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Technical Approach for Determining Key Parameters Needed for Modeling the Performance of Cast Stone for the Integrated Disposal Facility Performance Assessment

March 2015

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U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
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Executive Summary

Radioactive wastes currently stored in underground tanks on the Hanford Site will be retrieved, treated, and converted to high-level waste (HLW) and low-activity waste (LAW) glass waste forms for disposal. Through the treatment and vitrification processes at the Hanford Tank Waste Treatment and Immobilization Plant (WTP), aqueous secondary waste streams will be generated that will be treated and solidified outside the WTP at the Effluent Treatment Facility (ETF). Current baseline plans are to solidify the treated secondary wastes in a cementitious waste form, called Cast Stone, which will be disposed of in the Integrated Disposal Facility (IDF) on the Hanford Site. Washington River Protection Solutions (WRPS) and its contractors at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) are optimizing Cast Stone to develop/refine the cementitious waste form for the wastes treated at the ETF, and to provide the data needed to support the IDF performance assessment (PA).

In accordance with DOE Order 435.1 and the associated manual, a radiological PA will be conducted for the LAW glass and solidified secondary wastes (Cast Stone) that will be disposed of in the IDF. This technical approach document is intended to provide guidance to the Cast Stone development program with respect to the waste form characterization and testing information needed to support the IDF PA. At the time of the preparation of this technical approach document, the IDF PA effort is just beginning and the approach to analyze the performance of Cast Stone has not been determined. Therefore, this document examines the approach for evaluating Cast Stone performance and describes the testing needed to provide data to support the approach.

There is a large contrast in the physical and chemical properties of the Cast Stone waste form versus the IDF backfill and surrounding sediments. Cast Stone exhibits low permeability, high tortuosity, low carbonate, high pH, and low Eh, whereas the backfill and native sediments have high permeability, low tortuosity, high carbonate, circumneutral pH, and high Eh. These contrasts have important implications for flow, transport, and reactions across the Cast Stone – backfill interface. Over time, with transport across the interface and subsequent reactions, the sharp geochemical contrast will blur and there will be a range of spatially-distributed conditions. In general, the contaminants of concern (COC) mobility and transport will be sensitive to these geochemical variations, which also include physical changes in porosity and permeability from mineral reactions. Therefore, the effectiveness of Cast Stone as a barrier to COC release is expected to evolve over the lifetime of the IDF. The technical approach to determining PA modeling parameters should therefore consider processes, properties, and conditions that alter the physical and chemical controls on COC transport in Cast Stone over time.

A key issue is that the understanding of the evolving geochemical conditions controlling Cast Stone performance is based on relatively short-term, small-scale experiments. Thus, an important role and challenge for PA modeling is to provide a mechanistic link between the laboratory and field tests and the prediction of Cast Stone performance over repository time frames (1,000 to >10,000 years) and length scales (~100s of meters). Because of the comprehensive nature of the large-scale system model, there are many sources of uncertainty in the model specification. The long time frames, the lack of complete understanding of all of the processes that affect performance, and the variability inherent in waste package materials, subsurface geologic media, and their performance characteristics, require that uncertainty analyses be performed. An important goal of the modeling strategy is to demonstrate that performance is acceptable when the relevant uncertainties affecting performance have been appropriately accounted for.

The development of cementitious low- and intermediate-level waste forms and their emplacement in the subsurface is ongoing in the U.S. and other countries. To address the assessments of risk, safety, and performance for these facilities, most organizations responsible for disposal facility operation and their regulators support an iterative hierarchical total system performance assessment (TSPA) modeling strategy. The strategy is conceptually represented as a pyramid with the high-level, stochastic TSPA modeling for decision-making at the top, supported by more mechanistically detailed deterministic modeling below, which in turn is founded on a base of previous knowledge and new information from characterization and experimental studies. In this document, the technical approach for determining key parameters needed for modeling the performance of Cast Stone is developed within the context of a hierarchical modeling strategy.

The objective of the structured uncertainty analyses in the TSPA modeling is to identify a statistical distribution for the range of possible disposal system performances and behaviors. Because of the comprehensiveness required to model the total waste form/waste package/disposal facility/subsurface system, the Monte Carlo methods typically used for the stochastic uncertainty analysis are not computationally tractable without simplifications to the representation and resolution of the modeled processes. For example, the chemistry in high-level TSPA-type modeling is often abstracted to a set of COC-specific distribution coefficients (i.e., K_ds), which may be linked to corresponding effective diffusion coefficients and/or solubility limits. These simpler lumped parameter models are computationally efficient, allowing comprehensive coverage of the system features, as well as stochastic treatment of uncertainties in parameters, process models, and conditions. However, they are not mechanistic. This means these lumped, single-parameter models are not sufficiently robust to address the spatial and temporal variation in geochemical processes, properties, and conditions that control COC behavior, which include reactions with non-COC components.

The hierarchical modeling strategy is intended to address limitations in the reduced-order models used in the high-level TSPA modeling. In this strategy, detailed property distributions and mechanistic process models are used to provide a technically defensible basis for assessing the level of rigor that is ultimately included in the PA modeling. In this way, the sensitivity of the estimated risk to simplifications and/or omissions of specific process models can be directly evaluated.

The principal COCs for groundwater risk in Cast Stone are ^{99}Tc, ^{129}I, Cr, and nitrate, which are highly mobile in many subsurface environments. Cast Stone, however, is expected to provide physical and/or geochemical controls over the transport of these COCs. In general, cracking cannot be avoided, yet it is difficult to predict the magnitude, extent, and transport consequences over a ~10,000 year time horizon. Cracks can allow liquids and gases to flow through the waste form, increasing the potential for leaching and adding advective transport pathways that may increase COC release. Carbonation reactions induced by ambient subsurface gas and liquid phase CO_2 entering Cast Stone can dissolve and decalcify the principal cement mineral phases, lower the waste form pH, increase the solid phase/mineral mass, and lower porosity. Changes in pH can affect the mobility of COCs, and the formation of calcium carbonate may fill/seal pores in a way that limits gas and liquid phase transport. Oxidation of Cast Stone via near-atmospheric levels of O_2 gas in the shallow Hanford vadose zone can potentially oxidize and mobilize

^{99}Tc and Cr, which are in immobile reduced mineral forms, TcO_2 and Tc_2S_7 for technetium and $Cr(OH)_3$ or $Fe_xCr_{1-x}(OH)_3$ solid solutions for chromium.

Unlike ^{99}Tc and Cr, ^{129}I and nitrate are not expected to be significantly associated with Cast Stone mineral phases (e.g., portlandite, calcium silicate hydrates) or to be directly affected by reactions. In the absence of iodide getters, ^{129}I is expected to be mobile as the stable anion, I^-, in Cast Stone with transport dominated by diffusion. While ^{129}I and nitrate, and the oxidized forms of ^{99}Tc and Cr are often assumed to be non-reactive, they can exhibit small but non-zero K_ds when interacting with cement, backfill, and native sediments. Over the IDF lifetime and space (hundreds of meters) scales, this retardation may need to be considered.

Within the last 15 years, the ability to integrate multicomponent reactions and rates into subsurface flow and transport simulators has enabled more comprehensive treatment of the geochemical barriers and attenuation processes afforded by cementitious waste forms. A critical use of these comprehensive models/simulators is to address the time-dependent variation in the “constant” properties of the lumped parameter models (e.g., diffusion and distribution coefficients) used in simplified TSPA modeling. A multicomponent reactive transport simulator can be used to mechanistically address the evolving geochemical conditions, including pH and Eh, and estimate changes in COC mobility with time. A two-dimensional, multicomponent reactive transport eSTOMP (scalable version of the STOMP computer code) simulation of the decalcification of cracked cement is provided to illustrate the process modeling and data requirements for Cast Stone analyses.

To evaluate the uncertainties in the process models and underlying assumptions used in the high-level TSPA modeling, process models and property distributions that go beyond previous Hanford analyses are considered: 1) gas-phase flow and transport, 2) fracture/matrix flow for cracked Cast Stone, 3) multicomponent solubility, redox, aqueous and surface complexation reactions, and 4) feedback to physical properties from mineral precipitation and dissolution. These analyses are supported, in part, by the development of relevant characterization data and modeling parameters. For example, the multicomponent reaction networks will require stoichiometry and thermodynamics for mineral phases and sorption involving Cast Stone solid phases, COCs, products from the oxidation and corrosion of the mild steel waste containers, and the backfill materials.

This technical approach document begins with background in Section 1.0 on the Hanford waste streams, the development of low-activity waste forms, the IDF, and the IDF PA process. Section 2.0 provides a description of Cast Stone as a waste form and the various Hanford waste streams for which it has been tested. This provides some perspective on the types of information that may currently be available with respect to Cast Stone as a waste form. Section 3.0 reviews past Hanford and Savannah River Site PAs, as well as approaches developed by other countries, the IAEA, and the Cementitious Barriers Partnership. A hierarchical modeling strategy is described before identifying potential COC release scenarios and mechanistic process models that could be used for the PA. Section 4.0 then describes the key data and parameters that would be needed to support the identified PA process models. Finally, Section 5.0 provides brief summaries of the testing methods used to measure the needed parameters for the PA analyses.

Acknowledgments

This work was completed as part of the Secondary Waste Cast Stone Formulation and Waste Form Qualification project. Support for this project was provided through Washington River Protection Solutions (WRPS).

The authors wish to acknowledge Dave Swanberg (WRPS) for programmatic guidance, direction, and support. We also acknowledge Yilin Fang for the eSTOMP simulation of decalcification in a cracked cementitious waste form and Kirk Cantrell, Mike Fayer, Vicky Freedman, and Nik Qafoku for their technical review of the document.

The authors wish to thank Heather Culley for editorial review and document production.

Acronyms and Abbreviations

ALK	alkali
ANL	Argonne National Laboratory
APT	atom probe tomography
AREST-CT	Analyzer for Radionuclide Source Term with Chemical Transport
ASCEM	Advanced Simulation Capability for Environmental Management
ASR	alkali-silica reaction
ASTM	ASTM International (Standards Development Organization www.astm.org)
BFS	blast furnace slag
BNI	Bechtel National, Inc.
Bq	becquerel
CBP	Cementitious Barriers Partnership
CFR	Cumulative Fractional Release
CMP	Configuration Management Plan
COC	contaminants of concern
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
CSFMA	Centre de stockage des déchets radioactifs de faible et moyenne activité
CSH (or CSH)	calcium silicate hydrate
DAS	Disposal Authorization Statement
DEF	delayed ettringite formation
DOE	U.S. Department of Energy
DOE-EM	U.S. Department of Energy Office of Environmental Management
DOE-RL	U.S. Department of Energy Richland Operations Office
DRF	dry reagent formulation
DSSF	double-shell slurry feed
EA	environmental assessment
ECN	Energy Research Centre of the Netherlands
EDL	electrical double layer
EFTEM	energy-filtered transmission electron microscopy
EM	DOE Office of Environmental Management
ERDF	Environmental Restoration Disposal Facility
ETF	Effluent Treatment Facility
FDC	future disposal cell
FY	Fiscal Year (October 1 through September 30, e.g. FY15 ends on September 30, 2015)
GRAAL	Glass Reactivity with Allowance for the Alteration Layer
HDPE	high-density polyethylene

HLW	high-level waste
HRTEM	high-resolution transmission electron microscopy
IAEA	International Atomic Energy Agency
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
IDF	Integrated Disposal Facility
IFR	Incremental Fractional Release
ILAW	immobilized low-activity waste
IRSN	Institut de Radioprotection et de Sûreté Nucléaire
k-S-p	permeability-saturation-capillary pressure
LAW	low-activity waste
LERF	Liquid Effluent Retention Facility
LFRG	Low-Level Waste Disposal Facility Federal Review Group
LILW	low- and intermediate-level waste
LLW	low-level waste
MCL	maximum contaminant level
MPC	maximum permissible concentration
NDAA	National Defense Authorization Act
NICA	non-ideal competitive adsorption
NIST	The National Institute of Standards and Technology
NRC	U.S. Nuclear Regulatory Commission
OPC	ordinary Portland cement
ORP	DOE Office of River Protection
PA	performance assessment
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
POM	particulate organic matter
PRI	passivating reactive interphase
PUF	pressurized unsaturated flow
QA	quality assurance
R&D	research and development
RAI	Request for Additional Information
RCRA	Resource Conservation and Recovery Act
RFP	request for proposal
SA	Special Analysis
SDF	Saltstone Disposal Facility
SDU	saltstone disposal unit
SPFT	single-pass flow-through

SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SST	single-shell tank
STOMP	Subsurface Transport Over Multiple Phases
STORM	Subsurface Transport Over Reactive Multiphases
STP	Software Test Plan
S/V	surface area-to-solution volume ratio
TC&WM EIS	Tank Closure and Waste Management Environmental Impact Statement
TCLP	EPA Toxicity Characteristic Leaching Procedure
TER	Technical Evaluation Report
THAMES	Thermodynamic Hydration and Microstructure Evolution Simulator
THM	Thermo-Hydro-Mechanical
TSPA	total system performance assessment
TST	transition state theory
TWRS	Tank Waste Remediation System
VHT	vapor hydration test
WAC	waste acceptance criteria
WIR	Waste Incidental to Reprocessing
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The federal facilities located on the Hanford Site in southeastern Washington State have been used extensively by the U.S. government to produce nuclear materials for the U.S. strategic defense arsenal. Currently, the Hanford Site is under the stewardship of the U.S. Department of Energy (DOE) Office of Environmental Management (EM). A large inventory of radioactive mixed waste resulting from the production of nuclear materials has accumulated, including high-level mixed waste stored in 177 underground single- and double-shell tanks located in the central plateau of the Hanford Site (Mann et al. 2001). The DOE Office of River Protection (ORP) is proceeding with plans to immobilize and permanently dispose of the low-activity waste (LAW) fraction onsite in the Integrated Disposal Facility (IDF), which is a shallow subsurface disposal facility.

Radioactive wastes currently stored in underground tanks on the Hanford Site will be retrieved, treated, and converted to high-level waste (HLW) and LAW glass waste forms for disposal. Through the treatment and vitrification processes at the Hanford Tank Waste Treatment and Immobilization Plant (WTP), aqueous secondary wastes streams will be generated that will be treated and solidified outside the WTP at the Effluent Treatment Facility (ETF). Current plans are to solidify the treated secondary wastes in a cementitious waste form that will subsequently be disposed in the IDF on the Hanford Site. Washington River Protection Solutions (WRPS) and its contractors at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) are conducting a development program to develop and refine the cementitious waste form for the wastes treated at the ETF, as well as to provide the data needed to support the IDF performance assessment (PA).

In accordance with DOE Order 435.1 and the associated manual, a radiological PA will be conducted for the LAW glass and solidified secondary wastes to be disposed of at the IDF. The PA estimates the impacts of disposal of the wastes with respect to potential doses to representative future members of the public due to releases of contamination from the disposal facility. As part of the PA, modeling will be conducted to estimate the release of contaminants from the waste form over the 1,000-year period of compliance, as well as longer times to look at longer-term impacts. This modeling requires information regarding the release of contaminants from the waste form over time. Testing programs are conducted to provide the data for those analyses.

Technical approach documents have been prepared for glass waste forms to outline the data and testing needed for modeling the long-term performance of glass in the disposal system (McGrail et al 1998, 2000; Neeway et al. 2014a). McGrail et al. (2003) provided a technical approach document for other supplemental waste forms. This technical approach document for Cast Stone is concerned primarily with the cementitious waste form, which is referred to as Cast Stone. Methods and parameters required for modeling of its performance within the near-field environment of the backfilled IDF trench are identified, and methods needed for determining these parameters are discussed.

The remainder of this section provides some additional information on the IDF, as well as the types of wastes that could be disposed in the IDF as cementitious waste forms. This section also describes the organization for the rest of the document and the QA program under which this technical approach document was prepared.

1.1 The Integrated Disposal Facility

Figure 1.1 shows a photograph of the excavated IDF trench, and an idealized cross-section through the facility showing the waste packages after emplacement and backfilling with native sediments. Waste packages are expected to consist primarily of glassified waste produced by the Hanford vitrification plant. Planned secondary waste treatment is expected to generate a cementitious waste form.

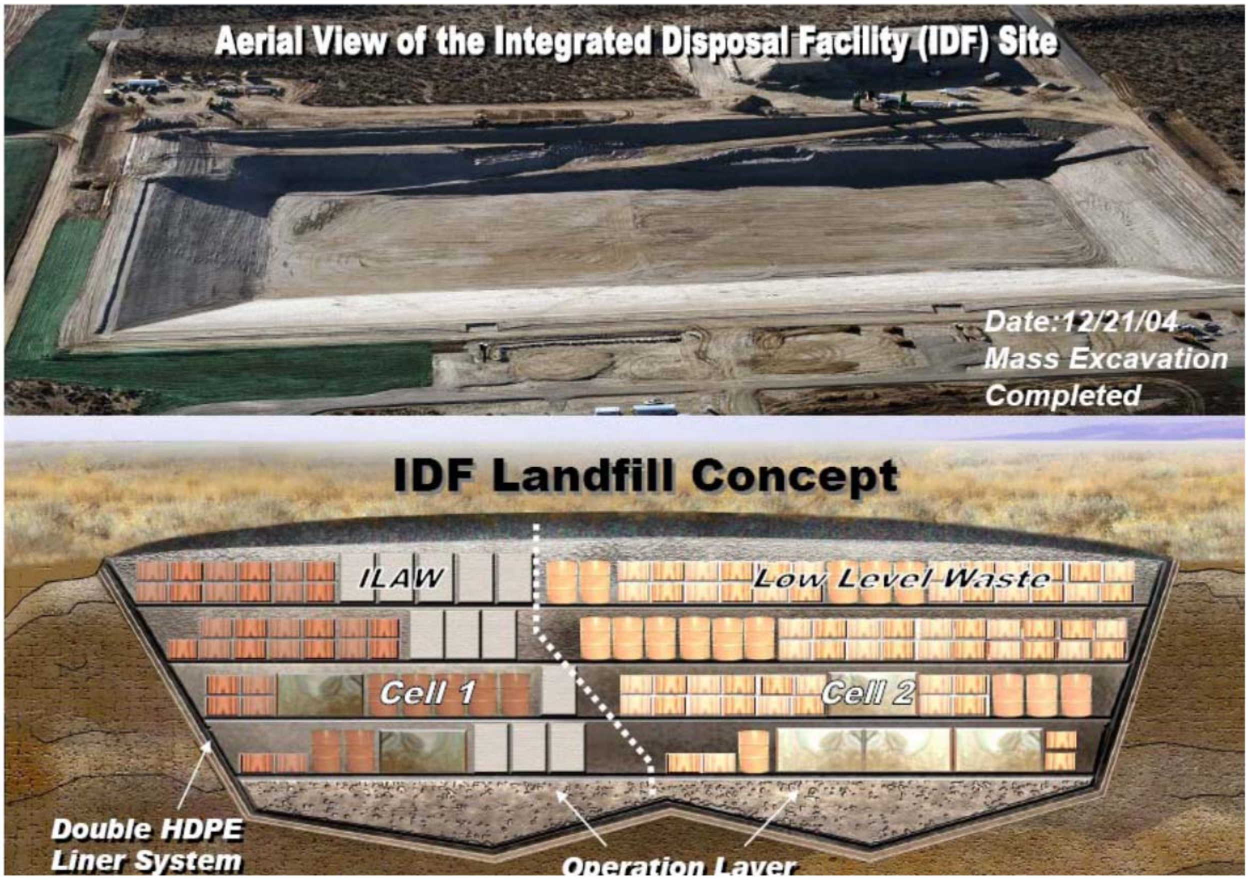

Figure 1.1. Aerial View of the Excavated IDF Trench Located in the South-Central Part of the 200 East Area (Top) and Artist's Rendition of the IDF Landfill Concept (Bottom)

Both the glass and cementitious waste forms will be placed in steel containers and co-disposed in the shallow IDF trench. The trench will be backfilled and covered with an infiltration barrier to limit percolation of meteoric water through the facility.

PNNL was contracted to provide the technical basis for estimating radionuclide release (the source term) from the engineered portion of the IDF as part of a Cast Stone testing program to support future IDF PAs.

1.2 Cast Stone as a Waste Form for Hanford Aqueous Wastes

Cast Stone was originally conceived as a supplemental immobilization technology for the solidification of Hanford tank LAW. It has subsequently been tested with other Hanford waste streams.

Cast Stone is the current baseline technology for the solidification of secondary aqueous wastes to be treated through the Hanford Site ETF.

1.2.1 Solidification of Treated Effluents from the Effluent Treatment Facility

The ETF currently treats aqueous waste streams, including evaporator condensates from the 242-A Evaporator, Environmental Restoration Disposal Facility (ERDF) and IDF leachates, laboratory wastes, and contaminated groundwater. The concentrated brine from the secondary treatment train within the ETF is currently fed to a thin film dryer producing a powdered salt waste form for disposal in drums. A stabilization and solidification treatment process is needed to provide a much more leach-resistant waste form for disposal in the IDF. The ETF is also planning to process secondary liquid waste from the Hanford Tank WTP operations, including Direct Feed LAW Immobilization. The ETF secondary waste immobilization process and waste form will be needed in time to support WTP operations. Accordingly, this waste form will need to be included and analyzed as part of the IDF PA being initiated in Fiscal Year 2015 (FY15).

Beginning in 2009, PNNL conducted a Secondary Waste Form Testing program for WRPS. Four waste forms, including Cast Stone, were developed and evaluated for solidifying the WTP secondary liquid wastes. That work provided input for a value engineering evaluation that led to the selection of Cast Stone as the baseline waste form for the solidification of the concentrated liquid wastes generated by the ETF process. PNNL and SRNL are continuing work on secondary waste performance into FY15, with funding from WRPS.

1.3 Purpose and Organization of the Report

WRPS is implementing a technology development program to address the technology needs in support of the application of the Cast Stone technology to immobilize aqueous wastes treated in the ETF. The program is also conducting work to provide long-term waste form performance data and information on degradation and release mechanisms to support the IDF PA.

The work in support of the IDF PA is the most complex, and will require a long-term testing program. Elements include measuring release rates for key risk driver contaminants over long periods of time, developing an understanding of the long-term degradation or weathering of the Cast Stone in the disposal environment, developing an understanding of the mechanism by which radionuclides and other contaminants are retained in the Cast Stone and the mechanism(s) of release, developing accelerated test methods and other test methods to characterize and predict the long-term performance of the Cast Stone, and characterizing transport properties of the key contaminants solidified in Cast Stone as water migrates through the IDF and the disposal packages contained within.

This technical approach document describes the work to determine key parameters needed for modeling the performance of Cast Stone for the IDF PA. At the time this technical approach document is being prepared, the IDF PA effort is just being initiated. As such, the specific modeling approach to be used in the PA for evaluating the impact of the disposal of Cast Stone waste forms has not been established. Therefore, this document is looking more broadly to identify different modeling approaches that have been, or are being, used in other cementitious waste form PAs to provide a more comprehensive suite of data needs to support whichever modeling approach is selected. This will then guide the collection of data from the waste form literature as input to a Cast Stone waste form data package. It will also guide current experimental work such that the pertinent data will be collected as part of the Cast Stone development work.

Section 2.0 of this technical approach document provides a description of Cast Stone as a waste form and the various Hanford waste streams for which it has been tested. This provides some perspective on the types of information that may currently be available with respect to Cast Stone as a waste form. Section 3.0 then looks at the different approaches that have been used to model the performance of cementitious waste forms. This then provides a basis for Section 4.0, which describes the data needs to support the various modeling approaches. Section 5.0 describes the testing methods used to generate the data needed for the PA analyses.

1.4 Quality Assurance

This work was conducted with funding from WRPS under contract 36437-168, Secondary Waste Cast Stone Formulation and Waste Form Qualification. The work was conducted as part of PNNL Project 66595.

All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research," and was planned, performed, documented, and reported in accordance with Procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

2.0 Development of Cast Stone as a Waste Form

Cast Stone was originally developed as one of three supplemental immobilization technologies as part of a mission acceleration initiative to provide the needed capacity to complete the Hanford tank waste cleanup mission in a timely manner (Raymond et al. 2004). The three technologies were containerized grout, bulk vitrification, and fluidized bed steam reforming. At the time, bulk vitrification was selected as the preferred supplemental immobilization technology, but it has subsequently been discontinued. The Cast Stone formulation selected for the containerized grout has since been tested with other Hanford waste streams and has been selected as the preferred waste form for WTP aqueous secondary wastes. In addition, Cast Stone is currently being developed for solidification of other ETF-treated aqueous wastes. Enhancements to the Cast Stone formulation are being pursued to further improve key risk driver contaminants of concerns (COC) retention in Cast Stone such that it could again be considered as a potential supplemental immobilization technology for Hanford LAW.

2.1 Containerized Cast Stone for LAW Supplemental Immobilization

The original Cast Stone formulation was selected from four dry blend mixes as part of the initial mission acceleration initiative work. Lockrem (2005a) documented work evaluating what were called dry reagent formulations (DRFs). DRF2, composed of 8 wt% Portland cement, 45 wt% class F fly ash, and 47 wt% blast furnace slag (BFS), was recommended by Lockrem (2005a) as the most robust of the four dry blends studied. DRF2 is the current Cast Stone standard dry blend mix. It is very similar to the saltstone dry blend mix of 10 wt% Portland cement, 45 wt% Class F fly ash, and 45 wt% BFS used for LAW solidification at the Savannah River Site.

The DRF2 dry blend mix was selected over three other mixes composed of Portland cement, fly ash, and attapulgite clay and/or Indian red pottery clay. Testing was done with a waste simulant of a single-shell tank (SST) blend based on analyses of saltcake from six SSTs (Rassat et al. 2003). DRF2 was selected because it had the best results in the EPA Toxicity Characteristic Leaching Procedure (TCLP) for chromium and selenium (Lockrem 2005a). Subsequent testing (Lockrem 2005a) with the SST blend waste simulant and with an actual LAW waste sample showed that the DRF2 blend had acceptable waste form properties, including:

- no bleed/free water after curing,
- compressive strength above 500 psi (3.45 MPa),
- meets Universal Treat Standards in 40 CFR 268 for land disposal restrictions,
- small volume decrease during curing,
- acceptable leachability indices for nitrate, nitrite, chromium, technetium, and iodide,
- reduced technetium leaching with addition of a bone char technetium getter,
- impermeable to fluid flow (negligible hydraulic conductivity), and
- produced with readily available, low-cost dry blend components.

2.2 Solidification Technology for WTP Secondary Wastes

The WTP will produce an aqueous secondary waste stream that will be sent to the ETF for treatment and solidification. This secondary waste stream is composed of a caustic scrubber solution from the secondary off-gas treatment system for the LAW vitrification process, plus evaporator condensates from the pretreatment facility. The caustic scrubber solution and the evaporator condensates are stored in process condensate collection tanks within the WTP pretreatment facility. There, the solution is sampled before being sent to the Liquid Effluent Retention Facility (LERF) Basin/ETF for final treatment and solidification.

Lockrem (2005b) conducted some initial work using a modified Cast Stone dry materials blend (8 wt% Portland cement, 46 wt% fly ash, and 46 wt% BFS) and a dilute (2M Na) caustic scrubber simulant. Lockrem's work showed that the caustic scrubber solution could be solidified with this modified Cast Stone dry blend mix. Lockrem (2005b) also showed that silver zeolite or silver mordenite could be added to the dry blend mix as a getter to reduce the leachability of iodine from the Cast Stone waste form.

Beginning in 2009, WRPS and PNNL began a project to identify and evaluate waste forms for the solidification of WTP secondary wastes. Cast Stone, a phosphate-bonded ceramic called Ceramicrete, and an alkali-aluminosilicate geopolymer called DuraLith were selected for evaluation through a development and testing program (Pierce et al. 2010a). Simulants of the secondary waste feed to ETF based on flowsheet modeling of the WTP process were used in the testing. The Ceramicrete and DuraLith developers were allowed to tailor their formulations for the simulants (Singh et al. 2011; Gong et al. 2011). All three waste forms were then subjected to a testing program to evaluate each with respect to anticipated waste acceptance criteria for non-glass waste forms into IDF (Mattigod et al. 2011). Finally, data packages were prepared for each waste form (Cantrell and Westsik 2011; Mattigod and Westsik 2011; Serne and Westsik 2011). The results of the testing program and the associated data package for each waste form were used as input to a value engineering exercise that led to the selection of Cast Stone as the baseline technology for solidification of the WTP aqueous secondary wastes. Cast Stone scored relatively high in the four evaluation areas of worker and public safety, environmental protection, cost/schedule, and operability.

The standard Cast Stone formulation with a dry blend mix (cement:fly ash: BFS) ratio of 8:45:47 was used in the waste acceptance testing. One specific secondary waste simulant was tested at 2M, 4M, and 6M Na at a water-to-dry blend ratio of 0.4. The Cast Stone had acceptable waste form properties with respect to free liquids, TCLP, and compressive strength. Effective diffusivities were measured using three different national standards, including:

- American National Standards Institute/American Nuclear Society (ANSI/ANS) Standard 16.1, *Measurement of the Leachability of Solidified Low-Level Radioactive Waste by a Short-Term Test Procedure* (ANSI/ANS 2003),
- ASTM C1308-08, *Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms*, and
- EPA draft method 1315, *Mass Transfer Rates of Constituents in Monolith or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test* (EPA 2009).

A key finding of this work on secondary wastes was that effective diffusivities measured for Tc, I, Na, and Re by all three leach test methods (ANS 16.1, ASTM C1308, and draft method EPA 1315) yielded comparable results (Mattigod et al. 2011).

2.3 Supplemental Immobilization for LAW Solidification

In 2012, WRPS, PNNL, and SRNL began a testing program to support a rigorous evaluation of Cast Stone as a potential supplemental low-temperature immobilization technology for Hanford LAW tank wastes. At the time, several alternative waste forms were being evaluated, including supplemental LAW vitrification, bulk vitrification, fluidized bed steam reforming, and Cast Stone. It was noted that limited data were available on Cast Stone for the immobilization of Hanford LAW. This lack of data was the impetus for initiating the Cast Stone development program for Hanford LAW. The objectives of the work were to:

- determine an acceptable formulation for the LAW Cast Stone waste form,
- evaluate sources of dry materials for preparing the LAW Cast Stone,
- demonstrate the robustness of the waste form for a range of LAW compositions,
- demonstrate the robustness of the formulation for variability in the Cast Stone process, and
- provide Cast Stone contaminant release data that could be used in PA and risk assessment evaluations.

Screening tests were conducted to evaluate the impact of waste composition, waste stream concentration, sources of dry materials, and mix ratios of waste (free water) to dry blend. The standard Cast Stone dry blend mix (8:45:47) was used. Four simulants, including the same SST blend used in the mission acceleration initiative (Rassat et al. 2003), plus average, high-aluminum, and high-sulfate simulants based on Hanford Tank Waste Operations Simulator (HTWOS) flowsheet modeling, were studied. Two simulant concentrations (5M and 7.8M Na) and two water-to-dry blend mix ratios (0.4 based on the secondary waste work and 0.6 based on the Savannah River Site (SRS) saltstone formulation) were used. Two sources each for fly ash and BFS were used in the testing. Twenty-six different Cast Stone mixes were prepared based on a statistically designed test matrix. Each of the mixes was characterized for processing properties and final waste form properties, including compressive strength, porosity, density, TCLP, and effective diffusivity using EPA draft method 1315. The results of the screening tests are documented by Westsik et al. (2013).

Twenty-four of the 26 Cast Stone mixes had acceptable properties with respect to processability and anticipated IDF waste acceptance criteria. For the 24 acceptable mixes, compressive strengths were above the minimum 500 psi (3.45 MPa). The leachates from the TCLP test met the Universal Treatment Standards in 40 CFR 268 to address land disposal restrictions. Effective diffusivities were measured for nitrate, nitrite, iodide, technetium, chromium, and uranium. Nitrate, nitrite, and iodide leachability indices were in the range of 8.0 to 8.7. Technetium and chromium leachability indices were in the range of 9.7 to 11.2 and 12.0 to 14.1, respectively. Uranium concentrations in the leachates were generally below detection limits such that only less than value effective diffusivities were calculated.

Subsequent to the Cast Stone screening tests work, testing has focused on 1) higher waste loadings, 2) the addition of fillers to reduce porosity, and 3) the addition of getters to enhance the retention of technetium and iodine in the Cast Stone waste form.

In FY15, the WRPS/PNNL/SRNL team is conducting the next phase of testing to refine the Cast Stone formulation for LAW supplemental immobilization. The planned testing includes the standard Cast Stone dry blend mix, as well as other dry blend mixes. Fillers to reduce porosity and getters for Tc and I retention are also included in the test matrix. The planned waste form testing includes effective diffusivity measurements, plus other properties such as hydraulic conductivity, porosity, density, water retention, desorption K_ds, and Tc solubility that may be needed for modeling contaminant release from Cast Stone in PA analyses, depending on the waste form release model selected. Data from this work will be made available for the analysis of solidified secondary waste performance in the IDF PA.

