

Three examples of dimensionless numbers have been used in analyses presented above: the retardation factor, the number of pore volumes, and the relative concentration. The relative concentration is the ratio of the eluate concentration to the (constant) input concentration:

$$C_r = \frac{C}{C_0}. \quad \text{(A.7)}$$

The pore volume is the volume available to the fluid passing through a porous column. The number of pore volumes passed during a particular test duration is calculated as

$$PV = \frac{v_w t}{L}, \quad \text{(A.8)}$$

where

PV is the number of pore volumes (—)
v_w is the linear velocity of the water in the column (L T^{-1})
t is test duration (T)
L is the column length (L).

The PV provides the dimensionless time. The retardation factor is the ratio of the contaminant velocity to the velocity of the groundwater (see Bouwer, 1991)

$$R = \frac{v_c}{v_w} = 1 + \frac{\rho_d K_d}{\theta}, \quad \text{(A.9)}$$

where

R is the retardation factor (—)
v_c is the linear velocity of the contaminant (L T^{-1})
v_w is the average linear velocity of the water in the column (L T^{-1}).

Two important dimensionless numbers that are used to characterize columns and interpret and scale test results are the Péclet and Damköhler numbers. These are used to characterize the relative effects of flow and hydrodynamic dispersion and the relative effects of flow and chemical reactions on test responses, respectively. It is important to design a column test to ensure that the measured response is sensitive to the process of interest relative to the imposed advection rate to correctly model the response and determine model parameter values. Different conditions (primarily flow rate and column length) will be required to highlight the diffusion, dissolution or leaching, and sorption processes. This is also important for relating the laboratory test results to the field conditions (and vice versa). The Péclet and Damköhler numbers are discussed in more detail in the following sections.

A.2 Pêclet Number

The Péclet number is a dimensionless quantity relating the effectiveness of mass transport by advection to that by either dispersion or diffusion. It relates the relative velocity and diffusion of a system as

$$\mathrm{Pe} = \frac{v\,x}{D_d}\,, \tag{A.10}$$

where

Pe is the Pêclet number (—)
v is the linear velocity of the leachant in the column (L T^{-1})
x is the spatial coordinate in the direction of flow (L)
D_d is the molecular diffusion coefficient in solution (L^2 T^{-1}).

The spatial coordinate could be the average grain diameter in a packed bed. The Pêclet number can be thought of as the ratio between the advective and diffusive time scales. The hydrodynamic dispersion coefficient is the sum of the longitudinal dispersion coefficient and the molecular diffusion coefficient in pure solution. The Pêclet number quantifies the effects of mechanical dispersion that arise from the variations of solute velocity in a porous medium due to friction with grains, flow paths, and mixing. As physical dispersion becomes more significant, the Pêclet number becomes smaller. From Equation A.1, high values of the diffusion coefficient or low flow rates give small Pêclet numbers, whereas small diffusion coefficients and high flows give large Pêclet numbers. Figure A.1 shows the ratio of the longitudinal dispersion and diffusion coefficients plotted against the Pêclet number for measurements in sand (data from Fetter, 1993 Figure 2.7), where D_L is the longitudinal dispersion coefficient and D_d is the molecular diffusion coefficient in solution.

