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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
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Hanford Site Composite Analysis Technical Approach Description: Waste Form Release

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Hanford Site Composite Analysis Technical Approach Description: Waste Form Release

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MODELING ~~ATMOSPHERIC TRANSPORT~~ WASTE FORM RELEASE

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5/30/17
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The approval signatures on this page indicate that this technical approach description has been authorized for information release to the public through appropriate channels.

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Terms

CA	composite analysis
CASH	calcium aluminate silicate hydrate
CDP	cellulose degradation products
CSH	calcium silicate hydrate
DAS	disposal authorization statement
DOE	U.S. Department of Energy
EMDT	electronic model data transmittal
ERDF	Environmental Restoration Disposal Facility
FEPs	features, events, and processes
ICF	integrated computational framework
IDF	Integrated Disposal Facility
PA	performance assessment
QA	quality assurance
QA/QC	quality assurance and quality control
STOMP	Subsurface Transport Over Multiple Phases (software)
VADER	VADosE Release (software)

1 Introduction

The U.S. Department of Energy (DOE) in DOE O 435.1 Chg. 1, *Radioactive Waste Management*, requires the preparation and maintenance of a composite analysis (CA). The primary purpose of the CA is to provide a reasonable expectation that the primary public dose limit is not likely to be exceeded by multiple source terms that may significantly interact with plumes originating at a low-level waste disposal facility. The CA is used to facilitate planning and land use decisions that help assure disposal facility authorization will not result in long-term compliance problems; or, to determine management alternatives, corrective actions or assessment needs, if potential problems are identified.

A CA is not prepared to demonstrate current compliance; rather, its purpose is to model potential future exposure events. In other words, a CA is a DOE planning tool, used to provide a reasonable expectation that DOE public radiation protection requirements will be met over the long term after the DOE site achieves its projected end state; and, the CA is a prerequisite to acquire and maintain an operational Disposal Authorization Statement (DAS).

CAs are closely linked with performance assessments for specific disposal facilities, which DOE uses to demonstrate that there is a reasonable expectation that the performance objectives will be met for a given facility. CAs may be documented in a companion report to the performance assessment, or integrated in the same report with a PA. At the Hanford Site, with numerous separate disposal facilities and tank farms, the CA has been developed and maintained as a separate document that includes all facilities contributing to dose at a specific boundary for supporting performance assessments for several low-level waste disposal facilities at the Hanford Site.

The currently maintained CA for the Hanford Site is documented in PNNL-11800, *Composite Analysis for Low Level Waste Disposal in the 200 Area Plateau of the Hanford Site*, and the subsequent Addendum 1 (PNNL-11800-Addendum-1, *Addendum to Composite Analysis for Low Level Waste Disposal in the 200 Area Plateau of the Hanford Site*). The annual summary report for this CA for fiscal year 2015 reached the determination that an update to the Hanford Site CA is necessary based on information reviewed for fiscal year 2015 as well as information presented in prior annual status reports. DOE has initiated work to develop a revised CA following a phased approach with planning, scoping, and analysis phases. The scoping phase will culminate in the development of a detailed technical approach for preparing the revised CA. This technical approach description document presents the approach for the integrated computational framework (ICF) as one facet of the overall technical approach. This is a companion document to a series of other technical approach description documents for various facets of the revised CA.

2 Overview

The purpose of this report is to review basic models for the release of radionuclides to be evaluated in the CA from waste forms that exist or may arise at the Hanford Site. Previous studies in support of the Hanford Site waste management system have reviewed and presented candidate models for known waste forms (see Section 3 of this report). In addition, recent performance assessments for C-Tank Farm and the Integrated Disposal Facility (IDF) have implemented such models for different waste forms into the GoldSim®[1] code.

Section 3 of this report provides a historical review of past reports on radionuclide release models for different waste forms. These reports form the core of the review with respect to identifying models for future Hanford Site waste forms. Selection of appropriate waste form release models (and data used in

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[1] GoldSim is a registered trademark of GoldSim Technologies, Issaquah, Washington.

such models), however, depends on an understanding of the disposal environment, boundary conditions, and design.

Section 4 briefly describes the basic features, events and processes (FEPs) that can influence the selection of release models for the specific disposal conditions at the Hanford Site. The purpose is to alert modelers that the choice of appropriate models and supporting data needs to be based on a clear understanding of the environmental "service" conditions under which current and future waste forms will be disposed. For example, conditions for disposal of future waste forms in shallow-trench disposal systems, similar to the IDF, would include unsaturated hydrogeological conditions with vertical, gravitationally controlled drainage of water, and water compositions buffered by contact with atmospheric gases such as O_2 and CO_2. One difficulty in modeling the release behavior of waste forms is that physical and chemical boundary conditions may evolve over time, so that models would need to be flexible to address these changes over appropriate compliance time scales.

Based on these review sections, Section 5 presents a table of recommended release models from previous Hanford reports. Specific parameters for these models are listed in the cited sections of Chapter 3. In addition, concerns regarding limitations to these models are also noted.

Potential future enhancements to modeling of waste form release and communicating safety performance are provided in Section 6.

Quality assurance / quality control considerations for implementation of selected models in the revision to the Hanford Site CA are briefly discussed in Section 7.

References cited in this report are provided in Section 8.

3 Previous Reports on Hanford Site Release Models

A historical review of past reports on models used to simulate release for different waste forms is presented in this section. These past reports are reviewed for the purpose of identifying appropriate release models for future Hanford Site waste forms. Selection of appropriate waste form release models (and data used in such models), however, depends on an understanding of the disposal environment, boundary conditions, and design discussed in later sections.

3.1 PNNL-11800, Kincaid et al. (1998), Hanford Site Composite Analysis, Appendix D "Hanford Composite Analysis Source Term Release Models"

Soil Debris Waste Form

In this appendix of PNNL-11800, *soil debris* is very loosely defined as the following: "unconsolidated wastes mixed with soil material." The assumptions made regarding this waste form type are as follows:

- All surfaces of the waste come into contact with the percolating water as it passes through the zone in a manner similar to how infiltrating water passes through natural vadose zone material;
- If contaminant inventories in the source zone are high enough, leaching of contaminants out of the bottom of the source zone is controlled by the solubility of the contaminant in the percolating water;
- Otherwise, the leaching is controlled by partitioning of the contaminant between aqueous and sorbed phases;

- Contaminants from wastes in the low surface-area-to-volume category (e.g., waste containers, personal protection equipment, and metal process equipment) readily leach into the surrounding soil; and therefore, their release from the source zone is controlled by the properties of the surrounding soil in the source zone; and
- Contaminants from wastes in the high surface-area-to-volume category (e.g., sludge, soil, and spent filters/adsorbents) can have high surface adsorption coefficients. Therefore, their release from the source zone is controlled by the properties of the waste material itself.

For all waste types, it is more generally stated: "In addition to the primary waste forms and surrounding soil, the source zone may initially contain other material, such as facilities/buildings, and waste containers, waste-zone structural components (e.g., asphalt pads, and plywood sheets separating layers of waste containers). In these analyses, no credit is taken for the ability of these other materials to inhibit contaminant release (i.e., the analyses now assume that these components degrade rapidly and offer no protection for the five generic waste form types for essentially the entire simulation time)."

The above assumptions seem generally conservative and would benefit from introducing a bit more realism into the system. Key limitations, however, are the lack of consideration of the overall context of the assessment (e.g. environmental evolution) and the need to acknowledge that some potentially important processes are not addressed (e.g., microbial activity or aqueous organic ligands) – as considered in Section 4 of this report.

There are a number of limitations for some of the equations used in the modeling and a few examples of this now follow. The basic equation that is introduced as the basis for "mathematical expressions" (D.1) tacitly assumes a degree of physical homogeneity and constancy in time that may not reflect reality for waste forms that are not engineered or conditioned under a quality control program. It is also stated that *"Equation D.2 implicitly assumes that the first-order decay coefficient of the contaminant is independent of the phase (aqueous, sorbed, or precipitated) in which the contaminant resides (this is strictly true for radionuclides)."* From a numerical standpoint, the decay process is efficiently simulated using a variable transformation of the concentrations. However, the limitation here is that this assumption neglects radioactive ingrowth, which would be a critical factor for radioactive daughters (e.g., Ra-226, Rn-222) growing in from decay of actinides. This issue becomes of greater concern for increasing lengths of compliance time scales.

The subsequent derived equations reflect the noted limitations. Some of the assumptions included are explicit (e.g. use of K_d – D.16), but justification is not provided. Suffice it to note that, for anything other than contaminants that are mono-isotopic with no natural stable background, subsequent derived equations based on this formulation do not adequately represent the system.

With respect to *soil debris*, the main presented release model equation is (Equations D.28-32):

$$\mathrm{M}_i^{\circ} = \left(\theta_\mathrm{w} C_{wi}^{\circ} + \beta K_{di} \mathrm{C}_\mathrm{wi}^{\circ}\right).V = \theta_\mathrm{w} R_i \mathrm{C}_\mathrm{wi}^{\circ} A h$$

Where,

M_i° = amount of contaminant *i* in the source zone without a precipitated phase (Ci)
C_{wi}° = aqueous concentration of contaminant *I* (Ci cm^{-3})
K_{di} = linear equilibrium sorption coefficient for contaminant *i* to the source zone soil (cm^3 g^{-1})
R_i = retardation factor defined as: $R_i = 1 + \frac{\beta K_{di}}{\theta_w}$ (unitless)
V = volume of the source zone (cm^3)

A = effective horizontal cross-sectional area of the contaminant source zone (cm^2)
h = average vertical thickness of the contaminant source zone (cm)
θ = the volumetric water content of the source zone soil or vadose zone soil (unitless; $cm^3\ cm^{-3}$)
β = the bulk density of the source zone soil or vadose zone soil ($g\ cm^{-3}$)

If $\mathrm{M}_i^\circ > \mathrm{M}_{maxi}^\circ$ (maximum amount of contaminant mass/activity existing in the source zone), a precipitated phase is assumed to be present and the aqueous concentration of the contaminant in the source zone is assumed to be solubility-controlled (C_{wi}^{sol}):

$$C_{wi}^\circ = C_{wi}^{sol}$$

Reactor Blocks Waste Form

With respect to *reactor blocks*, the presented release model equation is (Equation D.64):

$$\frac{dM_i}{dt} = -M_{oi}(365)\left[565\left(1 + 100e^{-(0.08)(365)t}\right)e^{-6640/T}\right]$$

Where,

M_{oi} = initial total activity of contaminant i in the source zone (Ci)
M_i = total activity of contaminant i in the source zone (Ci)
T = absolute temperature of the reactor block (K)
t = the time since initial condition of the source zone (yr)

This generic waste form type was developed to apply to the loss of radionuclides from irradiated graphite reactor blocks disposed of in the vadose zone. The blocks release contaminants into the water percolating past them via unspecified loss processes from the solid graphite matrix as well as via corrosion of the solid graphite matrix and irradiated metal components over time.

Saltcake Waste Form

With respect to saltcake, in this appendix, salt cake/sludge is defined as the following: “consolidated waste that is permeable to water, and that dissolves over time because some major structural component of the solid waste dissolves in the water percolating through the waste form.”

The major assumption made regarding this waste form type is that, as the solid waste dissolves, all of the contaminants associated with the portion of the waste form that dissolved are released into the percolating water congruently at constant rates related to their concentration in the waste form. Other assumptions are the following:

- Contaminants are assumed uniformly distributed throughout for all times;
- Sorption is not simulated;
- Chemical interactions between contaminants are not simulated; and
- Solubility into the percolating water is the key driver.

The mass of the major structural component remaining in the source zone as a function of time is (Equation D.46):

$$\mathrm{M_{msc}(t) = M_{msco} - q_w A C_{wmsc}^{sol} t}$$

Where,

M_{msc} = the mass of the major structural component in the source zone (g).

M_{msco} = the initial mass of the major structural component in the source zone (g).
q_w = the Darcy flux density of water flowing through the source zone or vadose zone (cm/s).
A = the effective horizontal cross-sectional area of the contaminant source zone (cm^2).
C_{wmsc}^{sol} = the aqueous solubility of the major structural component (g cm^{-3}).
t = the time since initial condition of the source zone (yr).

The saltcake model developed in this chapter is therefore very conservative, and may largely overestimate contaminant leachate, especially considering that residuals remaining after tank waste recovery may likely have a composition closer to sludge than saltcake.

Cement Waste Form

For *cement* waste form types, the contaminant release mechanism to the leaching pathway is diffusion through the solidified waste material to the outer surface of the waste form where it is carried away by the water percolating past the surface.

For this conceptualization, it was assumed that the rate of loss of activity from the source zone by leaching at any time is given by (Equation D.61):

$$\frac{dM_i}{dt} = -M_{0i}\left(\frac{A_{sc}}{V_{cc}}\right)\sqrt{\frac{D_{ci}}{\pi t}}$$

Where,

M_{oi} = initial total activity of contaminant *i* in the source zone (Ci).
M_i = total activity of contaminant *i* in the source zone (Ci).
A_{sc} = total external surface area of the cement waste form in the source zone (cm^2).
V_{cc} = volume of the cement waste form in the source zone (cm^3).
D_{ci} = effective diffusion coefficient of contaminant *i* within a cement waste form (cm^2 yr^{-1}).

This equation derived from the solution to the diffusion equation for mass/activity lost through an infinite plane that bounds a semi-infinite solid source when no decay occurs.

The cement model implemented excludes any impact of the chemistry (sorption, precipitation) or the formation of daughter products from radionuclides decay. It also assumes that the cement waste form never fails or evolves with time. This model is therefore probably overly conservative in many cases.

Conclusions

The report makes no mention of environmental conditions of the disposal system (e.g., Eh, pH, microbial activity, …) that can affect parameters used in the models and additionally, parameters are assumed to remain constant. As such, this means that the models may not adequately represent contaminants in a real disposal context over appropriate compliance time scales. In addition, no account is taken of retardation by either co-disposed materials or the engineered barriers, which is likely highly conservative. Finally, a description/illustration of the release model would have been a useful addition to better interpret and understand this model.

Notwithstanding these concerns, the release models presented can be applied to releases of contaminants from unconsolidated, porous wastes, assuming proper precaution is made regarding concerns about factors affecting input parameters.