2.4 Solidification Technology for ETF-Treated Wastes

The ETF currently treats liquid effluents from various waste cleanup activities on the Hanford Site. In the current ETF flowsheet, contaminants in aqueous wastes are removed and/or destroyed through a series of filtration, ultraviolet oxidation, reverse osmosis, and ion exchange processes. The treated liquids are disposed in a Washington State-approved land disposal site. Residual solids are dried on a thin film dryer and are packaged in 55-gallon drums for disposal in ERDF.

Aqueous wastes to be treated in ETF are collected in one of three surface impoundments (Basin 42, Basin 43, and Basin 44) as part of the LERF in the northeast corner of the 200 East Area. Liquid wastes in the individual basins are processed through ETF on a campaign basis. Historically, the wastes processed through LERF to ETF have included (in decreasing order by volume) 200-UP-1/200-ZP-1 groundwater treatment wastes, ERDF leachates, 242-A evaporator condensates, mixed waste burial trenches' leachates, K-basins' leachates, and purge water from sampling wells (CHPRC 2013). Looking beyond 2018, the wastes to be processed through ETF will include 242-A evaporator condensates, leachates from ERDF and IDF WTP secondary liquid wastes, liquid wastes from the LAW supplemental treatment system, mixed waste burial trenches' leachates, purge water, and other miscellaneous wastes (May et al. 2009).

Cooke and Lockrem (Cooke and Lockrem 2005; Cooke et al. 2006), conducted a study to identify a formulation for solidification of LERF Basin 42 wastes. Basin 42 wastes are composed primarily of 242-A evaporator condensates. In their initial work, they used a DRF with 10 wt% cement, 44 wt% fly ash, and 46 wt% BFS. Two Basin 42 simulant loadings were used (25 wt% solids and 40 wt% solids). A calcium aluminate (SECAR 51®[1]) was added to bind sulfate in the wastes as calcium sulfate to accelerate the formation of ettringite, which can cause swelling of the waste form, leading to cracking if the ettringite forms late in the curing process. In the next phase of testing, Cooke et al. (2006) tried a number of mixes with Portland cement, BFS, fly ash, Secar 51, and/or hydrated lime (an alternate source of calcium to facilitate the rapid formation of ettringite). Bucket tests and a 3 ft × 3 ft × 3 ft monolith test followed. The final recommended formulation was for a dry blend mix with 36 wt% Portland cement, 36 wt% BFS, and 28 wt% hydrated lime.

In FY15, the WRPS/PNNL/SRNL team will begin testing to evaluate the Cast Stone standard formulation and the dry blend mix recommended by Cooke and Lockrem (2005) for the Basin 42 waste. The testing will be conducted on treated ETF waste simulants, including 242-A evaporator condensates, WTP aqueous secondary wastes, and low level waste (LLW) disposal trench leachates. The planned

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[1] SECAR is a registered trademark of Lafarge Calcium Aluminates, Inc, Chesapeake, VA.

testing includes the standard Cast Stone dry blend mix, plus other mix ratios. Fillers to reduce porosity and getters for Tc and I retention will be included in the testing program. The planned waste form testing includes effective diffusivity measurements, along with other cured Cast Stone properties, such as hydraulic conductivity, porosity, density, water retention, and desorption K_ds and Tc solubility that may be needed for modeling contaminant release from Cast Stone in PA analyses, depending on the waste form release model selected.

2.5 Immobilization of Other Wastes Using Cast Stone

The saltstone facility at the SRS uses a dry blend mix similar to the Cast Stone formulation. The basic saltstone dry blend is composed of 10 wt% Portland cement, 45 wt% fly ash, and 45 wt% BFS. Serne and Westsik (2011) list a number of documents where the saltstone formulation was used for other waste streams at the SRS.

Wastes planned for disposal in the IDF will include LLW and mixed low-level waste (MLLW) from Tank Farm Operations and WTP Operations. Interface Control Document ICD-3 calls for WTP to characterize solid secondary wastes from WTP operations, quantify inventories of COCs associated with those wastes, and recommend treatment for disposal.

The IDF Waste Acceptance Criteria for these waste streams are expected to require grouting for mechanical stabilization and to provide encapsulation to minimize or retard the release of COCs. To the extent possible, data from the literature on cementitious barriers will be collected to allow PA modelers to predict long-term stability and release of contaminants from these waste forms.

3.0 Modeling Approach for Contaminant Release and Migration from Cementitious Waste Forms

Predicting the release of COC from cementitious waste forms and subsequent transport through the waste package and disposal facility into the shallow Hanford vadose zone over a 10,000-year time horizon will require a systematic and technically defensible understanding of the processes controlling COC behavior. The link between short-term experimental data and long-term performance is achieved through modeling.

The purpose of this chapter is to 1) summarize PA modeling approaches at Hanford, Savannah River, and in other countries, 2) outline an anticipated hierarchical modeling strategy for the PA, 3) identify the mechanistic modeling scenarios, and 4) describe the process modeling and simulation requirements.

3.1 Past and Ongoing Cementitious Waste Management Risk and Performance Assessments

3.1.1 Hanford

Hanford PAs related to solidified tank waste and the IDF (formerly called the ILAW facility) were first performed in the mid-1990s and have been updated as new data became available. This includes LAW glass compositions and release rates, as well as characterization data from sediments collected from new IDF site boreholes for geologic, hydrologic, and geochemical properties.

3.1.1.1 ILAW Early PAs

Mann et al. (1996, 1997) document two very similar interim PAs that evaluated the disposal of LAW glass in concrete vaults to be located in the 200 East Area and the vaults disposal system's long-term performance. Mann et al. (1996) evaluated disposed glass in future concrete vaults, while Mann et al. (1997) considered the use of four existing concrete vaults (each 37.6 m long × 15.4 m wide × 10.4 m tall and capable of holding ~8% of the projected LAW glass) built for disposal of grouted double-shell slurry feed (DSSF) for the abandoned Hanford Grout Technology program, as well as additional concrete vaults identical in design to those used in Mann et al. (1996). Both PA activities evaluated a base case and numerous sensitivity cases for key input parameters such as recharge rate, inventory, or glass release rate, where each was varied in a separate case. The base case for both PAs was performed using a fixed glass release rate of 4.4 parts per million per year that was requested by DOE-RL, with an assumed recharge rate of 0.5 mm/year for the first 1,000 years based on a working surface barrier, followed by a recharge rate of 3.0 mm/year thereafter. The concrete vaults were assumed to "instantaneously" degrade after 500 years. The glass inventories for the two most problematic radionuclides (^{99}Tc and ^{129}I) were set at 22,300 and 6.62 curies, respectively. In the vadose zone after release from the glass, the leachate interactions (reversible sorption-desorption) for these two contaminants with the sediments were quantified by K_d values of 0 and 3 mL/g, respectively. The release of contaminants (at the constant value of 4.4 ppm/year), and subsequent moisture migration, contaminant transport, and contaminant interactions with the vadose zone sediments were analyzed using the PORFLOW computer code, and subsequent contaminant-laden water transport in the unconfined aquifer was modeled using VAM3D-CG. Analyses were run out to 10,000 years for compliance comparisons (with Nuclear Regulatory Commission (NRC) regulations despite DOE regulations only requiring calculations to 1,000 years), and then out to time periods to find peak concentrations at a 100-m down-gradient well. The overall predictive methodology for the groundwater pathway is portrayed in Figure 3.1. In all ILAW/IDF PA activities, the groundwater pathway is found to be the most probable way humans would be exposed to released contaminants.

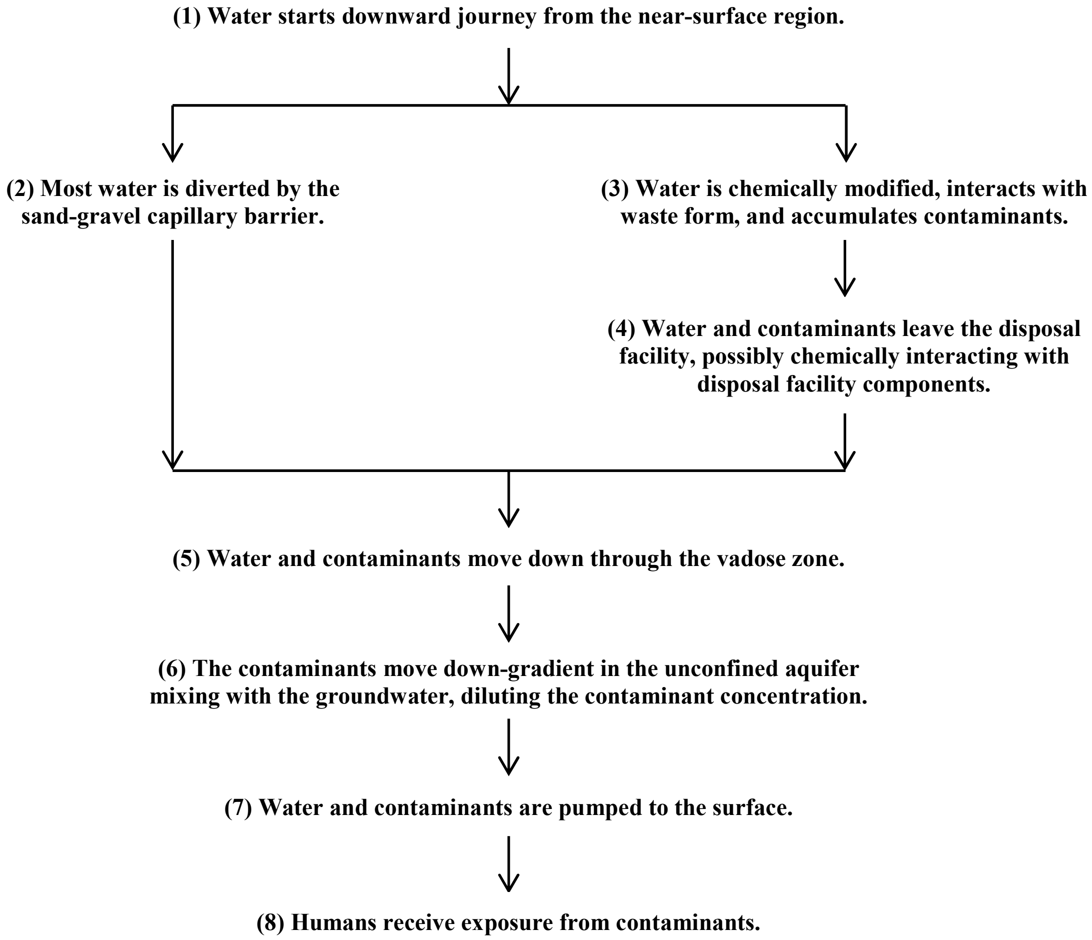

Figure 3.1. Early ILAW PA GW Exposure Pathway (after Mann 1996)

Besides providing the first comparison of the ILAW facility performance versus DOE O 435.1 (DOE 1998) and Washington State dangerous waste regulations, key goals of these early PAs (the base case and especially the sensitivity cases) were to gain understanding on what processes and input data were most sensitive and impactful to long-term environmental and human health impacts, as well as to gain insight on how to better design the disposal facility. These early PAs did not include disposal of any cementitious grout waste forms and the conceptual disposal facility differs from the current IDF design. Due to differences in glass composition and the facility design (i.e., concrete vaults), as well as the fact that no grout waste forms were included, these early PAs are not relevant to the current IDF. Thus, results and comparisons to regulations for these early PAs are not discussed here.

3.1.1.2 IDF PA-2001

Mann et al. (2001) documents the first version of the IDF PA that focuses on the current facility design (shallow trenches that will be covered by a surface barrier and undergirded with a leachate collection system and located southwest of the PUREX plant). The analysis was a full comprehensive PA that evaluated the long-term environmental and human health effects of disposing of vitrified LAW waste removed from Hanford tanks and processed into a glass waste form. All pathways (air, surface water, groundwater, and inadvertent intruder) were considered. Input data to perform the PA came from a suite of site-specific data packages that documented the site geology, hydraulic properties of the site and construction materials, geochemical attributes of the native sediments and construction materials, glass corrosion properties (LAWABP1 glass composition), and site recharge (infiltration) ranges. Besides predicting the long-term performance, the PA was used to underpin the Disposal Authorization Statement that was required before the IDF facility construction could begin.

Four major changes occurred since the early ILAW/IDF PA work. First, the IDF facility design changed from concrete vaults to shallow trenches. Second, all of the LAW generated at Hanford would be disposed to the facility (formerly 90%). Third, a glass had been chosen as the desired waste form (although the final composition had not been set). Fourth, much site-specific and glass-specific data had been generated. The time periods that the 2001 PA focused on were the 1,000-year "DOE compliance," a 10,000-year time interval (NRC desired), and the time of peak impact (effectively determined by running analyses out to 100,000 years+). The input data used in the 2001 IDF PA were consolidated into one large report (Mann and Puigh 2001), but are also available as stand-alone documents cited in Mann and Puigh (2001) and Mann et al. (2001). Besides radionuclides, the impacts of disposed chemicals (e.g., nitrate, chromium, and many others) were also reported.

A "base case" that did not include a sand-gravel capillary barrier and a "best case" analysis that included a sand-gravel capillary barrier above the wastes were run to evaluate impacts. Neither the "base case" nor the "best case" included the RCRA-compliant surface barrier that is part of the current IDF design. Approximately 45 sensitivity cases were also run, with certain key input values varied one-by-one and slightly different conceptual models considered. The infiltration water flow into the disposal trenches was modeled in two dimensions, but the glass corrosion and subsequent release of contaminants to the near-field vadose zone below were modeled in one dimension. Then the transport of released contaminants that reached the deeper vadose zone and aquifer were modeled in two dimensions. The computer codes used in the IDF 2001 analyses were the STORM code for glass corrosion and "near-field" (Bacon et al. 2000), VAM3DF (Huyakorn and Panday 1999) for the vadose zone "far-field", and CFEST-96 (Gupta 1987) for the aquifer. Impacts from the disposal system were quantified using the INTEG code (Mann 1996). This code combines the results from the far-field calculations, the groundwater calculations, and the dosimetry data to estimate impacts related to the performance objectives at various points of compliance.

The 1998 ILAW PA showed that the key variable in the analysis is the waste form release rate, which had to be calculated over thousands of years. The glass corrosion methodology pursued in the 2001 IDF PA was evaluated using computer modeling based on basic physical and chemical processes known to control dissolution behavior instead of using empirical extrapolations from laboratory "leaching" experiments commonly used in other PAs. Unfortunately, the robust methodology employed for the 2001 PA does not come without penalties. The principal penalty is the increased amount of information that is needed regarding the reaction mechanisms controlling the dissolution behavior of the waste form. Significantly more laboratory experiments are required to parameterize the models used for mechanistic glass release simulations. Second, the model and computer code itself are markedly complex. Execution times with today's fastest workstations can take weeks for one- and two-dimensional simulations.

Some key input parameters and their values chosen for the 2001 IDF PA are summarized in Table 3.1.

Table 3.1. Values for Key Parameters Used in IDF 2001 PA Compared to the 1998 PA

Parameter	Units	Value (2001)	Value (1998)
Recharge Rate	mm/y	4.2	0.5 (First 1000 Years) 3 (Thereafter)
^{99}Tc Inventory	Ci	5790	22300
^{129}I Inventory	Ci	22	6.62
^{99}Tc K_d for sediment	mL/g	0	0
^{129}I K_d for sediment	mL/g	0	3
Glass release rate	ppm/yr	NA[(a)]	4.4 (fixed value) was mandated by DOE-RL
Glass forward rate of reaction	$g \cdot m^{-2} \cdot d^{-1}$	3.4×10^6 (LAWABP1) 1.0×10^7 (HLP-31)	NA[(b)]

(a) Not applicable. For 2001 PA glass release was based on a Transition State Theory of chemical kinetics rate law (see McGrail et al. 2001) for details. This kinetic rate law conceptual model is dependent on several variables and is not a constant versus time. Two glass compositions (LAWABP1 and HLP-31) were used in the 2001 IDF PA. The former glass for the base case and the latter glass for a "pessimistic" sensitivity case.

(b) Not applicable. For the 1998 IDF PA only a simple constant glass release rate was used. No Transition State Theory of chemical kinetics conceptual model or the required data were used.

Overall, the conclusions from the 2001 IDF PA confirm the conclusions of the 1998 ILAW PA; a base case can meet the performance objectives even when the concrete vault design is changed to a trench disposal concept. In fact, the impacts to groundwater (based on the federal drinking water standards, a time of compliance of 1,000 years, and a point of compliance at a 100-m down-gradient well) predicted in the 2001 IDF PA are much lower than predicted impacts in 1998, due in large part to the slower release of contaminants from the waste glass (based on the use of the more mechanistic glass dissolution conceptual model. The Transition State Theory chemical kinetics model results predict that the maximum release of ^{99}Tc is 0.93 ppm/yr, which is lower than the fixed 4.4 ppm/yr value for all glass constituents used in the 1998 PA (see Bacon and McGrail 2001 for details)..) The estimated groundwater impact from beta emitters, such as ^{99}Tc and ^{129}I, for the base analysis case at 1,000 years is over four orders of magnitude less than the performance objective. At 10,000 years, the estimated impact for the base analysis case from beta emitters remains small (still a factor of almost 400 below the 4 mrem/year goal). Groundwater impacts from contaminants were found to be very small. The most important drivers for determining peak groundwater impacts are the inventory of ^{99}Tc for beta/photon emitters and neptunium for alpha emitters. However, ^{129}I and ^{237}Np, which were treated as relatively immobile in the 1998 ILAW PA, are now known through disposal site-specific information to be more mobile. Thus, whereas 75 percent of the drinking water dose was from ^{99}Tc in the 1998 ILAW PA, only 50 percent was due to ^{99}Tc in the 2001

IDF PA. Therefore, the relative contribution to groundwater impact from other mobile contaminants had increased.

3.1.1.3 Supplemental Waste Form Risk Assessment-2003

In 2003, a risk assessment for supplemental waste forms was prepared (Mann et al. 2003b). The purpose of this risk assessment was to document the evaluation of the long-term release behavior of baseline WTP glasses and the supplemental waste forms under consideration at that time [bulk vitrification (BV), Cast Stone and Fluidized Bed Steam Reformer (FBSR)] and, as well as the impacts of the release on groundwater below the IDF. However, because of budget, schedule, and technical limitations, Mann et al. (2003b) acknowledged that the risk assessment was less rigorous and detailed than a PA, but of sufficient technical credibility to support decision-making. A full PA would look at the impacts to surface water and air resources, as well as groundwater. However, as shown from previous full PAs (Mann et al. 1998, 2001, and 2003a), such impacts are small compared to the ground water impacts. A full PA also investigates the impacts to an inadvertent intruder, and the Mann et al. (2003b) risk assessment provides such an analysis in its Section 5.1.3.

The Mann et al. (2003b) risk assessment not only presents estimated numeric values for groundwater and intruder impacts, but stresses concerns and issues that have been identified with the methods and data used in its analyses. The authors state that further evaluations of long-term environmental impact from burial of supplemental waste forms in the IDF will need to be performed when more data become available.

Mann et al. (2003b) describes how transport through the vadose zone affects groundwater impacts caused by the burial of the various supplemental waste forms. Most of the input data for the near-field simulations in Mann et al. (2003b) were from the *Hanford Immobilized Low-Activity Tank Waste Performance Assessment: 2001 Version* (Mann et al. 2001; DOE/ORP-2000-24 Rev. 0). Only six contaminants (^{99}Tc, ^{129}I, Cr, NO_2, NO_3, and U) were considered in Mann et al. (2003b); however, they are considered the most mobile once released from the various wastes. Total inventories to be disposed of for these six constituents were based on the values used in the 2001 IDF PA (Mann et al. 2001). Mann et al. (2003b) used the assumption that 25% of the low-activity waste inventory would go into each of the four candidate supplemental waste forms (baseline LAW (WTP) glass, BV, FBSR, and Cast Stone).

An important input to these calculations for the “thermal” waste forms (i.e., WTP LAW glass, BV, and FBSR) is the amount of inventory that goes into the product (waste form) and the amount that becomes a secondary waste (e.g., via volatilization and off-gas capture). This split was provided by the Tank Farm Contractor, CH2M Hill Hanford Group, Inc.

A major conclusion from the 2001 IDF PA (Mann et al. 2001) is that the release rate of radionuclides from the WTP glass by reaction with water is one of the key parameters that determines the impacts of the disposal action and is the most uncertain. Consequently, a sound scientific basis for determining the long-term release rates of radionuclides from WTP glasses or any supplemental waste form is essential to ensuring acceptance of such disposal by regulatory agencies, stakeholders, Native Americans, and the public. A general approach for the evaluation of material behavior in a disposal site has been developed that outlines logical steps to validate and confirm the release behavior of materials whose life expectancies must greatly exceed the length of time over which experimental data can be obtained

(ASTM C1174-91). These steps include determining the likely range of environmental factors in the disposal system, identifying and characterizing materials that are likely to be present in the disposal system, performing tests under site-relevant conditions to determine important alteration processes for those materials, developing models for key alteration processes, and performing tests that accelerate those processes. The contaminant release from BV, FBSR, and WTP glass in Mann et al. (2003b) is based on classical silicate dissolution theory, which was also the basis of the 2001 IDF PA (Mann et al. 2001). However, for some waste forms, in particular cementitious waste forms, far less fundamental/scientific work has been conducted with respect to evaluating long-term release behavior. This includes identifying (or confirming) the weathering processes that will control the long-term release of contaminants, measuring parameters needed to perform model calculations for PA, and conducting accelerated and service condition tests to confirm and provide confidence in those calculations.

The contaminant release conceptual model for Cast Stone used in Mann et al. (2003b) was based on the classical advection-diffusion theory. In particular, the release of constituents from Cast Stone was quantified by the use of an effective diffusion coefficient for each constituent (see McGrail et al. 2003 for more discussion). The effective diffusion coefficients for Cast Stone contaminant release were derived from literature values for similar cementitious grouts, as well as some very short-term leaching results for one specific Cast Stone formulation, DRF 2, and one LAW waste loading produced by the Hanford Cast Stone vendor (Fluor Federal Services, Inc.). The effective diffusion coefficient has been shown to be dependent on the waste loading for a given formulation. This dependence has been observed in other cementitious grouts, such as the SRS saltstone formulations (see Serne and Westsik 2011 for more discussion and references).

Risks were calculated by Mann et al. (2003b) for:

- contaminant fluxes from the product at the bottom-most layer of packages in the IDF disposal facility,
- contaminant fluxes from the product at the bottom of the IDF disposal facility,
- contaminant fluxes from the product entering groundwater,
- contaminant concentrations in a groundwater well 100 meters down-gradient of the IDF facility,
- inadvertent intruder analysis, and
- groundwater impacts from secondary waste generated (for the “thermal treatment” waste forms).

Mann et al. (2003b) cautioned that there were major uncertainties in the risk analyses that could affect the conclusions, including the total tank waste inventory that was considered, the amount of inventory allocated to secondary waste for the thermal treatment waste products, the empirical nature of the conceptual release model for Cast Stone, the limited database for release from BV, and presence and release of mobile constituents from the froth layer observed in BV product. Finally, Mann et al. (2003b) caution that it is possible that processes not modeled in this preliminary risk analysis will turn out to be important.

For Cast Stone, the major question is how contaminants are released from the waste form. The classical advection-diffusion model was used in this analysis, but there are doubts whether this is the most appropriate model, especially for the vadose zone environment at Hanford and for the geologic time scales important in a risk assessment. Given all the cautions, the major conclusions of the Mann et al. (2003b) risk analysis are:

- Groundwater impacts from the disposal of secondary waste created from thermal processes (BV, FBSR, and LAW glass) will be comparable to or higher than the impacts from the products themselves.
- Cast Stone has the highest peak groundwater impacts, driven by the inventory and the use of an upper limit for a key parameter (the effective diffusion coefficient).

3.1.1.4 IDF PA-2005

Calculations for the IDF performed in 2005 were never published as a PA. Near-field source term release modeling results were published (Bacon and McGrail 2005), as well as several data packages. A few of these publications contain information important to evaluating the release of contaminants from cementitious grout waste forms and the subsequent fate of grout waste form leachates. The IDF 2005 PA included grouted secondary wastes originating from the WTP vitrification process. However, the description of the types of WTP secondary wastes in the 2005 IDF PA emphasized solid wastes, such as spent HEPA filters and spent ion exchange resins, more so than the liquid secondary wastes created by capturing solutes and particulates from off-gas treatment systems. Regardless, the conceptual model for contaminant release from grout used most extensively in the 2005 IDF PA was a diffusion-controlled model similar to that used in the 2003 supplemental waste risk assessment discussed in Section 3.1.1.3. However, one predictive modeling exercise using a kinetically controlled solubility conceptual model, embedded in the STORM code, for release of ^{129}I, was performed (see discussion below; for more details, see Bacon and McGrail 2005). Effective diffusion coefficients, time-invariant values for each key contaminant, used in the 2005 IDF PA, were documented in Pierce et al. (2004; Table 3-9) and reproduced herein as Table 3.2. For the base cases used in the 2005 IDF PA, the most probable effective diffusion coefficients were used. The conservative effective diffusion coefficients were used in sensitivity cases evaluated in the 2005 IDF PA.

Table 3.2. Most Probable and Conservative Estimates for "Proxy" Effective Diffusion Coefficients ($cm^2\ s^{-1}$) for Key Contaminants in Secondary Waste Solidified in Cementitious Waste Forms

Waste Form Species	Waste Form Type	Effective Diffusion Coefficient (cm^2/s)		Reference/ Rationale
		Most Probable	Conservative	
NO_2^-, NO_3^-	Any Cement/Grout	5×10^{-9} (a)	3×10^{-8}	(Serne et al. 1992)
I^- (free), IO_3^-(free)	Any Cement/Grout	2.6×10^{-9} (a)	1×10^{-8}	(Atkins et al. 1988)
TcO_4^-	Any Cement/Grout	5×10^{-10} (a)	1×10^{-8}	(Serne et al. 1992)
Cr(VI)	Any Cement/Grout	5×10^{-11} (a)	5×10^{-10} (guess)	(Serne et al. 1992)
Hg(I) free	Any Cement/Grout	1×10^{-11} (a) (guess)	1×10^{-10}(guess)	
U(VI)	Aged Cement/Grout	1×10^{-11} (a) (guess)	1×10^{-10}(guess)	

(a) Values used in the base analysis case calculations. All other contaminants assumed to have an effective diffusion coefficient of 5×10^{-9} cm^2/s.

The values in Table 3.2 were extracted from literature that was dominated by past studies of Hanford grout and not directly related to more current studies on Hanford secondary waste streams solidified in Cast Stone.

The most probable effective diffusion coefficients for the key groundwater risk drivers in Table 3.2 are compared to the recommended effective diffusion coefficient values chosen in the Mann et al. (2003b) risk assessment, shown in Table 3.3.

Table 3.3. Recommended Effective Diffusion Coefficient Values Chosen in the Mann et al. (2003b) Risk Assessment

Waste Form Species	Effective Diffusion Coefficient Most Probable Used in 2005 IDF PA for WTP Secondary Wastes	Recommend Values used in 2003 Supplemental Waste RA
	-------------------- cm^2 s^{-1}	--------------
NO_2^-, NO_3^-	5×10^{-9}	2.5×10^{-8}
I^- (free), IO_3^-(free)	2.6×10^{-9}	2.5×10^{-9}
TcO_4^-	5×10^{-10}	3.2×10^{-10}
Cr(VI)	5×10^{-11}	1.6×10^{-11}
Hg(I) (free)	1×10^{-11} (guess)	Not Considered
U(VI)	1×10^{-11} (guess)	3.2×10^{-10} (a)

(a) In 2003 RA uranium effective diffusion coefficient set equal to pertechnetate to be conservative.

In the 2005 IDF PA predictions, the effective diffusion coefficient used for nitrate and nitrite is five times smaller than the effective diffusion coefficient used in the 2003 RA; the chromate effective diffusion coefficient used in the 2005 IDF PA is about three times larger. The 2005 IDF PA used about the same effective diffusion coefficient for iodine species as was used in the 2003 supplemental waste RA. The 2005 IDF PA used a Tc effective diffusion coefficient that was 1.6 times larger than the Tc effective diffusion coefficient used in the 2003 RA.

When using the diffusion-controlled contaminant release model along with the effective diffusion coefficient, the contaminant flux out of the waste form depends on the physical dimensions (the key being the grout waste form surface area-to-volume ratio). In the 2005 IDF PA, the assumed dimensions of the grout wastes were 1.22 m (L) × 2.44 m (W) × 1.22 m (H) [4 ft (L) × 8 ft (W) × 4 ft (H)]. For example, a grout waste package with these dimensions would release a contaminant at a rate of about one-half that of a comparable grout monolith formed as a typical 55-gallon drum. Once released from the grout monolith at its surface, contaminants would be swept away in the recharge water that passes by the disposed grout. Thus, the flux of contaminants from the grout is also influenced by the recharge rate.

Differences between the 2005 IDF PA and the 2001 IDF PA included the evaluation of an expanded scope of waste types (LAW glass, BV, grouted secondary wastes from WTP, and other Hanford and DOE-Complex miscellaneous solid wastes). In addition, different estimates of recharge rates were used, and there were new estimates of contaminant-sediment K_d values, as well as better modeling of LAW glass release. The recharge rates used in the 2005 IDF PA were 0.5 mm/year for base cases and 0.1 mm/year for the best case, which relied upon the sand-gravel capillary break placed right above the uppermost layer of waste packages in the IDF trench. The recharge rate chosen has implications on the time of arrival of contaminants to the water table and the concentration of each contaminant that enters the water table. Given the thick vadose zone underlying the IDF (>80 m or 250 ft) and such a low recharge value (0.5 mm/year) no contaminant can reach the groundwater during DOE's time of compliance (1,000 years). For the base analysis cases (recharge equal to 0.5 mm/year), the mobile contaminants (K_d=0 in vadose zone) peaked at about 14,000 years. Retarded species (those that have positive K_d values) were predicted to have peak groundwater concentrations at much later times (significantly >10,000 years).

The assumed inventory in each type of waste form disposed in the IDF also influences the calculated impacts to humans and the environment once the fate and transport predictions are generated. Thus we have documented the assumed inventories for each PA discussed. The inventories of the two most problematic radionuclides (^{99}Tc and ^{129}I) used in the 2005 IDF PA were 22,700 and 41.3 Ci, respectively; however, only 388 and 25 Ci, respectively, were allocated into the secondary waste (grouted) and miscellaneous solid waste (not grouted) categories.

The same computer codes were used in the 2005 IDF PA as were used in the 2001 IDF PA. STORM (with a more robust glass release algorithm and more data on improved LAW glass formulations as documented in Bacon et al. 2004) was used for the near-field waste package contaminant release for the LAW glass and BV. However, the 2005 IDF PA contaminant release was performed in two dimensions, such that a lot of the infiltrating water travelled around the vitrified and grouted secondary waste packages as opposed to having to flow through the vitrified waste when using a one-dimensional version of STORM as used in the 2001 PA.

The grouted secondary waste package domain used in the 2005 IDF PA was assumed to be a 2-D vertical stack of four waste packages near the center of a single IDF trench. The grouted secondary waste packages are 2.44 m tall, 1.22 m wide, and filled to the top with grout. The grout waste packages in the IDF trench were assumed to be 1 m apart vertically, 30 cm apart horizontally, and offset horizontally by 10 cm relative to adjacent packages (see Bacon and McGrail 2005 for more details).

For the one case mentioned above where the release of ^{129}I from grouted secondary waste was modeled using STORM, a simple solid phase representation of the starting grout was chosen (Bacon and McGrail 2005, Table 12 with literature solubility constants and assumed kinetic rate constants). This grout composition and release conceptual model allowed the STORM code to predict release of ^{129}I (the only contaminant in grout that was modeled using STORM). The assumed "kinetically controlled" solubility release of three potentially iodide- or iodate-solids were then compared to the releases predicted by simple effective diffusion coefficient calculated releases. As shown in Table 3.2, the effective diffusion coefficient of the radioactive iodine (both I^- and IO_3^-) chosen was 2.6×10^{-9} cm^2/s (value from Pierce et al. 2004; which cites Atkins et al. 1988 as the original source). The STORM predicted results showed that barium iodide kinetically controlled solubility was unrealistically high, such that the iodide release rate assuming this controlling solid would more realistically be modelled using diffusion-limited release. However, if the ^{129}I inventory was assumed to be controlled by either barium iodate or silver iodide, that iodine release could be controlled by solubility. That is, lower concentrations of iodide and iodate in the pore water after leaching would be observed, assuming solubility control by either of these two solids instead of assuming that the cited empirical effective diffusion coefficient controlled release of all ^{129}I.

The LAW glass, BV, and grout contaminant fluxes were passed to the VAM3DF code (Huyakorn and Panday 1999). The VAM3DF code structured as a two-dimensional horizontally layered system computed the contaminant and water fluxes from the near-field through the rest of the vadose zone to the water table. This contaminant transport conceptual model was essentially the same in both the 2001 and 2005 IDF PAs. The water and contaminant transport in the groundwater aquifer were performed using the Hanford Site model and associated code, CFEST-96 (Gupta et al. 1987), in both the 2001 and 2005 IDF PAs. For both the 2001 and 2005 IDF PAs, no credit was taken for increased travel time in the unconfined aquifer because of geochemical retardation (sorption); thus K_d =0 for all contaminants in the aquifer. This is because the contaminants spend significantly less time in the unconfined aquifer than in the vadose zone. The results from the three release/transport codes were combined with inventory and dosimetry data to provide radionuclide and chemical concentrations in groundwater, as well as dose rates, chemical hazard indices, and cancer risks.