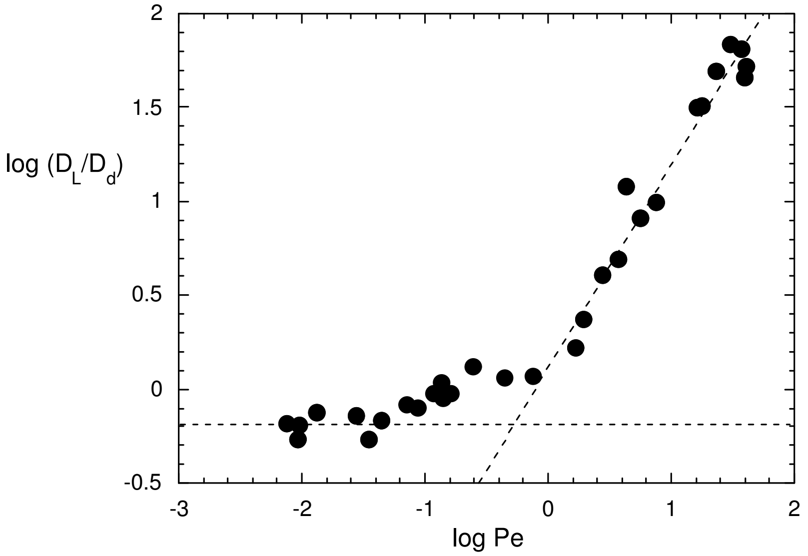

Figure A.1 Plot of dispersion coefficients against Pêclet number for measurements in sand.

The dispersion at values of Pe less than about 0.1 (log Pe < -1) is independent of the flow rate and indicates a dominance of diffusion, whereas the dispersion of values greater than about 1 (log Pe > 0) is proportional to Pe and indicates dominance by advection. At Pe values between these limits, dispersion is affected by both advection and diffusion. The spatial coordinate x is related to the average size of the particle and the y-value under diffusion control reflects the tortuosity for transport through the sand.

Column design and test conditions yielding sufficiently high Pêclet numbers that dispersion effects can be neglected allows the reaction transport equation representing the test system to be simplified. Selection of both the flow rate and grain size used in column tests will affect the relative contributions of mechanical dispersion and diffusion on the measured transport properties. Bear (1972) related the diffusional Pêclet number to transport zones through columns with different particle sizes, which is illustrated in Figure A.2 for the case of a solution diffusion coefficient with the value $D_d = 1 \times 10^{-5}$ cm^2 s^{-1} at 25 ºC (modified from Figure 12 in Oelkers, 1996). Mechanical dispersion becomes more important than diffusion as the particle size and flow rate increase. The horizontal dashed red line indicates an average particle size of 0.05 cm, which corresponds to 35-mesh. In this case, molecular diffusion dominates mechanical dispersion at flow rates below about 25 m y^{-1} (0.07 m d^{-1}) and longitudinal mechanical dispersion dominates at flows above about 316 m y^{-1} (0.9 m d^{-1})[10]. Both processes contribute at intermediate flows.