3.2 PNNL-14852 Volume 1, Eslinger et al., (2004), User Instructions for the System Assessment Capability Rev. 1, Computer Codes Volume 1: Inventory, Release, and Transport Modules

Section 5 of PNNL-14852, *User Instructions for the Systems Assessment Capability, Rev. 1, Computer Codes, Volume 1: Inventory, Release, and Transport Modules,* discusses the Vadose Zone Release Module (the VADosE Release, or VADER, code), "which calculates quantities of a given analyte, either a specific radioisotope or a non-radioactive chemical released from waste containment to the vadose source zone at regular (annual) time steps based on physicochemical release models generally expressed as differential equations."

This section does however acknowledge model limitations, which include:

- No chain-decay between analytes.
- No attempt to simulate chemical reactions that change the released contaminants into different chemical forms.
- VADER considers each analyte as being chemically and radiologically independent from all other analytes in terms of releases into the environment.
- VADER calculates quantities released to or injected into the release zone (vadose zone or river) without attempting to account for transport away from the release zone. Releases are considered to be at a point source.

It is assumed that if considered for use, the VADER code would be revised to provide a proper user-interface, or transposed to a more modern coding platform such as GoldSim. The advantage of this would be not only to improve the aspect of user-friendliness, but improved interfaces and more standardization of modules might allow some form of verification and validation against field data, laboratory tests or natural analogues.

Conclusions

In Section 5.2.3 of PNNL-14852, it is stated that the mathematical derivations for the release models implemented into VADER are fully documented in Appendix D of PNNL-11800, in which case the comments and concerns made previously in Section 3.1 are also applicable here.

3.3 PNNL-15965, Riley et al. (2006), Release Data Package for Hanford Site Assessments

PNNL-15965, *Release Data Package for Hanford Site Assessments,* acknowledges the fact that "*the Engineered waste systems have a number of features that influence the rate at which contaminants can be released from waste.*" It contains an illustration of the "Basic Features of a Waste Containment Facility," but not the actual system to be modeled. Additionally, it is noted that "*an effort has been made to provide detail on features of engineered systems in this section recognizing that not all of these features are addressed in SAC assessment modeling (e.g., the effects of liners at the bottom of a burial ground like ERDF are not modeled in SAC at this time except as a time delay on release).*" (ERDF here refers to the Environmental Restoration Disposal Facility; SAC refers to the System Assessment Capability.) The roles of contaminant precipitation, abiotic and biotic degradation of organic contaminants are acknowledged in that they may limit the amount of contaminant reaching the vadose zone. Processes that influence release from the waste to the migrating pore water include desorption, diffusion (e.g., diffusion out of permeable waste such as sludge or grout), solubility, solid phase dissolution/precipitation, and corrosion are acknowledged as well. In addition, the cement model, rather than the saltcake model, is used to simulate contaminant release from tank high-level waste residuals in a Hanford Site assessment.

The models in this report make more realistic assumptions than in the models presented in Sections 3.1 and 3.2. However, there several conservative assumptions remain that might affect the release rate of contaminants from waste forms. For example, simulating chemical reactions while assuming no impact of waste packaging/containment (or degraded packaging/containers) whose influence on retardation can affect the release rate of contaminants while structural integrity persists.

The waste form release models in Section 2.3 of PNNL-15965 are empirical (similar to previous reports), introducing parameters that are also assumed to be constant and, and where specified in detail (e.g. Equation 2.6), have high implied precision without any discussion of uncertainties or limitations on applicability. Uncertainties in the reported data are not discussed in detail. Where uncertainties are expressed (e.g., Table 5.3 of PNNL-15965), these appear to not account for natural heterogeneity. It is also clear from the treatment of sorption and solubility (last two paragraphs of Section 5.2, p. 5.7 of PNNL-15965) that the importance of environmental chemistry is not accounted for. This report also uses the same measurement units as in the models reviewed in Sections 3.1 and 3.2, and would benefit from adoption of the SI (international system of units) system.

Conclusions

This set of release models represented improvement over prior models by recognizing that many environmental factors can affect the parameters used in release modeling. However, these concerns are not always implemented into the models presented, particularly with respect to biotic processes. Nonetheless, this set of models are basically suitable for use in evaluating contaminant release rate behavior of waste forms, assuming appropriate caution is used in selection of parameters values and how such values might change over compliance time scales for the planned disposal context.

3.4 DOE/EIS-0391 (2012), Tank Closure and Waste Management Environmental Impact Statement, Appendix M “Release to Vadose Zone”

Soil debris as a waste form type is not listed in Table M-2 in this appendix of DOE/EIS-0391, *Final Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington,* nor indeed is there a mention of soil debris anywhere throughout the text. However, it can be noted that Appendix M incorporates most of the issues mentioned in the previous sections of this report, including a non-standardized mixture of units e.g., m and cm. The data included show also a lack of a chemical overview, parameters defined without any clear background, or assessment of chemical consistency.

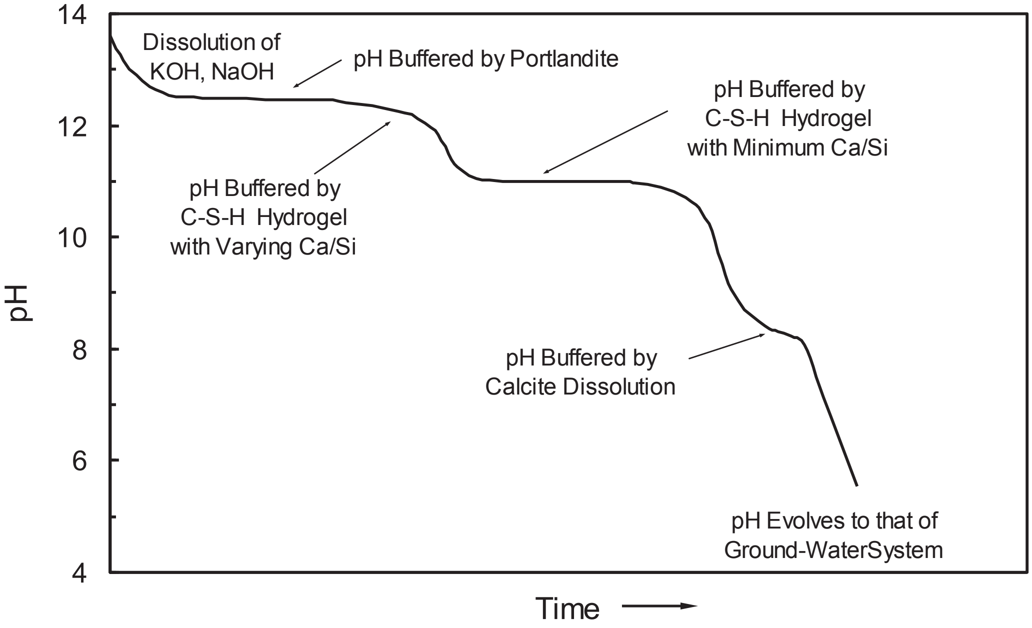
Most of the report is a catalogue of output data that has no clear meaning. However, a notable exception here is Section M.5 of DOE/EIS-0391, which attempts a form of sensitivity analysis. This is very positive and potentially useful, but one drawback would be that it adopts a bottom-up approach. Unfortunately, this approach makes it difficult to integrate all the results presented, which is required to develop a feeling for how realistic or conservative the assessment is and what the main uncertainties are in terms of long-term performance. It was beyond the scope of this review to examine in detail all sensitivity cases presented, but an example (M5.5) of where perhaps more caution should be applied. In this instance, empirical laboratory data are mixed with equilibrium thermodynamic modeling, without discussion of how either would be applicable to the expected conditions within a disposal trench, and how the very different uncertainties from such sources should be reconciled.

Conclusions

Adoption of a more modern approach (e.g. based on storyboards or argumentation models) would allow context (and limitations) to be better defined.

3.5 RPP-CALC-61030, Senger et al. (2016), Cementitious Waste Form Release Calculations for the Integrated Disposal Facility Performance Assessment

In RPP-CALC-61030, *Cementitious Waste Form Release Calculations for the Integrated Disposal Facility Performance Assessment*, the cement model is recent, showing a move towards modern, consistent units. The physical model is well described and its limitations are highlighted. The hydrogeological system is assessed in detail, but the consideration of chemical evolution within the waste form could benefit from a more in-depth treatment. This is a key issue, particularly for releases of contaminants from cement-based systems, where both physical (e.g., porosity) and solute release and transport properties (waste degradation rates, solubilities, sorption, colloid stability and transport, microbial activity) depend on the evolution of concrete. This is well described (at least empirically) and the major differences between “phase 1” Na/K OH and “phase 2” $Ca(OH)_2$ conditions are highlighted in almost all models in other national programs (see Figure 1).



Note: CSH hydrogel is the Amorphous calcium (C) silicate (S) hydrate (H = H_2O) solid formed.

Figure 1. Evolution of Cement Pore Water pH during Weathering due to Contact with Infiltrating Water and Air [Figure modified from Atkins and Glasser, (1992)]

A physical/hydrogeological/chemical reaction approach may be a useful first step, to consider evolution of cement-based waste forms and their release performance over extended compliance time scales. While near-surface disposal conditions at the Hanford Site will be unsaturated, the capillary effects of micro-porous cement may quickly lead to fully saturated porosity of cement-based waste forms, as indicated in RPP-CALC-61030.

RPP-CALC-61030 describes a comprehensive unsaturated flow and convective/diffusive transport model, using the *Subsurface Transport Over Multiple Phases* (STOMP)©[2] code, and its abstraction into the GoldSim® simulator. The STOMP simulations demonstrated that the release of contaminants is dominated by radial diffusion because of the much lower permeability of the cementitious waste than the surrounding backfill. The diffusive flux depends on the concentration of the contaminant in the backfill, which depends on the advective flow rate specified over the surface area of the backfill and the water content in the backfill, transporting the contaminant to the bottom for release to the vadose zone.

This outcome allowed the development into GoldSim of a shrinking core diffusion model. Key assumptions of the shrinking core diffusion model are that the interface moves slowly in comparison with the time needed for a quasi-steady state profile to develop across the depleted shell, and that the amount of diffusing constituents in the depleted shell is negligibly small. Possible degradation of the waste form is represented by a step increase in tortuosity of the waste form, representing an increase in the effective diffusion coefficient.

The GoldSim® model couples and solves numerically the following mass balance equations (A-5 to A-7):

$$(A_f - A_{wf}) H_{wf} \varepsilon_{svz} R_{d,vz} \frac{dC_{vz}}{dt} = R_{wf} - R_{vz}$$

$$R_{vz} = A_f q_{inf} C_{vz}$$

$$R_{d,vz} = (\theta_{vz}/\varepsilon_{svz}) + [(1 - \varepsilon_{svz})/\varepsilon_{svz}]\rho_s K_{d,vz}$$

Where:

A_f = area in horizontal plane for infiltration of water (m^2)

A_{wf} = area in horizontal plane intersected by stacks of waste packages (m^2)

H_{wf} = height of a stack of waste packages (m)

q_{inf} = infiltration rate (mm yr^{-1})

θ_{vz} = water content in the vadose zone (unitless)

ε_{svz} = saturated porosity of the vadose zone between waste packages (unitless)

$R_{d,vz}$ = retardation factor for the constituent in the vadose zone between waste packages (unitless)

R_{vz} = rate of release of the constituent from the vadose zone between the waste packages to the vadose zone below the waste packages (Ci yr^{-1})

C_{vz} = concentration of the constituent in the vadose zone between the waste packages (Ci m^3)

The main limitations are the following:

- Radioactive decay/ingrowth is neglected;
- Concentration profile within the degraded shell is linear;

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[2] Battelle Memorial Institute (Battelle) retains copyright on all versions, revisions, and operational modes of the Subsurface Transport Over Multiple Phases (STOMP) software simulator, as permitted by the U.S. Department of Energy. STOMP is used here under a limited government use license.

- Concentration within the core zone is uniform and constant;
- Release of contaminants from the backfill region surrounding the waste form is by advection only; and
- Concentration within the backfill is uniform and controlled by mass balance in the backfill.

3.6 SRNL-STI-2009-00473, Kaplan (2010), Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site

SRNL-STI-2009-00473, *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site*, focuses on the geochemical processes and data as well as the numerical parameters needed for performance assessment (PA) modeling efforts at the Savannah River Site. It discusses the assumptions made to assure that the conceptual and numerical models are reasonable, recommendations on geochemical input values and an identification of critical data needs.

Compared with previous document discussed in this document, SRNL-STI-2009-00473 highlights the limitations inherent to the classical K_d approach and proposes significant improvements to narrow the range of “empirical” K_d values used:

- Cellulose degradation products (CDP)
- Aging of the cementitious solids (3 stages)
- The notion of geological environment (sandy, or clayey, sediment).
- The notion of chemical environments:
    - Oxidized or reduced conditions
    - Cementitious-leachate impacted sediments

The above variables were combined into 15 classes of environmental conditions for which 62 K_d values and/or apparent solubility values are provided.

The author proposes additional directions of interest:

1. Incorporate more mechanistic approaches to describe geochemistry, for example, modeling Eu sorption using a K_d based on an Eu–NOM-sediment ternary system at several pH values.
2. Improve knowledge on the range and distribution of sorption parameters for cementitious or cementitious impacted materials.
3. Add kinetics, for instance, to compute Tc interaction with reducing grout.
4. Implement a degradation rate for the cellulosic materials.
5. Improve colloid-facilitated transport.

Many of these same topics are explored more fully in the following Section 4 of this report.