A key assumption for the IDF PA calculations (for all the PAs discussed herein) is that the contaminant release and transport from the different waste forms can be modeled separately and temporal and spatial superposition can be used to estimate the cumulative impacts from the different waste forms.

As mentioned above, once a contaminant was released from the waste package, its fate through the far-field vadose zone was modeled with the VAM3DF code that relies upon the linear isotherm sorption-desorption construct (i.e., K_d) to quantify interactions with the sediments. Therefore, for convenience, the K_d values used in the IDF calculations are provided for comparisons. In the 2005 IDF calculations, K_d values were documented in a geochemical data package (Krupka et al. 2004), and are summarized in Table 3.4

Table 3.4. Kd Values (mL/g) for the Vadose Zone Sediments- Base and Best Reference Cases

Element	**Impacted Sand**		**Non-Impacted Sand**	
	"Best"K_d $^{(a)}$	**Base-Case K_d**	**"Best"K_d $^{(b)}$**	**Base-Case K_d**
NO_3, NO_2, Cr, Tc	0	0	0	0
I	0.1	0.1	0.25	0.2
U	0.2	0.2	1	1
Np, Pa	0.8	0.6	15	10

(a) Taken from Table 5.5 of *Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility Performance Assessment (IDF PA)* (Krupka et al. 2004).

(b) Taken from Table 5.6 of *Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility Performance Assessment (IDF PA)* (Krupka et al. 2004).

The K_d value for the most important radionuclide in the 2001 ILAW PA (^{99}Tc) remains at 0 mL/g. The K_d value for ^{129}I increased from 0 (in the 2001 PA) to 0.2 mL/g in the non-impacted vadose zone and to 0.1 mL/g in the glass leachate-impacted vadose zone. This increase effectively slows the ^{129}I groundwater arrival times and its impacts at the 100-m down-gradient well and the Columbia River beyond 10,000 years.

For radionuclides, the key groundwater risk driver in the 2005 calculations was ^{99}Tc. Other radionuclides having a significant inventory are retarded, and hence do not reach groundwater in significant amounts in 10,000 years. ^{99}Tc is estimated to contribute over 95 percent of all pathways or beta/photon drinking water doses during the first 10,000 years. At far later times, ^{129}I, uranium, and ^{237}Np become important radionuclides. The most important non-radioactive contaminants that reach the groundwater are arsenic and chromium for the incremental lifetime cancer risk, and fluorine, nitrate, mercury, and zinc for the hazard index.

The 2005 calculations used many sensitivity cases by varying the inventories of tank waste proportioned to different types of waste, glass compositions for the LAW glasses, recharge rates, effective diffusion coefficients for grouted secondary waste, K_d values for key mobile contaminants, and other parameters to investigate which parameters impact the overall human health and environmental impacts. For the most part, other geotechnical data, such as hydraulic parameters for the materials in the IDF near-field environment, were less important than the inventory distribution, recharge rate, and K_d values chosen for the mobile contaminants.

One key observation was that for the groundwater pathway, the waste form that dominated the risk was the grout containing the secondary waste from ILAW production, even though the ^{99}Tc inventory is much higher in the ILAW glass than the grouted secondary wastes. The faster release rate from the grout relative to the glass overcomes the inventory difference.

3.1.1.5 TC&WM EIS (2012)

The Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington (TC&WM EIS; DOE/EIS-0391[1]) evaluates a number of alternatives, including waste treatment options that solidify liquid secondary waste and supplemental LAW in a grout waste form such as Cast Stone.

A diffusion-limited release model, along with assumed waste form size (key variable surface area-to-volume ratio), estimated waste form contaminant inventories, and pore-water flux rates (dominated by the recharge rate), was used in the TC&WM EIS impact analyses to estimate the release of contaminants from Cast Stone waste forms. The diffusion-limited release model relies on the Cast Stone waste form being configured with a known geometric surface area to volume ratio. The conceptual release model uses a bulk retardation factor or contaminant capacity (α) approach for each key contaminant, and physical attributes for the Cast Stone, such as its bulk density (ρ), tortuosity (τ), constrictivity (δ), and effective porosity (ε), as well as values of aqueous diffusivity (D_f) for key constituents as portrayed in the suite of equations shown in Eq. 1. Effective diffusivity ($D_{e)}$ is defined as the intrinsic diffusion coefficient, D_i,

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[1] available at http://www.hanford.gov/page.cfm/FinalTCWMEIS

divided by the contaminant-specific retardation or capacity factor (α), which is related to the K_d for each constituent. The intrinsic diffusion coefficient of a constituent within a grout (porous media) is related to its free diffusion coefficient, D_f, in water modified by physical attributes of the grout solid [tortuosity (τ), effective porosity (ε), and constrictivity (δ)], as shown in the last equation in the suite (Eq. 1).

$$\begin{aligned} D_e &= \frac{D_i}{\alpha} \\ \alpha &= \varepsilon + \rho * K_d \\ D_i &= D_f \frac{\varepsilon\delta}{\tau} \end{aligned} \qquad \text{Eq. 1}$$

Within the TC&WM EIS Cast Stone conceptual model, the aqueous diffusivities are based on ion conductivity data (Weast and Selby 1966) with values for key species, iodide (I^-), pertechnetate (TcO_4^-), and nitrate (NO_3^-) of 1.1 × 10^{-5}, 1.5 × 10^{-5}, and 1.9 × 10^{-5} cm^2/s, respectively, at 25 °C (77 °F); these values are given in Table 3.5. The total porosity of the Cast Stone grout was estimated to be 0.43, based on a crystal density of 2.65 g/cm^3 $/cm^3$for natural silicates (Freeze and Cherry 1979; Mason and Berry 1968) and a bulk density of 1.5 g/cm^3 for grout (DOE 2003). Because the value of effective porosity had not been established for Hanford Cast Stone under the IDF burial site conditions at the time that the TC&WM EIS was produced, the value of total porosity was used for the effective porosity as a conservative limit of release rates.

The TC&WM EIS used the Eq. 1 definition of effective diffusivity, but supplemented this approach using the Technical Guidance Document (DOE 2005) recommended values of effective diffusivity; the implied values of the distribution coefficient (used in the retardation or capacity factor) (α) for technetium and iodine in Cast Stone grout are 1 and 50 mL/g, respectively. Values of aqueous diffusivity and effective diffusivity for Cast Stone, consistent with the Technical Guidance Document (DOE 2005), are summarized in Tables M–9 and M–10 of the TC&WM EIS for radioactive and chemical constituents, respectively (values for key constituents are reported in Table 3.5).

Table 3.5. Effective Diffusion Coefficients (cm^2/s) Used in TC&WM EIS for LAW Cast Stone

Constituent	Aqueous Diffusivity (D_i)	Effective Diffusivity (D_e)
Tc (pertechnetate)	1.5 × 10^{-5}	5.2 × 10^{-9}
I (iodide)	1.1 × 10^{-5}	1.0 × 10^{-10}
U (uranyl)	4.3 × 10^{-6}	5.5 × 10^{-11}
Cr (chromate)	1.13 × 10^{-5}	1.81 × 10^{-8}
Nitrate	1.90 × 10^{-5}	3.04 × 10^{-8}

The TC&WM EIS analyses also used the effective diffusivities of 5.2 × 10^{-9} cm^2/s for Tc and 1.0 × 10^{-10} cm^2/s for I in solidified secondary waste from both ETF and WTP operations that were solidified in grout or Cast Stone.

Note that the Washington State Department of Ecology, in their foreword to the TC&WM EIS, calls for improving the performance of grout forms for WTP secondary wastes by lowering the effective diffusivity for all risk driver constituents to a performance standard of 1×10^{-12} cm^2/s, “thus deleting this waste from the list of dominant contributors to risk.” The Washington State Department of Ecology only mentions grouted secondary wastes in the foreword to the TC&WM EIS, and does not address or acknowledge use of Cast Stone for LAW. Whether such low effective diffusion coefficients are necessary can be debated seeing as the release of contaminants from waste forms and their subsequent migration to the groundwater rely on many other parameters besides the effective diffusion coefficient as mentioned above. For example, the inventory of contaminants in the waste forms, the size of the waste forms, the porewater flux passing by or through the waste forms, and the subsequent interactions of leached contaminants with vadose zone and aquifer sediment also influence the mass of contaminants reaching compliance points (e.g., the 100-m down-gradient well). Many combinations of Waste Management alternatives coupled with Tank Closure alternatives are found in Chapter 5 of the TC&WM EIS. The Waste Management and Tank Closure alternative that most closely represents the current baseline types and inventories to be disposed into the IDF facility located in 200-E is (Waste Management Alternative 3-Tank Closure Alternative 2A for Disposal Group 2 Subgroup 2-A)[2].

The inventories of the key risk driving radionuclides and chemicals for this alternative that are predicted to reach the groundwater in the 10,000 yr time “regulatory” period are shown in Figure 3.2 and Figure 3.3. The maximum groundwater concentrations and the calendar year at which the maximum groundwater concentration occurs are shown in Table 3.6. The key groundwater risk driver radionuclides are ^{99}Tc and ^{129}I, and the key groundwater risk driver chemicals are chromium and nitrate.

Figure 3.2 shows the waste form that contributes the largest mass of ^{99}Tc that reaches the groundwater— secondary solid wastes originating from WTP processes, followed by grouted wastes processed through ETF. The mass of ^{99}Tc that leaches from the LAW glass and from spent melters is insignificant over the 10,000-yr time period. For ^{129}I, the grouted waste from the ETF facility leaches the most mass that reaches groundwater, followed by the miscellaneous solid secondary wastes from WTP processes. Again LAW glass and spent melters contribute insignificant amounts of ^{129}I to groundwater in the first 10,000 years. Figure 3.3 shows that most of the chromium that reaches groundwater below the IDF facility emanates from the miscellaneous solid secondary wastes from WTP processes, with several percent also originating from both grouted ETF waste streams and the LAW glass. Essentially all the nitrate that reaches groundwater below the IDF originates from the grouted ETF waste streams.

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[2] The reader should review the nomenclature used in the TC&WM EIS to categorize the various alternatives and waste groupings. Suffice it to state there is a “complicated” and large number of alternatives/categories presented. Further, the types of waste categories assumed to be disposed of in IDF are designated as LAW glass, ETF generated secondary wastes (herein assumed to be grout solidified), retired or spent melters, and tank closure secondary wastes. The last category is not well defined in the TC&WM EIS but herein we assume this category to represent solid low-level radioactive waste and mixed low-level radioactive waste streams that would be generated by the waste treatment operations. Such waste streams would include debris waste, melter consumables, failed process components, analytical laboratory waste, spent resins, spent carbon adsorbent, high-efficiency particulate air filters, and other process-related waste. We also assume that the TC&WM EIS encapsulated these tank closure secondary wastes in grout and thus used the effective diffusion coefficient conceptual release model.

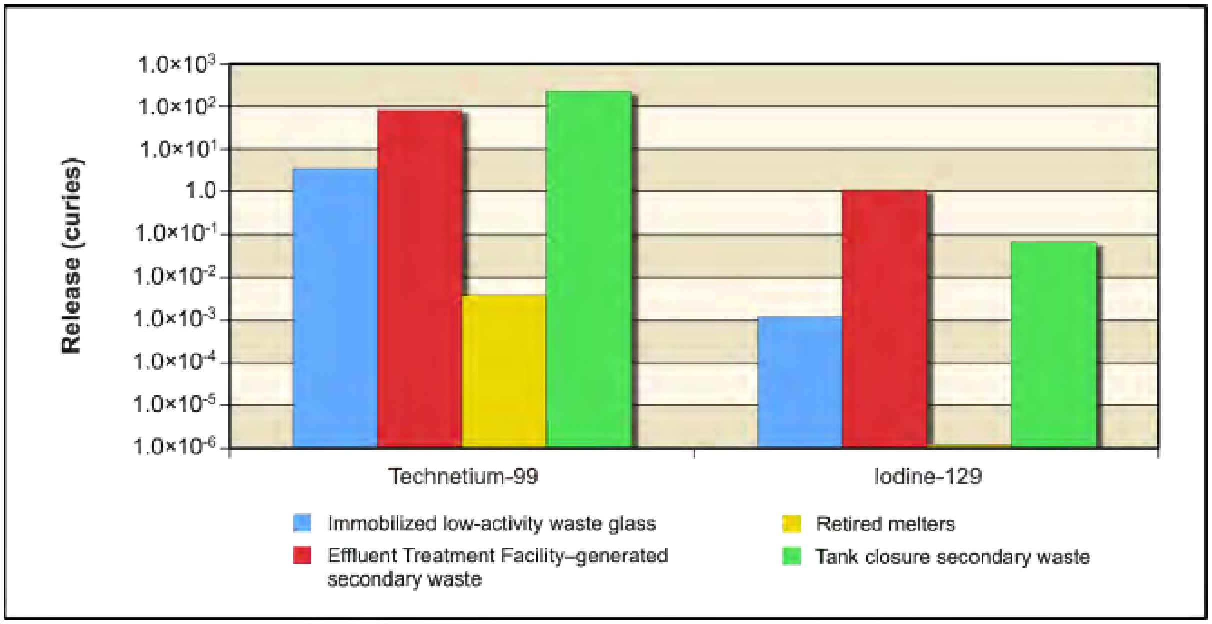

Figure 3.2. Inventory of Key Groundwater Risk Driver Radionuclides Reaching Groundwater below the IDF Facility for WM Alternative 3-Tank Closure Alternative 2A-Disposal Group 2, Subgroup 2-A (Figure 5-954 in TC&WM EIS)

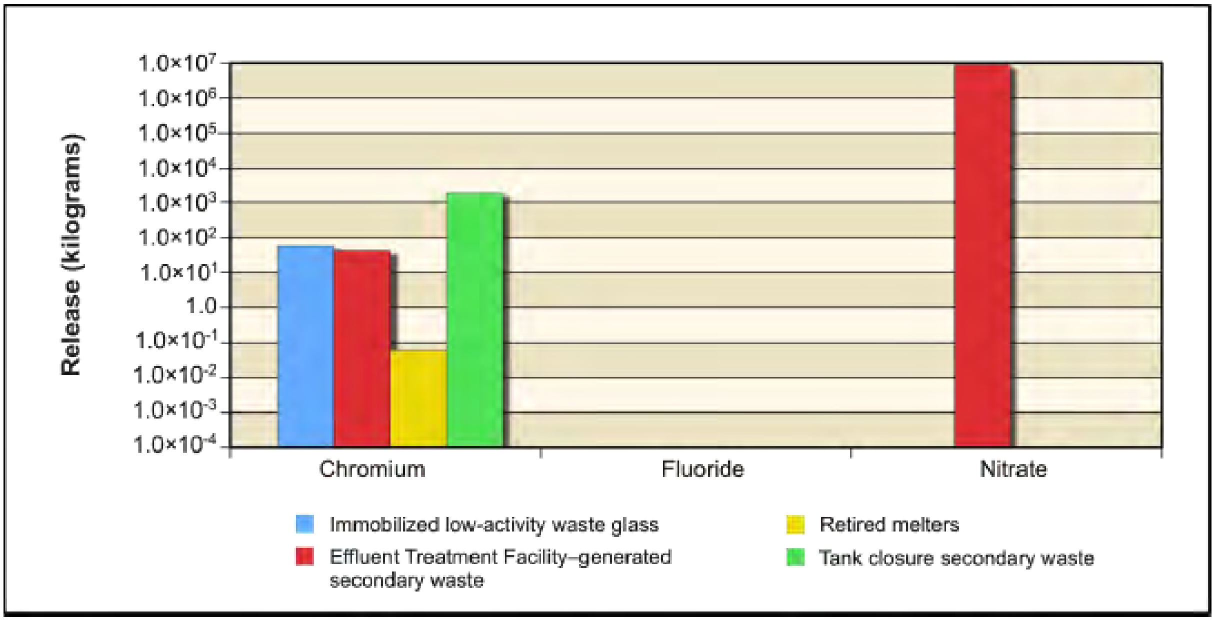

Figure 3.3. Inventory of Key Groundwater Risk Driver Chemicals Reaching Groundwater below the IDF Facility for WM Alternative 3-Tank Closure Alternative 2A-Disposal Group 2, Subgroup 2-A (Figure 5-955 in TC&WM EIS)

Table 3.6 shows the predicted maximum groundwater concentrations reaching the IDF 100-m down-gradient well, as well as the calendar year that the maximum groundwater concentration is predicted to occur. For this disposal alternative that most closely represents the current envisioned waste forms and inventories to be disposed in IDF, none of the four key groundwater risk driving contaminants (^{99}Tc, ^{129}I, chromium, and nitrate) exceed their maximum allowable concentrations in the 10,000-yr "compliance" period. The maximum peaks for these four key contaminants arrive at the 100-m downgradient well between ~8000 and 10,000 years.

Table 3.6. Peak Groundwater Concentrations (pCi/L or µg/L) and Calendar Year of Peak Arrival at the 100-m Downgradient Well for the TC&WMEIS Disposal Alternative Most Representative of the Current Baseline

Constituent	Units	IDF Down-gradient Well Concentration	Drinking Water (MPC)	Calendar Yr that GW Peak Arrives
^{99}Tc	pCi/L	193	900	10,188
^{129}I	pCi/L	0.8	1	9907
Cr	µg/L	2	100	8251
Nitrate	µg/L	9,590	45,000	7983

No other radionuclides or chemicals are predicted to arrive at the IDF 100-m down-gradient groundwater "regulatory" well at concentrations close to their drinking water maximum permissible concentrations. The TC&WM EIS peak groundwater concentrations at any of the regulatory points of compliance (100-m down gradient well, boundary of the core zone, or at the shore of the Columbia River) for ^{99}Tc,^{129}I, chromium, or nitrate are predicted assuming that there is no adsorption of any of these contaminants to the vadose zone or aquifer sediments. Data are available that suggest iodide and iodate do in fact adsorb to a small degree to Hanford formation sediments (see Um et al. 2004; Kaplan et al. 2000, 1998), thus the peak concentrations and year of arrival for ^{129}I shown in Table 3.6 likely are over- and under-estimated, respectively.

3.1.1.6 Comparison of Effective Diffusion Coefficients Used in Hanford Site PAs

In this subsection, the Cast Stone effective diffusion coefficient values for key groundwater risk drivers are compared for past predictions of the performance of the IDF. Bear in mind that the overall performance of the IDF is controlled by more than the contaminant release from the waste packages. Thus, solely comparing the effective diffusion coefficients for each risk-driving contaminant from the Cast Stone waste forms does not yield the entire story on groundwater impacts. However, using the simple diffusion-controlled release model, as was done in all past Cast Stone performance predictive modeling, does directly relate to the groundwater impacts; that is, the larger the effective diffusion coefficient for a particular contaminant, the larger the potential impact on the groundwater if all other variables are held constant.

Table 3.7 compares the effective diffusion coefficients used in the three past predictive modeling efforts that included a grouted or Cast Stone waste form. In the risk assessment performed by Mann et al. (2003b), for supplemental waste forms, some target or desired effective diffusion coefficient values were developed based on the modeling results that would be protective of future groundwater. The desired effective diffusion coefficients selected by Mann et al. (2003b) for ^{129}I and ^{99}Tc were 1.0×10^{-11} and 1.0×10^{-9} cm^2/s, respectively, but the authors warn that these target/desired effective diffusion coefficients are subject to change as updated modeling is performed. A desired effective diffusion coefficient for sodium, 1.0×10^{-6} cm^2/s, is also listed in preliminary IDF waste acceptance criteria (Burbank 2005).

As shown in Table 3.7, the effective diffusion coefficients for the mobile anions (nitrate and nitrite) used in past IDF PA analyses varied over a relatively small range of 0.5 to 3×10^{-8} cm^2/s. For Cr(VI), the effective diffusion coefficient used in the TC&WM EIS is much higher (three orders of magnitude) than the value used in other PAs, and the high value used in the TC&WM EIS is not supported by available short-term leaching data for Cast Stone containing BFS (see Westsik et al. 2013). The effective diffusion coefficient for U(VI) used in Mann et al. (2003b) was a very conservative guess because no data were available at the time. An effective diffusion coefficient for U(VI) for any waste simulant solidified in fresh Cast Stone has recently been found (see Westsik et al. 2013) to be $< 1 \times 10^{-11}$ cm^2/s, the approximate value used in the 2005 IDF calculations and TC&WM EIS. The effective diffusion coefficients for ^{99}Tc used in past PA analyses ranged from 3.2×10^{-10} to 52×10^{-10} cm^2/s, with the TC&WM EIS using a value. of 5.2×10^{-9} cm^2/s. Recent leach tests (Westsik et al. 2013; Mattigod et al. 2011; Sundaram et al. 2011) suggest that Tc effective diffusion coefficients are generally below the target value of 1.0×10^{-9} cm^2/s and mostly in the range or below the 3 to 5×10^{-10} cm^2/s used in the Supplemental LAW Waste RA and 2005 IDF PA. The effective diffusion coefficients for ^{129}I used in past PA analyses ranged from 0.1 to 2.6×10^{-9} cm^2/s, which is significantly higher than the target/desired value of 10^{-11} cm^2/s. Recent short-term leach tests (Westsik et al. 2013; Mattigod et al. 2011; Sundaram et al. 2011) found that ^{129}I does leach from Cast Stone at rates much higher than the target value of 10^{-11} cm^2/s, and for many Cast Stone waste simulant formulations, a median value of $\sim 5 \times 10^{-9}$ cm^2/s was realistic. This median value is larger than the values used in past IDF predictive modeling exercises, suggesting that ^{129}I release from Cast Stone might cause larger groundwater impacts unless there are other mechanisms, such as sorption on vadose zone sediments, that delay and reduce the transport of ^{129}I released from Cast Stone waste forms. Another process under investigation is adding ^{129}I getters to the Cast Stone dry blend or to the liquid waste prior to mixing with the dry blend.

Table 3.7. Comparison of Effective Diffusion Coefficients (cm^2/s) Used in Past IDF PAs

Contaminant Recommended / Most Probable / or Base Case D_e	2003 Supplemental LAW Waste RA	2005 IDF PA 2nd Waste	2012 TC&WM EIS (both LAW and 2nd Waste)
NO_3 (nitrate)	2.5×10^{-8}	5×10^{-9}	3.04×10^{-8}
NO_2 (nitrite)	2.5×10^{-8}	5×10^{-9}	Not Reported
Cr (total) (chromium)	1.6×10^{-11}	5×10^{-11}	1.81×10^{-8}
^{99}Tc	3.2×10^{-10}	5×10^{-10}	5.2×10^{-9}
^{129}I	2.5×10^{-9}	2.6×10^{-9}	1.0×10^{-10}
U (total uranium)	3.2×10^{-10} (a)	1×10^{-11}	5.5×10^{-11} (b)

(a) Conservative guess – assumed value of mobile Tc.
(b) There is a discrepancy in the TC&WM EIS; Table M-9 value for radioactive U shown in Table but Table M-10 in TC&WM EIS gives a value for “chemical” uranium as 2.19×10^{-9} cm^2/s.

Again as mentioned above effective diffusion coefficients are just one of the key variables that determine the release rate of contaminants from grout waste forms and subsequent impacts on groundwater. Other key variables are starting inventory, grout waste form surface to volume ratio, pore water flux, and leachate sorption properties.

3.1.1.7 LFRG Comments

Previous Hanford IDF PAs have been reviewed by the Low-Level Waste Disposal Facility Federal Review Group (LFRG). LFRG review comments fall into three broad categories (1. PA is Complete, 2. PA is Thorough and Technically Supported, and 3. PA Conclusions are Valid and Acceptable) with numerous subcategories (see Mann et al. 2003a for detailed descriptions of review criteria and comments).

The two primary areas in which previous IDF PA calculations appear to have been deficient are: 1) insufficient evidence was provided to satisfy reviewers that the assumed performance of the glass waste form could actually be achieved, and 2) there was a lack of consistency between base case and sensitivity cases and a need for additional sensitivity cases to address vadose zone heterogeneities. Note that previous IDF PA calculations that were reviewed by LFRG did not consider the performance of Cast Stone as a secondary waste form or supplemental LAW waste form. Thus, one can only assume that LFRG would have questioned whether sufficient data were available for the release of contaminants from the grout waste form, similar to their concern about data for glass release.

3.1.2 SRS Saltstone + NRC Review

In this section, PA activities related to saltstone disposal at the SRS are summarized, with emphasis on the most recent PA that was published in October 2009 (SRR-CWDA-2009-00017). In addition, formal comments on the SRS 2009 PA generated by the NRC are summarized from its “Technical Evaluation Report.”

3.1.2.1 SRS Saltstone PA Activities

Approximately 136 million liters (36 million gallons) of liquid waste resulting from reprocessing spent nuclear fuel are stored in 49 underground carbon steel tanks at SRS. This waste is being separated into two streams based on activity. The high-activity fraction, or high-level waste (HLW), is made into a glass waste form. The low-activity fraction, called salt waste, is treated to reduce the concentrations of certain key radionuclides and then mixed with dry materials (i.e., cement, BFS, and fly ash) to form a grout waste form called saltstone.

At the SRS, several PAs have been performed to support construction of the Saltstone Disposal Facility (SDF). The first PA (WSRC-RP-92-1360) was published in 1992 and included only radionuclides. This 1992 PA was written in accordance with the requirements contained in DOE Order 5820.2A, a precursor to DOE Order 435.1-1. The second PA (WSRC-RP-98-00156), an addendum to the 1992 PA, was produced in 1998 in order to address comments from the DOE PA Peer Review Panel and DOE Headquarters. There was no change in the conclusions of the 1992 PA. A third document, called the Special Analysis (SA) (WSRC-TR-2002-00456), was generated in 2002. The 2002 SA was prepared in response to updated facility inventory information. Further, DOE O 435.1-1 had also been promulgated, and the 2002 SA used this order for a compliance determination. Rather than calculating specific doses from a fixed radionuclide inventory, the 2002 SA calculated radionuclide inventory limits against specific objectives of 25 mrem/year from all pathways, and EPA maximum contaminant levels (MCLs) for the groundwater pathway. Updated information on the SDF feed solutions, modeling methods, closure cap design, and evaluations was captured in a 2005 SA (2005 SA) (WSRC-TR-2005-00074). The 2005 SA supplements the analyses in the 1992 PA and supersedes the analyses in the 2002 SA. The 2005 SA used three conceptual model components: a closure cap, the vadose zone, and the saturated zone. These same three conceptual models were used for the most current SRS PA (SRR-CWDA-2009-00017), issued in October 2009, which will be the focus of this subsection. The 2009 SRS PA revised analyses for the existing vaults and future disposal cells to address the new designs and the results of new experiments, as well as performance issues (such as cracking in the walls of Vault 4). DOE provided this revised PA to NRC in November 2009. Most recently several more special analyses have been performed to augment the 2009 SRS PA and these special analyses are briefly described below in Section 3.1.2.3.

A few other key assumptions for the SRS PAs are that no federal protection of the SDF is assumed beyond the 100-year period of institutional control. A 100-year period of institutional control is assumed to begin in year 2030, when the last SRS tank wastes will be processed into saltstone. At SRS, the appropriate measure for protection of water resources has been determined to be the Safe Drinking Water Act MCLs. In addition, the National Defense Authorization Act (NDAA) stipulates that 10 CFR 61 performance objectives are also applicable in order for DOE to seek classification of the saltstone waste as non-HLW for purposes of onsite disposition[3].

The hydraulic and physical properties of the cementitious materials associated with the saltstone disposal units after closure (i.e., roof and walls, floor, clean grout fill, and saltstone) are integral to the integrated saltstone conceptual model. Property estimates for these cementitious materials are utilized as input to the PA modeling. Some properties (e.g., dry bulk density, particle density, and the water retention characteristic curves) are expected to remain the same over time while other properties (e.g., hydraulic conductivity and contaminant retardation) are modeled as changing over time due to both aging and physical degradation. Degradation of the disposal unit concrete (walls, roof, and floor) is assumed to be dominated by external sulfate attack. Sulfate is present in saltstone feedwater (the liquid tank waste) and, after grout curing, remains at significant concentrations in saltstone internal pore water. Sulfate reacts with cement paste and creates ettringite, an expansive mineral phase often associated with spalling or cracking.

The 2009 Saltstone PA includes three distinct disposal facilities: two large above-ground rectangular concrete vaults [Vault 1(600 feet long, 100 feet wide, and 27 feet high) and Vault 4 (600 feet long, 200 feet wide, and 30 feet high)], and 64 (most to be built in the future) smaller cylindrical (150 feet diameter, with an interior height of 23.5 feet) cells. The cylindrical, reinforced, sulfate-resistant concrete disposal cells will be constructed below grade. These disposal facilities are designed for a dual role that limits releases of contaminants out of the saltstone and limits the migration of oxygen into the disposal unit via dissolved oxygen in moisture, thus delaying oxidation of the saltstone. The design intent of the disposal vaults and future cylindrical concrete tanks is to limit contaminant release to a controlled and low rate. Over time, disposal unit materials are expected to degrade through a variety of mechanisms, leading to higher contaminant releases. These saltstone disposal facilities are designed to retain ^{99}Tc through the use

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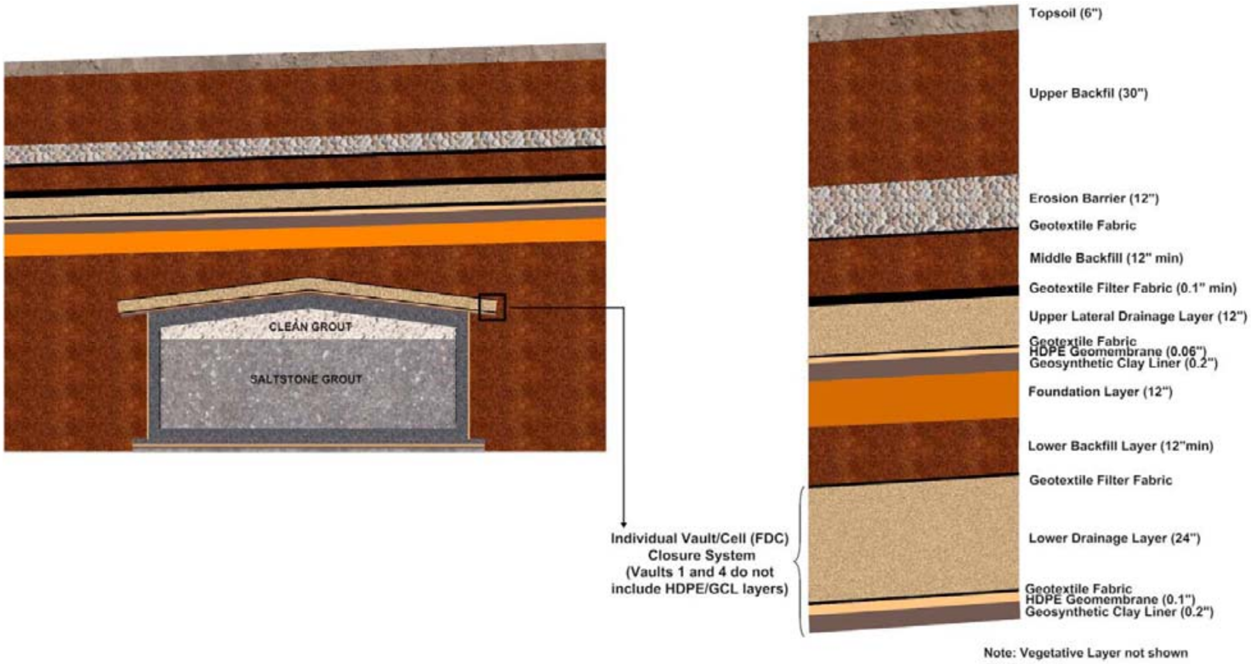
[3] Note that NDAA Section 3116 is applicable only to South Carolina and Idaho, and not Washington.

of BFS-bearing saltstone and disposal unit walls and floors, also containing BFS concrete mixes that all create a low-Eh environment.

All of these disposal facilities will be covered by a multi-layer closure cap (see Figure 3.4) that includes, from top to bottom: a 6-inch layer of topsoil with vegetative cover, 30 inches of upper backfill, a 12-inch erosion layer, a geotextile fabric, a 12-inch-plus middle backfill, a geotextile filter fabric, a 12-inch upper lateral drainage layer, a geotextile fabric, a 60-millimeter HDPE geomembrane, a 0.2-inch geosynthetic clay liner, a 12-inch bentonite-backfill foundation layer, a 12-inch-plus lower backfill layer, another geotextile filter fabric, and a 24-inch geosynthetic clay liner. The closure cap, to be constructed over the disposal units at the end of the 100-year operational period, is primarily intended to provide physical stabilization of the site, minimize infiltration, and provide an intruder deterrent. After the institutional control period, a 10,000-year post-closure performance period is assumed to begin, during which no active maintenance will be conducted on the disposal facilities. Degradation of the closure cap will accelerate once active operational period maintenance has ceased. Over the course of time, the mobile contaminants in the various saltstone disposal units are expected to be released and gradually migrate downward through unsaturated soil to shallow aquifers underlying the various disposal units.