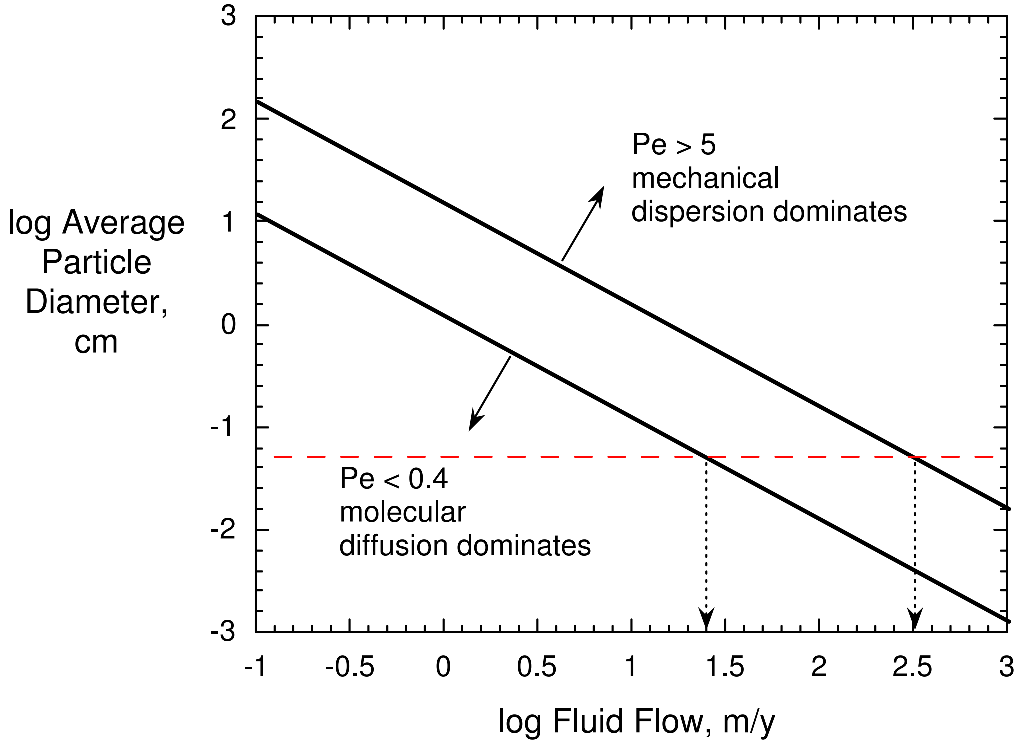

Figure A.2 Illustration of relationship between particle size, flow, and transport process.

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[10] Note that Figure A.2 is a log-log plot.

A.3 Damköhler Number

The Damköhler number relates the time scale of a chemical reaction rate to the flow rate as:

$$\text{Da} = \frac{\text{chemical reaction rate}}{\text{advective mass transport rate}} \tag{A.11}$$

or

$$\text{Da} = \frac{\text{characteristic fluid residence time}}{\text{characteristic chemical reaction time}} \tag{A.12}$$

The definition of the Damköhler number depends on the system being evaluated. In a continuous reactor, the Damköhler number for a general reaction A → B is

$$\text{Da} = k_c \, C_o^{n\text{-}1} \, \tau , \tag{A.13}$$

where

Da is the Damköhler number (—)
k_c is the rate constant of the chemical reaction (T^{-1})
C_0 is the initital concentration ($M\ L^3$)
n is the reaction order (e.g., 1)
τ is the mean residence time (T).

Low values indicate low conversions of reactant to product and high values indicate high conversions. For example, Da < 0.1 may result in 10% conversion while Da > 10 generally result in 90% conversion. When applied to the dissolution of contaminant-bearing host phases present as inclusion in a waste matrix, the degree of conversion could represent the extent of dissolution to free the contaminants or sorption of contaminants. For a column dominated by advective transport, the Damköhler number can be expressed as

$$Da = \frac{k_c \, L}{v} , \tag{A.14}$$

where

Da is the Damköhler number (—)
k_c is the rate constant for first-order chemical reaction (T^{-1})
L is the column length (L)
v is the velocity of the leachant ($L\ T^{-1}$).

In the column tests, both the dissolution reactions and the sorption/desorption reactions must be considered; these will likely have different Damköhler numbers. These provide a useful indication of the relative importance of the reaction kinetics. For high Da, the reaction can be considered to be at local equilibrium, whereas for low Da, the reaction should be treated kinetically. There is always a theoretical length scale over which local equilibrium could be attained under steady state conditions, but that length may not be attainable in laboratory test columns or even geological environments (Steefel and Maher 2009). Where local equilibrium is reached, the reaction becomes transport-controlled. Steefel and Maher (2009) have emphasized the important consequent that rates measured at length scales less than the equilibration length (typical for laboratory tests) will be controlled by reaction kinetics whereas rates measured at length scales greater than the equilibration length (typical for field scale) will be controlled by transport and be necessarily slower than the former. Because the objective of the column tests recommended in this protocol is to calibrate the parameter values describing the dissolution and sorption reactions, test conditions should be selected such that most data represent control by reaction kinetics. This can be done through the column length, solution flow, and/or particle size.

A.4 Combined Pêclet and Damköhler Numbers

The product of the Pêclet and Damköhler numbers relates the chemical reactions to dispersion irrespective of advection. For example, a key design factor for membrane reactors is the ratio of maximum reaction rate per volume over maximum permeation rate per volume. Figure A.3 shows the conversion of cyclohexane to benzene, using a molecular sieve membrane catalyst, becomes more efficient at smaller PeDa numbers (Battersby et al., 2006). The system is optimized (i.e., provides maximum conversion) when the transport rate of reactants is equal to the chemical reaction rate, which occurs when PeDa = 1. The efficiency of a conventional reactor, which is shown by the dashed line, is not affected. This example, though for a system different than water percolating through a waste pile, shows the possible artifacts that can be imposed by the design of a column test system. In the column tests, the particle size, column length, dissolution and sorption rates, and the solution flow rate will all contribute to the test response. The dependence of the dissolution and sorption rates on the solution composition will also impact the test response. It is important to understand the column behavior before relating the response to the behavior of a natural system. Conversely, it is important to design the column test such that the measured responses will reflect the processes being evaluated, whether reaction, sorption, advection, or dispersion.