4 Understanding the Disposal System

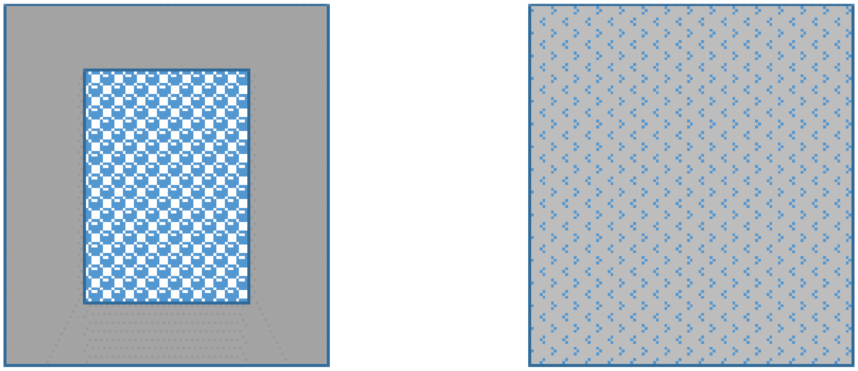
The basic FEPs that can influence the selection of release models for the specific disposal conditions at the Hanford Site are discussed in the section. The purpose is to alert modelers that the choice of appropriate models and supporting data needs to be based on a clear understanding of the environmental “service” conditions under which current and future waste forms will be disposed. For example, conditions for disposal of future waste forms in shallow-trench disposal systems, similar to the IDF, would include unsaturated hydrogeological conditions with vertical, gravitationally controlled drainage of water, and water compositions buffered by contact with atmospheric gases such as O_2 and CO_2. One difficulty in modeling the release behavior of waste forms is that physical and chemical boundary conditions may evolve over time, so that models would need to be flexible to address these changes over appropriate compliance time scales.

4.1 Basic Features and Processes of Waste Form Release Models

There are several basic features and processes (part of so-called features, events, and process, or FEPs) of waste forms that need to be considered first in identifying appropriate models for the release of contaminants. These are, in a sense, initial boundary conditions, and introduce the importance of understanding environmental conditions of the disposal system that must be considered in the selection of appropriate release models.

The initial basic features are the physical location and chemical form of contaminants within the waste form. In one case, contaminants may occur as a surface coating on the waste form. Upon contact by water, this coating may dissolve instantaneously, resulting in initial (but not fixed over time) concentrations of contaminants equal to the contaminant masses in the surface coating divided by the volume of the contacting water. Over time, this initial spike in concentration will dissipate as the contaminants are transported away from the waste form surface, a so-called instant release fraction.

An alternative, more common case with respect to physical location is contaminants that are located within a waste form. Here there are two possible sub-cases; the contaminants may be physically, or chemically, incorporated into the waste form matrix, or the contaminants may be located in a piece of waste that is surrounded and encapsulated by the waste form matrix. Figure 2 shows these two cases schematically.



Encapsulation **Incorporation**

Figure 2. Schematic Diagram of Two Types of Physical Location of Contaminants (represented by blue color) within Waste Forms

With respect to chemical form, this entails the oxidation state of a contaminant and/or whether the contaminant is chemically bound into a specific compound. For example, the release behavior of Tc^{2+} (reduced form) and Tc^{7+} (oxidized form) are quite different, the former being insoluble and the latter being extremely soluble in near-surface disposal conditions. The release behavior of I-129, as another example, will be quite different comparing I_2 (highly soluble) versus AgI (insoluble).

A second basic feature is physical form, that is to say, whether the waste form is an impermeable condensed phase or is porous (or containing through going fractures). Condensed waste forms include both liquids and solids, the latter represented by examples such as glass, metals, or reactor blocks. Cements (both incorporated and encapsulated forms) and "soil debris" are examples of porous waste forms. The importance of physical form is whether water[3], the phase necessary for the release of contaminants from the waste form, contacts only the surface or the entire volume of a waste form.

Permeability of porous waste forms can be construed as sub-cases of physical form. If a porous waste form has sufficiently low permeability, then the release of contaminants through the waste form matrix (e.g., cement) will be restricted to diffusion. Conversely, if the waste form matrix is relatively permeable (e.g., soil debris), then the release of contaminants may be controlled by advective flow of water through the waste form. For the unsaturated disposal environment expected in the arid climate at the Hanford Site, infiltration rates may be so slow that diffusive release rather than advective release may lead to release rates faster than even than for relatively permeable waste forms.

Whether advective or diffusive transport dominates in the disposal environment may also affect the selection of appropriate release models for solid waste forms. As is well-verified from diagenesis of minerals in long-term, near-surface geological settings (Berner, 1978), a flux ratio (R_r) can be defined as the ratio of waste form dissolution rate (R_d) and the rate of mass transfer of dissolved contaminants away from the waste form surface (R_t). Two limiting cases for release models can be identified:

$$R_r = \frac{R_d}{R_t} \ll 1, surface - reaction\ control,$$

$$R_r = \frac{R_d}{R_t} \gg 1, transport\ control$$

For the surface-reaction control case, effectively the rate at which dissolved contaminants move away from the waste form surface is much greater than the rate that new contaminants are released by dissolution, so that contaminant concentrations at the surface remain low and controlled by the dissolution rate. IDF glass is an example of this case. For the transport control case, dissolution rate is much faster than the rate of contaminant transport away from the waste form surface, so that the surface concentrations of contaminants can continue to increase until they may reach a *solubility* limit. At this point, a new, secondary reaction-solid would precipitate that incorporates the contaminant and imposes a solubility-limited concentration (C_{eq}). Note that a contaminant typically occurs as a minor or trace phase in such a precipitated phase, but still has its concentration limited by the solubility of that phase. These two cases are shown schematically in Figure 3.

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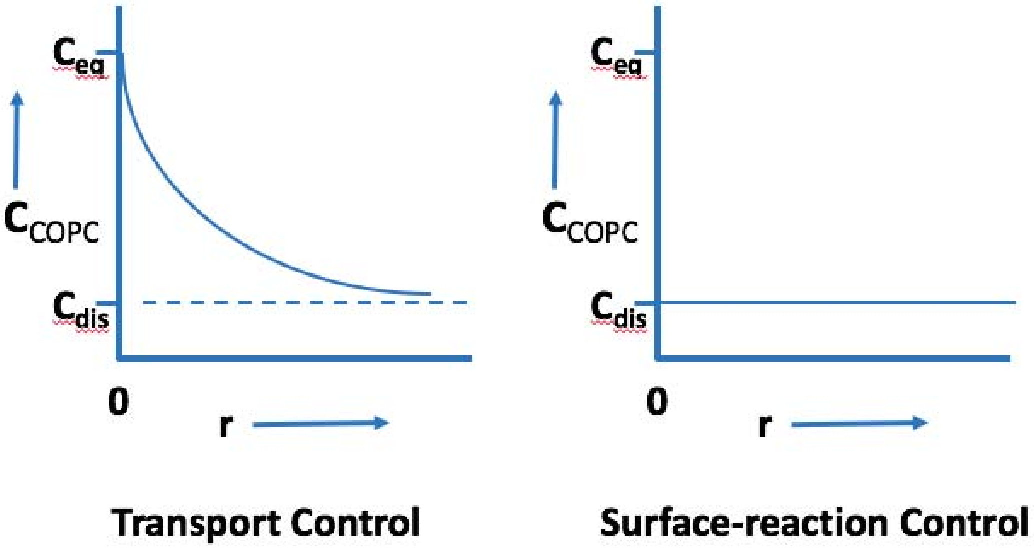
[3] Volatile contaminants, if present, could be released as a gas if a continuous air pathway exists in the disposal system.



Note: “C_{eq}” is a potential solubility-limited concentration for a contaminant, “C_{dis}” is the concentration set by the dissolution rate of the waste form, and “r” is distance from waste form surface

Figure 3. Schematic of Transport Control and Surface-reaction Control Cases for Solid Waste Forms (modified from Berner, 1978)

A basic decision flowchart of generic waste form features to be considered in selecting appropriate release models is presented in Figure 4. This top-level figure could be applied to future Hanford Site waste forms not yet anticipated.

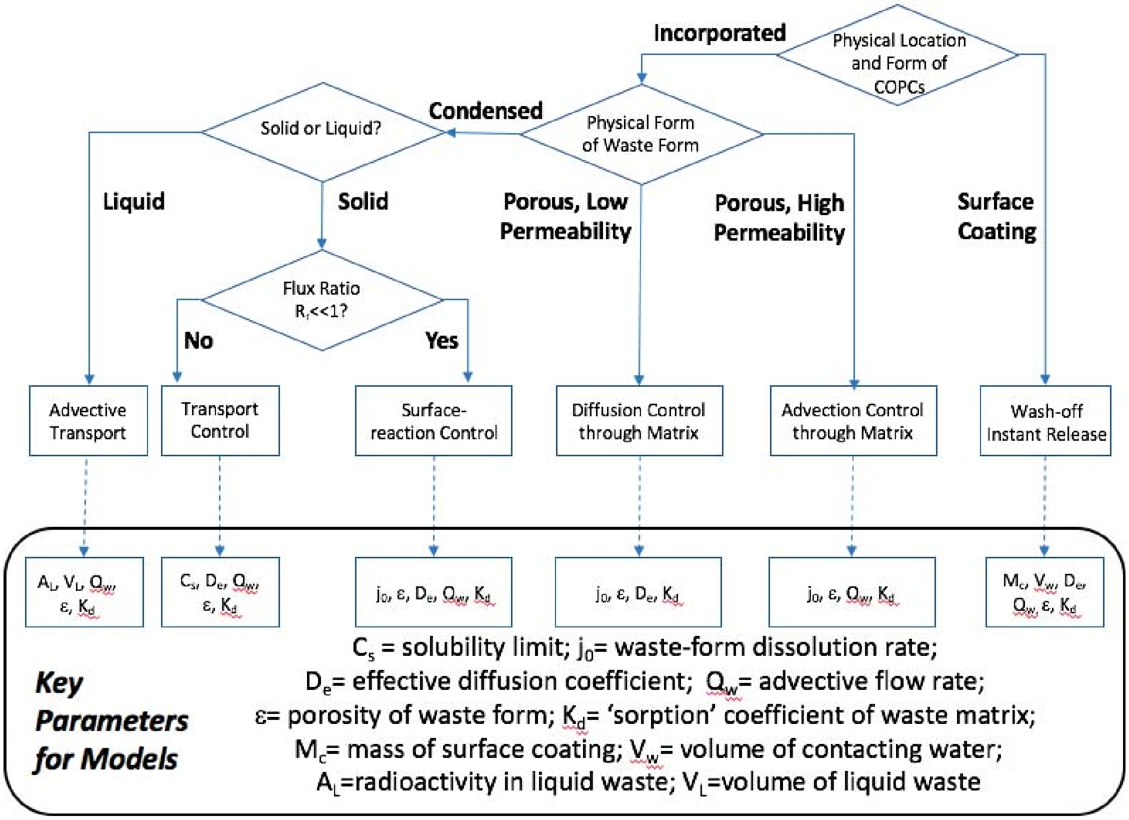


Figure 4. Decision Flowchart for Selecting Appropriate Release Models Based on Key Waste Form Features

One important process for inclusion in all release models is the degree of sorption/retardation of contaminants in the near-field materials immediately surrounding a waste form (e.g., corroded container, backfill). The many separate processes affecting sorption/retardation are often (but not optimally) lumped together in a K_d term. The importance of considering sorption/retardation processes is that they remove (either reversibly or irreversibly) dissolved contaminants from solution; this removal acts to maintain steep concentration gradients within porous waste forms and near the surface of solid waste forms, which will enhance and extend the diffusive transport rates of contaminants.

In some previous waste forms, the presence of reactive/sorptive materials in the waste form can even affect whether secondary precipitates form, which may impose solubility limits on some contaminants. For example, the inclusion of reactive blast furnace slag, containing sulfide and ferrous-iron phases, in formulations of low-level waste Cast Stone is intended to impose a local condition within the waste form that will cause highly soluble Tc^{+7} to be reduced to highly insoluble Tc^{+2}. Other so-called getter phases may be introduced into waste form formulations to cause the sorption or precipitation of a given contaminant (e.g., Ag added to cause soluble I-129 to precipitate as insoluble AgI).

There are a number of test procedures that may be used to evaluate whether surface reaction, or transport, will control the release of contaminants from the waste forms in which those contaminants are incorporated. These tests include simulation of either saturated or unsaturated conditions, as well as for advective or diffusive-controlled transport. As noted in subsequent sub-sections of this report, however, other factors such as physical form (e.g., permeability; fracturing) and chemical composition of contracting water (e.g., pH, redox potential [Eh]) can also affect the effective dissolution rates of waste forms. Relevant environmental service conditions, therefore, should be employed in such waste form testing to confirm appropriate contaminant release models for specific waste forms. These basic factors are discussed in more detail in the following sections in order to alert PA modelers as to important considerations of disposal conditions in order to select applicable release models for future Hanford Site waste forms.

4.2 Biogeochemical Features and Processes

During the last couple of decades, there has been an explosion of interest in the chemistry of the environment, particularly in the following areas:

- the basic processes determining the behavior of chemical contaminants and their effects on human health;
- the remediation of contaminated soils, natural waters, and the atmosphere; and
- the safe disposal of toxic and radioactive waste from past and present weapons production/nuclear power generation as well as from agricultural, manufacturing, and mining activities.

The main scientific issues concern the concentration and chemical forms (or speciation), distribution, reactivity, transformations among forms, mobility, and bioavailability of contaminants. These issues ultimately depend on molecular-scale structure and properties. The chemical processes affecting contaminants are interrelated and enormously complicated, as illustrated in Figure 5. This is true because contaminated natural systems such as soils are chemically and physically heterogeneous mixtures containing many different solids, aqueous species, gases and organisms.