Note: Vegetative Layer not shown
[NOT TO SCALE]

Figure 3.4. Schematic of the Closure Cap to be Used Over Each Saltstone Disposal Facility (from SRR-CWDA-2009-00017 Figure 3.2-20)

The 2009 Saltstone PA employed a hybrid modeling approach. In this approach, the PORFLOW computer code was used to model water and contaminant flow through the vadose zone as well as groundwater flow and transport. The water and contaminant flow predictions from PORFLOW provided radionuclide concentrations used for the calculation of dose for comparison to the relevant performance measures. PORFLOW water flow results were abstracted so that uncertainty and sensitivity analyses could be performed using the GoldSim computer code. The probabilistic sensitivity analysis was supplemented with multiple deterministic sensitivity analyses using the PORFLOW code.

Five disposal unit scenarios were employed in the groundwater model to simulate potential conditions in the SDF closure system over the 10,000-year performance period. While only one scenario (Case A) was simulated in the baseline analysis, the other four were considered in the deterministic sensitivity and probabilistic analyses. All PORFLOW transport analyses were carried out for at least a 20,000-year time period to ascertain when contaminant groundwater concentrations would peak, even though the compliance period is only 10,000 years. The groundwater concentrations are assumed to be at their highest at 100-m down-gradient wells strategically placed around all the various disposal facilities. The resulting contaminant groundwater concentrations suggest that the key radionuclides with potential to impact groundwater are ^{99}Tc, ^{129}I, ^{226}Ra, ^{237}Np, and ^{231}Pa. One key observation from the 2009 SRS saltstone PA is that groundwater concentrations scale linearly with inventory because, as inventory is increased (or decreased), there is a direct correlation to an increase (or decrease) in predicted groundwater concentrations. Alternatives to this linear relationship are possible if the waste in the saltstone were to be controlled by solubility or a nonlinear sorption isotherm. Neither of these alternative conceptual models was considered in the 2009 PA.

The flow model used available SRS site-specific data to simulate a future precipitation rate and the resulting infiltration rate, which is expected to change over time as the closure cap degrades. The flow rate out of the cap was calculated using the HELP code, with the closure cap modeled as degrading over time. The infiltration rate reaching the saltstone increases from 0.0011 cm/year at closure to 2.54 cm/year at 560 years, to 5.8 cm/year at 1,000 years, to 17.3 cm/year at 3,200 years, and reaches a steady-state value of 26.9 cm/year after 5,400 years. The depth of the vadose zone in which the various saltstone disposal units reside varies from 38 to 48 ft.

For saturated-zone contaminant transport, the contaminant flux leaving the bottom of the vadose zone model becomes the source of contamination entering the aquifer. Each water table flux contribution from an individual saltstone disposal unit was assigned to the aquifer transport grid by uniformly distributing the flux to those water table cells with centroids lying within the footprint of each of the disposal units.

Contaminants released from the disposal units are assumed to interact with the vadose zone and aquifer sediments via adsorption-desorption processes. Estimates of the K_d values for each contaminant and soil type were based primarily on SRS site-specific experimental data, and are provided in Table 4.2-15 of the SRS 2009 PA.

Of interest to this technical approach document is the conceptual model for contaminant release from the saltstone waste form. The SRS 2009 PA assumes that the mechanism controlling the release of contaminants from the saltstone and entire disposal facility (i.e., concrete vault or concrete cylindrical disposal cells) is the adsorption characteristic of the saltstone and concrete disposal facilities expressed by the K_d (distribution coefficient), which is element-dependent, and differs as the system redox and pH conditions change over time. In the 2009 SRS PA, contaminant concentrations in saltstone were not generally expected to be limited by solubility[4]. BFS is included in the saltstone dry mix to create reducing conditions that immobilize ^{99}Tc, Cr(VI), and likely other redox-sensitive constituents. Thus, a key issue is how long the BFS maintains reducing conditions within the saltstone and when added to the concrete used for the vault/future cylindrical disposal units' walls and floors. Transport behavior of contaminants

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[4] See section 3.1.2.3 where the most recent Special Analysis does in fact use a solubility conceptual model for release of Tc from saltstone under reducing conditions.

out of the saltstone disposal units depends on redox conditions (Eh) and pH of pore fluids. As saltstone ages, its internal pore water composition changes, thus impacting the release of contaminants. Calculations of pore fluid Eh and pH in saltstone and disposal unit concrete were done using The Geochemist's Workbench® (geochemical modeling software) and a suite of saltstone/concrete minerals chosen based on the dry blend ingredients and cement literature. Saltstone pore water pH and Eh calculations were done for three different infiltrating fluid compositions – unreacted groundwater, groundwater reacted with fresh concrete, and groundwater reacted with aged concrete – to identify the number of pore volumes needed to effect a transition from one state to another. Eh and pH transitions for the disposal unit concrete were calculated for reaction with only groundwater. The calculations considered only the case of advective flow where each pore volume of fluid that enters the solid material displaces the existing fluid and equilibrates with the solid materials. In this conceptual model, the initial saltstone and disposal unit concrete pore fluids were flushed out with the first pore volume of infiltrate. Thus, issues with high ionic strengths and calculation of activity coefficients by the extended Debye-Hückel method were ignored.

This chemical degradation of the cementitious materials is modeled by transitions from one defined age-redox or age-pH state to another. The "age" of the cementitious material is determined based on the pH value of the pore liquid traversing through the cementitious material. A pH value of 11 or greater indicates Region II (middle age) and a lower pH level indicates Region III (old age). The number of pore volumes calculated for the transitions from one Eh (reducing to oxidizing) and pH (highly caustic "fresh" to moderately aged to fully aged) state to another is presented in Table 3.8.

Table 3.8. Predicted Number of Pore Volumes of Recharge Water Needed to Transition from Middle Age to Old Age in the Aging Process

Case	E_h Transition		pH Transition	
	Pore Volume	Value Range	Pore Volume	Value Range
Saltstone wth GW	2,734	-0.45 to +0.66	2,274	11.0 to 9.5
Saltstone wth GW + calcite	2,775	-0.45 to +0.61	2,558	110. to 10.3
Saltstone wth GW + CSH[(a)]	2,806	-0.45 to +0.56	10,422 (extrapolated)	11.0 to (not defined)
FDC[(b)] concrete with GW[(c)]	3,230	-0.46 to +0.57	4,206 (extrapolated)	11.0 to (not defined)

(a) CSH = calcium-silica-hydrate cement gel
(b) FDC = future cylindrical disposal cells or units
(c) GW = groundwater

That is, the cementitious materials in the contaminant-release model are assigned an age-redox state based on the pH and Eh of the system, which transitions as the pH decreases [from Region II (middle age) to Region III (old age)] and the Eh increases (from reducing conditions to oxidizing conditions). Table 3.9 summarizes the results of an analysis conducted on the saltstone and disposal unit cementitious materials to determine the number of liquid pore volumes required to transition from one age-redox state to another. More details on the specific SRS calculations can be found in Denham (2008) (SRNL-TR-2008-00283) and more details on the regions (age categories) for cement weathering are found in Bradbury and Sarott (2008).

Flow into and out of the disposal unit is impacted by the material properties of the closure cap, the cementitious materials comprising the disposal unit, and the saltstone waste form. Time-varying degradation of the closure cap and cementitious materials is included in the conceptual model of contaminant release. The closure cap degradation causes the infiltration rate to increase with time as mentioned above; the contaminant-release model relies on transitions from one state to another based on infiltrating water pore volumes as just described. The pore volume simulations to establish the transition from one state to the next do not consider physical degradation of saltstone, such as fracturing, even though physical degradation may ultimately affect the rate of chemical degradation by influencing the rate that infiltration passes through the grout. Based on PORFLOW results for infiltration and water flux through and past the saltstone and concrete disposal units, the following times (see Table 3.10) were predicted for when the various transitions from one state to the next will occur.

Table 3.9. Predicted Number of Pore Volumes of Recharge Water Needed to Change the Age-Redox State of Saltstone and Disposal Unit Concrete[5] (SRNL-TR-2008-00283)

Age – Redox State Transition	**Number of Pore Liquid Volumes**	
	Saltstone	**Disposal Unit Concrete**
Region II Reducing → Region III Reducing	2,274(a)	N/A
Region III Reducing → Region III Oxidizing	2,734(a)	N/A
Region II Reducing → Region II Oxidizing	2,806(b)	N/A
Region II Oxidizing → Region III Oxidizing	10,422(b)	N/A
Region II Reducing → Region II Oxidizing	N/A	3,230
Region II Oxidizing → Region III Oxidizing	N/A	4,206

(a) Pore fluid is groundwater with no contact to disposal unit concrete.
(b) Pore fluid is groundwater equilibrated with middle age disposal unit concrete.

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[5] These transition times have been revised in the 2014 SA.

Table 3.10. Transition Times for the Various Cementitious Materials as Computed Within the PORFLOW Model (after Table 4.2-17 in SRS 2009 PA) (SRNL-STI-2009-00115)

Cementitious Material	**Vault 1**		**Vault 4**		**FDCs[(c)]**	
	E_h Transition (years)	**E_h Transition (years)**	**pH Transition (years)**	**E_h Transition (years)**	**pH Transition (years)**	**pH Transition (years)**
Roof	N/A(a)	25,400	N/A(a)	16,547	25,640	27,387
Clean Grout	NR(d)	NR(d)	NR(d)	NR(d)	NR(d)	NR(d)
Saltstone	NR(d)	NR(d)	NR(d)	NR(d)	NR(d)	NR(d)
Wall	20,781	21,043	15,519	16,018	16,334	16,753
Floor (b)	NR(d)	NR(d)	NR(d)	NR(d)	22,498	23,274

(a) Material is oxidized at the start of the model.
(b) Includes the Upper Mud Mat for the FDCs.
(c) FDC = the future cylindrical tank disposal cells or units
(d) NR = Not reported, computed transition time greater than 30,000 years

Based on the infiltration rate through the closure cap and entering the disposal units, saltstone remains in its initial condition—a reducing middle age cementitious material—throughout the 10,000-year performance period. The Vault 4 and future cylindrical waste unit walls will transition from reducing middle age, to oxidizing middle age, and then to oxidizing old age during the 20,000-year period modeled. When an Eh or pH transition is reached, according to Table 3.10, the K_d of the disposal unit concrete changes to "oxidizing" (if in a "reducing" condition), or to "old" from middle aged," respectively. Thus, the sorption coefficients used to simulate the release of contaminants from the saltstone and concrete Vault 1 and Vault 4 floor initially are the K_d values for reducing middle age cementitious material shown in Table 3.11 (Table 4.2-18 in the 2009 SRS PA) in bolded red type. Then, for the Vault 4 and future cylindrical tanks, there is a transition to oxidizing middle age, and then finally to oxidizing old age, but these transitions occur out beyond the 10,000 years compliance period. Thus for the 10,000-yr compliance period, the desorption K_d highlighted in bolded red type are used to predict the release of all but ^{99}Tc. Of particular note is the assumption that contaminant transport is retarded by the disposal unit's concrete walls and floor, with some radionuclides being slowed, greatly depending on their K_d values as shown in Table 3.11 as a function of aging, with the cementitious material "age" dependent on the pH of the concrete pore water, which in turn is dependent upon the amount of water (number of pore volumes) that has passed through the concrete over time.

There is one exception to the desorption K_d release conceptual model. A more sophisticated shrinking-core treatment of oxidation is used for ^{99}Tc release and transport simulations. The shrinking-core model is used both for the evolution of the saltstone reduction capacity and oxygen invasion, which is supported by site-specific test data. The saltstone starts with a high reduction capacity, which inhibits ^{99}Tc release, and leads to a decrease in reduction capacity of the saltstone over time. Reduction capacity and oxygen concentrations are explicitly tracked in each grid cell of the shrinking-core numerical model. Oxygen entering the disposal unit in the infiltrating water oxidizes the BFS within the saltstone and reducing concrete (when present), thereby depleting the reduction capacity. The conceptual model assumes that the fresh infiltrating water has an oxidation capacity saturation value of 1.06 meq e-/L. Gas-phase oxygen transport is ignored because the saltstone and disposal unit pore waters are practically

100% water saturated. When the reduction capacity in a disposal unit has been consumed by infiltrating oxygenated water, previously immobile ^{99}Tc is made mobile.

In the shrinking-core conceptual model, the initial ^{99}Tc is made immobile by setting K_d to 1,000 mL/g. The 1,000 mL/g used as the pseudo-K_d is considerably smaller than the value of 5,000 mL/g recommended in Table 3.11, and was chosen to conservatively increase the magnitude of ^{99}Tc release. Figure 3.5 (Figure 4.2-41 in the SRS 2009 PA) was used to describe how the ^{99}Tc sorption coefficient is artificially varied to achieve ^{99}Tc initial immobilization and then subsequent release as a function of local reduction capacity. The underlying physical process is not one of sorption; rather, K_d variation is simply used as a convenient means to control ^{99}Tc release in the model. Accordingly, Figure 3.5 identifies the ^{99}Tc K_d as a “pseudo-sorption coefficient” to call attention to its non-physical nature. The pseudo-^{99}Tc K_d remains at 1,000 mL/g as long as the reduction capacity of the saltstone or reducing concrete remains above 0.0053 meq e-/mL (volume basis). Then, as the reduction capacity drops below this value, the pseudo-^{99}Tc K_d drops, and eventually would be zero when the reduction capacity is totally consumed. That is, the pseudo-^{99}Tc K_d evolves from the right-hand side of Figure 3.5 to the left-hand side as time progresses.

Table 3.11. Recommended K_d (mL/g) Values for Cementitious Materials (From SRS 2009 PA)[6]

1000

Component	Reducing Cementitious Material				Oxidizing Cementitious Material			
	Young Age	Middle Age[d]	**Old Age**	**Reference**	**Young Age**	**Middle Age**	**Old Age**	**Reference**
Tc[c]	*5000*	*5000*	*5000*	*a*	*0.8*	*0.8*	*0.5*	*a*
I	5	9	0	b	8	15	4	a
Na	0.5	1	0.5	a	0.5	1	0.5	a
NO_3	0	0	0	a	0	0	0	a
NO_2	0	0	0	a	0	0	0	a
Cr	5000	5000	1000	a	20	20	2	a
U	2500	2500	2500	b	250	250	70	a
Cs	20	220	102	b a	2	20	10	a
Sr	0.5	3	20	b	3	30	15	a
Ra	0.5	3	20	a	100	100	70	a
Se	300	300	150	b	300	300	150	a
Np	4000	4000	3000	b	1600	1600	250	a

[a] Kaplan and Coates (2007)

[b] Kaplan et al. (2008)

[c] For Tc a separate explicit redox simulation coupled with a reduction capacity dependent pseudo-K_d value is used instead of the Tc values in this table in the PORFLOW analysis for reducing cementitious material, see Flach et al. (2009; SRNL-STI-2009-00115).

[d] The middle-age desorption K_d values were used for most of the PORFLOW calculations during the 10,000 yr compliance period based on the predicted longevity of reducing conditions within the vaults, cylindrical disposal units and saltstone

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[6] Note that in Section 3.1.2.3 the more recent Special Analyses (SRR-CWDA-2014-00006, Revision 2) has revised some of these desorption release K_d values based on new experimental data and/or further geochemical considerations. The new recommended values are shown in Table 4.1-4 within SRR-CWDA-2014-00006, Revision 2. The revised desorption K_d values for reducing conditions for Cr and Np were lowered but the K_d values were increased for Sr, Ra, and NO_3. For oxidizing conditions, the desorption K_d values for Np, U, and NO_3 were increased and the values for Cr and Sr were lowered. The desorption K_d for Tc under oxidizing conditions for all ages of cementitious materials was set to 0.5 mL/g.

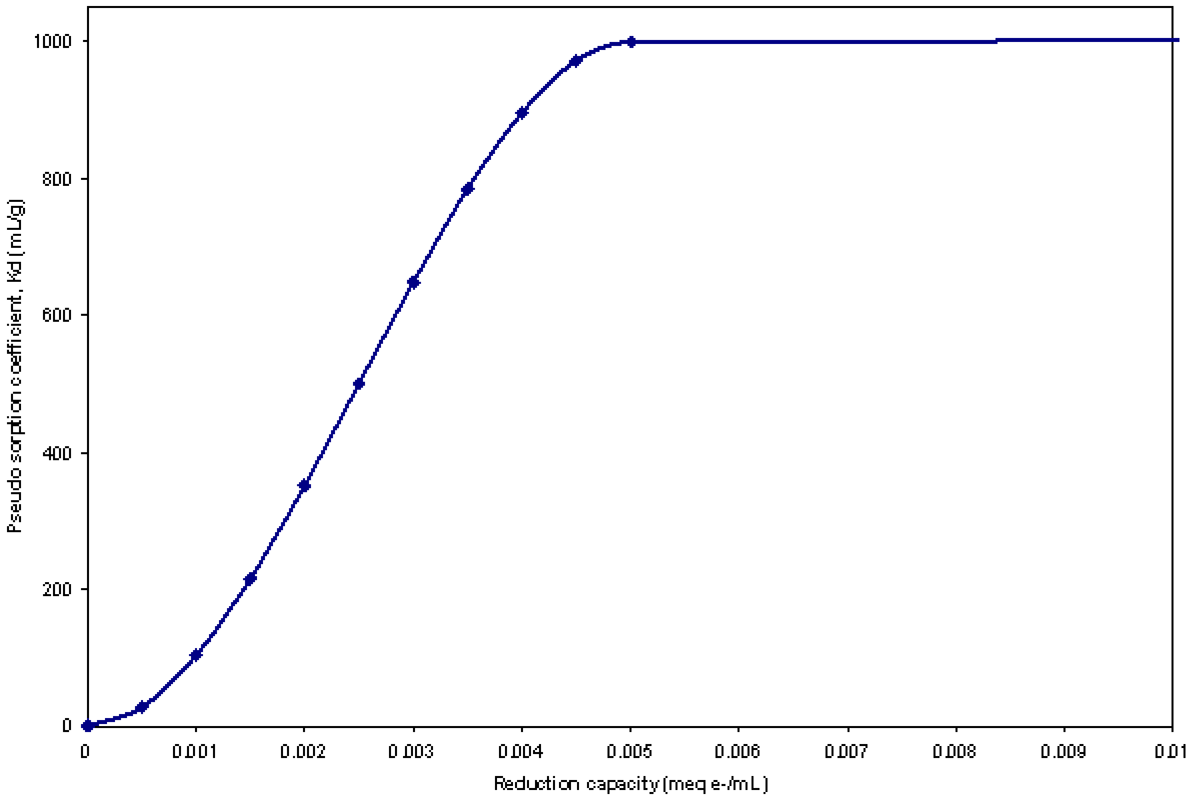

Figure 3.5. Pseudo-Desorption Coefficient for ^{99}Tc as a Function of Reduction Capacity

In summary, the rates of contaminant release and movement from saltstone are principally controlled by the following factors:

- chemical properties of the contaminants (e.g., desorption K_ds),
- physical properties (e.g., void structure and hydraulic conductivity, etc.) and “age” state (e.g., integrity) of the saltstone and disposal unit,
- chemical properties (e.g., reduction capacity) and “age” state (e.g., Eh and pH) of the saltstone and disposal unit, and
- moisture flux reaching the saltstone through the disposal unit from the overlying soil.

3.1.2.2 NRC Technical Evaluation Report

Section 3116(b) of the Ronald W. Reagan National Defense Authorization Act (NDAA) requires NRC to monitor DOE’s disposal actions concerning certain wastes associated with spent fuel reprocessing that DOE, in consultation with the NRC, has determined to be non-HLW. Although radioactive material resulting from the reprocessing of spent nuclear fuel typically is defined as HLW, DOE may determine certain reprocessing waste is non-HLW, or Waste Incidental to Reprocessing (WIR), if it does not need to be disposed of as HLW to manage the risks it poses. Per the definition of NRC monitoring in the NDAA, the NRC Technical Evaluation Report (TER) review focuses on DOE’s compliance with the third criterion of the NDAA, which is that the disposal actions must comply with the performance objectives of NRC’s LLW disposal facility regulations as presented in the Title 10 of the

Code of Federal Regulations (CFR) Part 61, Subpart C. The TER documents the NRC review and their confirmatory analysis of the 2009 PA. NRC's review results are not intended to represent any regulatory authority related to DOE's disposal activities.

The NRC staff concluded that it had reasonable assurance that waste disposal at the SDF meets the 10 CFR 61 performance objectives for protection of individuals against intrusion (§61.42), protection of individuals during operations (§61.43), and disposal site stability (§61.44). However, based on its evaluation of DOE's SRS 2009 PA (SRR-CWDA-2009-00017) results and independent sensitivity analyses conducted with DOE's models, the NRC staff did not have reasonable assurance that DOE's disposal activities at the saltstone disposal facilities meet the performance objective for protection of the general population from releases of radioactivity (§61.41). The NRC only performed independent analyses using the SRS deterministic codes because they had concerns about the design and implementation of the probabilistic model that relied on the GoldSim code.

NRC's evaluation focused largely on the technical factors related to the oxidization and mobilization of Tc. The staff questioned several of the 2009 PAs assumptions in its base case analysis, including: 1) the lack of saltstone fractures, given that cracking of saltstone already has been observed, 2) the performance provided by the roof and lower drainage layer in shedding over 99% of the water around the disposal units throughout a 10,000-year performance period, and 3) the basis for a number of parameters (e.g., hydraulic conductivity, Tc sorption coefficients), because recent research did not support parameter values/assumptions used. More specifically, recent research did not support assumptions in the 2009 Saltstone PA regarding 1) the way cracks develop over time (i.e., the PA predicts most of the cracks develop after 8,000 years) and 2) efficient Tc retention in the disposal units' floors, which results in predicted peak doses being delayed by several thousand years to approximately 12,000 to 14,000 years. The NRC review concluded that the information supporting the delay of the groundwater peak concentrations of ^{99}Tc by these two assumptions was weak and, therefore, did not provide reasonable assurance that these peak doses would occur after 10,000 years. The NRC review expected that any exceedance of the §61.41 releases of radioactivity to the general public would occur many years after site closure, but the 2009 Saltstone PA did not provide a sufficient basis for the conclusion that any exceedances would occur beyond the 10,000-year compliance period.

The NRC review found that the base case (Case A) in the 2009 SRS saltstone PA was not an appropriate compliance case because it did not accurately reflect current site conditions, did not account for the full range of measured values of key parameters or expected differences between laboratory-scale and full-production-scale (as-emplaced saltstone) properties, and did not appropriately account for potential changes in parameter values with time. In the base case, NRC contends that the surface cover was assumed to degrade with time, but there was no degradation of the saltstone and limited degradation of the future disposal units assumed over a 20,000-year evaluation period. The walls in Vaults 1 and 4 were assumed to be initially cracked, while the new future disposal cells walls, like the floor and roof of the vaults, experienced only minimal degradation. Due to a combination of the material properties assumed and the lack of roof degradation, over 99% of the water was diverted around the disposal units from 400 to 10,000 years after site closure. This assumption significantly limited water contact with the saltstone, and thus, the modeled transport of radionuclides out of the waste. In addition, because oxidation from gas-phase transport of oxygen was not included in the base case, the low water contact (1%) with the saltstone significantly limited the modeled oxidation of saltstone, limiting Tc mobilization and release.

NRC also concluded that the 2009 SRS saltstone PA "pessimistic" sensitivity cases were not truly "pessimistic." Instead, the NRC concluded that the "pessimistic" sensitivity cases were based on a combination of both overly-optimistic and conservative assumptions. The NRC staff's independent analyses suggested that the timing of DOE's predicted peak dose to an offsite general member of the public in its "pessimistic" case (Case K, at 12,900 years after site closure) was sensitive to, and delayed by assumptions about, saltstone fracture growth, use of an average K_d value to simulate release of ^{99}Tc, and seemingly overly-optimistic assumptions about Tc retention in disposal unit concrete. Because almost all of the infiltrating water bypassed most of the saltstone inventory in both the base case and most of the sensitivity cases, these cases did not appear to realistically predict potential doses from saltstone. Although more water flowed through the disposal units and saltstone in Case K, DOE assumes that the disposal unit concrete acts as a significant barrier to Tc release. Because DOE changed the way Tc sorption was modeled, from a discrete fracture model to a model based on an average sorption coefficient, Tc did not leave the system through oxidized pathways. Instead, in the Case K model, intermediate model outputs showed that Tc is retained in the disposal unit floor for thousands of years until it nears complete oxidation. Thus, in the Case K model, the disposal unit floor captured nearly all of the Tc, like a filter. For example, in the future disposal cells (FDCs), this filtering effect leads to the disposal unit floor having a modeled Tc concentration approximately 13 times greater than the original concentration in the saltstone waste itself. The disposal unit floors were also modeled as releasing the Tc much more gradually than the saltstone does, which lowered the predicted peak dose. Therefore, the change in the conceptual and mathematical models for Tc retention in the floor caused an unintended significant improvement in floor performance.

This NRC assessment is not a precedent for any future decisions regarding the efficacy of the saltstone disposal performance. The NRC encouraged DOE and its contractors to continue to perform more experiments that collect data on key parameters and to improve conceptual models for contaminant release from saltstone and transport out of the disposal units.

3.1.2.3 Special Analyses for SRS Saltstone Performance

Special Analyses (SAs) are performed to evaluate the significance of new information, new conceptual models, or using new analytical and/or numerical simulators on the conclusions reached in an approved PA. As summarized in Section 3.1.2.1, the SRS 2009 PA was prepared and issued in October 2009 to support the operation and eventual closure of the SDF. The 2009 SRS PA was prepared to demonstrate compliance with the pertinent requirements of DOE O 435.1, DOE M 435.1-1, and 10 CFR Part 61, Subpart C, as required by NDAA-3116. After approval by DOE, and upon initial review of the 2009 SRS PA, the NRC issued Requests for Additional Information (RAIs) in March 2010 (ML100820097), for which DOE provided a response (SRR-CWDA-2010-00033) in July 2010. In December 2010, the NRC provided a second set of RAIs (ML103400571), for which DOE provided responses (SRR-CWDA-2011-00044) to the NRC in August 2011. Subsequent to the review of the second set of RAI responses, the NRC issued a TER on the SRS 2009 PA. As summarized in Section 3.1.2.2, the TER concludes that current proposed disposal activities for salt waste may result in releases that exceed the performance objective in §61.41 of 10 CFR Part 61, for the protection of the general population at a time much greater than 1,000 years, but within 10,000 years. Based on the NRC independent calculations and interpretations documented in the TER in April 2012, the NRC issued a Type IV letter of concern (ML120650576) indicating that the performance objectives in §61.41 may not be met.

DOE issued a Disposal Authorization Statement (DAS) transmittal letter, dated May 22, 2012, for the SDF, with a stipulation that a sensitivity analysis would be performed to ensure that the performance objective in §61.41 of 10 CFR Part 61 is met (WDPD-12-49). In accordance with the DAS, a sensitivity analysis (SRR-CWDA-2012-00103) was prepared in October 2013 that assumed a more recent inventory of ^{99}Tc, as well as some other updates. Then, another more recent SA was prepared based on new information, plans, and data collected in ongoing saltstone studies (SRR-CWDA-2014-00006, Revision 2). This most recent SA is the main topic of this subsection.

The primary purposes of SRR-CWDA-2014-00006, Revision 2 are to 1) reflect the change in future disposal unit design from 150-foot diameter FDCs to 375-foot diameter saltstone disposal units (SDUs), 2) update the inventory for all SDUs, 3) increase the saltstone fill height (i.e., no clean cap) for the 150-foot and 375-foot diameter SDUs, 4) address remaining LFRG secondary issues as presented in the LFRG Review Report on the SRS Salt Waste Disposal SA to the 2009 Performance Assessment, DOE-OS-2013-10-15-01, and 5) include enhancements to the ^{99}Tc release model. In SRR-CWDA-2014-00006, Revision 2, dose results were presented both deterministically and probabilistically to provide further evidence to support that there is reasonable expectation/assurance that all applicable performance objectives associated with the operation and closure of the SRS SDF will continue to be met.

Specific technical revisions/changes included using 1) more detailed degradation conceptual models of cementitious material (e.g., sulfate attack, carbonation, and decalcification) to predict the long-term fate of chemical and physical properties, 2) a solubility-controlled release of ^{99}Tc from reducing cementitious materials, 3) revised distribution coefficients for the release of some radionuclides from the cementitious materials, 4) evaluation of flow through joints in the cementitious disposal cells, and 5) new dose pathway exposure methodology. Many of these improvements are discussed in Flach and Smith (2013). Of particular interest to this document is the inclusion of a solubility-controlled release for ^{99}Tc when the saltstone and other BFS-containing cementitious disposal units remain under reducing conditions created mainly by the BFS used in the dry blend mix.

In the 2014 SA, the conceptual release model for ^{99}Tc from the saltstone and BFS-containing concrete disposal units under reducing conditions was assumed to be controlled by solubility rather than by a desorption K_d value. Once the cementitious materials transition to oxidizing conditions, the release of ^{99}Tc, as well as all other COCs, is controlled by desorption K_d values the same as assumed in the 2009 SRS PA. A solubility control for Tc for saltstone, clean cap grout, and for concrete containing slag was used in the 2014 SA, based on a study that compared thermodynamic modeling results to recent laboratory measurements (Kaplan and Dien 2012; SRNL-STI-2012-00769). Thermodynamic saturation index calculations described in Kaplan and Dien (2012) were conducted to evaluate which Tc solid phase might be controlling the observed Tc solution concentrations in laboratory experiments (performed under reducing conditions). In addition to evaluating likely solid phases, Kaplan and Dien (2012) also evaluated different thermodynamic databases. The conclusions from Kaplan and Dien (2012) suggested that either $TcO_2 \bullet 1.6H_2O$ or $TcO_2 \bullet 2H_2O$ were most likely controlling Tc concentrations in the laboratory experiments where crushed saltstone was leached in various solutions under anoxic conditions until steady-state Tc concentrations were observed. The likely solid is generally described as being hydrated $TcO_2 \bullet xH_2O$ (with $TcO_2 \bullet 1.6H_2O$ being most likely). This assumed solid controlled the Tc concentration in reducing saltstone leachates as long as the Eh remained < -0.38 V. However, as the Eh increased just above -0.35 V, the highly soluble Tc(VII) species, TcO_4^-, became the more dominant species due to the re-oxidation of Tc(IV) in the aqueous and solid phases. Further, under even more oxidized environmental conditions (i.e., above Eh values of -0.35 V at the alkaline pH values generated by saltstone), the TcO_4^- concentration increased dramatically in the leachates. Kaplan and Dien (2012) also concluded that the experimental data were not consistent with assuming that TcO_2(c) was the solubility-controlling solid (i.e., saturation index calculations using the K_{sp} for TcO_2(c) showed large oversaturation). In many past PA activities around the world, this crystalline Tc dioxide was often assumed to control Tc solution concentrations under reducing conditions. Based on their experimental results using SRS site-specific materials, Kaplan and Dien (2012) concluded that TcO_2(c) was not an appropriate choice, and that a more soluble Tc-bearing solid phase must be controlling the ^{99}Tc concentrations in the reduced SRS disposal environment.

The influence of pH on Tc solubility was also evaluated by Kaplan and Dien (2012) because pH is used to help define the "age of the saltstone". Saltstone pore water is initially ≥ pH 12, then as saltstone ages, the evolving mineral assemblage of the saltstone and the air and recharge water that contact the saltstone buffer the pH to approximately 10.5. After extensive leaching/weathering, the saltstone is expected to degrade and eventually take on the pH of the background sediment at pH 5.5. Under reducing conditions (Eh < -0.38 V), the calculated Tc solubility decreased as the pH decreased. For example, when pH changed from 12.7 to 10.5 (the approximate pH decrease between the young and moderately-aged saltstone stages used in the SA) at a fixed Eh of -0.38 V, the calculated solubility of $TcO_2\bullet1.6H_2O$ is predicted to significantly decrease from 6.3×10^{-7} M to 5.2×10^{-9} M.

In summary, the 2014 conceptual model for ^{99}Tc release from saltstone and BFS-containing concrete is as follows. During the two early stages of cement aging, thermodynamic modeling, described in Kaplan and Dien (2012), indicates that $TcO_2\bullet xH_2O$ (with x being ~1.6) is the solubility-controlling solid phase for Tc concentrations in the pore water within and surrounding saltstone. Once the near-field disposal system becomes oxidized, generally anticipated to occur during the second stage of cement aging, then solubility no longer controls aqueous Tc concentrations. Under oxidizing conditions, Tc adsorption to solid phases and subsequent desorption becomes the predominant mechanism controlling the concentration of Tc in pore water, and thus the K_d construct is appropriate to use for predicting Tc concentrations for oxidizing conditions.

Based on this more mechanistic and evolving Tc release conceptual model, laboratory experiments and thermodynamic calculations similar to those described in Kaplan and Dien (2012) are recommended for parameterizing Tc release from Cast Stone buried in the IDF. In Section 5.0, details on the recommended experimental methods to measure both Tc solubility under reducing conditions and Tc desorption K_ds under all redox conditions are provided.