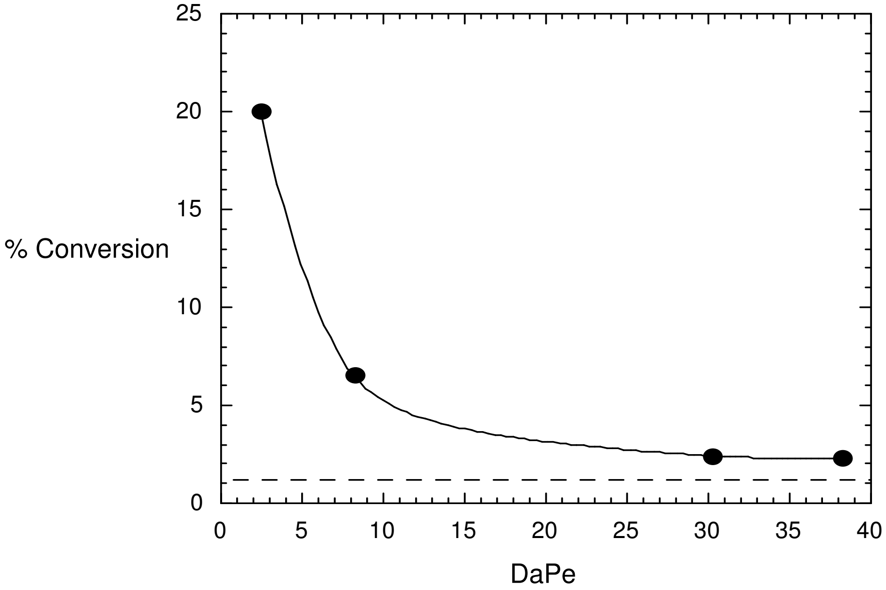

Figure A.3 Effect of the product of the Pêclet and Damköhler numbers on catalytic efficiency.

APPENDIX B

FORMULATION OF SURROGATE PORE WATER SOLUTION USING GEOCHEMIST'S WORKBENCH

Formulation of a Simplified Pore Water Solution Using Geochemist's Workbench

The objective of formulating a simplified surrogate pore water formulation is to facilitate production of large volumes of a stable and reproducible solution that represents water that has percolated through the waste pile for use in batch and column tests over several months period. The approach is to evaluate the stability of the composition generated in the ASTM C1285 test by calculating the electrical balance, theoretical pH, and saturation indices of potential precipitates using geochemical models such as Geochemist's Workbench (Bethke and Yeakel, 2009). The same calculations are then made with the proposed simplified composition, except the pH is adjusted to match the value measured in the C1285 solution by the addition of strong acid or strong base. The stability of the resulting solution is then evaluated, including the saturation indices of potential precipitates, and compared to the stability of the C1285 solution. The proposed composition can be adjusted to better match the C1285 solution. In most cases, matching the pH will be most important. This is because the dissolution and sorption rates are expected to be most sensitive to the pH. Solutions generated in C1285 are dominated by degradation of the solid material and continued degradation will occur in all subsequent uses of the simplified pore water solution. The buffer capacity of the simplified porewater solution is not expected to be important.

As an example, Table B.1 summarizes the compositions measured for tests with four waste material samples and the proposed simplified composition for a surrogate pore water based on the composition measured in Test 2. The measured composition is not electrically neutral and no measure of the fO_2 is provided. The pore water is assumed to be air-saturated. The simplified composition contains Ca, Na, Si, and HCO_3^-. The other components are excluded from the formulation (but retained at trace levels in the Geochemist's Workbench calculations).