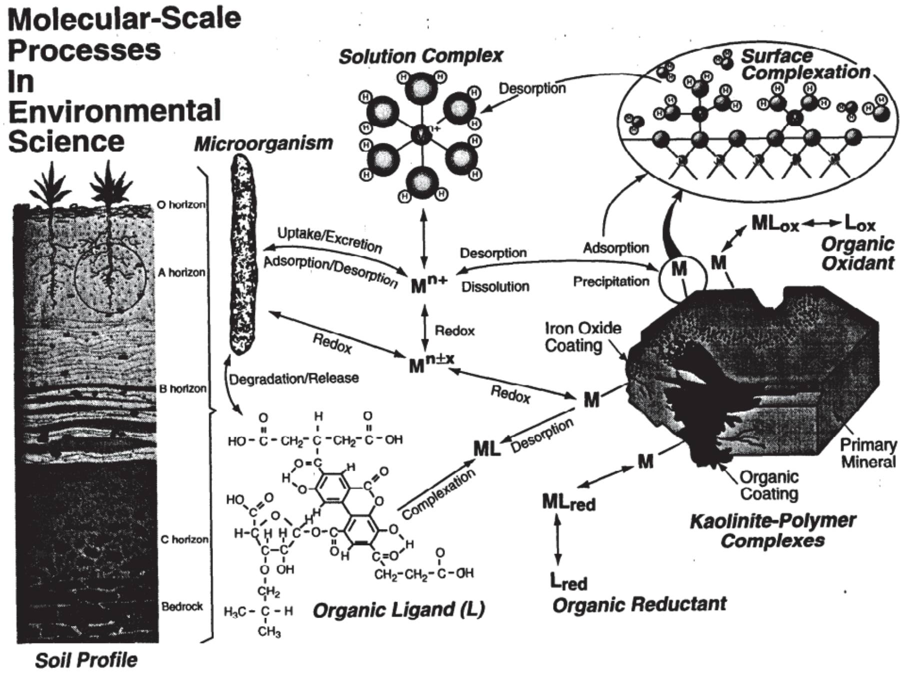


Figure 5. Schematic Illustration of *some* of the Processes that Affect the Fate of Environmental Contaminants [e.g., misses processes associated with macro-organisms (animal and plant)]

Other components can include petroleum, volatile organic compounds such as benzene and trichloroethylene, and a host of other organic and inorganic pollutants. Their behavior is dominated by chemical interactions at solid-water and solid-gas interfaces. Natural systems also contain a complex array of organic matter, plants, fungi, enzymes, and organisms that mediate these reactions and thus affect the forms, transformations, and transformation rates of environmental contaminants. Additionally, all of these processes will vary hugely both on spatial and temporal scales and so must be individually determined for a given site. Due to variations in temperature, transpiration, biological activity, rainfall, etc., rates of processes may show diurnal and/or seasonal cycles and, over longer periods, be susceptible to the impacts of climate change and variations in anthropogenic activity (e.g. land use, water management).

4.2.1 Chemical Environment at the Disposal Site

An important starting point that needs to be considered before discussions on the chemical environment at any site can be discussed, is of the position of the water table/air interface and how this will vary with time, as these changes can all involve fluxes of solute into the system.

Saturation/desaturation of the Vadose Zone

The vadose zone is a zone of natural and anthropogenic activity. Its constituents do not passively reside in place or steadily pass through. There are transport processes of various kinds, thermodynamic interactions, and chemical reactions involving both natural and artificial substances. There is the biological activity of plant roots, rodents, worms, microbiota, and other organisms. The flow rate of water is often directly of interest: for example, in estimating how fast water moves down to the water table, that is the aquifer recharge rate. It also is critical in the transport of contaminants, whether dissolved or in the form of a non-aqueous liquid or solid. The usual first step in assessing the rate of spreading of contaminants in the subsurface is to assess the flow rate of water that moves the contaminant along with it. Hydrologically, the vadose zone is often the main factor controlling water movement from the land surface to aquifers. Flow rates and chemical reactions in the unsaturated zone control whether, where, and how fast contaminants enter groundwater supplies.

A whole range of factors will affect the chemical environment at the site and these factors can be natural or anthropogenic and vary on a number of different timescales, e.g., diurnal (e.g., day-night temperature cycles), seasonal (e.g., precipitation events), high/low atmospheric pressure zones, river level, decadal and more (e.g., natural and anthropogenic climate change). Saturation and de-saturation in the vadose zone will depend on the level of the water table, which in turn is controlled by parameters such as temperature (diurnal effect) and atmospheric pressure. Zones of both high and low pressure have the ability to change the gas phase within the air-filled porosity of the vadose zone. The air phase above the water table is generally static, but will be driven by changes in the water table and by atmospheric pressure. A high-pressure zone above the surface of the ground will drive air into the vadose zone and a low pressure zone will allow air/gas to be emitted from the vadose zone. What this effect does is to change the gas phase in the vadose zone. Biological respiration takes place within the vadose zone resulting in a build-up of CO_2 during times when the air phase is static. An increase in CO_2 is generally associated with a decrease in pH of soil water.

The air-filled zone within the vadose zone will exchange gas with the atmosphere, flushing out CO_2, which will in turn affect the pH of soil water, e.g., thin films around grains and within pores. So, diurnal temperature cycles and atmospheric pressure can both affect the position of the water table, but additionally so will the level of any major drainage in the system, e.g., river level. Generally, when the river level rises, so does the water table, although there may be some inertia in the system depending on how far the vadose zone that you are studying is from the water table.

Finally, anthropogenic activities on-site such as remediation activities and off-site activities such as water abstraction may also have a significant impact on the position the water table, especially in the short term.

In the longer term, anthropogenically induced climate change will have an impact on the position of the water table.

4.2.2 Mineralogy

Minerals are generally coated with surface layers e.g., biofilms, oxides etc., but it is the surface coatings of minerals with which radionuclides will interact. However, the mineralogy of any site is not constant with time; it can change because of a number of factors. For example, the use of concrete in a repository or indeed as a contained waste type will lead to the release of high pH/alkaline leachate, which can lead to changes in the mineralogy. Any changes in the mineralogy can lead to changes in porosity, which can change the water flow characteristics that implicitly means that the transport pathways for radionuclide/contaminant transport will evolve with time.

4.2.3 pH and redox (Eh) Buffering

In the natural environment, pH generally ranges from slightly acidic to slightly alkaline (pH 5-8), but there are exceptions, e.g., highly organic waterlogged soils. Depending on the circumstances, pH can change considerably with distance and time as environmental conditions change. Buffering is the ability of a system to resist changes in pH resulting from addition of acid or alkaline ions (e.g., high pH plume from concrete). Biological activity is significantly influenced by pH, as many microbes only function in a very narrow "optimum" pH range, above and below which their activity is inhibited, as is the activity of animals such as arthropods. On the other hand, microbial activity may change pH, both on a large scale (e.g., due to the oxidation of sulfides by sulfur oxidizing bacteria, the source of acid mine drainage) and on a micro-scale (within biofilms).

Many soil components have a pH-dependent surface charge that influences their properties, e.g., humic organic matter has an overall negative charge that depends on the extent of dissociation of phenolic and carboxyl groups. Hydrous oxides and clay minerals are negatively charged at high pH and positively charged at low pH, the magnitude of which depends on pH (greater at higher pH). Clearly, then, pH will have a large impact on the transport or retardation of contaminants.

Eh is a measure of the extent to which a system is reducing or oxidizing and, in groundwater, may define the stability (thermodynamic) of redox-sensitive dissolved species and minerals and hence the solubility and transport of elements and their interactions with available surfaces. Eh is determined by redox reactions, which involve the transfer of electrons from one chemical species to another and, as hydrogen ions are involved in many cases, pH has a direct impact on Eh. The fundamental problem with Eh is that, for environmental systems, it is not a well-defined parameter as many redox pairs are not in equilibrium in natural waters (Lindberg and Runnells, 1984). As a result, different redox electrodes will commonly give different readings in a specific water and bear little relationship to key redox couples that require catalysis by microbes or reactive surfaces.

Importantly, the chemical species of many key contaminants is dependent on both pH and Eh, as illustrated in the Pourbaix diagram in Figure 6. The production of such diagrams does, however, depend not only on assumptions about Eh (generally based on "chemical common sense"), but also the presence of complexants that can stabilize particular redox states and the thermodynamic data used (very poor for many of the species of interest and generally measured only at 25 °C).

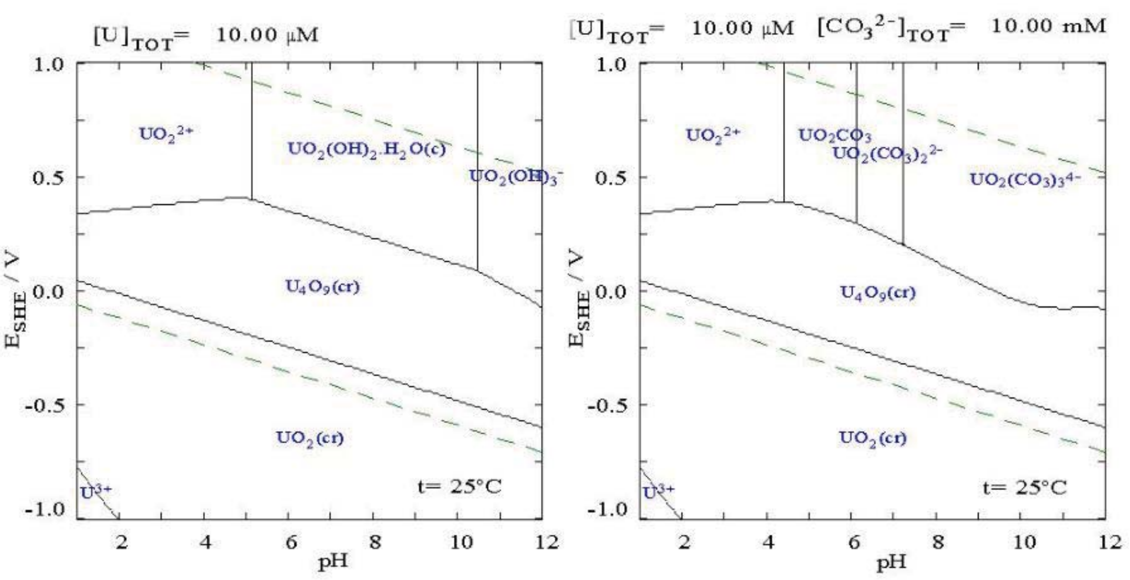


Figure 6. Pourbaix Diagrams of Uranium in a Non-complexing Solution (left) and Carbonate Solution (the dashed lines indicate the stability limits of water)

Speciation of an element (contaminant) is extremely important as ultimately it controls the mobility, interaction and fate in the environment. This may be influenced by Eh/pH changes within a disposal facility or along a transport path. In the most extreme cases, reaction fronts showing sharp changes in Eh and/or pH may exist; these are commonly observed, but particularly difficult (or impossible) to model using equilibrium thermodynamics, requiring representation of reaction kinetics if not explicit consideration of key microbial processes.

At reaction fronts, precipitation/dissolution of minerals can be high and these are key areas where colloid formation/destabilization may take place. The energy released from inorganic redox reactions can be harnessed by chemotrophic organisms for their life processes and therefore high microbial activity levels can be found at redox fronts. Eh can vary widely in a system, as regards the vadose zone in particular, air-filled pores will clearly be more oxidizing whereas water filled pores lined with organic material may be reducing. During the onset of reduction, microbial populations will go from being dominated by aerobic ones to anaerobic ones (first facultative anaerobes followed by obligate anaerobes) and the use of electron sources other than oxygen will take place, in the order NO_3^-, Mn(IV), Fe(III), SO_4^{2-} and lastly CO_2.

4.2.4 Major and Minor Element Concentrations

The concentration of elements in soils and other surficial materials is determined not only by the elemental content of the bedrock or other deposits from which the surface materials have been produced, but also by the effects of climatic and biological factors as well as any influences of land use (e.g. agricultural and industrial operations) that have acted on the surface environment for various periods of time. Soil factors such as organic matter, type and amount of clay, pH and cation exchange capacity influence the quantity of trace elements available for mobilization and release or sorption in a soil. However, in arid soils, trace elements can be mobilized through plant uptake and erosion/leaching processes, but these soils usually contain higher contents of trace elements than other soils. Minor element concentrations are particularly important for the stable isotopes of radionuclides of interest, especially in arid soils where concentrations can be high.

It is also noted that solubility and sorption are elemental concepts, meaning all concentrations of stable and radioactive isotopes of an element that are present in a system are summed to define chemical behavior. It is inappropriate and can be non-conservative to assign a radionuclide an elemental solubility or sorption if other stable or radioactive isotopes exist in the system. For example, in the Hanford Site river corridor work it is necessary to recognize carbon-14 exists in two forms with very different sorption behavior: carbon-14 in liquid form typically associated with reactor gas condensate is extremely mobile (K_d = 0 mL/g) and carbon-14 in solid form typically associated with graphite that is very immobile (K_d = 200 mL/g). Other national radioactive waste disposal programs have been careful to consider all stable and radioactive isotopes in their release and transport modeling (e.g., TR-02-06, *Project Opalinus: Models, Codes and Data for Safety Assessment*).

4.2.5 Natural Colloids (Solid Phases Transported in Water)

Colloids are naturally occurring solids made up of organic or inorganic substances found in all groundwater. Colloids are operationally defined as being between 1 and 1000 nm in size. Colloids can be operationally defined as in suspension or in true solution are organic or inorganic substances to which a radionuclide or contaminant has sorbed. It is now generally accepted that mobile organic or inorganic particles or colloids are ubiquitous in groundwater and that these solid materials have the potential to transport contaminants long distances.

Increased understanding of the conditions under which colloids facilitate transport of radionuclides is necessary to be able develop reliable transport models needed to predict radionuclide migration and improve models of risk assessment. The extent (how much, how fast, under what geochemical conditions) to which contaminants are transported via colloids as well as the mechanisms (e.g., adsorption, or surface precipitation onto mineral colloids, co-precipitation or intrinsic colloid formation) control the rate of contaminant transfer through a given groundwater system. If colloids facilitate transport of low-solubility radionuclides, these contaminants will be detected at much higher concentrations down gradient than simple solubility and retardation calculations would predict. Increases in both pH and salinity lead to the destabilization of colloids through particle dispersion.

However, fate and transport models neglecting colloid-facilitated transport therefore often under-predict contaminant movement. Long-term predictions of contaminant fate and transport as well as risk assessment rely on an accurate representation of subsurface processes, and in the case of strongly sorbing contaminants, need to consider mobile colloids as potential contaminant carriers. Modeling of colloid-facilitated contaminant transport involves various interactions, including colloid attachment to and detachment from the solid matrix and the air–water interface, contaminant adsorption to, and desorption from, colloids and transport with mobile colloids, and contaminant adsorption to and desorption from the solid matrix (Figure 7).