3.1.3 International Repository Development

The use of cement to stabilize radioactive waste is fairly common outside of the U.S. PAs for cement-based systems are ongoing in several European countries (e.g., France, Belgium, Switzerland, Sweden, and Spain), as well as Canada, the Russian Federation, and China. The International Atomic Energy Agency (IAEA) has programs supporting the PA process and recommended procedures in its member countries.

3.1.3.1 European Repository Development

In France, hazardous waste stabilization in cement with subsequent near-surface disposal is currently being used under the auspices of the regulatory entity, Institut de Radioprotection et de Sûreté Nucléaire (IRSN), which has developed European criteria for acceptance of hazardous waste landfilling. Optimization of recipes and procedures for cementing complex LLW waste streams has been performed. For example, waste containing elevated borate and phosphate can adversely lengthen setting times with ordinary Portland cement (OPC). Coumes et al. (2009) showed that adding calcium sulfoaluminate to OPC eliminated the setting inhibition by allowing the formation of significant amounts of ettringite and calcium monosulfoaluminate hydrate, which incorporated borates into their structure. Two notable benefits of this approach include 1) sulfates, which can induce swelling and cracking due to delayed formation of ettringite in OPC-based materials, were rapidly depleted by the hydration reactions to form non-expansive ettringite, and 2) waste loading can be increased from 30% to 56% wt.

In the development of acceptance criteria for these cement-based systems, one difficulty was accounting for fracture mechanisms in the cement waste monoliths. For repository time scales, cracking is expected and the objective is to minimize and manage the impacts. It is recognized that the exchange of reactive fluids between cement and the surrounding subsurface environment is the initiating mechanism for conditions leading to the formation of cracks. In these reactions, chemical and physical alterations to the cement microstructure create weaknesses and strain that facilitate cracking. Many of the factors that contribute to mechanical damage of cement can be minimized by properly designing cement mixtures and using good construction practices. The absence of steel reinforcement and aggregates in cementitious waste forms is seen to be advantageous from the standpoint of late-stage precipitation of expansive minerals involving chloride, carbonate, and silicate. However, a general weakness is the lack of information on the impact of liquid waste composition on the resistance of the cement to the degradation processes.

Low- and intermediate-level short-lived cementitious waste has been disposed at the Andra Centre de stockage des déchets radioactifs de faible et moyenne activité (CSFMA) waste disposal facility situated in the Aube district in France for a dozen years. The Belgian government is currently developing a similar near-surface disposal system in Dessel, with a surface barrier over backfilled concrete caissons. A comprehensive modeling study for this effort by Jacques et al. (2014) describes the evolution of radionuclide sorption and physical parameters (porosity, bulk density) as a function of concrete degradation. In this approach, the long-term decalcification of cementitious engineered barriers is divided into four degradation states, depending on the geochemical conditions (principally pH) and controlling cement phases. The chemical evolution is based on multicomponent thermodynamic geochemical modeling for hardened cement paste of OPC using a specific choice of calcium silicate hydrate (CSH) model and chemical composition of the soil pore water percolating through the cementitious materials. The modeling calculates the evolution of pH, the total amount of CSH in the system (i.e., control on sorption sites), and the molar volume of the solid phases (i.e., control on bulk density and porosity). This information, and the distribution coefficients (K_ds) for each COC in each of the four degradation states, is incorporated into coupled-flow and reactive-transport models to address radionuclide migration in the disposal system. Uncertainties in the composition of infiltrating water (pH, dissolved carbon, major cations, and anions) and the chosen CSH dissolution model are taken into account in the derivation of the evolution of the parameters. This Belgian team has also proposed a benchmark on cracked concrete in the framework of the Subsurface Environmental Simulation Benchmark workshop series (Steefel et al. 2014).

In this case, the core of the benchmark is the feedback of chemistry to porosity and bulk density of the cementitious material based on mineral volume fraction changes.

As in most countries with plans for underground high-level radioactive waste disposal, cement behavior (hydration, degradation, and geochemistry) is of great interest because concretes and mortars play key roles in mechanical repository support as well as barriers to COC transport. A common implementation is the use of engineered cementitious barriers in clay formations, which is studied in Belgium, France, Netherlands, and Switzerland. An important aspect of these studies is the detrimental effect of the alkaline plumes emanating from the cement on the surrounding clay barriers (Gaucher et al. 2006).

Multicomponent geochemical reactive transport modeling is used to address the interactions between the waste form, waste package, vault, and receiving environment. In particular, HYTEC from MINES ParisTech is a thermal-hydrological-chemical simulator used in French HLW and LILW repository analyses for mm-scale cement hydration processes to km-scale radioactive waste storage, augmenting the reaction modeling with thermal processes to address decay heating and multiphase flow to address the redox transients driven by gas-phase transport of oxygen and hydrogen (De Windt and Devillers 2010; De Windt et al. 2008).

Most, if not all, of the safety/performance assessments in Europe use a hierarchical modeling approach where decision-making is based on simulations with hydrodynamic codes whose chemistry was reduced to a set of distribution coefficients (i.e., K_ds) linked to corresponding effective diffusion coefficients, as well as solubility limits. These simpler, abstracted models are computationally efficient, allowing comprehensive, though not necessarily mechanistic, coverage of the system features, as well as stochastic treatment of parameter sensitivity and model uncertainty. More mechanistically detailed multiphase and geochemical models are used to simulate the waste form/near-field behavior leading to the estimation of source terms, distribution coefficients, and solubility limits for the abstracted decision-making models that vary during cement degradation. For example, the Swiss radioactive waste management program, NAGRA, has several reports available for download (http://www.nagra.ch/en/downloadcentre.htm/s_element/285400/s_level/10190) describing the degradation of repository materials under low- and intermediate-level waste (LILW) emplacement conditions. In particular, Wieland and Van Loon’s (2002) Technical Report NTB 02-20 contains a cement sorption database for relevant radionuclides in the planned Swiss repository. Reactive transport modeling has been used for this purpose and for estimating material lifespans.

In both geochemical and reactive transport modeling, the European PA efforts have primarily used two thermodynamic databases:

1. THERMODDEM (http://thermoddem.brgm.fr): a database for standard thermodynamic data for chemical compounds encountered in most water-solid-gas systems, including environmental contaminants, cement phases, and clay minerals (Blanc et al. 2012). A major objective is for these data to be integrated into coupled reactive transport modeling codes.
2. CEMDATA07 (http://www.empa.ch/plugin/template/empa/*/62204/---/l=1): a thermodynamic database for hydrated solids in the Portland cement system ($CaO-Al_2O_3-SiO_2-CaSO_4-CaCO_3-Fe_2O_3-MgO-H_2O$) (Lothenbach et al. 2008). It contains thermodynamic data (solubility product, Gibbs free energy, enthalpy, entropy, heat capacity, and molecular volume) for a number of cement phases.

Kinetics is generally not considered in the modeling of classical cement like CEM I/OPC, but it seems to be more important for BFS or other low-pH cements where the hydration of the clinker solid phases can be slow.

The most recent European repository studies include gas-phase analyses, in particular, the effect of carbonation on pH lowering (chemical effect) and pore clogging (physical effect) caused by calcite precipitation. In summary, these cement/concrete modeling studies demonstrate a general consistency between the various codes used for a given conceptual model. Consequently, most of the variability that exists between different groups is in the conceptualization of the system model and not in their simulators (computer codes). Finally, multicomponent reactive transport modeling and its coupling to hydrologic models has become an integral component in the performance and safety analyses in Europe.

3.1.3.2 IAEA

The IAEA is an independent international organization for scientific and technical cooperation in the nuclear field. One aspect of its mission is to promote the safety of radioactive waste management through international programs, which, in part, focus on the long-term behavior of LILW packages under repository conditions. In its reports, cementitious binders for the solidification of liquid radioactive waste have been reported by Argentina, Canada (e.g., AECL Chalk River), Czech Republic, Finland, India, Republic of Korea, Norway, Romania(IFIN-HH), Russian Federation (SIA RADON), Spain, and UK (IAEA 2013). The IAEA supports an iterative hierarchical safety/performance assessment approach with a general philosophy that modeling provides the critical link between the short-term understanding from laboratory and field tests, and the prediction of repository performance over repository time frames and scales. One recommendation is that experiments be designed to permit the appropriate scaling in the models.

The concept of the total system PA (TSPA) process, similar to that used for Yucca Mountain in the U.S., is seen in projects (e.g., China) where the system-level modeling using GoldSim is being used to compare far-field modeling approaches and geosphere conceptualizations. The GoldSim modeling uses a compartment approach, in which mass is transferred between the compartments, and contaminant sinks/sources for each contaminant are accommodated in each compartment. More mechanistically detailed deterministic process modeling simulations are performed to study the impact of simplifications needed for the TSPA parameterizations for geologic disposal. Sensitivity and uncertainty analyses are then conducted with GoldSim to identify the most sensitive parameters with respect to the radionuclide concentration in the receiving environment as well as the dose rate. In this iterative system-level PA modeling approach, these results can be used to help design future laboratory and field tests and data-collection activities, and to reduce prediction uncertainties of key components of the natural system.

The hydrologic setting of the repositories in Spain is most similar to the Hanford Site. Both are located in dry regions where minimal infiltration into the subsurface occurs. Parameters being monitored in Spain’s PA activities to assess concrete durability include temperature, deformation, electrical resistivity, corrosion potential, corrosion rate, and oxygen migration (Santos 2004). Several other countries are using cementitious binders for solidification of the liquid LILW wastes. AECL Chalk River (Canada) is focusing specifically on the development of performance criteria for waste forms that arise from the treatment of liquid LAW (Rowat 2004, 2002). A cementitious binder has been selected, with physical and chemical properties being evaluated to assess the durability and leaching requirements for waste forms. Work has focused on the assessment of waste form performance, definition of vault chemical conditions in the presence of cementitious materials, and establishment of source terms for safety-relevant radionuclides present in both reactor operational and decommissioning waste. The potential for gas generation from both corrosion and microbial degradation of waste package components was evaluated. Calculations were performed to estimate the type and magnitude of gases likely to be generated under disposal conditions and their impact on repository performance and integrity.

The Russian Federation effort is notable for performing a 12-year field test of pilot- and full-scale waste packages subjected to repository conditions. The waste packages consisted of cemented, bituminized, and vitrified waste forms, with the latter two placed in carbon steel containers. The field testing focused on evaluation of the leaching behavior of the waste forms and corrosion degradation of steel containers. The experimental results, based on 12 years of field testing, have been used to develop a model that represents the leaching behavior of the waste forms studied. The model can be used to extrapolate long-term waste form behavior in order to predict radionuclide releases over repository time scales (Sobolev et al. 2004). Interestingly, the ^{137}Cs leaching rate from the cement waste form was ~2 orders of magnitude lower in the field repository test versus the laboratory test (Ojovan et al. 2011). It should be noted that the wastes, waste form dry mix recipe, and the waste loading are very different from Cast Stone. Observations of carbon steel corrosion led to the following estimates of container lifetime: 25 years for 1.5 mm-thick steel and vitrified waste, 30-60 years for 2 mm-thick steel and vitrified waste, 50 years for 2.5 mm thick steel and bituminized waste.

3.1.4 CBP/CRESP

The Cementitious Barriers Partnership (CBP) is a collaborative program with eight member organizations from the U.S., Canada, and Netherlands. U. S. participants include the Department of Energy Office of Environmental Management (DOE-EM), SRNL, Vanderbilt University Department of Civil and Environmental Engineering, Consortium for Risk Evaluation with Stakeholder Participation (CRESP), The National Institute of Standards and Technology (NIST), and the U.S. NRC. The two international organizations participating in CBP are Energy Research Centre of the Netherlands (ECN) and SIMCO Technologies, Inc. (SIMCO), located in Quebec, Canada.

A central tenet of CBP is that cementitious materials could be used in more nuclear applications if more realistic treatments of their properties and the processes that control contaminant release were available. Accordingly, the CBP mission is to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious materials and waste forms used in nuclear waste disposal (see the CBP web site, cementbarriers.org). A key component of the CBP mission is the development of software tools that support nuclear waste management PA modeling. The simulation tools and data developed under this program will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems. Test methods and data needs to support the use of the simulation tools for future applications are also a component of the planned activities.

Before embarking on the development of modeling tools and data, the CBP performed a review of existing PAs in the U.S. involving cementitious barriers (Seitz et al. 2009). In the reviewed PAs, cementitious materials functioned as both physical and chemical barriers to COC release. In general, the effectiveness of cementitious waste forms as a barrier to COC release is expected to evolve with time. PA modeling must therefore anticipate and address processes, properties, and conditions that alter the physical and chemical controls on COC transport in the cementitious waste forms over time.

A common occurrence identified by CBP in the various dose and risk assessments was the use of gross simplifying assumptions that were conservative (i.e., would lead to COCs arriving earlier, at higher concentrations, and/or longer durations than the real system). These conservative assumptions (e.g., no attenuation for the waste form container) were typically made because of a lack of information, or to avoid having to perform analyses to account for the detail and complexity of more realistic conditions. The logic was that if the assessment was acceptable without considering a known COC attenuation process, it would not be necessary to include that attenuation process in the analysis. CBP points out potential consequences of the additional conservatism, including unnecessary limitations on future land use.

A general assumption of the reviewed PAs is that releases from the cementitious waste forms are controlled by diffusion, with CBP noting that different assumptions have been made for different COC diffusion rates. Cracking is therefore a critical consideration, as it allows liquids and gases to flow through the waste form, increasing the potential for leaching, and adding advective transport pathways, which may significantly increase COC release over that supported by strictly diffusional transport. Because of the difficulty quantifying the extent and impact of cracking in cementitious barriers, gross simplifying assumptions were often made (e.g., the cementitious barriers fail completely at the onset of through-wall cracking). This failure is typically represented as a change in bulk hydraulic conductivity. CBP observed that there appears to be a lack of confidence in taking credit for more gradual changes in flow and transport as cracking progresses, but the resulting conservative assumptions did not appear to have a negative impact on the conclusions of the assessments. However, as described in Section 3.1.2.2, the NRC was critical of how cracking impacts were modeled in the SRS 2009 PA.

From a chemical barrier perspective, the most common assumption in the reviewed PAs was the use of K_ds to account for the waste stabilization properties of cementitious materials. There were many cases where the presence of reducing conditions in a grouted waste form was an important consideration for the results of the COC release assessment (e.g., U, Tc, and Cr). More recently, solubilities are also being developed for specific radionuclides stabilized in cementitious matrices. There have been substantial successes in the use of these types of assumptions. This illustrates the apparent improved confidence related to taking credit for long-term performance from a chemical perspective.

The following table (Table 3.12) from the CBP review of past PAs gives some details that led to their conclusions that were briefly summarized in this section.

Table 3.12. Summary of Examples of Assessments (after Seitz et al. 2009)

Example	Description	Role of Cementitious Barriers and Processes	Important Assumptions and Conceptual Models	Relative Importance of Cementitious Materials
INTEC Tank Farm (Idaho Site)	Tank Closure under section 3116. Tanks cleaned to maximum extent practicable and filled with grout.	Voids in tanks filled with grout, many tanks surrounded by concrete walls. Cementitious materials assumed to serve as physical and chemical barriers.	Multiple degradation mechanisms quantitatively assessed. Physical failure of concrete represented as step change in hydraulic conductivity. Timing based on conservative degradation scenario. Chemistry assumed unchanged.	Reducing conditions in cementitious materials were significant factor. Hydraulic properties important early, but degradation expected to occur later than assumed.
Radioactive Waste Management Complex (Idaho Site)	LLW disposal facility managed in accordance with DOE Order 435.1.	Cementitious materials used in vaults and containers. No credit taken for cementitious materials, except releases are diffusion-controlled for one type of concrete cask container.	Diffusion assumed to occur without considering tortuosity or chemical effects.	Diffusion-controlled release with conservative diffusion rate was sufficient to demonstrate compliance for cask containers. No credit needed for other cementitious barriers.
Integrated Disposal Facility (Hanford Site)	Combination LLW and RCRA waste disposal facility managed respectively under DOE Order 435.1 and RCRA.	“Treated” LLW form assumed to be grouted. Diffusion-controlled release assumed for grouted waste.	More probable and conservative diffusion coefficients were developed for each key species. The diffusion coefficients account for tortuosity and chemical reactions in the cementitious material.	Diffusion-controlled release sufficient to contain radionuclides. Overall grouted waste not a major contributor.
Solid Waste Storage Area 6 (Oak Ridge)	LLW disposal facility managed in accordance with DOE Order 435.1.	Cement silos and tumulus pads with concrete containers used for disposal. Cementitious materials are assumed to function and physical and chemical barriers.	Detailed coupled structure and degradation modeling conducted to predict onset of cracking, which is assumed to compromise role as a physical barrier in a step change. Diffusion and chemical reactions in cementitious materials also considered with K_ds and solubilities.	Results were shown to be sensitive to several parameters associated with cementitious materials. Performance was deemed sufficient, even with assumption of total failure as a physical barrier at the onset of cracking.
F Tank Farm (Savannah River Site)	Tank Closure being conducted under Section 3116.	Multiple tank designs, in general with steel liners inside concrete walls and tanks filled with grout after cleaning. Cementitious materials assumed to serve as physical barrier to water flow and chemically limit releases of radionuclides and also to delay onset of corrosion of steel tank.	Multiple degradation mechanisms were considered, including physical changes and chemical changes in the cementitious materials. Distributions of degradation times were developed for changes in hydraulic conductivity and for changes from reducing to oxidizing conditions.	Results were dependent on performance of the cementitious materials in delaying the onset of corrosion of the steel tank. The chemical properties of the cementitious material were important after failure of the tank.

Example	Description	Role of Cementitious Barriers and Processes	Important Assumptions and Conceptual Models	Relative Importance of Cementitious Materials
E-Area (Savannah River Site)	LLW disposal facility managed in accordance with DOE Order 435.1.	Multiple disposal concepts using different types of cementitious barriers. Cementitious materials serve as physical and chemical barriers. Cracking is assumed to compromise performance as a physical barrier.	Structural and degradation models were used to determine timing of cracking and failure of cementitious materials. Transitions from reducing to oxidizing conditions were also calculated.	The grout used for components in grout trenches was important in terms of limiting releases of tritium. The vault walls are assumed to maintain a physical barrier until after the time of compliance, which precludes significant releases.
Engineering Test Reactor (Idaho Site)	Decommissioning under non-time-critical CERCLA removal action. ETR reactor vessel removed and disposed on-site.	Voids in pressure vessel were filled with grout for on-site disposal. Credit taken as a means to limit subsidence and resulting impact on water movement through cap.	None made specific to cementitious materials other than voids are filled to preclude subsidence that would increase infiltration rate through the cover.	Performance and properties of the grout actually used in disposal were inconsequential in the risk assessments and modeling performed.
Radioactive Waste Management Complex (Idaho Site)	Closure under the CERCLA remedial investigation/feasibility study (RI/FS) process.	No credit taken for diffusional release from concrete or the effect of containment in concrete casks in final baseline risk assessment. Some credit taken in previous assessments.	Cement forms treated as soil for modeling release for materials with surface contamination leached by infiltrating water and controlled by partitioning between the waste form and water.	Performance and properties of cementitious materials were inconsequential in the risk assessment modeling.
Waste Calcining Facility (Idaho Site)	Landfill closure under RCRA supported by NEPA Environmental Assessment (EA).	Credit taken in detailed modeling phase (using PORFLOW) for grouting and concrete cap including cracking. No credit taken in initial screening phase (using GWSCREEN).	In the detailed modeling phase, cementitious materials impact source release and transport when estimating risks to the future resident.	Significant impact on predicted groundwater concentrations and risks and provided assurance that landfill closure would be protective of human health.
Tanks 17-F and 20-F (Savannah River Site)	Operational closure under SCDHEC industrial wastewater permits supported by NEPA Environmental Impact Statement (EIS).	Credit taken for grout and concrete in modeling fate and transport (using MEPAS) of residual contaminants from grout to the aquifers and receptors.	Basemat, grout, and tank top remain intact for 1,000 years and then fail instantaneously, resulting in significant increase in hydraulic conductivities and infiltration rate.	Not taking credit would likely result in predictions that violate performance objectives – properties and performance of these materials likely important to the risk analysis.
P Reactor (Savannah River Site)	In-Situ Decommissioning under CERCLA.	Concrete and grout are physical and chemical barriers controlled by the assumed hydraulic conductivity and distribution coefficients.	Concrete and grout behave as porous media. Hydraulic conductivity changes as a function of time. Distribution change as concrete or grout ages.	Grout-water distribution coefficient for Ni was also shown to be important to risk.

Example	Description	Role of Cementitious Barriers and Processes	Important Assumptions and Conceptual Models	Relative Importance of Cementitious Materials
221-U Facility (Hanford Site)	CERCLA RI/FS process used to evaluate potential actions and identify preferred alternatives supported by inclusion of NEPA values in process.	Credit taken for grouting as a "defense-in-depth" measure if the engineered barrier fails during the 1,000-yr simulation period.	No assumptions pertain to the use of cementitious materials or their properties even though vessels will be grouted prior to cap emplacement.	Properties and performance of these materials are not relatively important; they only provide defense-in-depth.
Tank Waste Remediation System (Hanford Site)	NEPA EIS needed because of potential environmental impacts for proposed actions concerning the management and disposal of Hanford tank wastes.	A potential option for treating retrieved low-activity tank wastes is grouting, and the EIS proposes that empty waste tanks be grouted instead of being removed entirely.	Grouting would produce acceptable waste forms for ex situ treatment of wastes and would be acceptable for tank closure after waste removal operations are complete.	Use of these materials for disposal could have a large impact in the future, safe and economic treatment of retrieved wastes possibly including Hanford LAW.
Big Rock Point Nuclear Power Plant	Decommissioned using a "Greenfield" approach under a license termination plan and demonstrating compliance with License Termination Rule supported by NEPA EA.	Considered for the dos assessment supporting certification of the cask used to transport the reactor pressure vessel to the Barnwell low-level disposal facility.	Shielding credit taken for the low-density cellular concrete used to fill voids in the pressure vessel and the annular space between the reactor vessel and package.	Concrete n reactor vessel voids likely to have small shielding impact relative to the assumptions made for the source term in the analysis that allowed certification of cask.

In its recommendations, the CBP observed that parameter uncertainties in the modeled PA processes, including temporal waste form degradation, were often not taken into account or were oversimplified. While these assumptions were considered conservative, the CBP points out potentially significant impacts on predictions used to characterize doses and risks for decision-making purposes. They conclude that improvements in both the characterization and modeling of these phenomenological properties for cementitious materials used in disposal would provide more accurate predictions and support their continued use in future disposal and other nuclear-related activities undertaken by the U.S. DOE.

In particular, the CBP uses the selection of vitrification for the immobilization of LAW at the Hanford Site to illustrate how the extensive body of work on vitrified waste forms for HLW provided the assurance needed for stakeholders to be comfortable on the use of glass waste forms when compared to the relative uncertainty in the durability of cementitious forms. One goal of the CBP is to provide more accurate models for cementitious materials used in nuclear application to ultimately provide technically defensible information/assurance on durability for future applications of cementitious materials. Improving both the characterization of the properties of cementitious materials and the accuracy of the models used to predict their performance, especially over long assessment periods, would increase the applicability of cementitious materials for nuclear applications.

After reviewing the nuclear waste PAs with cementitious materials, CBP reviewed process models and uncertainty methods (CBP 2009). At the time of their review in 2009, the CBP concluded that performance and risk assessments for nuclear waste management with cementitious materials did not fully incorporate the effectiveness of the engineered barriers because the processes that influence performance are coupled and complicated. They performed a literature review to document existing knowledge with respect to 1) mechanisms and processes that directly influence the performance of cementitious materials, 2) methodologies for modeling the performance of these mechanisms and processes, and 3) approaches to addressing and quantifying uncertainties associated with performance predictions.

A key goal of the review was to provide a road map for improvements in conceptual understanding, measurements, and performance modeling leading to significant reduction in the uncertainties, as well as improved confidence in estimating the long-term performance of cementitious materials in nuclear applications. Accordingly, the review identifies 1) technology gaps that may be filled by the CBP project and 2) information and computational methods that are currently being applied in related fields, but have not yet been incorporated into PAs of cementitious barriers.

3.1.4.1 CBP Software Tools

In response to the technological gaps identified, CBP developed software tools that are intended to reduce the uncertainties in current PA methodologies. The principal CBP software tools are 1) LeachXS, for estimating short- and long-term releases of COCs, 2) ORCHESTRA, for modeling geochemical speciation in fluids such as cementitious waste form leachates, and mass transport of the leachates through subsurface environments, 3) STADIUM, for modeling cement degradation (e.g., sulfate attack) and reactive transport in cement paste, and 4) THAMES, for estimating evolving cement paste physical properties (e.g., changes in porosity and solid-phase volumes). These tools can be used independently or in tandem for local-scale modeling to support more comprehensive field-scale or simplified total system PA modeling performed at DOE sites. For example, LeachXS/ORCHESTRA has been implemented with the GoldSim Monte Carlo simulation software to assess vault degradation via sulfate attack (Hanford CBP Workshop 2014). These analyses augment the Savannah River Saltstone PA field-scale modeling predictions, which are used to evaluate uncertainty in key parameters (see Section 3.1.1 for more discussion).

CBP software tools are intended to provide modern, mechanistically detailed process models to address important features of the PA modeling of cementitious waste forms. In most of the CBP tools, the reaction processes are treated as systems of multi-species reactions with standardized stoichiometry and thermodynamics. This mechanistic approach is necessary to address situations where chemical speciation changes in space and time affect COC mobility via adsorption/desorption and precipitation/dissolution reactions. Reaction processes that affect chemical controls on COC mobility often do not involve the COCs themselves. For example, uranium mobility is dependent on pH, Eh, and alkalinity, as well as concentrations of Ca, Fe, and surface complexation sites. Any reaction that is significantly affecting one of these controls should be included in any detailed COC release conceptual model.

The following is a summary of the current CBP software tools.

LeachXS

The Leaching eXpert System, LeachXS, is an environmental impact assessment tool based on estimated contaminant release as derived from leaching tests. Leaching tests are interpreted in an expert system to provide estimates of the short- and long-term releases of constituents of interest. The LeachXS materials leaching database includes leaching/extraction test data, field data, and composition data that are used to address a wide variety of materials and scenarios, including cement-based systems. The expert decision system assists in guiding and evaluating laboratory tests, managing and evaluating data, estimating source terms, and evaluating impact. A regulatory database allows comparison of test data against criteria for disposal conditions.

Geochemical speciation and chemical reaction/transport modeling capabilities are integrated into the system using another CBP tool, ORCHESTRA. The geochemical processes in ORCHESTRA include mineral solubility (based on the extended MINTEQ thermodynamic database), surface complexation on hydrous ferric oxides (Dzombak and Morel 1990), and Al-oxide, dissolved organic carbon (DOC), and particulate organic matter (POM) interaction [according to the non-ideal competitive adsorption (NICA)-Donnan model (Kinniburgh et al. 1996)]. The LeachXS coupling to ORCHESTRA can be used to estimate contaminant release as a function of time for granular and monolithic materials from sequential data sets (liquid-to-solid ratio or time dependency from monolithic or compacted granular tank leaching tests, column testing, and lysimeter testing), including geochemical speciation and mass transfer parameter estimation. It can also be used for statistical evaluation of leaching data (pH stat, percolation tests, and monolith leach test).

The software for the database/expert system includes data conversion tools based on Microsoft Excel and data import tools for the Microsoft Access database. In this way a user may insert their data into LeachXS and obtain the desired answer or result.

ORCHESTRA

ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) is a computer program for modeling multicomponent equilibrium chemistry with the option of including kinetics and/or transport processes. In ORCHESTRA, reactive transport processes are implemented by a mixing-cell concept. The cells contain the information on the local physical and chemical composition, while the connections between the cells contain the mass transport equations (e.g., diffusion, convection).

Multi-surface adsorption modeling of cations and anions on organic matter, clay, and Fe-oxides, and the determination/interpretation of model parameters, has been implemented [e.g., CD-MUSIC, NICA-Donnan, Donnan ion exchange, and Ligand and Charge Distribution (LCD) model]. ORCHESTRA has capabilities to model both saturated and unsaturated zones, and has been extensively applied to model data from leaching tests, landfill leachate, pilot studies, and groundwater data. Recent applications of the model include coupling of ORCHESTRA with the LeachXS™ database to improve understanding and prediction of the long-term performance of cementitious barriers used in nuclear applications. This Thermo-Hydro-Mechanical (THM) coupling has also been used to assess long-term carbonation-induced corrosion in HLW tanks (Brown et al. 2013).

STADIUM

Software for Transport and Degradation in Unsaturated Materials (STADIUM®) can be used to predict the transport of ions and liquids in reactive porous media. The model has been used to predict the degradation of unsaturated concrete structures exposed to chemically aggressive environments. The results provided by STADIUM® have been validated on the basis of laboratory test results and field exposure observations. The model has been used to predict the behavior of numerous existing structures exposed to various forms of chemical degradation phenomena.

The calculations in the STADIUM® model are divided into two primary modules. The first module accounts for coupled transport of ions and water without considering chemical reactions (e.g., dissolution, precipitation). Transport is modeled with a volume-averaged version of the extended Nernst-Planck equation, which accounts for the electrical coupling between the ions, as well as for the chemical activity of the species in solution. Terms are added to consider the impact of fluid flow and temperature gradients on ionic fluxes. The transport equations are coupled to Poisson's equation, which gives the electrical potential in the material as a function of the ionic profiles distribution. Coupling with moisture conservation and heat conduction equations is also taken into account.

The second STADIUM® module is a chemical equilibrium code. After each transport step, this module equilibrates the concentrations at each node of the finite-element mesh with the phases of the hydrated cement paste. Solid phases can also be formed as a result of the penetration of aggressive species into the porous network of the material. The variation of solid phases will lead to local variations in porosity. These variations will likely affect the transport properties of the material locally. STADIUM® takes this locally varying phenomenon into account in the transport module described above.

THAMES

THAMES (Thermodynamic Hydration and Microstructure Evolution Simulator), is a model of evolving cementitious microstructures that can be used to calculate important engineering properties during hydration and degradation. THAMES can be called by other programs to update physical cement paste properties (e.g., porosity, connectedness, diffusivity, elastic moduli) as hydration and degradation proceed through the projected lifetime of the material. THAMES is built around a thermodynamic engine, which predicts bulk mineral phase volume fractions as a function of time in cement paste microstructures evolving by hydration or degradation phenomena. However, the bulk information alone is insufficient to make accurate predictions of transport properties and mechanical properties—microstructure information is also required. THAMES ultimately will include: 1) a module for generating a representative 3-D initial microstructure of cementitious particles in water (GENMIC), 2) a module for simulating microstructure changes (THAMES) guided by the thermodynamic calculations (e.g., GEMS), and 3) a module for calculating the elastic moduli, DC conductivity/diffusivity, and permeability on the predicted cement paste and mortar/concrete microstructure (CONCPROPS).

3.1.5 Summary of Past and Ongoing PAs with Cementitious Barriers

3.1.5.1 General Observations

Hierarchical Modeling Approach

To assess the long-term (~10,000 years) safety of an underground repository where the variability in processes, properties, and conditions is evolving and not completely understood, a hierarchical modeling approach has necessarily been adopted in the U.S., Europe, and by other countries and international organizations (e.g., IAEA). At the top of the hierarchical modeling pyramid (Figure 3.6) is the high-level total system PA (TSPA) model for decision-making, which must demonstrate that performance is acceptable when the relevant uncertainties have been accounted for. The Monte Carlo methods typically used for the stochastic uncertainty analysis generally require large numbers of simulations to adequately span the space of possible performance outcomes. Simplifications and/or omissions to the representation and resolution of the TSPA modeled processes are commonly employed to make the stochastic uncertainty analysis computationally tractable. The simplified modeling abstraction for the high-level TSPA is intended to be conservatively representative but not necessarily mechanistic.

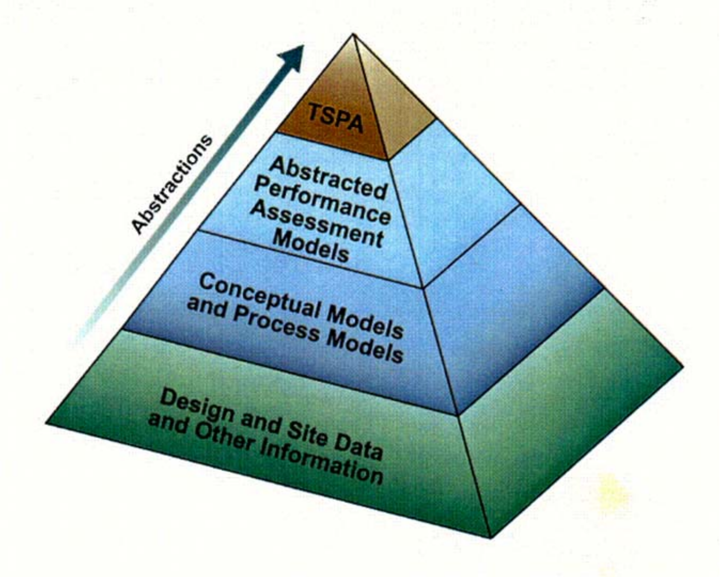

Figure 3.6. Total System Performance Assessment Information Pyramid (TRW 2000)

In the hierarchical modeling approach, the simplifications and assumptions in the high-level TSPA modeling are underpinned by mechanistically detailed field-scale and refined smaller-scale models of flow, transport, and reactions. These modeling analyses are used to link relatively short-term monitoring and/or experimental observations with characterization data, and with databases in the development of technically defensible assumptions for long-term performance.