Table B.1 Measured compositions and proposed simplified composition, in mg L^{-1}

	Measured Test 1	Measured Test 2	Measured Test 4	SPW
Al	0.63	0.43	<0.1	—
Ca	9.08	7.10	11.9	8
Li	0.04	0.04	0.05	—
K	0.02	0.01	0	—
Mg	0.96	0.25	0.95	—
Na	46.5	49.3	45.4	50
Si	34.4	35.7	30.6	36
HCO_3^-	118	120	121	120
F^-	2.4	2.8	2.5	—
Cl^-	7.2	8.4	7.7	—
NO_3^-	7.6	7.2	8.4	—
U	0.05	0.25	0.11	—
Cs	0.42	0.05	0.11	—
pH	8.25	8.10	7.61	8.10

Representative concentrations of 0.3 mg L^{-1} U and 0.5 mg L^{-1} Cs are determined as the surrogates for the pore water, but are excluded from the SPW solution used in the tests to measure the dissolution and desorption rates in Steps B2 and B4. The concentrations are used for generating Solutions A, B, C, and D used in the sorption tests in Step B3.

The measured composition in Test 2 and the proposed simulated pore water composition were evaluated using Geochemist's Workbench (Bethke and Yeakel, 2009). Seven calcuations were performed by Dr. James L. Jerden, Jr. (ANL) to support the following analyses:

1. Evaluate the stability of the as-measured solution without precipitation.
2. Equilbrate the as-measured solution allowing precipitation.
3. Evaluate the stability of the proposed simplified solution without precipitation.
4. Equilbrate the proposed simplified solution allowing precipitation.
5. Add HCl to match pH of proposed simple solution without precipitatation.
6. Add HCl to match pH of proposed simple solution allowing precipitation.
7. Evaluate synthesis of proposed simplified solution with various chemicals with and without suppression of silica polymorphs.

The input files for nine calculations are provided in Table B.2 and the results of those calculations are summarized in Table B.3. Calculation 1 determined the as-measured composition to be supersaturated with 45 mineral phases in the data base. The calculated pH for the solution (at 25 ºC) is 8.302, which is only slightly higher than the measured pH of 8.10. Allowing quartz, calcite, and mesolite ($Na_2Ca_2Al_6Si_9O_{10}$•$3H_2O$) to precipitate in Calculation 2 resulted in a small increase in the solution pH to 8.501 and the solution becoming undersaturated with respect to the other 42 phases (due in most cases to decrease in SiO2(aq) concentration from 1.22 m$\underline{M}$ to 0.10 m$\underline{M}$). Calculation 3 showed the simplified solution composition to be supersaturated with seven phases, although precipitation was suppressed in the calculation. The calculated pH of the equilibrated solution is 9.388. Allowing quartz and calcite to precipitate from that solution (as was done in Calculation 4) resulted in a small increase in the pH to 9.609. Calculation 5 showed that adjusting the solution generated in Calculation 3 to pH 8.1 while suppressing the precipitation of all phases required the addition of 0.593 mmoles HCl. If the phases are allowed to precipitate, as they were in Calculation 6, slightly more HCl must be added to maintain the pH (0.611 mmoles HCl); only quartz precipitates under those conditions. The Cl^- concentration was about 22 µg mL^{-1} in Calculation 6, which is only slightly higher than what was measured. The difference represents the F^- and NO_3^- that was excluded from the simple formulation. From the results of Calculation 1, the as-measured solution contained 0.234 m$\underline{M}$ Cl^-, 0.145 m$\underline{M}$ F^-, and 0.115 m$\underline{M}$ NO_3^-., which total to 0.494 moles total anions.

For most applications, this simplified solution will adequately represent the as-measured solution because the key properties affecting dissolution and sorption are pH and ions common to the dissolving phases. That was the objective in this example. These are well-represented by the simple solution. Other compositional effects may be important for some systems, for example, the concentration of Cl^- will affect the corrosion of steel-based phases and F^- is an effective ligand for actinides. In those cases, the simplified solution should be formulated to match concentations of the key elements. In most cases, the solution pH will be the most important property to be matched.