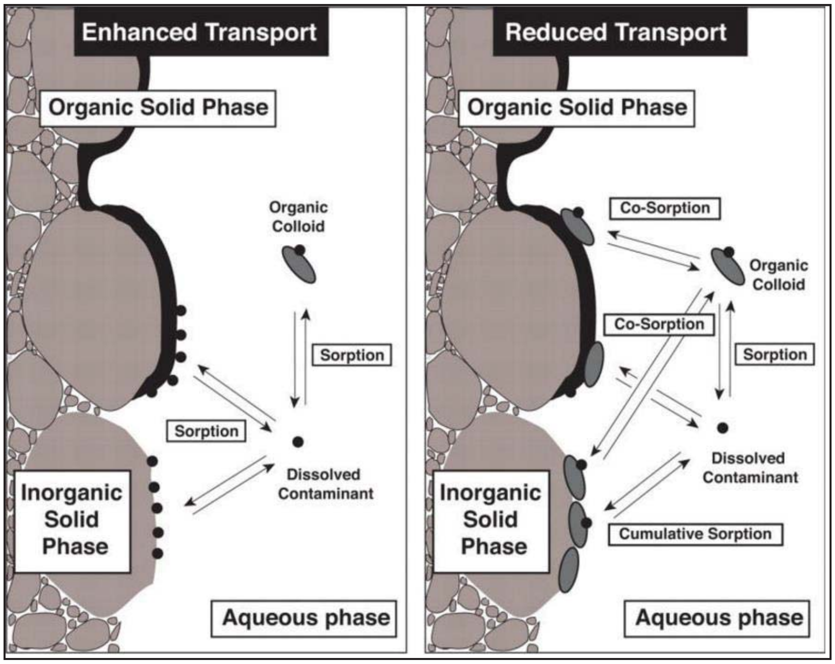


Figure 7. Colloidal Interaction with Contaminants Can Both Enhance and Reduce Transport

Most of these processes in colloid-facilitated contaminant transport models have been described by first- or second-order kinetics. The unique feature of the vadose zone is the presence of an air phase, which affects colloid and contaminant transport in several ways. Colloids can be trapped in immobile water, strained in thin water films and in the smallest regions of the pore space, or attached to the air–water interface itself. Colloidal transport in unsaturated conditions is expected to be very low with water being restricted to films around grains and very small pores.

4.2.6 Microbial Ecology and Biofilms

Microbial activity in any environment is generally located on chemical or physical interfaces, usually within biofilms, and the impacts can be both chemical (e.g., changing redox conditions, pH) and/or physical (e.g., altering porosity) and may result in extracellular or intracellular formation of minerals or indeed mineral degradation in addition to alteration of metal speciation, toxicity and mobility. Microorganisms in subsurface environments play a major role in the cycling of elements, as well as weathering of rocks and sediments, and can affect the geochemical properties of groundwater by modifying the fate and transport of organic and inorganic contaminants. Microbial cell walls, outer layers, and exopolymers can sorb, bind or entrap many soluble and insoluble metal species, e.g., clay minerals, colloids, oxides, etc., which also have significant metal-sorption properties.

The formation and development of biofilms in the subsurface environment will depend on the presence of the microbes themselves, the availability of energy sources, nutrients and of course water necessary for life processes (West and Chilton, 1997). A biofilm is an agglomeration of microbial cells and their excreted organic and inorganic products that is attached to, or coats, mineral surfaces or other substrates (Taylor and Jaffé, 1990) and are very common in the geosphere and biosphere, forming in a range of diverse environments.

While the vadose region of the subsurface generally does not support robust microbial populations, particularly in arid regions, there have been numerous reports of viable microorganisms associated with unsaturated zone soils and sediments including at the Hanford Site as far back as the early 1990s

(Brockman et al., 1992; Fredrickson et al., 1991; Fredrickson et al., 1993). Water potentials in the vadose zone generally do not directly restrict microbial activity, because many microorganisms are relatively tolerant to the matric water potentials typical of vadose sediments. Rather, it is relatively thin, discontinuous water films that will retard the diffusion of solutes, including nutrients and metabolic waste products that restrict microbial metabolism. In the vadose zone, microbes will dominate everything and therefore need to be explicitly included in any models of release of contaminants. Reactions that occur may alter the pH and the redox conditions, therefore it is very difficult to define them; concomitantly, solubility and sorption will also change. Furthermore, properties in the vadose zone will not be constant; they will all vary in space and time both due to changing climate and human activities, and accordingly it is very difficult to extrapolate a few centuries into the future. Therefore, developing system understanding is extremely important.

It should also be noted here that microbes in the near field of a waste disposal system could degrade waste, produce gas (stable and radioactive), and could cause degradation of the engineered barrier system.

4.2.7 Organic Degradation Processes

Cellulosic materials (e.g. paper, wood, cotton wool…) and other organic polymers readily degrade under alkaline anaerobic conditions to form CDPs. CDPs consist of soluble organic compounds that are able to form aqueous complexes with radionuclides and react with surface complexation sites, potentially together with radionuclides. Isosaccharinic acid is expected to be the most abundant CDP, but numerous other short chain carboxylic acids are also produced during the degradation process such (e.g., acetate, formate, lactate, etc.). These carboxylic acids will eventually further biodegrade, especially when environmental conditions become aerobic.

4.2.7.1 Retardation Processes

The transport of radionuclides through materials and along migration pathways in the surrounding rock is controlled by diffusion and advection in both groundwater and pore water. Some radionuclides are so poorly adsorbed that they effectively move at the same rate as the water containing them (e.g., ^{3}H, ^{14}C, ^{129}I), but the majority do in fact interact with materials in the engineered barrier system and rock surfaces across which water passes. The radionuclides may also be subject to changes in solution behavior depending on the extent of rock-water interactions along the pathway. Retardation processes can be defined as either chemical of physicochemical and have a range of different mechanisms (illustrated in Figure 8).

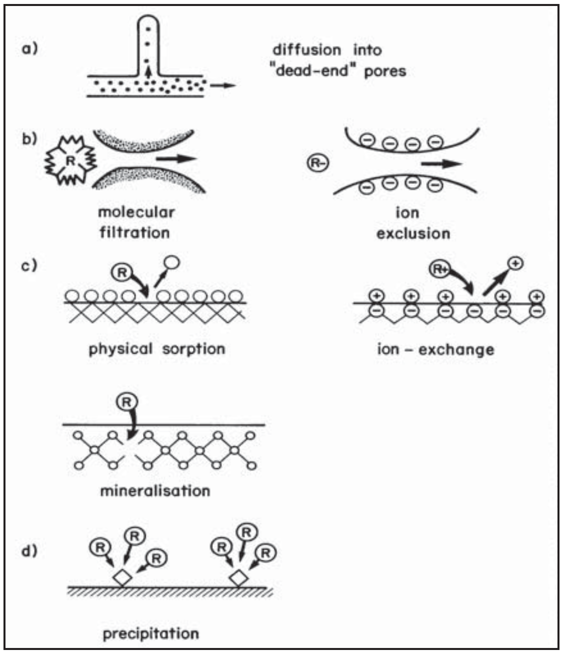


Figure 8. Retardation Mechanisms that can Affect Radionuclide Transport (from McKinley and Alexander, 1992)

Physicochemical retardation mechanisms illustrated in Figure 8 are as follows: (a) matrix diffusion, (b) molecular filtration and ion exclusion, (c) chemical retardation mechanisms including ion exchange, adsorption (physical sorption) and mineralization, and (d) precipitation and co-precipitation.

Chemical Retardation Mechanisms

Generally, ion exchange and adsorption and termed sorption and both retard transport of radionuclides. Sorption is usually modeled as a reversible process, although desorption kinetics are slower than sorption kinetics and there can be instances where sorption is irreversible e.g., cesium (Fuller et al., 2015). Precipitation is not a sorption process but can be difficult to discriminate from sorption in both field and laboratory experiments. This happens when concentrations of the elements of concern have exceeded the linear sorption range/solution saturation range (Figure 9).

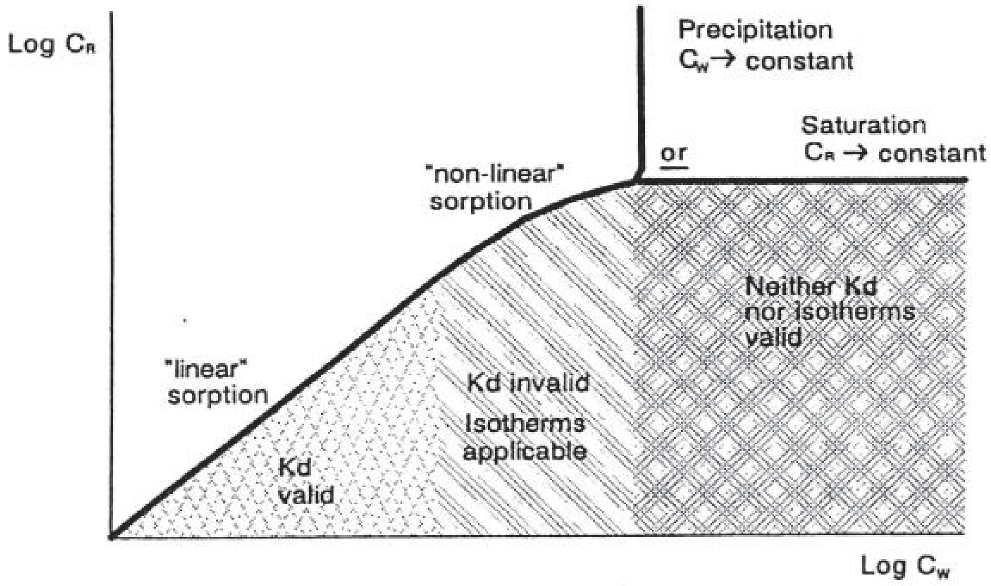


Figure 9. Schematic Representation of the Variation of C_R (the concentration sorbed on the rock phase) with C_w (solute concentration in the aqueous phase) for a General Isotherm, showing the Effects of Precipitation and Saturation (from McKinley and Alexander, 1992)

Radionuclides can also co-precipitate if total dissolved solids are high. When this occurs, an extremely complex environment can develop, resulting in radionuclides co-precipitating as solid solutions in a variety of different mineral phases. Radionuclides can also be effectively co-precipitated if they are scavenged by amorphous precipitates such as iron oxyhydroxides. The stability of amorphous phases and precipitated minerals is dependent on the maintenance of high solution concentrations. When concentrations begin to drop (below saturation) then precipitated minerals will begin to re-dissolve and amorphous phases will begin to destabilize thus releasing any contained radionuclides back into solution.

Physicochemical Retardation Mechanisms

Matrix diffusion is the process where water that is flowing in distinct fractures penetrates into the surrounding rock matrix. Diffusion occurs into the rock matrix by way of a system of connected pores or microfractures and diffusion through the solid phase is considered negligible in comparison (Valkiainen, 1992). The important aspect of matrix diffusion is that it greatly increases the surface area on which transported radionuclides can sorb. However, if the flow of groundwater is relatively fast, matrix diffusion will not be as significant a retardation process as it can be with slower flowing groundwater (e.g., as with a deep geological repository). Anion exclusion is a process whereby negatively charged mineral surfaces cause anions to be repelled and therefore, access to surfaces for sorption is limited. This correspondingly promotes their transport through the geosphere. In addition, when it comes to matrix diffusion, more narrow pores may be inaccessible and therefore again reduce the amount of retardation that takes place. Molecular filtration is self-explanatory; this process will serve to enhance radionuclide transport if smaller pores inhibit radionuclide penetration into the rock matrix. In practice, many retardation mechanisms are often hard to distinguish as many/all may occur simultaneously. Representation in models is very different, so assumed dominant processes have to be proven (validation).

4.2.8 Radioactive Decay, Ingrowth, Radioysis, and Hot Atom Effects

The decay in activity of unsupported parent radionuclides is set by the half-life of the parent and the ingrowth (important in all cases) of activity of a daughter takes place at a rate set by its own half-life. Common cases are:

- Secular equilibrium ($t_{1/2}$ daughter << $t_{1/2}$ parent)
- Transient equilibrium ($t_{1/2}$ daughter < $t_{1/2}$ parent)
- No equilibrium ($t_{1/2}$ parent >> $t_{1/2}$ daughter)

Where $t_{1/2}$ is the radioactive half-live.

Radiolysis depends on activity levels and is generally significant only when activities are highest – i.e., within or near engineered barrier systems. Most focus on radiolysis is on the radiolysis of water, but can be significant for some waste matrices (e.g., bitumen, resins). Radiolysis is characterized by linear energy transfer for specific radiation/matrices, so usually dominated by alphas (due to their mass and the fact that they give up nearly all their energy in the first interaction).

Hot atom effects are generally deemed unimportant but they group together effects of physical recoil during decay (especially alpha) and chemical effects of the highly active daughter. These effects are usually subtle and generally more significant for interpretation of analogues than influencing radionuclide release and transport.

4.3 Transport

Consideration of transport processes is provided in this section.

4.3.1 Advection/Dispersion

Advection corresponds to the movement of dissolved species with the bulk displacement of the fluid. Advection is controlled by pressure gradients and by the hydraulic conductivities of the porous/fractured medium, and is typically expressed through some variant form of Darcy's Law.

Kinematic dispersion is a mixing phenomenon reflecting essentially in the heterogeneity of the microscopic flow velocities inside the porous medium. This effect causes a spreading of solute concentration. The spreading of concentration is larger in the direction of the velocity than in transverse (lateral) directions.

For unsaturated (vadose), near-surface disposal conditions at the Hanford Site, advection is driven by gravity in the downward direction. This advective flow is often called either "recharge rate" or "infiltration rate." Therefore, vertical advective flow, combined with lateral dispersion, will likely be the transport boundary conditions affecting the release of contaminants from many forms of radioactive waste and debris disposed in unsaturated, near-surface facilities at the Hanford Site.

The one-dimensional differential equation of transport can be written as:

$$\frac{\partial}{\partial t}\left(\theta_w \overset{\circ}{C}_{wi} + \beta \overset{\circ}{C}_{si}\right) = -\frac{\partial}{\partial z}\left(-\theta_w D_{si}\frac{\partial \overset{\circ}{C}_{wi}}{\partial z} + q_w \overset{\circ}{C}_{wi}\right) - \lambda_i\left(\theta_w \overset{\circ}{C}_{wi} + \beta \overset{\circ}{C}_{si}\right)$$

Where,

θ_w = volumetric water content of the source zone soil or vadose zone soil.
$\overset{\circ}{C}_{wi}$ = concentration of contaminant i in the aqueous phase.
B = bulk density of the source zone soil or vadose zone soil.