Multicomponent Reactive Transport Modeling

Within the last 15 years, the ability to integrate multicomponent reactions and rates into subsurface flow and transport simulators has enabled more comprehensive treatment of the geochemical barriers and attenuation processes afforded by cementitious waste forms and concrete structures surrounding waste forms. A critical use of these models is to address the time-dependent variation in the “constant” properties of the lumped-parameter models (e.g., diffusion and distribution coefficients) used in the simplified high-level TSPA modeling. . In this case, the mechanistically detailed models are used to identify how the lumped parameters vary as the hydrogeochemical conditions evolve. For example, COCs incorporated into waste form minerals will be released as a dissolution process subject to changing redox potential and/or pH. The use of a lumped-parameter diffusion or K_d model cannot mechanistically address the evolving geochemical conditions controlling COC release. It may be possible, however, to use a sequence of time periods, each with a different but constant diffusion coefficient and/or K_d, to represent the dissolution behavior. Multicomponent reactive transport modeling can be used to mechanistically address the evolving geochemical conditions, including pH and Eh, and estimate representative lumped parameters that vary in time and space. Similarly, mineral precipitation and dissolution reactions [e.g., $Ca(OH)_2$, CaO, $CaCO_3$] that alter porosity, tortuosity, and permeability can be used to update the modeling of flow and transport processes.

Fracturing/Cracking of Cement Paste

A key difficulty in the prediction of long-term COC release is accounting for fracturing and cracking of cement paste or the cementitious waste form. There are many processes, properties, and conditions that can potentially lead to or affect crack formation in cement, including the liquid components in the LAW, the dry ingredients in the Cast Stone recipe, hydration reactions and conditions, late-stage ettringite formation due to reactions with sulfate, dissolution of $Ca(OH)_2$ and calcium silicate hydrate (CSH) phases due to reactions with carbonate, and precipitation of calcite. While there are 2,000-year-old Roman concrete analogues (van der Sloot et al. 2000), there is general difficulty predicting rates for cement weathering, cracking, and rubblization over a 10,000-year time horizon. These processes have important ramifications for the flow, transport, and reaction controls on COC release.

3.1.5.2 Cementitious Waste Form

Cementitious Waste PAs and Safety Analyses

Cementitious radioactive waste forms have been addressed in U.S. DOE PAs for Hanford grout and Savannah River Saltstone as discussed earlier in Section 3.1. Safety analyses for cementitious waste forms have also been performed in several other countries.

Chemical Gradients

A key feature of cementitious waste forms is the strong chemical gradient between the cementitious waste form [e.g., high pH (~13), anoxic, low carbonate, high salt, strong influence of electrical double layer (EDL)] and the backfill (e.g., circumneutral pH, oxic, high carbonate, low salt, minimal EDL effects). The exchange of pore fluids across this interface creates an evolving range of geochemical conditions. Depending on the COC, mobility can be sensitive to the variation in these conditions and other species concentrations. Consequently, the common usage of constant lumped parameters, such as diffusion coefficients, or K_ds, to represent these processes must be supported by more mechanistic multicomponent analyses to address evolving parameter variations in space and time.

Cast Stone and Previous Hanford PAs

The present conception of the Cast Stone waste form has not been addressed in any mechanistic detail in previous PAs. At best, Cast Stone performance was the subject of a risk assessment in 2003 (Mann et al. 2003b). Thus, the pending 2017 IDF PA will be the first opportunity to bring more mechanistic underpinnings for COC release from Cast Stone at Hanford. Once COCs are released outside of the waste package, there is general commonality with the processes, properties, and conditions as described in previous Hanford PAs.

3.1.5.3 Cast Stone Waste Form and Waste Package

Cast Stone Processes, Properties, and Conditions

While Cast Stone has commonality with other cementitious waste forms, there are some key differences in the waste form and the setting. The principal groundwater risk-driving COCs in Cast Stone are ^{99}Tc, ^{129}I, Cr, and nitrate. Mixing of LAW, WTP secondary or ETF-treated liquid wastes with the cement, fly ash, and BFS, lowers the oxidation-reduction potential of the waste form. In this process, the oxidized ^{99}Tcand Cr species in the LAW are reduced to their immobile mineral forms. Consequently, near-atmospheric levels of O_2 gas in the shallow vadose can potentially invade the Cast Stone via the gas-phase. This gas phase reoxidation process would be relatively ineffective in saturated systems (e.g., Savannah River saltstone), where the water-filled pores are barriers to gas-phase flow and transport.

3.1.5.4 Simulation Requirements

Flow and Transport Modeling

To more rigorously model the performance of the Cast Stone waste package in the shallow, variably saturated Hanford IDF backfill, a range of flow process modeling would be considered. Previous PA analyses have used a multidimensional, isothermal, single-phase, unsaturated flow modeling approach (i.e., Richards equation). In the hierarchical modeling pyramid, the validity of this single-phase modeling approach for the Cast Stone TSPA would be established by experiments and/or more mechanistically detailed, deterministic multiphase process modeling. The multiphase modeling would be used to assess the importance of the transport of gas-phase components (e.g., O_2, CO_2) that can react with the Cast Stone and affect COC release rates. Because of the low permeability of Cast Stone, a passive gas-phase with multicomponent diffusion may be sufficient to address the principal gas-phase transport processes, but this assumption must have a technically defensible basis that considers the impact of cracking of the Cast Stone.

Previous PA and safety analyses have assumed that transport through the small pores and tortuous pathways of cementitious waste forms can be modeled with diffusion alone. This may be the approach for the large-scale simplified TSPA modeling, although an alternative modeling approach is to model the release of COCs as a source term developed from more detailed coupled-process modeling in the supporting layers of the hierarchical modeling pyramid. Once again, the validity of the TSPA modeling approach should have a technical basis in more detailed deterministic liquid flow modeling with advection and diffusion process modeling.

Multicomponent Reaction Modeling

There are precedents for using lumped-parameter diffusion coefficients and K_ds to represent COC release from cementitious waste forms in high-level, stochastic, TSPA-like modeling. While this approach may be adjusted with time- and space-dependent parameters to better represent the behaviors of interest, these lumped parameter models are not mechanistic. For example, there is ample evidence that the release of ^{99}Tc and Cr from cementitious waste forms is a dissolution process controlled by pH and Eh conditions (Cantrell and Williams 2012; Lukens et al. 2005). In this case, the reduced Tc minerals are TcO_2 and perhaps Tc_2S_7, whereas the likely reduced chromium phases are $Cr(OH)_3$ and Cr(III)/Fe(III) hydroxide. On the other hand, ^{129}I is often assumed to be nearly non-reactive as the stable anion, I^- (Krupka et al. 2004). However, Xu et al. (2014) reported iodine speciation in Hanford groundwater from the 200 West Area to be 75.9% IO_3^-, 1.8% I^-, and 22.3% organo–I. It was also observed that iodate, IO_3^-, sorbs to Hanford sediments appreciably more than I^-.

In the safety assessment for a Belgian radioactive waste repository, Jacques et al. (2014) used multicomponent reactive transport modeling to develop time-dependent K_d values for a COC that was pH-sensitive. In this hierarchical modeling approach mechanistically detailed coupled-process modeling was used to determine different radionuclide K_ds for different chemical degradation states. In this case, the reaction network included equilibrium and kinetic reactions for cement minerals (e.g., CH, CSH phases), ion exchange, surface and aqueous complexation, and oxidation reactions from the migration of O_2 gas.

3.2 Modeling Strategy

3.2.1 Scope

The focus of the modeling strategy development for the Cast Stone PA is on COC release from the waste package. Subsequent migration through the backfill and natural vadose zone sediments has largely been addressed in other IDF PA studies. In general, the modeling strategy is designed to address the hierarchical modeling needs of the Cast Stone PA. This includes the development of 1) simplified, computationally efficient process models that will be integrated into the high-level stochastic TSPA simulation and 2) mechanistically detailed field-scale and refined small-scale models to provide a technically defensible basis for the assumptions, simplifications, and omissions in the TSPA modeling.

3.2.2 Hierarchical Modeling Approach

Prior to the disposal of LAW and secondary waste forms, an assurance that disposal of the waste can be accomplished while protecting the health and safety of the general population is required. The long time frames over which public safety must be assured necessitate that the safety case relies, in part, on computer simulations of events and processes occurring well into the future. Safety assessment requires, in part, an understanding of the performance of the waste containers, waste forms, and engineered backfill. Other important roles for modeling include identification of data, design, and model development needs for defensible decisions about regulatory compliance, and development of waste acceptance criteria (WAC) related to the quantities of COCs permitted for disposal. In this technical approach document, the focus has been on the identification of data and the models necessary to evaluate the performance of cementitious waste forms in steel waste packages.

The modeling that is performed in the PA processes is necessarily intertwined with the data collection, waste form characterization and testing, and laboratory and field experiments. To illustrate this context for the PA modeling, the following general approach is cited from IAEA (2004) for developing defensible, long-term waste package performance evaluations:

1. Identify the chemical/physical conditions of the repository environment and waste characteristics (e.g., inventory, physical and chemical forms).

2. Perform sensitivity studies, based on the available data and simple models.

3. Identify important radionuclides and hazardous chemicals, waste form, container, and backfill parameters that have the largest impact on performance.

4. Perform durability and leach tests on waste package components to assess the various processes that may affect their behavior and performance. Initially, these tests should be on a laboratory scale to gain experience on test methods. As the project evolves, field- scale tests may be necessary to obtain the appropriate supporting data.

5. Develop more complex models of the waste package behavior to evaluate its performance over time. Mechanistic models are generally preferred; however, empirical models may be used if data are insufficient to support mechanistic models.

6. Validate models by comparison with experimental results (e.g., lysimeter studies and leach tests) and/or with natural and archaeological analogues.

7. Determine whether performance goals are met based on existing models and data. If not, return to the sensitivity analysis step and repeat the process with the more complex models and enhanced data. Repeat the steps until performance goals are met.

A hierarchical modeling strategy is generally used to support the achievement of the above PA objectives (Figure 3.6). There are multiple modeling objectives that require different levels of modeling detail. At the top of the modeling pyramid is a total system PA (TSPA) model for with the ultimate objective to provide a probabilistic basis for assessing the uncertainty in the predicted performance of the Cast Stone waste form-waste package-disposal facility-subsurface environment system for a minimum of 10,000 years. In the past, IDF PA calculations have not used a probabilistic TSPA, relying instead upon simulations of numerous deterministic sensitivity scenarios/runs to address uncertainty. The SRS saltstone PA used the GoldSim Monte Carlo simulation software package for this purpose.

In the hierarchical modeling strategy, the validity of any abstracted/simplified representation of a process, property, or condition in the TSPA model at the top of the modeling pyramid is supported by more mechanistic and detailed predictive codes and modeling analyses that include more scientifically defensible constructs. These supporting analyses provide the technical justification that the TSPA model will generate results that are more protective (i.e., conservative) than a more realistically detailed depiction of actual subsystem performance. The key modeling parameters identified in this technical approach document address the data requirements for all hierarchical modeling analyses.

It should be emphasized that the goal of the hierarchical modeling framework is to ensure that the process models used in the TSPA are appropriate for the level of risks posed by uncertainties in the scenarios, conceptual models, and parameter sets. This implies a graded approach based on the assessment of risk. For example, if the risk-driving radionuclide inventory is sufficiently small, there should be more latitude in using a simpler, more conservative, modeling approach if the associated risks are still acceptable. In this respect, the hierarchical modeling framework is necessarily iterative as the conservativeness of the assumption must be established (presumably using experimental observations and/or more mechanistic modeling approaches) and the resulting risk must be calculated.

3.2.2.1 Total System IDF PA (TSPA) Model

The objective of the TSPA model is to provide a probabilistic basis for assessing the predicted performance of the Cast Stone waste form–waste package–disposal facility–subsurface environment system for a minimum of 10,000 years. The stochastic modeling approach systematically propagates uncertainties in the modeled scenarios, processes, properties, and conditions to the predicted dose from COC concentrations in the subsurface for the relevant period of performance at specified compliance points. The objective of the structured uncertainty analyses is to identify the range of possible disposal system performances/behaviors.

Because of the comprehensive nature of the large-scale system model, there are typically many sources of uncertainty in the model specification. The long time frames, the lack of complete understanding of all of the processes that affect performance, and the variability inherent in waste package materials, subsurface geologic media, and their performance characteristics, drive the performance of uncertainty analyses. Although short-term experiments may provide the best available data for PA, these data may not reflect processes that govern contaminant release over repository time scales. As materials age, their properties change. However, short-term laboratory data collection usually does not take into consideration the degradation-induced changes over time. In some cases (e.g., compressive strength of cementitious materials), the performance may improve over time. In other cases, the performance may degrade over time. In order to consider the variability that may occur, uncertainty analyses are performed using current models and understanding. Uncertainty analysis allows an examination of potential changes in system behavior as a function of changes in model specification. A Monte Carlo-type analysis, in which multiple variables for an individual realization are sampled from probabilistic distributions and then repeated for a large number of realizations, produces a distribution of potential outcomes. This technique is typically used in TSPA models (e.g., GoldSim) to demonstrate that performance is acceptable under a wide range of conditions. An important objective is to show that all the uncertainties relevant for safety and important to safety functions have been considered and will be managed appropriately. This includes a range of scenarios, conceptual models, and parameter sets. Sensitivity analyses should also be conducted to identify the processes and parameters that have the greatest influence on the performance of the disposal facility. Sensitivity analyses and uncertainty analyses should also be used to identify parameters or processes that can significantly impact safety when subjected to a relatively small change.

The use of Monte Carlo methods leads to the generation of massive numbers of model realizations to adequately sample the probabilistic distributions for all the characterized uncertainties. The potentially prohibitive computational requirements for simulating the large number of realizations for a minimum of 10,000 years can be reduced by simplifying the representation and resolution of the modeled processes.

Typically, only the most essential process models will be retained (i.e., principal controls on COC release and transport). Simplifications may include reduced dimensionality, coarser grid resolution, simpler boundary conditions and source terms, and lumped/empirical-parameter process models. In general, it must be demonstrated that the use of any simplification or assumption will result in a more conservative modeling scenario (i.e., one that does not generate results that appear to be more protective than a more realistic depiction would provide).

The resulting modeling abstraction of the total system is intended to be conservatively representative, but not necessarily mechanistic. A key requirement is that any abstracted/simplified representation of a process, property, or condition in the total system PA model must be valid. The general philosophy is that the omission or simplification of a feature in the total system PA model must be justified by an analysis that accounts for that feature or shows that the omission or simplification is conservative. The validity of the representation can be based on monitoring or experimental observations, characterization, technically defensible assumptions, and/or more mechanistic and detailed modeling analyses. The IDF total system PA model should be an integration of parsimonious models of flow, transport, and reactions that are based on more detailed modeling. This integration may take advantage of predictions from smaller-scale refined models that can be approximated (e.g., as source terms, process model simplifications and omissions) in the total system IDF PA model.

3.2.2.2 Field-Scale Modeling

The abstractions in the TSPA model at the top of the modeling pyramid are supported by coupled-process field-scale models (e.g., eSTOMP) that provide the most mechanistically detailed modeling that will be performed at the scale of the total system model. These models systematically account for the geochemical reaction processes controlling COC behavior in the context of the field-scale flow through the subsurface environment, disposal system, waste package, and waste form. As such, the field-scale models can be used to support simplifications invoked in the total system IDF PA model. While there might be larger-scale models that are used to generate boundary conditions for the field-scale models, they will not be as detailed in terms of process representations, or in temporal or spatial resolution, as the coupled-process field-scale models.

Mechanistic modeling of field-scale processes in the context of the detailed specification of the system fluid flow is comprised of process models for 1) liquid and gas flow, 2) transport of COC and reactive macro components, and 3) reactions controlling COC mobility. With respect to the IDF, which will house the Cast Stone waste packages, there will be considerable commonality with the field-scale modeling approach for the vitrified LAW. In fact, the hydrology, transport, and pore water chemistry associated with the far-field vadose zone and aquifer (sediments and groundwater) will be nearly the same. The principal differences will be the COC release mechanisms from the waste form and the interaction of 1) the waste form with the ambient liquid and gas-phase chemistry, 2) the waste form with the waste package chemistry, 3) the waste package chemistry and the backfill chemistry, and 4) the evolving geochemistry of the plume as it travels from the waste form to the ambient vadose zone.

In accordance with a graded approach and the assumptions made in the safety case, modeling and/or testing of the behavior of waste forms should be undertaken to ensure the physical and chemical stability of the different waste packages under the conditions expected in the disposal facility. Further, to ensure their adequate performance in the case of accidents, unforeseen incidents, or abnormal conditions, testing of extreme scenarios should be considered.

3.2.2.3 Fundamental, Detailed, and Targeted Models

Consideration should be given, as part of the safety case and safety assessment development, to conducting more detailed modeling studies for particular parts of the disposal system and for particular events and processes, in order to understand their contributions to system performance. Accordingly, below the level of coupled-process field-scale models in the modeling pyramid (Figure 3.6) is modeling that targets specific processes (e.g., liquid and gas flow, transport of each COC and reactive components, reactions controlling COC mobility), specific scales (e.g., waste form, waste package, disposal facility, vadose zone), and specific situations (e.g., thermodynamics, speciation, saturation indices for the pore water or waste form leachate in a column experiment, moisture migration into the Cast Stone, Cast Stone hydration behavior). These targeted modeling efforts provide the foundation for the coupled-process field-scale modeling and the TSPA model.

Another important modeling approach that can be used to optimize detailed or subsystem model development and data collection needs is sensitivity analysis. In sensitivity analysis, an evaluation similar in approach to an uncertainty analysis is performed, with the objective of determining if a change in a parameter significantly impacts the release or fate of key COCs or the overall performance of the disposal system. For example, two parameters often measured in backfill performance studies are bulk density and the radionuclide distribution coefficient. After analysis, it may be found that changes in the distribution coefficient of a COC have a major impact on performance, while changes in bulk density indicate only a minor impact. Thus, in this example, it is more important to accurately measure the distribution coefficient of the COC than the bulk density of the backfill.

3.2.2.4 Lumped-Parameter and Mechanistic Modeling

The cementitious waste form, Cast Stone, was included in the Mann et al. (2003b) document, "Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies, RPP-17675, Rev. 0." In that analysis, the Cast Stone waste form release rates for ^{99}Tc, ^{129}I, Cr, nitrite, nitrate, and U were based on empirical lumped-parameter effective diffusion coefficients supplied by the Cast Stone vendor, Fluor Federal Services, Inc., in coordination with CH2M-Hill Hanford Group, Inc. and available grout waste form literature. The source term was simulated with diffusion-controlled liquid transport in the continuous pore network of the Cast Stone coupled with diffusive-advective transport in porous matrix and idealized fractures. A different effective diffusion coefficient was used for each contaminant. The authors pointed out the preliminary nature of the calculations and the principal uncertainties. An important observation was that there is no fundamental scientific reason that empirical diffusion coefficients based on short-term laboratory tests for each contaminant accurately describe Cast Stone performance for 10,000 years.

One significant issue is that the release of COCs from Cast Stone is not governed by physical diffusion alone. The belief that modeling a simple diffusive release without modeling the geochemical sequestration of COCs in Cast Stone is conservative requires confirmatory analyses. This is because the effective radionuclide-specific diffusion coefficients used to model the diffusive release are often based on simple leaching test protocols (e.g., EPA 1315) that enforce a diffusion process conceptualization for situations that may be governed by other processes (e.g., pH- and Eh-controlled Tc solubility). If the measurement of a diffusion coefficient occurs when most of the ^{99}Tc in the Cast Stone monolith is still in reduced mineral form, the modeled diffusive release will under-predict subsequent Tc oxidation and mobilization. Mechanistic process modeling is needed to address how the waste form degrades, over what time scales, and how degradation affects the waste form porosity, permeability, tortuosity, and dispersivity as well as fracturing. Knowledge of geochemical processes is also needed to address 1) chemical forms of the COCs (species, oxidation state, COC association with grout minerals, including substitution and incorporation), 2) mobility of the various COC chemical forms, 3) geochemical/ thermodynamic conditions controlling the COC forms as a function of waste form aging (redox potential, pH, alkalinity, aqueous and surface complexation, ion exchange, solubility), and 4) geochemical/ thermodynamic conditions that feedback to flow and transport (e.g., dissolution, precipitation) as a function of waste form weathering. Gas-phase flow and transport modeling may be needed if significant oxidation and carbonation is induced by the exposure of Cast Stone to gas-phase oxygen and carbon dioxide, respectively. This is particularly important because of the vadose zone setting of the IDF and experimental evidence for enhanced Tc oxidation in the presence of unsaturated sediments and pore water (Langton 2014).

The near-field water saturation condition controls the gas-phase O_2 and CO_2 access to the waste form, and provides a conduit for diffusion. Water and water vapor can be driven to the waste form via capillary, osmotic, and hygroscopic forces. Depending on the liquid fraction in the waste form recipe, the cement hydration reactions may require additional moisture from the surrounding backfill material in order to progress to completion.

The waste package size and geometry also have an influence on the magnitude of the release of COCs from the waste form. In a diffusion-controlled liquid release, larger monoliths have a smaller surface area-to-volume ratio, which should lower the diffusive release rate. The baseline waste container to be used to contain the Cast Stone wet slurry before it sets/hardens/cures is mild steel rectangular boxes. The corrosion of the mild steel container was not previously accounted for in Hanford IDF PAs. Possible container corrosion effects include 1) Fe(II)-induced reduction and immobilization of Tc, Cr, or U, 2) sorption/incorporation of COCs into Fe(III) secondary minerals, 3) pore clogging by secondary minerals, and 4) access to the waste form by backfill pore water through deteriorated containers. In the latter, the backfill pore water might also include chemical components leached from the glass waste that may be co-disposed with Cast Stone in the IDF.

Numerical simulation of the near-field flow coupled to complex and evolving waste form chemistry provides a means to systematically integrate the 1) characterized waste form properties, 2) knowledge from relatively short time-scale laboratory experiments, and 3) subsurface conditions to predict the degradation of Cast Stone and release of COCs for 10,000 years or more. Existing subsurface simulation capabilities (e.g., eSTOMP) can comprehensively address the processes, properties, and conditions controlling the Cast Stone source term. In the most general case, the analysis would require 3-D, multiphase (gas and liquid) flow, dual-porosity modeling for fractures and the porous matrix, and multicomponent reactive transport including feedback to flow due to changes in mineral volume fractions. eSTOMP, and a few other simulators, can address the required process and property detail via massively parallel processing. In particular, the multicomponent reactive transport simulation of evolving geochemical conditions controlling COC mobility and release from waste packages is a part of every major radioactive waste management program in the world (e.g., France, Belgium, U.K., Switzerland, Sweden, Spain, Canada). The coupling of geochemical processes to flow and transport includes the simultaneous solution of equilibrium and kinetic reactions for redox, acid-base, aqueous, and surface complexation, ion exchange, and mineral precipitation and dissolution with feedback to flow and transport. DOE-EM is actively supporting the development of these modeling capabilities through the CBP (e.g., LeachXS, ORCHESTRA, STADIUM) and the Advanced Simulation Capability for Environmental Management project (ASCEM, http://esd.lbl.gov/research/projects/ascem/) and associated software (e.g., Amanzi simulator).

3.2.3 Simplified Processes for TSPA

3.2.3.1 Liquid-Phase COC Diffusion from Cast Stone

In some PAs and safety assessments, the low permeability of cementitious waste forms has been used to justify the omission of liquid- and gas-phase flow and advection from high-level stochastic total system modeling analyses. In fact, many of these analyses have used only liquid-phase diffusion to describe COC transport through cementitious barriers. Technically, diffusion is a non-reactive process, driven only by the concentration gradient for a particular COC. However, the mobility and, consequently, the release of ^{99}Tc and Cr from Cast Stone, are known to be controlled by redox reactions (see discussion in Serne and Westsik 2011) that involve other chemical components (e.g., O_2). Clearly, the use of non-reactive diffusion to account for reactions and other processes is not mechanistic. In this case, diffusion is treated as a simple lumped-parameter analogue of the speciation-controlled release. The use of this lumped-parameter model must be justified by more detailed modeling and analyses. A key issue is the estimation of time- and space-dependent COC-specific diffusion coefficients to account for evolving conditions in the waste form due to fracturing, mineral dissolution/precipitation (including feedback to porosity and tortuosity), and oxygen invasion, as well as varying aqueous chemistry.

3.2.3.2 COC Partitioning to Cast Stone

Another simplified modeling approach used in high-level stochastic TSPA and safety analyses is COC-specific desorption based on constant distribution coefficients (K_ds). In this approach, the partitioning of a particular COC between solid and aqueous phases is assumed to be linearly dependent on aqueous COC concentration, as defined by a constant K_d. The desorption K_d assumes that the partitioning is instantaneous, the solid has infinite capacitance for the COC, and the process is not affected by changes in the concentrations of other chemical species or the concentrations of those species are unchanging. Once again, this is not consistent with ^{99}Tc and Cr behavior in Cast Stone, and likely, most COCs. In their initially chemically reduced state in Cast Stone, these two COCs are controlled by the solubility of the technetium minerals, TcO_2 and Tc_2S_7, and likely, the chromium mineral $Cr(OH)_3$ and/or mixed-phase $Fe_xCr_{1-x}(OH)_3$ (Eary and Rai 1988). Furthermore, aqueous Tc solubility is pH- (Cantrell et al. 2012) and O_2-dependent (Langton et al. 2014). In an approach similar to the COC-specific diffusion model described above, this simple desorption model is treated as a non-mechanistic lumped-parameter analogue of the speciation-controlled release. This approach must be shown to address time- and space-dependent waste form conditions (e.g., fracturing, porosity, tortuosity, and speciation).

3.2.4 Mechanistic Process Modeling to Support TSPA Modeling Simplifications

The benefits of using COC-specific lumped-parameter diffusion and K_d models in radioactive waste management assessments include simplicity, computational efficiency, and convenience. This approach allows standard flow and transport simulators to be used on all realizations performed in the high-level TSPA modeling. The principal liability of this approach is that, beyond Fickian diffusion and retardation based on K_ds, the modeling cannot mechanistically address the evolving hydrogeochemistry controlling COC release over the operational lifetime of the IDF.

In general, the technical viability of the simplifications used in the high-level TSPA must be justified and defensible. Typically, the lumped-parameter approach can only be employed with time- and space-dependent diffusion coefficients and K_ds to address the evolving hydrogeochemistry. To determine these changes in a systematic and mechanistic manner, multicomponent reactions and rates with feedback to flow and transport properties must be incorporated into the modeling assessment.

The simplifications and assumptions employed in the high-level stochastic TSPA calculations (i.e., the top level of the hierarchical modeling pyramid) must be implemented in a way that is representative of the behaviors controlling the COC release from Cast Stone. In general, this requires time- and space-dependent specifications of COC-specific lumped parameters (e.g., diffusion and/or distribution coefficients) to account for the evolving conditions relevant to COC release from Cast Stone.

In the hierarchical modeling strategy, the simplified modeling choices made for the TSPA modeling at the top of pyramid are supported by a foundation of more mechanistically detailed modeling below. Below the TSPA modeling in the modeling pyramid (Figure 3.6) is the systematic and mechanistic coupling of flow, transport, and multicomponent reaction process models at the field scale. The simulations performed at this level will determine the time- and space-dependent diffusion and distribution coefficients that best represent COC release from Cast Stone over the operational lifetime of the IDF (> 10,000 years).

In the next echelon down in the hierarchical modeling pyramid (Figure 3.6), the mechanistic coupled-process modeling at the field scale is supported by modeling that targets specific processes, locations (e.g., waste form/waste package interface), and events (e.g., Cast Stone rubblization). This modeling can be more fundamental and/or spatially-refined with shorter-term (e.g., hydration reactions) or longer-term (cement degradation) focus. The foundation of the hierarchical modeling pyramid is data from laboratory and field experiments, characterization studies, and analogue studies (e.g., ancient Roman concrete).

3.3 Mechanistic Modeling Scenarios

The long time horizons and the absence of a significant degradation mechanism for the principal COCs (i.e., ^{99}Tc, ^{129}I, Cr) underscore the importance of a sound understanding of the controlling processes, properties, and conditions for COC release and transport. To build and test this system level of understanding, there are several key modeling scenarios that should be considered, each with potentially different modeling requirements. At a minimum, the Cast Stone and waste package weathering scenarios should be mechanistically addressed by the fundamental and field-scale modeling echelons of the hierarchical modeling pyramid (Figure 3.6) discussed above. Of interest are the processes, properties, and conditions that affect COC mobility and timing of COC release from Cast Stone, as well as transport through the waste package. Different scenarios will emphasize different mechanisms and pathways.

The scenarios describing the mobility, release, and transport of COCs in Cast Stone are of fundamental importance because they will be the basis for the time-dependent source term in the high-level TSPA modeling that will be used to assess the overall performance of the disposal facility. Cast Stone is expected to provide some degree of COC containment and retention. The physico-chemical properties of the waste form, including the nature of the COCs and environmental conditions, will determine the rate of COC release. Once the mild steel container degrades, giving rise to access of water to the waste, releases of radionuclides are determined primarily by the Cast Stone. In the absence of getters, Cast Stone is expected to exhibit diffusion-controlled release for ^{129}I and redox/dissolution-controlled release for ^{99}Tc and Cr.

Both the behavior and performance of a waste package will depend on the nature of the waste package and repository site-specific conditions. Waste packages can be expected to exhibit a large degree of variability in their behavior and performance due to the diversity in the types of wastes, the types of waste stabilization/solidification, and the complex chemical, physical, and microbiological processes and interactions that are likely to take place in the IDF disposal units.

Waste package performance refers to the combined performance of the waste form and container. From a safety assessment point of view, the essential features of waste package performance are structural integrity and COC containment. Waste package performance contributes to the source term of the IDF disposal unit (i.e., the COC flux leaving the IDF). Releases of COCs from a disposal unit are the result of a number of physical and chemical processes occurring primarily in the presence of vadose zone water and air. For Cast Stone, the initiation of waste form degradation and COC mobilization will be from the invasion of gas-phase oxygen and carbon dioxide. In addition, infiltrating water will enhance container degradation and leaching of the waste form, giving rise to releases of COCs from the disposal facility.

Controls on the COC source term include processes, properties, and conditions affecting 1) COC mobility and 2) flow and transport in and near the waste package. Mobility, in this context, is directly controlled by COC adsorption/desorption and precipitation/dissolution of COC-containing minerals. Indirect controls on COC mobility include any process, property, or condition that affects the concentration of any species involved in the COC solid-phase reactions. Flow and transport properties can be directly controlled by cracking/fracturing of the Cast Stone and the precipitation/dissolution of minerals in, on, and near the Cast Stone waste form. Modeling of liquid- and gas-phase flow is subject to the surface boundary conditions and failure scenarios for the Cast Stone, mild steel container, backfill, and surface barrier system. The movement of water vapor to and from the waste form can affect the moisture content of the waste form, which is a control on transport and reactions.

3.3.1 Mobilization of Cast Stone COCs

3.3.1.1 Tc and Cr Minerals

In the secondary waste stream from the ETF and LAW liquid waste streams, ^{99}Tc and Cr are in their respective oxidized forms—the pertechnetate ion (TcO_4^-) and the chromate ion (CrO_4^{-2}). The +7 oxidation state for Tc and the +6 oxidation state for Cr are mobile, whereas their reduced state Tc(IV) and Cr(III) form immobile sparingly soluble solid phases. There are reducing agents associated with the Cast Stone cement mixture that mediate the reduction and immobilization of the Tc(VII) and Cr(VI) species. Most effective are the sulfides in the BFS, which have been identified as enhancing the formation of TcO_2 and Tc_2S_7/Tc_3S_{10} minerals, but there are other reducing agents in Cast Stone (e.g., SO_3^{-2}) that can also contribute to the reductive immobilization of Tc(VII) and Cr(VI) (Lukens et al. 2005). XANES and EXAFS experiments performed by Lukens et al. (2005) showed that O_2 was the most efficient Tc(IV) oxidizer, even in the presence of high NO_3^-.

The pH of fresh Cast Stone pore water is high (~12-13), and the solubility of these Tc and Cr solid phases under reducing conditions is pH-sensitive (Cantrell and Williams 2012). Under these conditions, the principal mechanism for mobilizing Tc and Cr in Cast Stone is an increase in the redox potential that will lead to the oxidative dissolution of the Tc and Cr solid phases. In the shallow vadose zone of the 200 East Area where the Cast Stone waste package will be emplaced, the principal oxidant is oxygen, which can be assumed to be at near atmospheric levels (pO_2 ~0.21) in the gas-phase of the unsaturated pores. O_2 is thermodynamically partitioned between gas and aqueous phases according to Henry's Law parameters. At 25 ºC, this results in aqueous O_2 concentrations of 8.7 mg/L, or 270 µM.