Table B.2 Input files for Geochemist's Workbench calculations

Calculations 1 and 2	Calculations 3[a] and 4	Calculations 5[a] and 6
T = 25	T = 25	T = 25
swap O2(g) for O2(aq)	swap O2(g) for O2(aq)	swap O2(g) for O2(aq)
f O2(g)	f O2(g) = 0.2	f O2(g) = 0.2
swap NO3- for NH3(aq)		
NO3- = 7.2 mg/l		
suppress N2(aq),		
suppress N2(g)		
Al+++ = 0.43 mg/l		
B(OH)3(aq) = 0.97 mg/l		
Ca++ = 7.10 mg/l	Ca++ = 8.0 mg/l	Ca++ = 8.0 mg/l
Li+ = 0.04 mg/l		
Mg++ = 0.25 mg/l		
Na+ = 49.3 mg/l	Na+ = 50.0 mg/l	Na+ = 50.0 mg/l
SiO2(aq) = 76.37 mg/l	SiO2(aq) = 77.0 mg/l	SiO2(aq) = 77.0 mg/l
HCO3- = 120 mg/l	HCO3- = 120 mg/l	HCO3- = 120 mg/l
F- = 2.8 mg/l		
Cl- = 8.4 mg/l		balance on Cl^-
balance on H+	balance on H+	pH = 8.1; fix pH

Calculation 7	Calculation 8[b]	Calculation 9[b]
T = 25	T = 25	T = 25
swap O2(g) for O2(aq)	swap O2(g) for O2(aq)	swap O2(g) for O2(aq)
f O2(g) = 0.2	f O2(g) = 0.2	f O2(g) = 0.2
swap CO2(g) for HCO3-	swap CO2(g) for HCO3-	swap CO2(g) for HCO3-
f CO2(g) = 4E-4	f CO2(g) = 4E-4	f CO2(g) = 4E-4
Na+ = 1E-10 molar	Na+ = 1E-20 molar	Na+ = 1E-20 molar
Ca++ = 1E-10 molar	Ca++ = 1E-20 molar	Ca++ = 1E-20 molar
SiO2(aq) = 1E-10 molar	SiO2(aq) = 1E-20 molar	SiO2(aq) = 1E-20 molar
react 19.9785 mg Calcite	react 19.9785 mg Calcite	react 115.2563 mg Na2CO3
react 11.6781 mg SiO2(am)	react 11.6781 mg SiO2(am)	react 23.1871 mg (CaSiCO3)
react 132.7364 mg Na2SiO3	react 132.7364 mg Na2SiO3	react 65.0358 mg SiO2(am)
swap HCl(aq) for Cl-	swap HCl(aq) for Cl-	swap HCl(aq) for Cl-
HCl(aq) = 1E-10 molar	HCl(aq) = 1E-10 molar	HCl(aq) = 1E-10 molar
react 2.357E-3 moles HCl(aq)	react 2.338E-3 moles HCl(aq)	react 1.457E-3 moles HCl(aq)
balance on H+	balance on H+	balance on H+

[a] Suppress all phases.
[b] Suppress Quartz, Chalcedony, Coesite, Cristobalite(alpha), Cristobalite(beta), Tridymite.

The nearly ubiquitous supersaturation of quartz demonstrates the limited information available from both thermodynamics and kinetics and the relationships between the two. The formation of quartz is kinetically prohibited (in a practical sense for laboratory tests).

Modelers often suppress phases having slow precipitation kinetic from forming (as was done in Calculations 1, 3, and 5), as their precipitation affects the solution concentrations of key components—in this case SiO_2(aq). Calculations in which phase precipitation is suppressed give what is considered to be a kinetically limited solution composition and calculations in which