C_{si}° = concentration of contaminant i in the sorbed phase.
z = vertical spatial coordinate.
D_{si} = effective diffusion coefficient of contaminant i in the soil.
q_w = Darcy flux density of water flowing through the source zone or vadose zone.

The presence of a gas phase in a porous medium affects the movement of the liquid phase. In unsaturated conditions such as are found at near-surface disposal sites at Hanford, pressure and hydraulic conductivity, and therefore the advective flow-velocity field, depend of the proportion of water in the pore (water saturation).

4.3.2 Diffusion

Molecular diffusion is a physical phenomenon associated with Brownian agitation. It results in a mass transfer from zones of high concentration to those of low concentration according to Fick's Law, which defines diffusion as the product between a diffusion coefficient and the concentration gradient. In porous media, solute movement is affected by the structure solid matrix. Thus, there is a reduction in the *free-water diffusion coefficient* of a contaminant (D_v) and in the *effective diffusion coefficient* (D_e) controlling the transport rate (hence, release rate) of a contaminant in a porous waste form. There are several relevant representations of diffusion in porous media that need to be described, so that appropriate measurements are made and applied to contaminant release behavior:

$$D_e = \varepsilon D_v \phi = \varepsilon D_v \delta_D / \tau^2$$

Where ε is the *effective solution-filled porosity* available for diffusion (can be less than total porosity), ϕ is the *geometric or tortuosity factor*, δ_D is the *constrictivity*, and τ is the *tortuosity*. Also, note that by this definition, the porosity term ε may need to be normalized by the *degree of partial saturation* (< 1) for release modeling of waste forms in the near surface vadose zone at the Hanford Site.

As noted earlier, there can be retardation of contaminants, expressed as a *sorption coefficient* or K_d, as contaminants are transported along and interact with solid surfaces, so that an *apparent diffusion coefficient* (D_a) needs to also be defined:

$$D_a = D_e / (\varepsilon + \rho K_d)$$

Where ρ is the density of the solid phase through which the diffusion is occurring.

In unconsolidated porous media, such as near-surface soils, diffusive transport is generally negligible with respect to advective transport with dispersion (although strictly depends on distance of interest, as defined by a Peclet number). Diffusion becomes the dominant transport process affecting the transport/release of contaminants, however, in materials with low hydraulic conductivity (permeability), which may include engineered backfills/liners of disposal systems or porous radioactive waste forms themselves, such as cements.

4.3.3 Evolution of Environmental Conditions from Interaction between Chemical and Hydrological Processes

Natural (i.e., atmospheric precipitation) or anthropogenic recharge is a major model component as it represents the driving force for the contaminants to migrate downwards and enter the underlying aquifer. In the context of the Hanford Site, recharge is the result of flow through the thick vadose zone.

Recharge is the result of infiltration from precipitation or manmade activities. The infiltration has two potential effects: it can affect the release rate from the waste forms as well as the advective flow rate through the vadose zone beneath the facility. Factors that influence recharge at sites ranging from undisturbed ecosystems to engineered surface barriers include climate, geology, soils, topography, ecology, hydrology, engineered barriers, surface features, and disturbances.

Recharge evolution in time, in terms of the rates, must be assessed to establish past vadose zone conditions during all waste disposal sites operations and to predict future hydraulic conditions prevailing during the time period considered in the analysis (i.e., until 10,000 years after closure). This implies, in particular, knowledge of historical and future: climate conditions, land use, manmade additions of water from water line leaks, ponds, watering…. It also requires an understanding of unsaturated flow through unaltered hydrogeological units as well as the impact of engineering barriers and of their degradation in time and space.

Note that chemical reactions occurring in the backfill surrounding a waste form, or beneath the waste form, can affect both retardation properties and the transport properties (e.g., porosity, permeability) of the backfill, in turn potentially affecting the release model behavior of waste forms. For instance, cementitious leachates with pH values of 12 and a high calcium content may react with minerals like silica and, in return, produce locally cementitious calcium silicate hydrate (CSH) phases. These secondary phases may significantly both reduce the hydraulic properties of sediments and increase sorption of radionuclides and organics. Thus, release, retardation and transport processes need to be considered together considering all coupling involved.

For example, if chemical precipitation takes place in the backfill immediately surrounding a waste form, precipitates could clog pores, possibly affecting advective flow (infiltration rate) of water. This, in turn, can change the boundary conditions affecting which process controls contaminant releases from some types of waste forms.

A further consideration is that degree of saturation in waste forms or backfill around waste forms may evolve in space and time, and directly influence, for example, $O_2(g)$ and $CO_2(g)$ partial pressures, thus potentially affecting pH and redox values as well as microbial activity. This could depend on the changes in water infiltration fluxes resulting from changes in rainfall/snowfall or degradation of surface caps/covers.

In addition, cementitious materials are typically assumed to degrade progressively through three stages, resulting in a change of their physical and chemical properties. From a chemical perspective, cementitious materials successively release sodium/potassium hydroxide, calcium hydroxide and finally silica (SiO_2). During this process, the pH of the pore water drops from values > 12 down to 5.5, together with a drop in the solution ionic strength. Furthermore, concrete containing blast furnace slag significantly increases sulfide concentrations in pore water, which reduces the solubility of many radionuclides. These reducing conditions are expected to progressively disappear as the concrete gets exposed to atmospheric $O_2(g)$.

Similarly, redox fronts generated, for instance, by reducing cements may affect sediments below and locally change radionuclide retardation factors. With time, these reducing conditions are expected to disappear progressively due to the action of atmospheric O_2. In the same line, atmospheric CO_2 may progressively buffer the pH solution through calcite precipitation.

Finally, waste components which are directly and significantly affecting the speciation of the pore water (such as CDPs) may also be totally released progressively. Thus, the physicochemical conditions of the pore water are expected to vary significantly during the period of interest with potentially significant impacts on radionuclide mobility.

4.3.4 Gaseous Transport

By definition, the porous medium in the vadose zone is filled by both a water and a gas phase. Volatile contaminants can be partitioned between the two phases according to their Henry's Law constants. It is generally assumed that the air phase is immobile in the unsaturated media but gas transport by advection (for instance when volatilization generates pressure gradients) or by diffusion could occur.

4.4 Other Factors

Additional concerns for representation of waste form release are noted in this section.

4.4.1 Co-disposal Concerns

Co-disposal inevitably increases system complexity and raises further concerns about the over-simplifications of release modeling. However, co-disposal may be a historical, operational or planned circumstance. For example, to increase overall disposal system performance in cases where contaminant releases are dominated by a small-volume waste, other types of waste with low-release rates or small inventories of contaminants, could be packed around the small-volume waste to act as additional barriers, e.g., JAEA and FEPC (2007).

A key issue to be addressed is potential, adverse interactions between different waste types – predominantly the impact of leachate from one waste (which could be high pH or contain microbial nutrients) on surrounding or down-flow packages. It is also possible that perturbations from some waste groups (e.g., gas pressurization, swelling, slumping, or in the worst case, spontaneous combustion) could degrade disposal facility barriers that influence other waste in the vicinity.

4.4.2 Age and History of Waste Along with Uncertainties and Degree of Heterogeneity

In general, confidence in characteristics of wastes will decrease with their age – especially if their history in terms of production, conditioning, packaging and storage is not fully documented. Another concern is to what degree it has been determined (or assumed) that a waste form (e.g., soil debris) is itself homogeneous, and contaminants are homogeneously distributed within the waste form.

4.4.3 Caliche Layers

Caliche is a sedimentary rock formed in arid environments from the precipitation of $CaCO_3$ (calcrete), SiO_2 (silcrete) or Fe_2O_3 (ferricrete), commonly referred to as "hardpans" or duricrusts (Langmuir, 1997). Caliche generally forms when minerals leach from upper sediment layers and accumulate in a lower-lying layer via precipitation arising from evaporation of water, aided by lateral dispersion of such leachates. Caliche may also form when water, carrying dissolved minerals from lower layers, rises through capillary action. Caliche layers typically have lower hydraulic conductivity than the surrounding sediments, and can create a flow-diversion barrier.

In an arid region such as at the Hanford Site, past liquid waste discharges into trenches sank into the ground. In the subsurface, it might have been possible for such liquid wastes to spread via lateral dispersion, increasing the exposed surface area available for evaporation, leading to precipitation of radionuclide-bearing solids. It has been reported that uranium- and iodine-bearing caliche layers are known to exist at depth in the Central Plateau of the Hanford Site. While natural uranium-bearing caliches are well known and often can be economically viable mineral deposits, the presence of radioiodine in such caliche layers would be confirmation that some past liquid wastes evolved into precipitates, or interacted with existing caliche layers, at the Hanford Site. If this is a credible scenario to be considered, note that none of the previous CA reports on release models has considered or modeled such a subsurface "waste form." Furthermore, if a precipitated layer from previous liquid wastes were to have formed near the surface, erosion/exhumation and air-borne dispersion of such a layer might be considered a credible scenario over a compliance times on the scale of 10,000 years.

4.4.4 Safety Significance of Release Rate Constraints

Key dose contributing radionuclides are likely to be Tc-99 and I-129, as well as possible U-238 decay-chain daughter nuclides, such as Ra-226, that might grow-in during a 10,000-year compliance period. The transport times, even with retardation, through both the vadose zone and saturated zone are likely to be far shorter than the half-lives of such dose contributing radionuclides, so that there will be insignificant radioactive decay during transit. This means, therefore, that the concentrations, hence doses, arising from such radionuclides will largely be determined by the release rate constraints of the waste forms in which such radionuclides reside. For example, this is certainly the conclusion from the IDF PA calculations. Of course, safety significance must be tested with Composite Assessment's own total system model. If confirmed, however, then due consideration of verifying inventory data, improving release models with the factors noted in this Section 3, and/or avoiding undue conservatisms in release model assumptions will provide the most likely options for enhancing confidence in overall safety assessment.

5 Assignment of Release Models to Specified Waste Forms

Table 1 presents a summary of recommended release models, as reviewed in Sections 3 and 4 of this report, for specific waste forms previously identified for the Hanford Site (PNNL-11800). "Cements" are included as a basic and well-studied model by which possible future wastes might be conditioned for disposal. In addition to the aqueous phase release models cited in Table 1, a bulleted summary of concerns regarding their application are also noted.

Table 1. Recommended Aqueous Phase Release Models by Waste Type

Waste Type	Recommended Previous CA Models	Concerns
Soil Debris	Equations D.28-32[1]	• absence of radioactive decay/ingrowth • assumes fixed parameter values (changes in in environmental chemical and hydrological conditions likely over 10,000 years) • assumes homogeneous waste form • assigns *radionuclides* to *radioelement* properties such as K_d and solubility • reformulate terminology and ensure it is consistent • check balance in all equations from the point of view of dimensions • impact of microbial activity not considered
Saltcake	Equation D.46[1]	• assumes fixed parameter values • assumes congruent dissolution and no retardation
Reactor Blocks	Equation D.64[1]	• source term controlled by the local temperature only

Table 1. Recommended Aqueous Phase Release Models by Waste Type

Waste Type	Recommended Previous CA Models	Concerns
Cement (encapsulated)	A-5 to A-7[2]	• assumes fixed parameter values (no evolution of cements through time) • assumes no retardation • simplified waste geometry (no shrinking core model)
Cement (solidified)	A-5 to A-7[2]	• assumes fixed parameter values (no evolution of cements through time) • assumes no retardation • simplified waste geometry (no shrinking core model)
Caliche (from Liquid Waste)	None	• existing caliche layers in Central Plateau • natural caliche known to include mineral precipitates containing cations and anions matching or analogous to contaminants
Organic Wastes	None	• impact of microbial activity particularly important

[1] PNNL-11800, 1998, *Composite Analysis for Low-Level Waste Disposal in the 200 Area Plateau of the Hanford Site*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0079141H.

[2] RPP-CALC-61030, 2016, *Cementitious Waste Form Release Calculations for the Integrated Disposal Facility Performance Assessment*, Washington River Protection Solutions, Richland, Washington.

Compared to the approach adopted for the Hanford 1998 CA (PNNL-11800), several improvements should be considered. The cement model used in PNNL-11800 could evolve towards a diffusive shrinking core model, such as the one described in RPP-CALC-61030, to simulate a more realistic geometry and incorporate a retardation factor.

When appropriate, a cement-type, shrinking core model could also be applied to other types of wastes like saltcake/sludge.

From a geochemical standpoint, studies that are more recent suggest that the source term release model should include a set of K_d corrections for soluble organics ligands (e.g., CDP), impacted sediments as well as cementitious K_ds, depending on the age of oxidizing or reducing cementitious solids. Such an approach would be recommended to account for releases of radionuclides at the Hanford Site more realistically.

Similarly, future release models should consider the impact of leachates on the nearby sediments that may locally change both the flow field and the radionuclide retardation factors.

Additional directions of interest could be:

1. Add a geochemical zone to account for the influence that the leachate from cementitious materials have on sorption properties in underlying vadose zone sediments.

2. Account for a potential formation of secondary CSH or calcium aluminate silicate hydrates (CASH) phases that may also locally alter the flow pattern.
3. Incorporate more mechanistic approaches to describe geochemistry. However, it should be noted that this approach could lead to complex calculations of K_ds when combining different pH, redox conditions, CDP concentrations… Following a similar objective, another approach could be based on tabulated radionuclide complexation coefficients for the relevant species (e.g., OH^-, CDP, surface sites …) for the computation of conditional reaction constants. Such an approach could be implemented relatively easily in a code like GoldSim to simulate more realistically the solution speciation.
4. Add kinetics, for instance to compute Tc interaction with reducing grout.
5. Implement a degradation rate for the cellulosic materials.
6. Modify solubilities for radioelements having stable isotopes or other radioisotopes (solubilities apply to *elements*, not individual *radionuclides*).
7. Microbiological effects.
8. Colloid-facilitated transport.