The transport of gas- and liquid-phase O_2 to the waste package will ultimately result in the oxidation of the reduced phases in the Cast Stone. Gas molecular diffusion coefficients are about four orders of magnitude greater than those of water; consequently, gas-phase diffusive fluxes are generally much greater than those of water. A key issue is the role of the non-COC Cast Stone reducing equivalents in protecting the reduced Tc and Cr from re-oxidation. These reduced phases may include additives (e.g., O_2 getters) in the Cast Stone recipe that are designed to scavenge O_2 to prevent or delay the oxidation of Tc and Cr. In the presence of O_2, reduced Tc is rapidly oxidized. Technologies for incorporating Tc and perhaps chromate into goethite mineral crystal structures that are less susceptible to dissolution and re-mobilization have been developed (Um et al. 2011a). Incorporation of these approaches will require characterization of the reactions, thermodynamics, and rates.

Shrinking-core models, which account for the diffusion of oxygen and the progressive reaction from the surface to the interior of an idealized sphere of material, have been used to represent these sub-grid mechanisms (Lukens et al. 2005). The rate of growth of the oxidation layer requires characterization of the transport of oxygen into the Cast Stone by both aqueous and gaseous phases, knowledge of solid-phase reactions with oxygen (including Tc, Cr species, getters, and other macro constituents in the Cast Stone solids), and the stability constants and rate laws for these reactions.

3.3.1.2 ^{129}I

In some PAs, ^{129}I was assumed to be non-reactive. This is because the stable anion, I^- (Krupka et al. 2004), which is the thermodynamically favored species in Cast Stone, has been characterized by very small distribution coefficients (K_ds) in laboratory experiments (Um et al. 2004; Kaplan et al. 2000, 1998). Under these conditions, the dominant control on ^{129}I release from Cast Stone would be liquid-phase diffusion. Recently, however, iodine speciation in Hanford groundwater from the 200 West Area was found to be 75.9% IO_3^-, 1.8% I^-, and 22.3% organo–I (Xu et al. 2014). This is significant because iodate, (IO_3^-), was observed to sorb to Hanford sediments appreciably more than I^-. If iodine in the LAW and secondary wastes is in the form of IO_3^-, the iodine speciation and sorption in the Cast Stone must be determined. This issue may be minimized by including iodine getters in the Cast Stone recipe to enhance retention of ^{129}I (Qafoku et al. 2014; Neeway et al. 2014b).

Recent leaching experiments underway at PNNL that will be documented in a May 2015 report[7] on LAW simulants solidified in Cast Stone monoliths (2 inches in diameter by 4 inches long), immersed in either deionized water or simulated IDF pore water, determined that over 60% of the iodine in the waste form was leached after ~500 days for the worst-performing Cast Stone-LAW simulant mixes and over 30% of the total iodide in the best-performing Cast Stone-LAW simulant mixes. These leach results suggest that iodine was not significantly retained in the waste form. It also demonstrated that the porosity was largely connected throughout the Cast Stone waste form. Another observation from these experiments was the temporal consistency of the fractions of released ions. If the pores are sufficiently small and the electric field from the net charge at the solid surface extends sufficiently far into the solution, the electrical double layer would be expected to selectively retain the sodium cation. This was not observed; the percentage of sodium leached for the various Cast Stone-LAW simulant mixes was quite similar to percentage of iodide leached.

3.3.2 Controls on COC Transport

Processes that can modify the Cast Stone waste package in a way that affects flow and transport properties include 1) flow scenarios, 2) cracking and fracturing of Cast Stone, 3) precipitation of minerals, and 4) dissolution of minerals.

A key issue is how changes in the waste form and waste package during 10,000+ years alter the transport rates of COCs out of the waste form and waste package into the backfill. Potential effects include the fracturing and rubblizing of the Cast Stone waste form and the corrosion of the mild steel waste container.

3.3.2.1 Cast Stone Curing and Hydration

Mineralogical and Microstructural Evolution

An important component of the PA is the prediction of chemical, mineralogical, and microstructural changes that will occur in Cast Stone during hydration and subsequent interactions with the environment (e.g., chemical and/or physical degradation). The Cast Stone microstructural properties will determine the hydraulic/pneumatic flow and transport properties of the material, whereas the mineralogy and the chemical stability of the solid phases can contribute to geochemical controls on COC mobility. The transport of ionic species in the aqueous pore solution that react with the insoluble mineral phases leads to a continuous evolution of the mineralogy and microstructure, beginning with hydration, followed by degradation. Modeling the evolution of the cementitious material consists of treating the material as a porous reactive matrix in contact with aqueous reactive components.

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[7] Serne RJ, JH Westsik, Jr., BD Williams, Hun Bok Jung, G Wang. 2015. "Extended Leach Testing of Simulated LAW Cast Stone Monoliths." Currently unpublished.

Table 3.13. Composition of Portland Cement with Chemical Composition and Weight Percent (Bye 1983)

Cement Compound	Weight Percentage	Chemical Formula
Tricalcium silicate	50 %	Ca_3SiO_5 or $3CaO \bullet SiO_2$
Dicalcium silicate	25 %	Ca_2SiO_4 or $2CaO \bullet SiO_2$
Tricalcium aluminate	10 %	$Ca_3Al_2O_6$ or $3CaO \bullet \bullet Al_2O_3$
Tetracalcium aluminoferrite	10 %	$Ca_4Al_2Fe_2O_{10}$ or $4CaO^{\cdot}Al_2O_3 \bullet Fe_2O_3$
Gypsum	5 %	$CaSO_4 \bullet 2H_2O$

Table 3.13 shows the typical constituents of Portland cement and their respective weight percentages. When water is added to Portland cement, the hydrolysis reactions involving the calcium silicates liberate calcium ions, hydroxide ions, and heat. The increase in hydroxide ions results in the elevation of pH to 12-13 in the paste. When caustic wastes such as LAW are solidified, the liquid waste also generates additional hydroxides (causticity and elevated pH). The reaction continues producing calcium and hydroxide ions until the system becomes saturated with respect to CSH minerals. Once this occurs, calcium hydroxide and CSH begin to precipitate. As the CSH mineral volume fraction increases, the hydration reaction is controlled by the rate at which water molecules diffuse through it. Consequently, the production of CSH becomes slower and slower. As long as the hydration reactions continue, the compressive strength continues to increase and the pore space is replaced by CSH mineral volume. Pore space not filled with the hardened hydrate is primarily calcium hydroxide solution. Hydration reactions can continue for years, as long as water is present and unhydrated compounds remain in the cement paste. In general, a low “free” water to cement ratio (< 0.4) is necessary for low-porosity, high-strength cement paste. When solidifying highly saline liquid wastes in grouts, such as Cast Stone, the free water-to-dry blend mix ratio is often raised to 0.6 or larger to obtain high compressive strength and leach resistance.

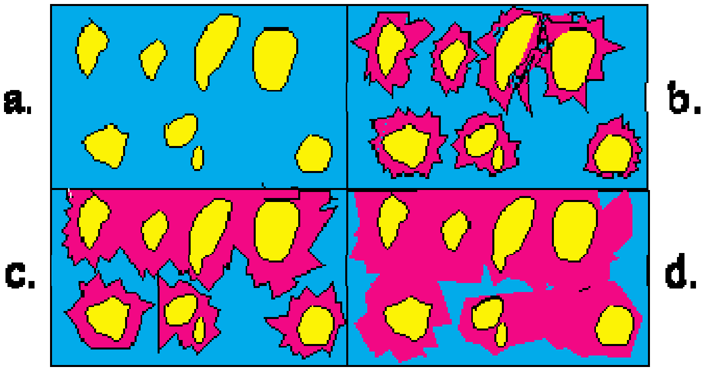


Figure 3.7. Schematic Illustration of the Pores in Calcium Silicate through Different Stages of Hydration (Chamberlain et al. 1995)

Figure 3.7 shows the progressive decrease in pore space as CSH is formed. Note in diagram (a), hydration has not yet occurred and the pores (blue-colored empty spaces between grains) are filled with water. Diagram (b) represents the beginning of hydration (red is the formation of calcium silicate solids). In diagram (c), the hydration continues. Although empty spaces still exist, they are filled with water and dissolved calcium hydroxide. Diagram (d) shows nearly hardened cement paste. Note that in diagram (d), the majority of space is now filled with CSH solids.

The IAEA (Ramallo de Goldschmidt 2009) has published laboratory measurements from an Argentinian case study that illustrates the changes in porosity and compressive strength over time. In this case, a cementitious waste form with a waste/cement matrix ratio of 0.45 and a water/cement ratio of 0.38 was studied. From 28 to 180 days, compressive strength increased from 53 Mpa to 57 Mpa, oxygen permeability decreased from 0.30 to 0.04×10^{-16} m^2, and air permeability decreased from 0.13 to 0.02×10^{-16} m^2.

3.3.2.2 Cast Stone Cracking and Fracturing

There is currently insufficient understanding to accurately predict fracturing, cracking, and rubblization of Cast Stone over the ~10,000-year period desired by regulators and the public for waste disposal facility performance. Under certain scenarios, the formation of fractures and rubble can enhance flow and transport through the otherwise low-permeability waste form. This potentially significant impact on COC release has been addressed in some assessments by assuming stages of degradation that are linked to changes in model parameters. This approach must be shown to be conservative. The principal changes of interest include changes to the Cast Stone flow properties (e.g., porosity, permeability), transport properties (e.g., tortuosity, diffusion coefficients), and reaction parameters (e.g., desorption coefficients, rates, surface area). Changes in these parameters will affect transport and mixing of reactive components in the fluids, as well as the interplay between the rates of transport (e.g., delivery of reactants) and the rates of reactions.

Fracturing may occur in the course of curing/hydration of the Cast Stone waste form. Early-age cracking (< 7 days of curing) can generally be avoided by controlling temperature rise and providing sufficient moisture to mitigate autogenous and drying shrinkage. In general, lower water-to-cement ratios produce hardened cement paste with higher strength and smaller porosity and permeability. High-salinity liquid waste requires higher ratios of free water to dry blend, in the range of 0.4 to >0.6, to obtain good hardened final solids. Under these conditions, water is rapidly drawn into the hydration process, and the demand for more water creates very fine open capillaries. The surface tension within the open capillaries causes autogenous shrinkage (sometimes called chemical shrinkage or self-desiccation), which can lead to cracking (Pabalan et al. 2009). With wet curing, water is drawn into the capillaries and the shrinkage does not occur. Note that autogenous shrinkage is separate from, and in addition to, conventional drying shrinkage, which will start when water curing ceases.

Sulfate attack can be “external,” due to penetration of sulfates from backfill pore water, or “internal,” due to sulfate in the liquid waste being incorporated into the Cast Stone at the time of mixing (Winter et al. 2012). External sulfate attack is characterized by a reaction front, behind which the composition and microstructure of the cement paste exhibits expansion and cracking to a varying extent. In general, the conversion of monosulfate phases to expansive ettringite and gypsum decalcifies the CSH that provides strength for Cast Stone. Magnesium can also take part in the reactions, replacing calcium in the solid phases with the formation of brucite (magnesium hydroxide) and magnesium silicate hydrates.

Internal sulfate attack from delayed ettringite formation (DEF) occurs where sulfate in the liquid waste is incorporated into the cement when mixed. DEF generally occurs when curing experiences elevated temperatures (>70 ºC), for example, in large concrete pours where the heat of hydration results in high temperatures within the concrete. Expansion of the concrete due to DEF within the paste can cause serious damage to concrete structures. Although excess sulfate in the cement would be likely to increase expansion due to DEF, it can occur at normal levels of sulfate in cement. It should be noted that a relatively small quantity of ettringite normally forms during early-stage hydration/curing of cement without adverse consequences. It is only when ettringite formation is delayed after the cement paste has hardened, that the local expansion has deleterious effects.

3.3.2.3 Influence of Cast Stone Formulation

Variability in the composition of the liquid wastes may require robustness and/or flexibility in the determination of the Cast Stone mix recipe. For recipes that satisfy the durability and compressive strength requirements (currently 500 psi for disposal in the IDF), it is important to understand how the waste composition and liquid/solid ratio (liquid waste to dry blend) affect the flow and transport properties (e.g., porosity, permeability, tortuosity, bulk density, surface area) of the Cast Stone, as well as the mobility of COCs (e.g., incorporation and/or mineral substitution, reduction, and immobilization). This extends to the potential addition of getters to the Cast Stone recipe, which are designed to permanently immobilize COCs, or at least extend the period of immobilization. The extent to which the cement and pozzolan hydration reactions affect the chemical form and mobility of COCs, flow and transport properties, and water saturation in the waste package/near-field environment is also important. Previous testing (Um et al. 2011b) has identified that increasing the fraction of liquid waste in the Cast Stone recipe leads to increasing connected porosity. Information regarding the permeability of concrete as affected by curing temperature, drying, and admixture composition is provided by Whiting and Walitt (1988). The physical and geochemical COC retention mechanisms (and their enhancement with additives) should be incorporated into the detailed waste form release sub-model, and subsequent near-field flow and reactive transport modeling.

3.3.2.4 Carbonation

Gas-phase CO_2 can access the Cast Stone after the mild steel container is breached. Diffusion is orders of magnitude faster in air than in water (as dissolved CO_2(aq), HCO_3, or CO_3^{2-} species). Cement exposed to a moist soil atmosphere will carbonate faster than when exposed at ground surface to the atmosphere (Langton et al. 2014). This is because the CO_2 concentration in the soil gas-phase of an arid vadose zone environment can be five times the atmospheric concentrations or higher (Smith et al. 1998) due to biodegradation of organic matter. The conceptual model is that gas-phase CO_2 partitions to pore water in the Cast Stone as (bi)carbonate, which then reacts with dissolved calcium to form calcite mineral. The carbonation reactions dissolve and decalcify the $Ca(OH)_2$ (CH in cement notation; ~25 %wt in normal cement) and $3CaO•2Si0_2•3H_2O$ (CSH in cement notation; 60% in normal cement) (Papadakis et al. 1991), lower the waste form pH from ~12-13 toward ~8 , increase the mineral mass, and lower porosity. The drop in pH can impact the solubility and sorption properties of Tc (Cantrell et al. 2013), and the formation of calcite may fill/seal pores in a way that limits further gas and liquid invasion. In particular, pH is a master variable for many reactions, including those controlling the mobility of some COCs. Significant pH changes could affect sorption/desorption reactions and the solubility of minerals containing COCs.

Water saturation of the Cast Stone pores is an important control on where the carbonation reactions take place. Saturation can potentially impede the gas-phase transport while increasing the volume for the aqueous phase reactions. Consequently, the interplay between the dynamics of the water saturation conditions and the CO_2 reactivity is important.

Water can dissolve soluble phases in the hydrated cement paste. These phases are stable under the alkaline pH of the cement pore waters, but are susceptible to dissolution when exposed to ambient pore water with much lower pH. Driven by the concentration gradient, calcium and hydroxide ions diffuse out of the cement, leading to the dissolution of the cement mineral phases. Portlandite is the first cement phase to dissolve because of its high solubility, followed by monosulfate, ettringite, and lastly, CSH, which is progressively decalcified and transformed into a silica gel (Pabalan et al. 2009) (Table 3.14).

Table 3.14. Concrete Leaching Zones (Lagerblad 2001)

	Zone 1	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 5**	**Zone 6**
Phases[(a)]	**Calcite Silica Gel Hydroxides**	**Silica Gel Calcite Hydroxides**	**Silica Gel CSH[(a)] Hydroxides**	**CSH(2) Ettringite**	**CSH(1) Ettringite**	**CSH Portlandite Ettringite**
Al_2O_3 content	High	Medium	Low	Low	Low	Low
MgO content	High	Medium	Low	None	None	None
CaO/SiO_2	< 0.1	< 0.5	0.5 – 1.0	~1.0	1.0 – 1.6	1.6 – 1.7
Ca concentration (mmol/kg)	Low	< 2	< 4	< 10	10 – 20	> 20
Si concentration (mmol/kg)	1.5	4.2	1.5	1.5	< 1	< 1
pH	7	~10	10.0 - 10.5	> 10.5	10.5 – 12.4	> 12.4
Porosity	Low	Medium	High	Medium	Low	Very Low

(a) CSH(2) has less volume than CSH(1). The silica gel also contains Al_2O_3 and MgO. The MgO content and CaO/SiO_2 ratio are approximate and relate to the content in silica gel.

Leaching can result in increased porosity and subsequent loss of strength. Increasing connectivity of the pore space results in higher diffusive transport of reactive species. The decrease in pore solution pH due to complete dissolution of portlandite could also cause CSH to decalcify and weaken. The extent of leaching depends on the qualities of the waste form, the rate at which water percolates through or flows over it, and the composition and concentrations of species in solution. It is a reasonable supposition that cements with reduced calcium contents, such as blends of fly ash and Portland cement, will exhibit better resistance to aggressive CO_2 than OPC (Pabalan et al. 2009). However, large increases in porosity, resulting from attack, may still adversely affect hydraulic properties and, as supplementary materials such as fly ash diminish the CaO content of cements, the matrix contains less portlandite to neutralize "aggressive" CO_2.

Modern cements exposed to soil and other environmental conditions are only slowly carbonated, unlike the much more porous Roman cements used to construct aqueducts. The ancient pozzolans (e.g., volcanic tuff or trass), have rather high porosity, which allows drying to occur more rapidly and carbonation to penetrate deeper. Lumps of Roman cement, sampled from ancient German aqueducts, were tested for trace element behavior and found to be fully carbonated to the depth of the core (~10 cm) after approximately 2,000 years (van der Sloot et al. 2000). The general concern is that the repository lifetimes far exceed any observational period for these materials.

It should be noted that the carbonation reaction discussion has not addressed the impact of the waste composition on the performance of Cast Stone retention of the principal COCs. In this case, high sodium and potassium concentrations are likely to influence the carbonation process as they affect the chemical activity of the pore solution, and consequently, chemical equilibrium with the hydrated paste.

3.3.2.5 Concrete Degradation

The absence of rebar and aggregates in the Cast Stone precludes some well-known chemical degradation mechanisms that are associated with concrete. These include chloride-promoted corrosion of steel reinforcement and alkali-silica reaction (ASR). Corrosion of reinforcing steel initiated by chloride in the vicinity of the steel surface produces iron oxides that can lead to stresses that may damage the concrete. The ASR mechanism occurs when the alkaline solution in the cement pores reacts with the siliceous aggregate (e.g., sand), resulting in expansive replacement by CSH. Cracking originates at the aggregate and surrounding cement paste.

3.3.2.6 Flow Scenarios

Infiltrating water will enhance container degradation and leaching of the waste form, giving rise to releases of COCs from the disposal facility. Because of the very long half-lives of ^{99}Tc (10^5 years) and ^{129}I (1.6×10^7 years), it is important to understand their chemical behavior if the disposal facility is breached by water.

3.3.3 Waste Package Interactions

Waste containers contribute to waste package and repository performance by delaying water or gases from reaching the waste form, and thus the release of COCs. The Cast Stone waste packages are expected to be more-or-less isolated from the accessible environment at early times, as a result of being placed in mild steel containers that will presumably be covered by steel lids. Therefore, the containerized waste packages should initially behave as impermeable objects within the backfilled IDF trenches.

Depending on the IDF emplacement geometry for the different waste forms, the interactions between the Cast Stone waste package and the backfill pore gas and liquids may also include products from the corrosion of the glass waste form and its waste package. As the mild steel containers corrode, the Cast Stone will eventually be in contact with backfill sediments. Given the expected lower permeability of the cementitious waste, the waste packages should be expected to behave as relatively impermeable objects for some length of time after complete degradation of the steel containers. However, fracturing and cracking of the Cast Stone could result in higher permeability and increased surface areas for reactions.

For the mild steel Cast Stone containers, the underlying corrosion mechanisms that contribute to container failure can also provide reactive surfaces with some degree of retention for some COCs (e.g., additional reductive capacity for redox-sensitive COCs and local O_2 consumption). Cement-stabilized waste forms may contain substances (e.g., chlorides) that accelerate corrosion of the steel containers and, depending on the nature of the soil geochemistry, lead to re-mineralization reactions on the surface of the monolith (Viani et al. 1997). This includes iron oxidation leading to the formation of Fe(III) minerals that can incorporate, adsorb, and/or inhibit the transport of COCs. Sorbents for the anionic COCs would require pH below the pH_{PZC} of the resultant iron oxides from the mild steel containers and the surrounding backfill. The pH_{PZC} for most ferric oxides and backfill sediments are above pH 7, and thus these materials will likely not adsorb anionic species given the highly caustic pH of Cast Stone pore waters. In summary, even after the mild steel containers fail to provide isolation of the Cast Stone from the environment, the degraded containers may still provide a source of sorption sites that retard the movement of released cationic COCs, and thereby improve waste package performance.

The estimation of container lifetime is necessary to establish how much credit should be assigned to the waste package for COC containment and retention. Container performance and its lifetime are a function of the container material type, thickness, and design, degradation mechanism and rate, environmental conditions, and groundwater chemistry. In a carbon steel drum corrosion test (Ramallo de Goldschmidt 2002), the results obtained indicate a moderate to low degree of degradation. Using a polarization slope with the normal corrosion parameters for the studied system, the corrosion current was calculated to be 10^{-6} to 10^{-5} Amp/cm^2, which represents a dissolution rate of less than 0.1 mm/year. However, due to the uncertainties associated with corrosion product formation, credit for sorption on container materials is generally neglected in PAs. If model evaluations were performed, data on the degree of sorption as a function of the amount of corrosion would be needed. As stated, modeling of this phenomenon is not usually performed.

3.4 Process Modeling and Simulation Requirements

In summary, the candidate simplified lumped-parameter Cast Stone aqueous COC release models that could be used in the high-level stochastic TSPA simulations can be categorized into two physico-chemical processes: 1) diffusion, requiring COC-specific diffusion coefficients and properties of the pore geometry of the waste form, and 2) linear solid/aqueous partitioning, requiring COC-specific K_ds and bulk solid properties. In Section 3.3, the mechanistic modeling scenarios that must be addressed to justify the use of the simplified lumped-parameter modeling in the high-level stochastic TSPA simulations focused on mechanisms controlling COC release and transport in the Cast Stone waste package. These mechanisms were the result of evolving hydrogeochemical conditions driven largely by reactions between the waste package and backfill components. The highest concentration gradients are expected across the Cast Stone monolith surface with interactions from gas and liquid phases in the IDF backfill, and container corrosion products.

The gas- and liquid-phase transport pathway for this exchange of reactive components between the ambient subsurface and Cast Stone waste package is through unsaturated sediments. Key issues are the ability of pore liquids and gases to access the waste form, leach resistance of the waste form, chemical reactions that directly (e.g., Tc oxidation) or indirectly (e.g., cement degradation and fracturing) lead to or accelerate the mobilization of COCs, and changes in mechanical durability. The principal external reactive components, products from reactions with cementitious waste forms, leaching processes, and interactions are summarized in the schematic diagram in Figure 3.8. The basic processes in the mechanistic modeling scenarios are summarized in Table 3.15.

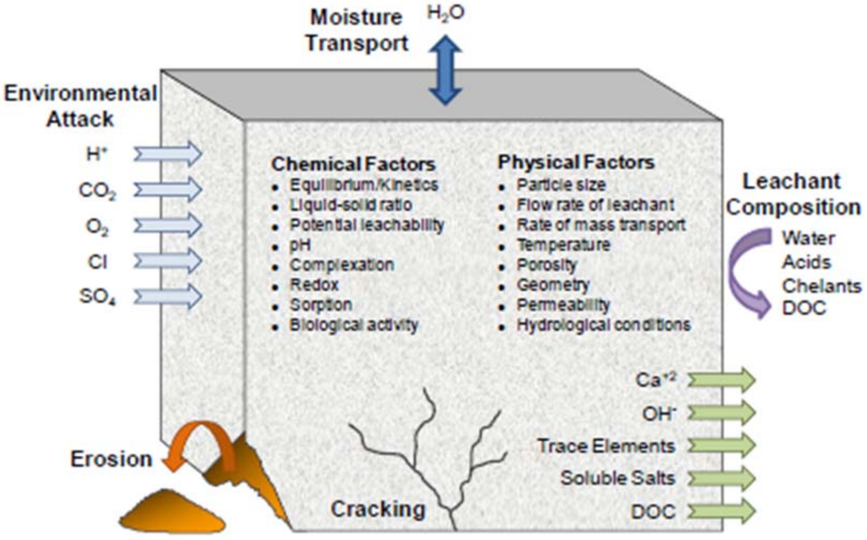


Figure 3.8. Factors Affecting the Rate of Leaching from Cementitious Waste Forms (Adapted from Garrabrants et al. 2005)

Table 3.15. Cast Stone Process Models

Mechanism	Applicability	Comments
Flow	Liquid and gas flow through Cast Stone.	Requires fluid and flow properties, saturations, driving force, and boundary conditions. Must address fractured Cast Stone and feedback to flow from mineral reactions.
Advection	Advection of O_2 and CO_2 and backfill aqueous chemistry into Cast Stone; COCs and cement pore solutions into backfill.	Gas and liquid phases require properties for fluid, flow, and transport as well as sufficient driving forces.
Diffusion	Diffusion of O_2 and CO_2 and backfill aqueous chemistry into Cast Stone; COCs and cement pore solutions into backfill.	Gas and liquid phases require concentration gradients, species-specific diffusion coefficients, and waste form geometry.
Mineral Dissolution	Dissolution of COC-bearing minerals, oxidative dissolution of reduced minerals, degradation of CSH.	Solubility-controlled COC release depends on reaction species concentrations, stoichiometry, thermodynamics, and possibly rates. Feedback to flow and transport requires linkage to porosity, permeability, tortuosity.
Mineral Precipitation	Incorporation of COCs into minerals, precipitation reactions that affect controls on COC mobility; pore clogging.	Solubility-controlled attenuation depends on reaction species concentrations, stoichiometry, thermodynamics, and possibly rates. Feedback to flow and transport requires linkage to porosity, permeability, tortuosity.
Adsorption / Desorption	COC surface complexation and anion exchange; competition for adsorbent sites.	Sorption-controlled attenuation depends on reaction species concentrations, stoichiometry, thermodynamics, and possibly rates.
Cast Stone Fracturing / Cracking / Degradation	Age- and degradation-related formation of fractures, cracks, and rubble in Cast Stone.	Feedback to flow and transport properties and accessible reactive mineral surfaces. Lack of mechanistically predictive process models for repository time scales.

3.4.1 Chemical Degradation

Chemical degradation of the Cast Stone is triggered by the exchange of reactive species across the Cast Stone–backfill–corroded container interface. In some cases, species are leached out of the Cast Stone, while in other cases, external species enter the Cast Stone and affect the microstructure. Because the transport of species is prominently involved in the chemical degradation of Cast Stone, the various mechanisms affecting the movement of ions in the pore solution of Cast Stone need to be characterized. Part of the characterization must necessarily be dedicated to unsaturated flow and transport. A more detailed treatment on this topic can be found in Section 0.

The principal waste package degradation mechanisms are corrosion of the mild steel container, carbonation/decalcification due to the leaching of hydroxide and calcium from the CSH phases, and external sulfate attack for Cast Stone.

Differences in pore structures at the Cast Stone–backfill interface can result in capillary suction between materials across the interface. The interface between Cast Stone and the steel container and/or backfill is characterized by gradients in pH, soluble salts, and redox potential. Organic matter from soil interacting with the Cast Stone can potentially mobilize COCs, although the organic matter content in Hanford sediments is generally very low. The rate of front movement (especially for pH, carbonate, and sulfate) is likely to significantly influence the mobility of COCs differently. However, as long as the monolithic product remains intact, the accessible interface is limited to the Cast Stone surface.

The following subsections describe other processes that may also be important to consider for near-field modeling in Hanford Site PA applications. The expected benefits, or expected impacts on PA calculations, are also discussed.

3.4.2 Liquid- and Gas-Phase Flow

This section discusses various processes and assumptions associated with the different types of models that have been used in previous IDF PA calculations. Justification is also provided for a more rigorous two-phase flow and reactive transport modeling that is recommended for near-field modeling.

Previous far-field modeling assumed isothermal conditions and used the Richards equation (Richards 1931) for modeling single- (aqueous-) phase flow in the vadose zone as well as the advection-dispersion equation for modeling non-reactive solute transport in both the vadose and saturated zones. Use of the Richards and non-reactive advection-dispersion equations implies the following assumptions:

1. Water flow is in the liquid (aqueous) phase only, which implies that the gas-phase is continuous, at constant atmospheric pressure, and does not directly affect the movement of liquid water.
2. Driving forces for water flow are gravity and matric potential gradients—gradients in water vapor pressure and solute or osmotic potential are neglected.
3. Solutes behave as dilute passive scalars—there is no interaction or coupling between solute concentrations or activities and water movement, or between solute properties and bulk fluid properties.

The first assumption is usually justified by the fact that the viscosity of air is about 50 times lower than that of water (Lide 1996), such that air may have very small or negligible resistance to flow relative to water. The assumptions implied by the use of the Richards equation may be reasonable in many cases, except when a soil becomes water-saturated and air contained in the pore space under the saturated region can become compressed under a wetting front. As liquid saturation increases, the air-filled porosity of a porous medium and its relative permeability to air become reduced. Resistance to air flow may become significant at higher water contents and in finer-grained porous media.

Consideration of coupled two-phase flow (of air and water) and non-isothermal conditions may be necessary when barometric pumping effects are significant (Massman and Farrier 1992), when biogeochemical reactions generate non-equimolar concentrations of partitioning species, such as $O_2(g)$ and $CO_2(g)$, so local gas pressures are affected (Rockhold et al. 2004), and/or when gas-phase diffusion and interphase exchange processes are thought to be important enough to warrant more rigorous mechanistic treatment owing, for example, to their effect on weathering or degradation of components of engineered or natural systems. Heat generated by the decay of radioactive materials may also influence moisture movement, but this should generally not be an issue for the low-activity solidified wastes destined for burial in the IDF.

Mechanistic modeling of coupled two-phase flow and reactive transport under non-isothermal conditions, which may be applicable to the near-field environment, involves other assumptions, some of which include:

1. Water flows in both liquid and vapor phases, and typically under non-isothermal conditions.
2. Driving forces are gravity, temperature, and water potential gradients in both liquid and gas phases, which can include so-called barometric pumping effects induced by fluctuations in atmospheric pressure, and solute or osmotic pressure effects (Cary and Taylor 1964).
3. Species concentrations or activities can affect bulk fluid properties (e.g., density, viscosity, interfacial tensions, vapor pressure, boiling and freezing points) and osmotic potentials (Pitzer 1987).
4. Concentration-dependent fluid properties in turn can affect the relative permeability-saturation-capillary pressure relations (k-S-p relations) of the porous media.
5. Precipitation/dissolution reactions can alter pore-size distributions and the porosity and permeability of the porous media (e.g., Cast Stone).

Motivation for using a more rigorous, mechanistic modeling approach to evaluate COC release and transport in the near-field environment around the waste packages includes the fact that initial conditions will likely be very far from equilibrium and species concentrations and activities will be relatively high. The equations associated with modeling coupled two-phase flow with non-isothermal conditions and reactive transport can capture non-linear feedbacks associated with process interactions and associated emergent phenomena. Such process interactions and feedbacks may be very important, but might not be apparent using conventional (single-phase flow and non-reactive transport) modeling approaches. For calculations of contaminant release from cementitious waste forms, several processes of potential importance are discussed in more detail below. The effects of some of these processes on PA calculation results can be anticipated or forecast. The effects of others may be less clear, owing to process interactions and feedbacks. We also note that many of the processes and effects discussed in subsequent sections may not have been given previous consideration because simulators capable of modeling these processes may not have been available in the past.

3.4.2.1 Osmotic Pressure Effects

Osmotic pressure effects are typically neglected when modeling single-phase water flow and non-reactive solute transport in variably saturated porous media using the Richards and advection-dispersion equations. This neglect stems from common assumptions that solute concentrations are low enough that the solute effectively behaves as a passive scalar relative to water, and that there is no (obvious) semi-permeable membrane in subsurface environments that would otherwise differentially affect the movement of solutes relative to water. These assumptions are not necessarily true for cementitious waste forms that have high concentrations of soluble species and small pore sizes. It has been shown, both theoretically and experimentally, that when dissolved species concentrations are high, and when water-filled pore sizes are small, the small pores can effectively behave as semi-permeable membranes, which can result in potentially significant osmotic pressure effects (Kemper 1961; Cary and Taylor 1964; Marine and Fritz 1981; Nobel 1991; Fakcharoenphol et al. 2014).

Marine and Fritz (1981) developed expressions to account for non-ideal membrane behavior for describing anomalous hydraulic heads observed in clay sediments at the SRS near Aiken, South Carolina. Osmotically-driven water flow has also been observed in experiments performed with cementitious materials being considered for waste disposal applications (Mattigod et al. 2001; CBP 2009). In general, it appears that osmotic pressure effects may need to be considered whenever there are high concentrations of dissolved species and materials with relatively small pore sizes, which would include cementitious waste forms. Such effects have not been previously considered in waste release calculations associated with earlier Hanford IDF PAs.