Table B.3 Comparison of various SPW compositions, in mg L^{-1}

Component	Measured	Proposed	Geochemist's Workbench Calculation Number				
	Test 2	SPW	5	6	7	8	9
Ca	7.10	8	7.63	7.63	7.965	7.96	7.84
Na	49.3	50	49.20	49.24	49.96	49.92	49.87
Si^a	35.7	36	35.52	2.817	2.815	35.45	35.46
HCO_3^-	120	120	115.0	115.0	12.77	12.77	65.36
Cl^-	8.4	—	21.01	21.67	83.52	82.84	51.62
pH	8.10	8.10	8.10	8.10	8.10	8.10	8.10
Precipitation of polymorphs suppressed?			yes	no	no	yes	yes

[a]Total Si in SiO_2, $HSiO_3$-, and $NaHSiO_3$.

phase precipitation is allowed give what is considered to be a thermodynamically limited solution composition. Which is more informative depends on the system being studied. Geological studies of pore waters in contact with minerals in aquifers for centuries are better served by the thermodynamic limit, with few phases suppressed, whereas studies on shorter time scales (of even thousands of years) are better served by the kinetic limit. As was done in this example, is is usually beneficial to run calculations in both limits to assess the differences.

Calculation 7 was run to evaluate production of the simplified solution with reagent chemicals as an easy way to assess chemical solubilities and compatabilities, in this case with Na_2SiO_3, $CaCO_3$ and SiO_2(am). Two additional calculations were run to evaluate this solution: Calculation 8 was run with the same input file, except the precipitation of silica polymorphs other than SiO_2(am) were suppressed. Calculation 9 was run to assess the use of $CaSiO_3$ and Na_2CO_3 to make the SPW solution.

The reagents used for Calculations 7, 9, and 9 are summarized in Table B.4. The impact of not suppressing kinetically limited Si-bearing phases (quartz) is clear by comparing the dissolved Si concentration in Calculation 7 in which quartz precipitation was suppressed with that in Calculation 6 in which quartz wasn't suppressed. Note that the concentrations of other solutes are not affected. In addition, the choice of chemicals to make the solution has a significant effect on the carbonate speciation. Further modification of the recipe could be used to increase the bicarbonate concentration. For example, $CaCO_3$ and $MgCO_3$ could be added to the mixture used in Calculation 9, since Tests 1 and 4 had higher Ca contents than Test 2 and Mg was

Table B.4 Reagents used in Geochemist's Workbench analyses of possible SPW solutions and concentrations, in mg L^{-1}

Component	Geochemist's Workbench Calculation Number		
	7	8	9
$CaCO_3$	19.9785	19.9785	—
$CaSiCO_3$	—	—	23.1871
Na_2CO_3	—	—	115.2563
Na_2SiO_3	132.7364	132.7364	—
SiO_2(am)	11.6781	11.6781	65.0358
HCl	85.9126	85.2201	53.1077

present in all test solutions. The contaminants of interest may influence the ultimate selection of the SPW to be used.

Some compositional flexibility will be required to match test solutions, and calculations such as these with Geochemist's Workbench facilitate the formulation of stable solutions that can be made in the laboratory. Knowledge of which component is important to match is beneficial, for example the relative importance of Si and Cl^- to the corrosion behavior will be different for silicate glass and stainless steel host phases. It is recommended that the SPW solution that is made be analyzed before use, including filtered solutions, and periodically during use to track its stability, for example in blank or control tests.

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A protocol of simple laboratory tests designed to measure values needed to model the release and transport of contaminants from large piles of waste materials at surface sites for regulatory analyses is presented. The system of discrete pieces of waste material forming a pile is modeled as a fractured matrix allowing use of volume or mass of the waste material, instead of surface area. This allows existing models for contaminant transport to be applied to the waste piles. A probability distribution based on the values measured for many small field samples can be used to represent the behavior of the entire waste pile. Simple batch tests are recommended for quantifying the effective contaminant release due to the dissolution or leaching of all host phases in the waste and the effective sorption/desorption behaviors of contaminants on the waste material. Simple modifications of standardized ASTM test methods are used to determine a representative pore water composition and range of contaminant concentrations (ASTM C1285), measure the contaminant release kinetics and rates, and the desorption rate (ASTM C1308), and measure the effective sorption properties (ASTM C1733). An optional column test is recommended to calibrate the measured dissolution and sorption values under well-controlled transport conditions.

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