As stressed in Section 4, improvements in release modeling (which would include inventory estimates) of waste forms is likely to be the most credible and safety-significant improvements that can be achieved for iterative CA analyses. The menu of suggested enhancements noted above could be adopted in part or in full. Some enhancements, such as revised solubility could be easily incorporated into previous CA models to improve their reliability. Other model enhancements would require more effort to implement. The initial advantage of implementing newer models is using such models in a scoping manner to explore possible sensitivities of additional processes on calculated doses. From such scoping results, guidance could be provided as to possible priorities for future research and development on a safety/risk basis.

Table 1 above summarizes input to models that include some very complex transport representations, but limited chemical and process understanding. Rather than beginning with equations, an improved approach is to start with a mathematical description of the waste, waste container and the trench. In such a case, even if simplifications are made, they are all explicitly documented during model development.

A critical starting point is definition of the boundary conditions at the time of trench closure (t=0). This can usefully be specified for a profile of any waste in the trench normalized to 1.0 m^3. The reference volume will contain a specific volume of packaged waste and backfill/infill/liner, which can be related to mass by appropriate densities. The porosity and degree of water saturation can be defined for both waste and infill (if any) to define the initial material inventories. Given an average (or reference) concentration of contaminant in the waste package, the inventory in the reference volume (in appropriate units – kg, mol or Bq) can be defined.

For all waste types, the contaminant content can be further refined in terms of distribution between possible reservoirs – e.g.:

1. homogeneously distributed through impermeable waste matrix
2. homogeneously distributed through permeable waste matrix
3. concentrated on surfaces
4. localized precipitates
5. pore water
6. gas filled voids

7. biofilms, etc….

It will be important to establish the starting point of each of these reservoirs at t_0 and then describe how the system evolves with time, giving a general description of release of contaminants from a waste package (that is applicable for all waste types), per m^3 of trench. Typical processes that could be considered as models for these would be:

1. congruent dissolution proportional to surface area (possibly microbially catalyzed)
2. leaching proportional to surface are and diffusivity
3. sorption/desorption
4. dissolution/precipitation
5. fluxes into and out of solution (incl. colloids), water flow through the waste package
6. fluxes into and out of gas phase, gas flow through the waste package
7. fluxes into and out of biofilms (incl. colloids) etc….

Note that some processes can be specified for specific isotopes, but some (e.g. 3, 4), require all isotopes (stable and radioactive) to be considered together. Surface area dependent processes depend on geometry of the reservoir. All (or most) processes will be influenced by gradual evolution of chemical conditions (esp. Eh, pH).

Equations can thus be developed to extrapolate the evolution of the waste package based on mass balances (taking into account radionuclide decay/ingrowth into account). The flux of water from the waste package would then interact with the backfill/liner (which may contain also several reservoirs) and then be released to provide the source term for far-field transport calculations.

Such a generic model can be simplified for specific waste types, based on expert judgment or scoping calculations, providing a transparent process for defining recommendations for Table 1.

6 Future Enhancements to Modeling and Communicating Safety Performance of Contaminant Releases from Hanford Waste

Looking to the future, there are opportunities to enhance the completeness, and therefore the reliability, of release rate models for Hanford Site wastes. In many cases, such capabilities are already being applied in other countries engaged in near-surface disposal of radioactive wastes. Thus, there is confidence that such improvements to release modeling at the Hanford Site have already been tested and verified, albeit that they employ new data in addition to the standard solubility limits, sorption K_d, infiltration rate, etc., that have been instituted into the previous Hanford Site release models reviewed in this report. While a great deal of demonstrated techniques and information already collected can be applied to Hanford Site release rate modeling, the vadose zone environment and possibly unique waste forms at the Hanford Site will likely require collection of site-specific data.

6.1 Microbes: Identify and Reference what is known about Possible Microbial Impacts on Waste Form Performance

With the development of geomicrobiology in the late 20th century and the recognition of the existence of microbial life in deep geological formations, some seminal studies of the potential influence of microorganisms on high-level waste and spent fuel repositories were carried out (Mayfield and Barker, 1982; West et al., 1982). For near-surface disposal, seminal research work on microbial impacts was carried out by American emeritus professor A.J. Francis (https://www.bnl.gov/envsci/bio/francis-aj.php) and pre-dates the research studies that were carried out in deep disposal systems. However, this early work showed clearly that microbial processes have the potential to affect the performance of a geological repository. These processes can have both direct (e.g., biodegradation and corrosion of some wastes and repository containment materials; gas production; blocking of pores by biofilms) and indirect effects (e.g., alteration of pH and redox resulting in changes to radionuclide mobility). Many radioactive waste management organizations now include applied geomicrobiology in their programs.

The varying materials that may be used in a repository (as waste matrices, canisters, overpacks, buffers, backfills, etc.) are all potential nutrient and energy sources for microbial use. These materials may also have a microbial load, as will the excavated repository itself. Internationally, considerable work has been carried out to understand and quantify microbial influences on many of these materials. Much of this work is site- or repository concept-specific but all investigations show the importance of considering microbial impacts in the context of a particular repository concept. The performance of the waste itself and repository construction materials was tackled in the early 1990s. The impacts of microorganisms on steel corrosion were studied (Philp et al., 1991) and considerable efforts were made to investigate cellulosic biodegradation and biogenic gas production in the context of I/LLW (e.g., Coutts et al., 1997).

6.2 Evaluate Relevant Other U.S. or non-U.S. Models for Specific “Waste Types”

It is extremely advantageous that near-surface disposal of radioactive wastes is being conducted and reported in numerous other countries, including the modeling of release of contaminants from similar waste forms to those at the Hanford Site. Review and comparison of such alternative reports on waste form release could provide independent confirmation of the past Hanford Site models, as well as identifying credible release models for processes not considered in past Hanford Site release models.

The United Kingdom, for example, has considered microbes and their impacts on waste and repository performance for some considerable time because, during the post-closure phase of a repository, for some forms of low- and intermediate-level radioactive wastes significant quantities of gas can be generated, primarily by the anaerobic corrosion of metals and the degradation of organic wastes. For example, in the Nirex report written by Agg et al. (1997) a description is given of work carried out within the “Nirex Safety Assessment Research Programme” to address the generation of gas within a repository and the migration of gas from the repository to the biosphere.

These reports describe the theoretical modeling capabilities that have been developed to address microbial and gas generation issues. In addition, model validation approaches are described:

- Agg et al. (1997), *GAMMON (Version 1A): A Computer Programme addressing Gas Generation in Radioactive Waste Repositories*
- Agg et al., (1994), *Gas Generation and Migration from Radioactive Waste Repositories.*

Since the development of the GAMMON model described in Agg et al. (1997), the Nuclear Decommissioning Authority in the United Kingdom has developed a simplified model of gas generation, which considers and represents processes of gas generation from cellulose, metals and other wastes in a geological disposal facility (Small and Dutton, 2009). Again, model validation against appropriate data sets is also discussed.

Other relevant reports include:

Switzerland

- Warthmann, R., Mosberger, L. and Baier, U. (2013). Anaerober Abbau und Gasbildungskinetik für SMA in geologischen Tiefenlagern (Anaerobic Degradation and Gas Formation Kinetics for

SMA in Deep Geological Repositories). NAGRA Arbeitsbericht NAB 13-52, Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Hardstrasse 73, CH-5430 Wettingen.

United Kingdom

- Nirex, (2003). Generic Repository Studies: Generic post-closure Performance Assessment. Nirex Report no. N/080, July 2003, Nirex Limited, United Kingdom.
- Humphreys et al. (2010), *Microbial Effects on Repository Performance*.

EU

- Rodwell, W.R., Harris, A.W., Horseman, S.T., Lalieux, P., Müller, W., Ortiz Amaya, L. and Pruess, K. (1999). Gas Migration and Two-phase Flow through Engineered and Geological Barriers for a Deep Repository for Radioactive Waste. A Joint EC/NEA Status Report published by the EC, European Commission Report EUR 19122 EN, 1999.

6.2.1 Models of Radionuclide Transport and Microbial Effects

In a similar vein as the modeling on gas-release modeling outside the United States noted in the sub-section above, there have been numerous attempts outside the United States to model microbial growth in subsurface environments and effects on contaminant transport in groundwater. These models may be grouped into a number of categories, depending upon the sophistication and the nature of the processes that they try to represent: "microbe mass balance" models, "coupled microbe growth and mass transport" models and "microbial transport and clogging" models. The microbe mass balance model is perhaps the simplest in concept because it only attempts to calculate the limits to growth from the available supplies of nutrients and energy provided by the flow of groundwater and the leaching of the solid phase. This style of model was first proposed by Grogan and McKinley (1990) and similar models were used by Baker et al. (1998) and Jolley et al. (2003) in a Yucca Mountain study.

There are numerous models of "coupled microbe growth and mass transport" reported in the literature over the past 30 or more years. A review of these models by Baveye and Valocchi (1989) divided them into three groups according to the treatment of the attached bacteria. The first group (I) consisted of those models that neglected pore scale processes and assumed that the bacteria respond directly to the macroscopic bulk fluid composition. The other two groups were based upon the assumptions of the bacteria forming microcolonies (II) or biofilms (III). Examples of the first group of models may be found in Corapcioglu and Haridas (1984), Corapcioglu and Haridas (1985), and Kindred and Celia (1989). Examples of the microcolonies approach are found in Molz et al. (1986) and Widdowson et al. (1988), while the biofilm approach was used, for example, in Rittmann et al. (1980) and Bouwer and McCarty (1984). Baveye and Valocchi (1989) noted the formal similarities in all the mathematical models with the differences arising in the detailed implementation of particular terms. Widdowson (1991), in commenting on this review, noted the particularly close association of model types I and II, but demonstrated that the differences in detail could result in noticeable differences in the calculated concentrations.

6.3 Storyboard Approach to Promote Stakeholder Understanding of Release

To aid in illustrating how release models for specific waste forms are applied at the Hanford Site, a top-down, scenario-driven approach could prove useful, both in internally organizing such modeling (and their data requirements) and in communicating with stakeholders as to the rationale and implications of models that are selected. A method outlining this approach has been implemented in the past using *scenario storyboards* to represent knowledge of a disposal system graphically (Kawamura et al. 2011). This *disposal system* necessarily includes the waste form(s) and disposal vault, but the environmental conditions at the disposal site as well. Thus, the starting point for this approach are detailed descriptions of the characteristics (and their evolution over time, as appropriate) of waste form(s), disposal vault, and disposal site.

A first consideration is characterizing the disposal environment, as illustrated in Figure 10. Three main areas of a site need to be described in detail; the soil zone, the vadose zone, and the saturated zone.

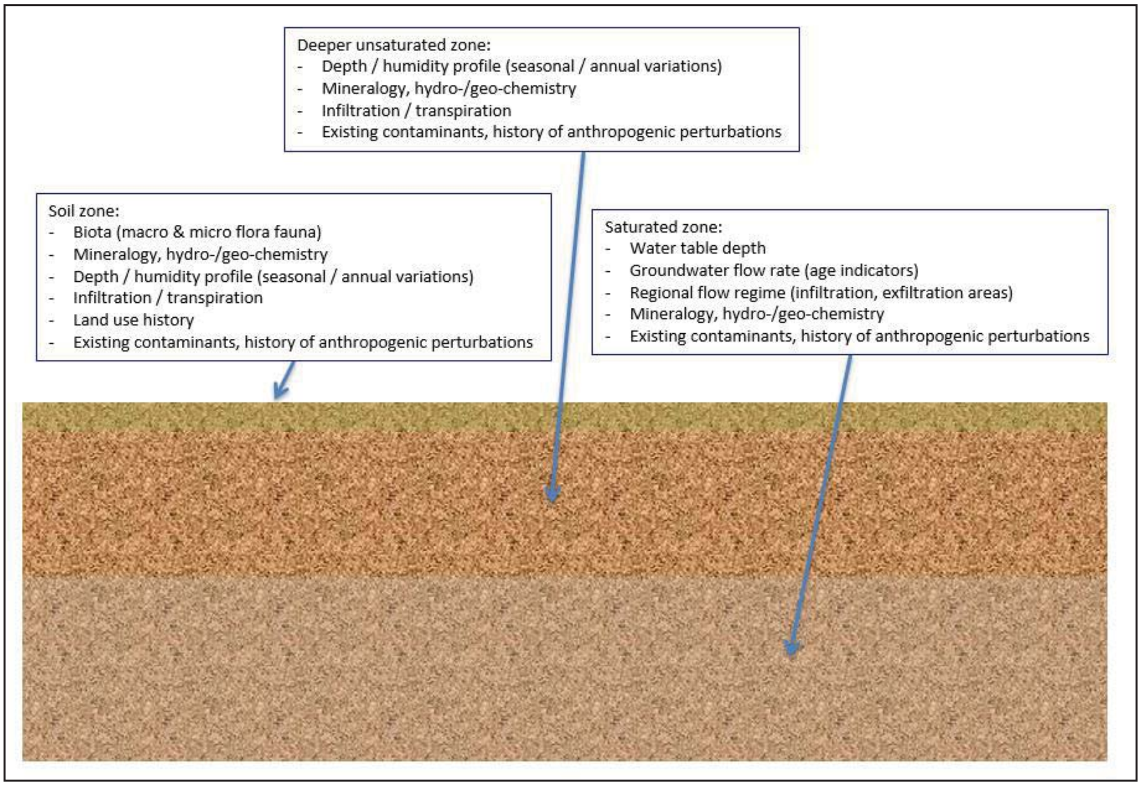


Figure 10. Site Description and Some of its Elements

Many of the features in Figure 10 are also described in more detail in Section 4. This figure summarizes the baseline that usually reflects a synthesis of measurements carried out over several years. In addition to being necessary for modeling release of contaminants from waste forms, such information is basic input for any monitoring program. A cogent monitoring plan needs to be able to distinguish inherent site variations and background contaminants from anything resulting from the disposal facility.

Once the disposal site has been adequately described in a graphical storyboard, the next step would be to add a detailed description of the disposal system itself, including such things as waste form(s) and their containers (if any), trench shape and dimensions, liners, drainage system, etc., and how these are implemented (Figure 11). This is related to both the monitoring baseline (noting changes resulting from the engineered structures) and the boundary conditions for contaminant release and transport models.

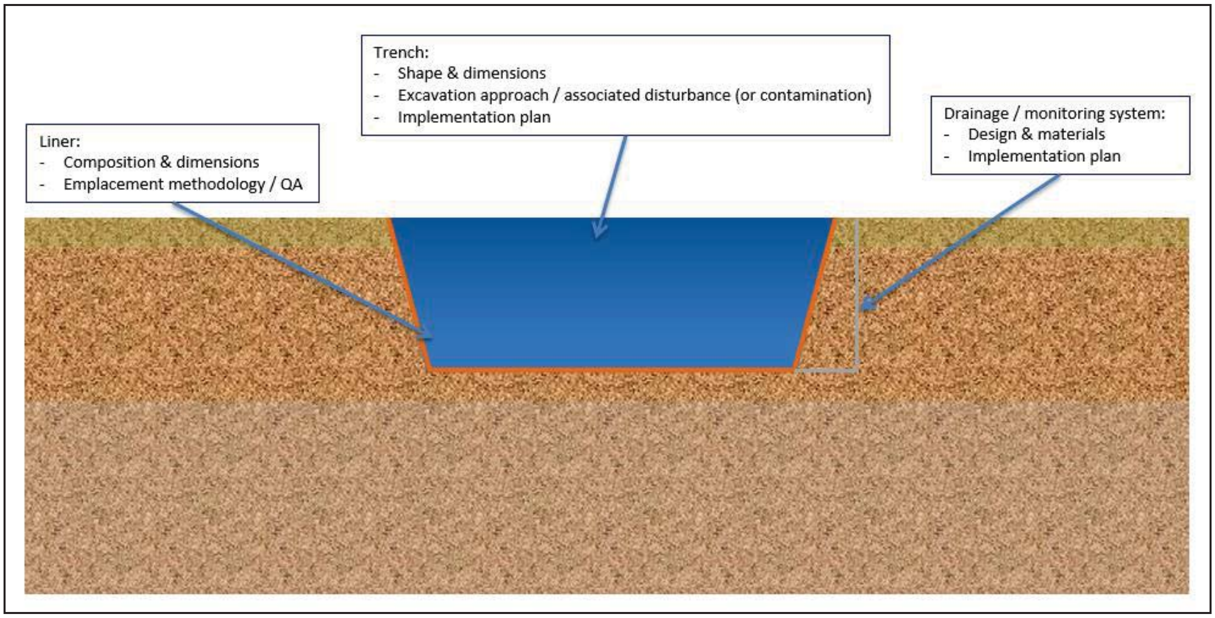


Figure 11. Disposal System Characteristics, Implementation, and Quality Assurance

Construction may precede or run in parallel to waste emplacement (Figure 12). The inventory of each type of waste can be related to its emplacement history and any other wastes in its vicinity, allowing an assessment of pre-closure evolution of groups of related waste packages (i.e., waste form and encompassing container).

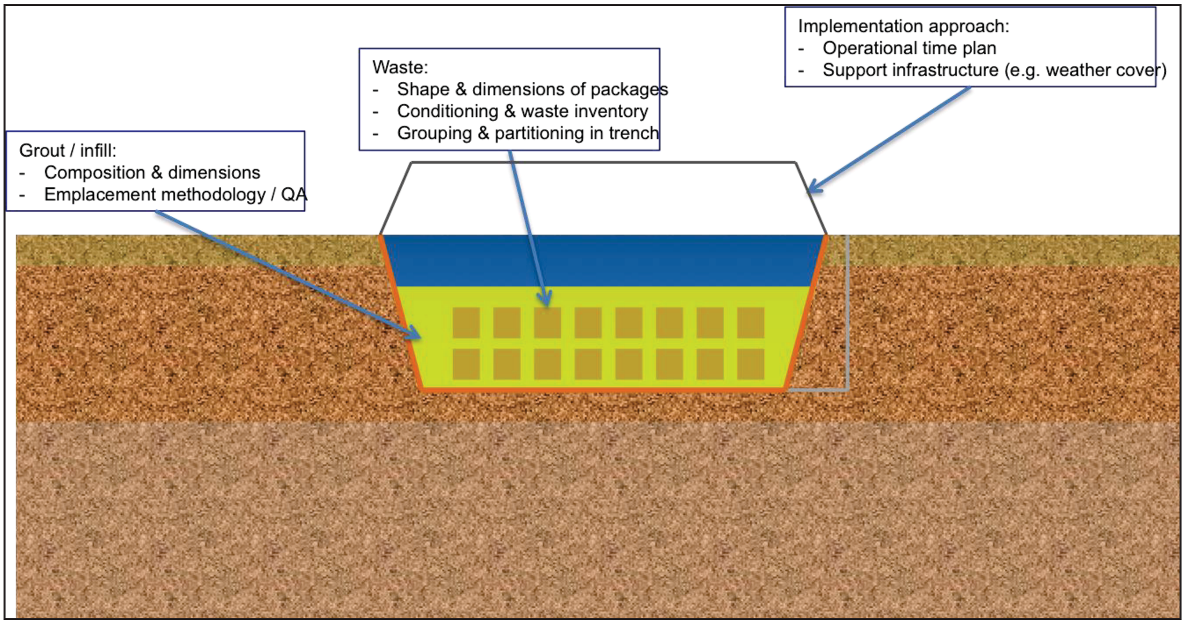


Figure 12. Waste Disposal System Operational Procedures

Depending on the timescale of operations, the grout/infill used and the extent of any control measures (e.g. weather cover), there could be potential for waste package degradation before final closure. Degradation processes possibly affecting eventual contaminant releases can include mechanical crushing of waste forms by over-burden loads or corrosion of containers leading to corrosion products that might chemically react with waste forms in a manner affecting the release rate behavior. These possible "what if?" concerns can all be readily represented in graphical storyboards.

As mentioned previously, in some past cases, "emplacement" of waste was simply pouring liquid waste into unlined trenches, allowing the liquid waste to drain into the subsurface. Again, a visual storyboard of how such liquid wastes evolve over time and space would be a benefit to both assessment modelers and to stakeholders interested in understanding what processes can affect the subsurface behavior of such liquid waste. Processes such as lateral dispersion, evaporation of the aqueous supernatant, various retardation processes, etc. could all lead to significant hold-up of the contaminants in the vadose zone, rather than assuming unretarded "pass-through/no-hold-up" of contaminants directly to the saturated zone beneath.

The storyboard approach, based on a structured synthesis of system knowledge and engineering plans, could be represented up to the point of closure (Figure 13). Based on simple scoping calculations, many of the FEPs identified can be screened out, to allow the initial boundary conditions for post-closure safety assessment to be defined. It is worth noting that, up until this point, uncertainties are rather small and may be related to QA and knowledge base limitations.

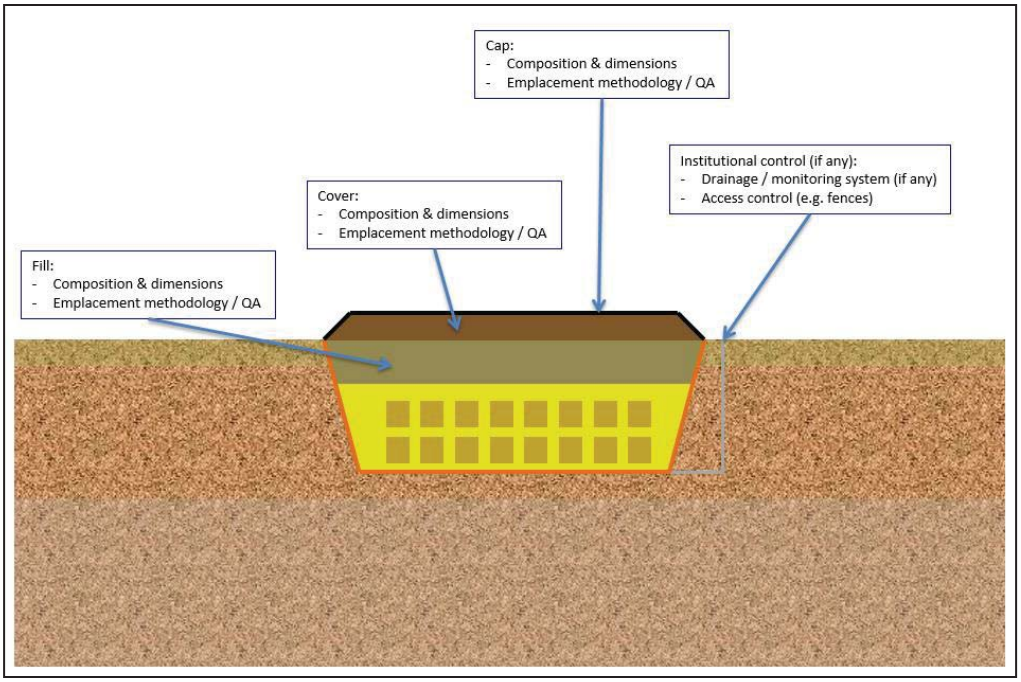


Figure 13. Disposal Facility Closure

After closure, alternative scenarios of future evolution can be defined and represented as storyboards based on extrapolation of system understanding into the future – which inevitably involves greater uncertainties. To explore both expected performance and credible alternative "what if?" scenarios of future conditions, a "starting case" of expected evolution and "variant cases" that bound the greatest uncertainties can provide a convincing basis for safety assessment. Key constraints on such scenarios are the assessment timescales, the degree of institutional control assumed, and specific regulatory boundary conditions (e.g., treatment of human intrusion scenarios).

For the expected evolution scenario, an example of the set of FEPs that will affect and control the release rate behavior of waste forms is shown in Figure 14.

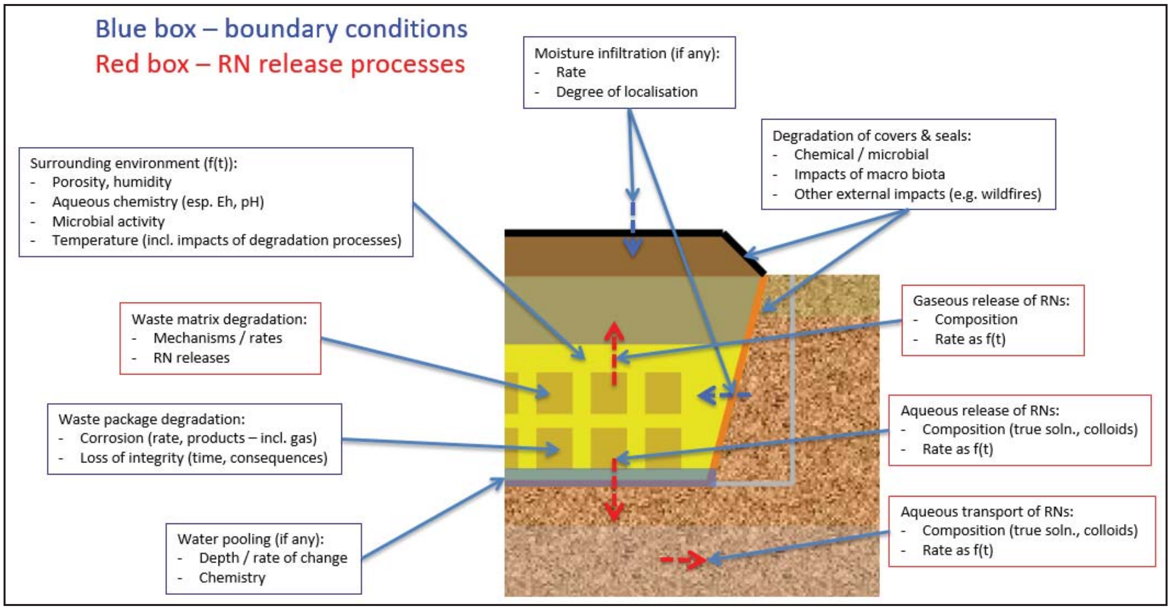


Figure 14. Details of Post-emplacement FEPs inside and outside of the Waste Disposal System

Scoping calculations using appropriate release rate models would be used to assess the relative importance of alternative evolution in disposal conditions (e.g., change in infiltration rate over time, change in porosity/permeability of waste forms). Such calculations, in turn, provide a basis for identifying key, safety-significant FEPs, for which further studies to better characterize their uncertainties would help confirm and optimize long-term, post-closure safety.

7 Quality Assurance and Quality Control

PRC-MP-EP-53107, *Hanford Composite Analysis Project Management Plan*, Appendix B ("Hanford Site Composite Analysis Quality Assurance Plan") specifies the QA/QC requirements for the CA update, noting the importance of QA/QC to this project:

> "A critical aspect of preparation of the revised Hanford Site CA is quality assurance and quality control (QA/QC). This Project-Specific Quality Assurance Plan documents the plan for QA/QC for the project that is consistent with CH2M HILL Plateau Remediation Company plans and procedures that implement DOE requirements, EPA guidance, and adds additional project-specific requirements deemed necessary to facilitate delivery of a successful product."

Guiding principles are provided in the project QA plan (Section 1.2 of Appendix B), including that QA/QC controls will address three key areas:

1. Software quality and control – to ensure use of only software that meets DOE requirements for use under a graded approach.
2. Data quality and control – to promote fully traceable development of model input parameters from traceable and qualified data.
3. Application quality and control – to promote fully traceable calculations using numerical software in which inputs are traceable to data (basis information), code use is traceable to inputs, and outputs are traceable to code use.

Software quality and control are to be addressed through the application of procedure PRC-PRO-IRM-309, *Controlled Software Management*, which implements requirements of DOE O 414.1, *Quality Assurance (*NQA-1-2008*, Quality Assurance Requirements for Nuclear Facility Applications;* NQA-1a-2009 addenda*, Quality Assurance Requirements for Nuclear Facility Applications)*, for software used for modeling and calculations in the CA. Software QA documents will be prepared for the ICF at an appropriate quality level under a graded approach.

Data quality and control are addressed through provisions of the project QA plan, including the designation of a data configuration manager for the CA update project, maintenance of data configuration control, and requirements for the use of electronic modeling data transmittal (EMDT) forms to document submittal and review of all data configuration items utilized in the updated CA.

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