Osmotic pressure effects are expected to result in the increased imbibition of water from host sediments into the cementitious waste, or towards the waste form if the cementitious waste is already water-saturated and incapable of imbibing more water. Water accumulation at the interface between the waste and host sediment may then lead to preferential vertical flow below the zone of water accumulation that could ultimately result in earlier arrivals and higher peak concentrations, owing to transport along preferential local flow paths. Accounting for osmotic pressure effects is therefore expected to result in more conservative PA calculation results.

3.4.2.2 Vapor Pressure Lowering Effects

It is well known that the vapor pressure of a solvent (e.g., water) is lowered by the addition of a non-volatile solute to form a solution (Poling et al. 2001). The extent of vapor pressure lowering is proportional to the mole fraction of the solute(s). Vapor pressure lowering in the vicinity of materials with high solute concentrations (such as cementitious waste forms) would result in larger gradients in water vapor pressure that would increase the driving force for movement of water vapor from surrounding geologic materials toward the waste form. This effect cannot be represented using a single-phase modeling approach based on the Richards equation.

Weisbrod et al. (2002, 2003) investigated this phenomenon in the context of leaking underground waste storage tanks at Hanford. They performed experiments in thin-slab, sand-packed, light transmission chambers to quantify changes in aqueous saturation resulting from vapor stripping by saline fluids. Their experimental results and calculations suggest that over long periods of time, a significant amount of water can be delivered from native sediments into a brine plume by vapor transport. Similar results were reported for numerical studies performed by Pruess et al. (2000).

Moisture movement from native sediments toward cementitious waste packages by a vapor transport mechanism may also lead to the formation of wetted flow paths. Cementitious wastes will likely have very low permeability, but may be nearly fully water-saturated (Rockhold et al. 1993), depending on the cement hydration behavior. Therefore, there may be relatively little capacity for imbibition of additional water into the cementitious waste from the native sediments. However, as moisture accumulates at the interface between waste packages and native sediment, downward vertical migration of water may occur, and a wetted path may become established that results in preferential or so-called fingered flow below this interface (Weisbrod et al. 2002). Accounting for two-phase flow and vapor pressure lowering effects is therefore expected to result in more conservative PA calculation results relative to simpler models that do not account for these processes.

3.4.2.3 Effects of Changes in Fluid Properties on k-S-p Relations

Densities, viscosities, and surface tensions of high-salinity fluids in the immediate vicinity of cementitious waste forms in the vadose zone may be significantly different than those of pure water. Such differences affect the contact angles between fluid and solid phases, and consequently, the water-retention characteristics and relative permeability of the porous media (Weisbrod et al. 2009). These changes may tend to magnify the significance of fingered flow phenomena that are noted above.

Current PA modeling of both near- and far-field flow and transport behavior do not account for changes in fluid properties resulting from locally elevated fluid concentrations associated with cementitious wastes. The changes in fluid composition and associated k-S-p relations would tend to amplify the potential preferential flow effects noted earlier. In combination, the effects of these processes are expected to result in more conservative PA calculation results – namely, faster arrivals and higher concentrations of contaminants at the water table.

3.4.2.4 Precipitation of Salts

Osmotic pressure gradients and vapor pressure lowering effects will likely result in concomitant precipitation of previously dissolved salts (e.g., $CaCO_3$, $Mg(OH)_2$) in the material from which water is removed. Observations from half-cell diffusion experiments performed by Mattigod et al. (2001) indicated water movement from relatively dry backfill sediment into the concrete that was placed in contact with it, and precipitation of salts at the interface between the concrete and sediment. These, and the aforementioned effects, may also confound the interpretation of data used for determining effective diffusion coefficients from such experiments.

3.4.2.5 Changes in Porosity and Permeability

Precipitation of salts should in turn reduce the porosity and permeability of the porous media in which the salts precipitate. Since this behavior is most likely to occur at the interface between waste packages and surrounding geologic media, the result could be a sealing or armoring effect that actually increases the effectiveness of the waste package in minimizing release of contaminants into the environment. These types of feedback mechanisms, which have been observed, cannot be modeled without considering coupled two-phase flow and reactive transport processes. Inclusion of some of the aforementioned processes is expected to result in more realistic transport behavior that can be more protective than simplified PA calculations. The extent to which one process or set of processes may dominate over others is difficult to predict without performing experiments and/or modeling to evaluate their combined effects.

3.4.2.6 Redox-Sensitive Contaminant Behavior

The aqueous and surface complexation behavior, and associated mobility, of several of the contaminants of concern (e.g., Cr, ^{99}Tc) are dependent on the oxidation-reduction (or redox) state of the environment (Section 3.3.1.1). Conventional modeling of single-phase water flow using the Richards equation, and non-reactive solute transport using the advection-dispersion equation, do not account for gas-phase diffusion or pressure-induced gas flow resulting from barometric pressure fluctuations. However, both of these processes may have an important influence on subsurface concentrations of species, such as O_2 and CO_2, that partition between the gas and aqueous phases. Consequently, the redox conditions in the vicinity of the IDF waste packages, and associated contaminant mobility, would be more accurately represented using a two-phase flow and reactive transport modeling approach.

Oxidized forms of ^{99}Tc are typically mobile. Higher water contents or fully water saturated conditions within the cementitious waste would tend to limit gas phase transport, and thus minimize the oxidation of immobile reduced ^{99}Tc minerals. Accounting for two-phase flow, reactive transport, and diffusive mass transfer of O_2 and CO_2 in both the gas and aqueous phases can result in transport behavior that is more conservative or less conservative than assuming that ^{99}Tc is simply controlled by an “effective” diffusion coefficient.

The above considerations concerning physico-chemical processes, interactions, and assumptions associated with different types of models suggest that more detailed process-based modeling of two-phase flow and reactive transport processes for near-field modeling of cementitious waste forms would provide more realistic results. The extent to which more mechanistically-based model results might be more or less conservative relative to results obtained using single-phase flow and non-reactive transport models is difficult to determine a priori, owing to the potential for both conservative and non-conservative effects by different processes, and process coupling that may amplify certain effects. The water-air-energy operational modes of the STOMP simulator (White and Oostrom 2006) and its parallel counterpart eSTOMP, will solve coupled equations for heat and mass transfer through both air and water phases and coupled equations involving multicomponent mixtures that partition between fluid phases. Application of eSTOMP to evaluate some or all of the processes and effects noted above is recommended.

3.4.2.7 Dual-Porosity and Permeability for Cracked or Fractured Media

Crack formation in Cast Stone may occur because of geochemical and other processes that occur during curing and/or later in time following exposure of the waste form to local environmental conditions within the backfilled IDF trench. Such cracking or fracture formation may effectively result in the formation of a dual-porosity system in which the fractures and bulk porous matrix have different porosities, permeabilities, and associated transport characteristics. Under unsaturated conditions, the fractures or cracks could be devoid of water, depending on their sizes and the flow conditions. If the fractures or cracks are air-filled and interconnected, they could be conduits for gas-phase O_2 and CO_2 diffusion into the Cast Stone. If the cracks become water-filled at some point (e.g., if the surface infiltration cover is breached), cracks or fractures could become conduits for migration of COCs out of the Cast Stone.

Modeling of flow and transport through dual-porosity–permeability porous media can be accomplished in several different ways (Šimůnek et al. 2003; Gerke and van Genuchten 1993a, 1993b, 1996; Peters and Klavetter 1988). All modeling approaches require additional parameters to describe fracture properties such as densities, widths, orientations, surface areas, and first-order mass transfer coefficients, depending on model assumptions. Šimůnek et al. (2003) provided a review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. Although their emphasis is on natural vadose zone materials rather than on engineered materials such as Cast Stone, the methods they review are generally applicable.

At the simple end of the spectrum, dual-porosity and permeability can be represented using an equivalent continuum approximation with composite relative permeability–saturation–capillary pressure functions (Peters and Klavetter 1988; Durner 1994). This approach assumes capillary equilibrium between fractures and matrix, and has been used to model variably saturated flow through unsaturated fractured tuff at the Yucca Mountain site in Nevada (Peters and Klavetter 1988). The dual-porosity/permeability functions of Peters and Klavetter (1988) are also available in the STOMP simulator.

Dual-porosity and permeability can also be represented using separate flow and transport equations for each domain (Gerke and van Genuchten 1993a, 1993b, 1996). Since separate mass balance equations are solved for each domain, the pressures in the fractures and matrix can be different. Gerke and van Genuchten (1993a, 1993b) used this approach to model preferential flow and transport processes with first-order mass transfer terms to account for exchange of water and solutes between macropores (or fractures) and matrix. The macropores (or fractures) are not represented discretely in this approach, but rather, effective fracture properties are assumed for each type of porous medium and are applied on a bulk volume basis. This approach was implemented in an early (currently unsupported) version of the CO_2 operational mode of PNNL's STOMP simulator.

Modeling of discrete fracture networks has also been performed for fractured natural gas reservoirs (Robinson 1989; McKoy and Sams 1997). Effective permeabilities and diffusivities for porous and fractured media can also be estimated using a variety of other numerical methods, including continuous time random walk particle tracking (McCarthy 1995), the Lattice-Boltzmann method (Lichtner and Kang 2007), and Smoothed Particle Hydrodynamics (Tartakovsky et al. 2008). Several of these approaches may be applicable for determining effective flow and transport properties of cracked Cast Stone.

The effects of accounting for or neglecting possible crack formation will likely be most apparent when comparing results for different future scenarios. Fractured or rubblized waste packages will have larger surface areas, porosities, and permeabilities relative to intact cementitious waste. Accounting for these features and their effects on physical, hydraulic, and transport properties would likely lead to more conservative transport behavior (faster arrival times and higher peak concentrations for COCs) relative to not accounting for them.

3.4.3 Multicomponent Reactive Transport

3.4.3.1 Liquid-Phase Reactions

The principal chemical retention mechanisms for COCs in Cast Stone are adsorption and mineral precipitation. The principal COCs, ^{99}Tc, ^{129}I, Cr, and nitrate are often considered mobile and non-reactive in oxidized circumneutral pH settings. However, partitioning to the solid phase is typically non-zero, although relatively small (Bondietti et al. 1979).

COC Adsorption and Desorption

COC adsorption is controlled by the local geochemical conditions, which include the individual COC species concentrations, competing ion concentrations, the aqueous species charge, the surface charge on the adsorbent solid, pH, and complexing ion concentrations in solution and at the reactive surface. Furthermore, the COC adsorption reactions operate in the context of other controls on COC concentrations and geochemical conditions, including mineral reactions, transport, and events (e.g., waste form cracking).

Modeling the mechanistic detail of adsorption in natural sediments can be challenging because the natural variability in mineral surface reactivity is difficult to characterize. Adsorption/desorption modeling options range from the complex to the simple, with commensurate characterization requirements. In general, however, there are two basic approaches — multicomponent reaction networks and lumped-parameter models. In the reaction network approach, the behavior of the individual solution components is predicted using elementary reactions based on the law of mass action. While equilibrium constants for many elementary reactions have been catalogued as a function of temperature in thermodynamic databases (e.g., EQ3/6, NEA), adsorption reactions are typically developed specific to observations in the geochemical environment of interest. In general, the reaction network accounts for the speciation of the adsorbate as well as the adsorbent. Electrostatic models consider the variation in the surface charging environment that can be the result of pH changes (Dzombak and Morel 1990). This approach requires knowledge of the reactivity of each participating adsorbent solid phase. Non-electrostatic conceptual sorption models have been used to address bulk mineral assemblages, where it is difficult to identify the contribution of specific minerals to adsorption/desorption (Davis et al. 2004). In the non-electrostatic “bulk” adsorbent models, the standardized aqueous reactions and thermodynamics are coupled to surface complexation reactions, in which the adsorbent’s sorption sites’ stability constants are fit from bench-scale laboratory experiments.

Ion exchange models, unlike surface complexation models, assume the continuous occupation of all exchange/adsorption sites. The exchange capacity and selectivity coefficients for each exchangeable ion reaction are fit from experimental data, usually under the assumption of a bulk mineral assemblage. However, multisite ion exchange models can be employed in this fitting process to account for the affinity and capacitance associated with different mineral abundances and forms (e.g., edge sites).

Kinetics can be included through parameterized but thermodynamically consistent rate laws. The benefit of the multicomponent reaction network is that it can potentially address a wide range of geochemical controls on the adsorption/desorption (e.g., pH, alkalinity, Eh, competition for adsorption sites, site density). The challenge is to characterize not only the reactions, thermodynamics, and rates directly controlling COC mobility and transport, but also the auxiliary reaction processes not involving COCs that significantly affect the direct controls (e.g., pH, porosity, macro solute composition).

Mineral and biological reactions are typically modeled as kinetic reactions. A variety of rate laws of varying sophistication have been employed. The availability of equilibrium constants for reversible reactions allows for transition state theory type rate laws (Lasaga 1998), driven by “distance” from equilibrium, to be used. An important time-dependent update for the mechanistic modeling will be the effects of precipitation/dissolution reactions on changes in the porosity and permeability of porous media. Freedman et al. (2003, 2004) describe one approach to link changes in the mineral volume fractions with physical properties for flow and transport.

In contrast to the reaction network approach, the constant-K_d distribution coefficient model is the simplest, most commonly used, and least robust model for adsorption/desorption. The K_d coefficient (e.g., with units of mL/g), an equilibrated ratio of solid-associated concentration (e.g., μg sorbed adsorbate/g solid) to aqueous concentration (e.g., μg dissolved adsorbate/mL solution), is a lumped parameter that applies only to the geochemical conditions in which it was measured. It further assumes a linear relationship between equilibrated liquid and solid-associated adsorbate mass. It does not account for interactions with other chemical components (e.g., pH, competing ion concentrations) or processes (e.g., solubility reactions) in the system. This limits its applicability, especially if geochemical conditions are evolving (e.g., oxidation and carbonation reactions) in space and time. The COC-specific K_d is a simple lumped-parameter approach that is typically used in the high-level stochastic TSPA simulations. It is usually necessary to provide a temporal sequence of COC-specific K_ds to address the evolving geochemical conditions over the operational life of the repository.

Lumped-parameter COC-specific diffusion coefficients have also been used in high-level TSPA simulations to represent reaction processes (Section 3.1.2.1). ^{129}I is the least reactive of the principal groundwater risk-driving Cast Stone COCs, and therefore, is the most consistent with the diffusion process model (Section 3.3.1.2). Diffusion coefficients for I^- in water at infinite dilution may be obtained from standard references (Lide 1996; Flury and Gimmi 2002). As derived in Eq. 1 above in Section 3.1.1.5, the appropriate lumped effective diffusion coefficient (D_e) for a COC requires modifying the infinite dilute diffusion coefficient (D_f) with both a physical correction factor to account for the porosity, tortuosity, and constrictivity of the porous Cast Stone, and a chemical factor to account for any interaction with the Cast Stone solid phases. In practical use, the time-varying partitioning of iodine between Cast Stone solids and its pore water (aqueous phase) will need to be addressed using experiments and/or modeling to estimate a series of time-dependent diffusion coefficients.

3.4.3.2 Reactive Gases

Gas-phase components of interest include carbon dioxide (~0.04 vol% in atmosphere), oxygen (~21% in atmosphere), water vapor (~0.96% in atmosphere), and nitrogen (~78% in atmosphere). It should be noted that subsurface soil CO_2 gas concentrations may be substantially higher than atmospheric concentrations, owing to biogeochemical reactions. Nevertheless, near-atmospheric O_2 gas concentrations are expected in the vicinity of the IDF waste packages due to their proximity to the ground surface. Although nitrogen is typically assumed to be relatively inert, it must be accounted for when estimating gaseous diffusion coefficients in multicomponent mixtures (Hirshfelder et al. 1964; Whitaker 1986; Jaynes and Rogowski 1983).

3.4.3.3 Geochemical Modeling

In considering transport processes over long time scales, interactions among multiple reactive chemical components are clearly important. Single-substance lumped-parameter calculations that do not account for multi-species interactions (e.g., as a function of pH and pore water composition) cannot, in general, address evolving geochemical system behavior (CBP 2009). Therefore, multicomponent modeling that can account for the competitive effects and multiple factors affecting solid-liquid partitioning over different chemical forms is required for mechanistic modeling. Furthermore, while local thermodynamic equilibrium is an appropriate assumption for most reactions over long time scales, some chemical reactions proceed at very slow rates, especially some mineral precipitation/dissolution reactions. For these cases, the progress of reactions is kinetically controlled, and should be taken into account accordingly in modeling the disposal system.

The system of relevant chemical reactions, stability constants, and associated rate laws comprise a reaction network that can be solved with a multicomponent geochemical speciation model to calculate the compositions of solid phases consistent with their associated pore solution, which often is evolving with time. The pore solution composition can change as the result of continued hydration, or through the interaction with the subsurface disposal environment. Changes in the mineral assemblage or amounts of the phases affect the porosity and transport properties of the Cast Stone. This approach can be used to evaluate the effects of multiple degradation mechanisms occurring simultaneously, provided thermodynamic data for the relevant solid, aqueous, and gaseous phase chemical reactions are available.

Thermodynamic and Adsorption Databases

The accuracy of the multicomponent reactive transport modeling approach is dependent on a comprehensive characterization of the starting material and the subsurface disposal environment, as well as the availability of comprehensive thermodynamic and kinetic data for the key reactions. A critical requirement for the physico-chemical reactive transport modeling is accurate thermodynamic data for the relevant cement species and mineral phases. There are well-known databases with specialization for cement (e.g., Matschei et al. 2007). Thermodynamic databases provide reference reactions, stoichiometry, and temperature-dependent stability constants that are used to build the reaction networks for predicting equilibrium species and mineral phase assemblages in cementitious materials. The solid-phase assemblage in the cementitious (paste) fraction of cementitious materials is for the most part responsible for the mechanical, hydraulic transport, and chemical properties of these materials. The thermodynamic data are used to determine the type and quantity of mineral phases dissolved or precipitated. These databases are extensive, but not exhaustive; in particular, gaps in the thermodynamic data for supplementary materials like fly ash, BFS, and degradation-produced materials need to be determined or defensibly estimated, as well as reactions involving the key COCs.

Kinetics

It is important to remember that thermodynamic data (i.e., stability constants) differ from kinetic data. The thermodynamic data will yield mineral composition at equilibrium, which may not occur until after a significant period of time. Kinetic coefficients are used in rate laws to determine reaction rates for non-equilibrium conditions. Few, if any, kinetic data exist for mineral phases relevant to cementitious systems. Over very long time scales, performance will be controlled by the properties of the very-low-solubility minerals, which are the minerals that will most likely have the slowest reaction kinetics.

3.5 eSTOMP Cement Benchmark Simulation

Numerical simulation provides a framework to systematically and quantitatively integrate the 1) characterized properties for waste form, waste package, and sediments; 2) identified system of reactions, thermodynamics, and rates; 3) knowledge from laboratory and field experiments; 4) required flow, transport, and multicomponent reaction processes; and 5) subsurface conditions to predict the degradation of Cast Stone and the release of COCs for 10,000 years or more. In the context of the hierarchical modeling strategy pyramid (Figure 3.6), the simulation of coupled mechanistically detailed processes supports the higher-level stochastic Cast Stone IDF TSPA modeling. Capabilities needed include 3-D, multiphase (gas and liquid) flow, dual-porosity modeling for fractures and matrix, and multicomponent reactive transport with feedback to flow due to changes in mineral volume fractions. For the most comprehensive and detailed 3-D coupled-process field-scale modeling scenarios, single-processing-node workstations will not be able to address the large memory and computational requirements.

eSTOMP can address the required process and property detail via massively parallel processing. This capability enables more realistic representations of the conceptual model without compromises on dimensionality, resolution, process, and property detail to make the run times tractable. In this respect, eSTOMP is among the most powerful simulation capabilities in the subsurface science and engineering community (Steefel et al. 2014).

eSTOMP is in the process of being NQA-1 qualified, including the development of an updated user manual. While there are several fundamental verification tests that demonstrate that individual process models in eSTOMP are working properly, benchmarking provides a means to establish the accuracy of simulators for realistically complex coupled process applications. We describe the eSTOMP application to a cracked cement degradation benchmark problem (Perko et al. 2015) that includes many processes, properties, and conditions discussed in previous sections of this report—cement mineralogy, high-pH pore fluids, cement degradation from decalcification reactions, and the impact of cracking on the degradation process.

3.5.1 Degradation and Leaching from a Cracked Cementitious Waste Form

This benchmark set developed by Perko et al. (2015) involves leaching from a cracked, hardened cementitious waste form similar to scenarios described in Section 3.3. Infiltration of ambient pore water, which is in strong disequilibrium with the cement mineralogy, leaches calcium from the hardened cement paste, resulting in the dissolution of cement minerals. In this two-dimensional reactive transport case, the dissolution of cement minerals progresses heterogeneously as a consequence of a small crack within the domain (Figure 3.9).

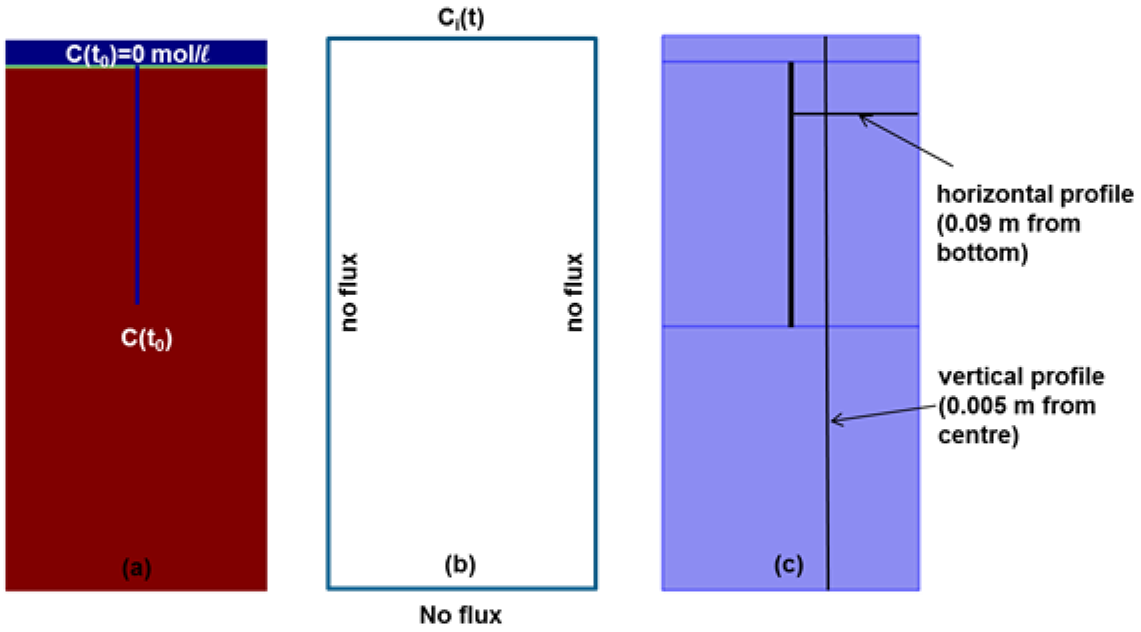


Figure 3.9. (a) Initial and (b) Boundary Conditions for the Tracer Case (Case 0); (c) Shows the Two Required Profiles

The modeling input includes physical properties (e.g., porosity, tortuosity, and diffusion coefficients) (Table 3.16), thermodynamic properties for the mineral and complexation reactions (Table 3.17), and initial and boundary conditions (e.g., volume fraction, pH, and major ions) (Table 3.18).

Table 3.16. Physical and Transport Properties for Presented Modeling Cases

Parameter	Symbol	Unit	Value
Free water diffusion coefficient	D_0	m^2/s	10^{-9}
Porosity top layer	θ	-	0.3
Porosity cement	θ	-	0.1
Porosity crack	θ	-	1
Tortuosity top layer	τ	-	0.0383
Tortuosity cement	τ	-	0.0383
Tortuosity crack	τ	-	1

Table 3.17. Thermodynamic Parameters for Cement Minerals

Phase	Formula	log K
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O = 6Ca^{+2} + 2Al(OH)_4^- + 3SO_4^- - + 4OH^- + 26H_2O$	-44.9085
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}:26H_2O = 6Ca^{+2} + 2Al(OH)_4^- + 3CO_3^- - + 4OH^- + 26H_2O$	-46.5085
Stratlingite	$Ca_2Al_2SiO_2(OH)_{10}:3H2O = 2Ca^{+2} + 2Al(OH)_4^- + 1SiO(OH)_3^- + OH- +2H_2O$	-19.7042
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}:5H_2O = 4Ca^{+2} + 2Al(OH)_4^- + CO_3^- - + 4OH^- + 5H_2O$	-31.4726
Hydrotalcite-OH	$Mg_4Al_2(OH)_{14}:3H_2O = 4Mg^{+2} + 2Al(OH)_4^- + 6OH^- + 3H_2O$	-56.0214
Hydrotalcite-CO_3	$Mg_4Al_2(OH)_{12}CO_3:3H_2O = 4Mg^{+2} + 2Al(OH)_4^- + CO_3^- + 4OH^- + 3H_2O$	-51.142
Calcite	$CaCO_3 = Ca^{+2} - H_2 + HCO_3^-$	1.84897
Portlandite	$Ca(OH)_2 = Ca^{+2} + 2H_2O - 2H^+$	22.79937
CSH(1.6)	$Ca_{1.6}SiO_{3.6}:2.58H_2O + 3.2H^+ = 1.6Ca^{+2} + Si(OH)_4 + 2.18H_2O$	28.002
CSH(1.2)	$Ca_{1.2}SiO_{3.2}:2.06H_2O + 2.4H^+ = 1.2Ca^{+2} + Si(OH)_4 + 1.26H_2O$	19.301
CSH(0.8)	$Ca_{0.8}SiO_{2.8}:1.54H_2O + 1.6H^+ = 0.8Ca^{+2} + Si(OH)_4 + 0.34H_2O$	11.050
$Pb(OH)_2$	$Pb(OH)_2 + 2H^+ = Pb^{+2} + 2H_2O$	8.15

Table 3.18. Solution Composition for the Different Cases. $c(t_0)$ is the initial concentration in the cement region and the crack. $c_0(t_0)$ is the initial concentration in the 5 mm top layer. $c_B(t)$ is the upper boundary solution composition.

Case	Initial & Boundary Concentration	Tracer	pH	Pe	pO_2	Nitrate	Ca
0	$c(t_0)$	$1.035 \cdot 10^{-3}$	-	-	-	-	-
	$c_0(t_0), c_B(t)$	0	-	-	-	-	-
1	$c(t_0)$, $c_0(t_0)$	-	12.48	11.54	-0.68		$1.948 \cdot 10^{-2}$
	$c_B(t)$	-	3			$1.035 \cdot 10^{-3}$	-

The eSTOMP-predicted aqueous concentrations are in excellent agreement (Figure 3.10) with the results from the other simulators for tracer transport after 100 days, as well as aqueous chemistry (pH, Ca++) after 100 years along a vertical transect near the crack. The eSTOMP-predicted spatial distribution of portlandite in the vicinity of the crack is also in agreement, in both geometry and concentrations, with the other simulators (Figure 3.11).

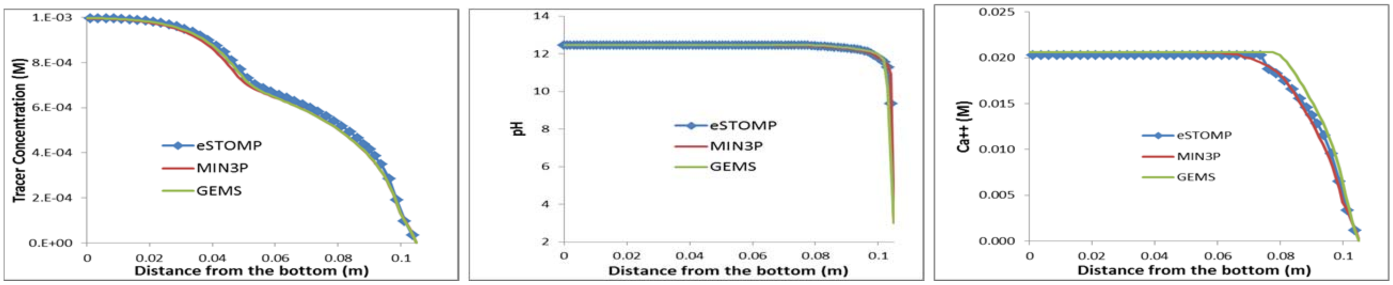


Figure 3.10. Comparison of Dissolved Tracer at 100 Days, pH and Ca^{++} Concentrations after 100 Years Along Vertical Cross-Section x=0.005 m. Unpublished eSTOMP simulation results courtesy of Yilin Fang and Steve Yabusaki.

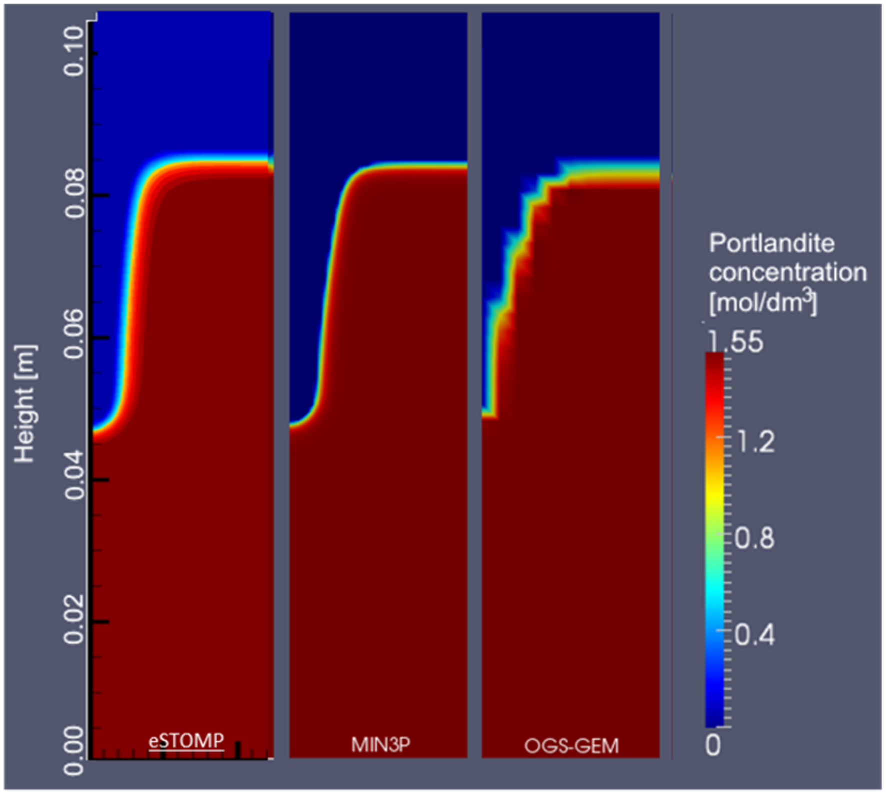


Figure 3.11. Portlandite Concentration Fields at 100 Years for Case 1. All x-axes extend from 0 m (center) to 0.025 m (side). Unpublished eSTOMP simulation results courtesy of Yilin Fang and Steve Yabusaki.

The simulation of relevant and realistically complex benchmark problems is especially important to the qualification of coupled-process simulators if they are to be used for the IDF PA. Cement-based benchmarks requiring varying degrees of sophistication are now available, developed primarily in collaboration with international teams who are involved in safety assessments of subsurface radioactive waste repositories. Members of the eSTOMP modeling team have convened and participated in the development and publication of these benchmarks through a series of Subsurface Environmental Simulation Benchmarking (SSBench) workshops (Berkeley 2011, Taipei 2012, Leipzig 2013, Cadarache 2014) that include modeling teams from Australia, Belgium, Canada, China, France, Germany, Korea, Netherlands, Spain, Switzerland, Taiwan, and the U.S. (Steefel et al. 2014). A special issue of the Journal of Computational Geosciences will be published in 2015 with this and other benchmarks, several of which are relevant to the Cast Stone IDF PA.

4.0 Key Parameters Needed for Modeling the Performance of Cast Stone

In this section we summarize the key parameters that need to be measured or estimated in a technically defensible fashion. The list of parameters may not be all-inclusive for the most detailed mechanistic models, but in general, are considered “necessary” for modeling the release of key groundwater risk-driver COCs.

4.1 Material Properties

Cast Stone waste form properties are being determined by PNNL and SRNL in ongoing or newly proposed experimental efforts. The sensitivity of model predictions to changes in the waste package properties (e.g., fracture-induced changes in surface area, porosity, and permeability) and associated release characteristics will be evaluated using sensitivity cases until direct measurements become available. Evolving properties of the waste package and disposal facility, such as fracturing and porosity and permeability changes due to precipitation/dissolution reactions, will need to be considered in the sensitivity analyses. For example, the Cast Stone waste package may be subject to fracturing or crack formation resulting from chemical reactions such as sulfate-induced post-hydration ettringite formation, which could result in the swelling and cracking of the waste form.

4.2 Waste Form Properties

The characterization and quantification of physical flow and transport properties in the Cast Stone waste form is critical because these processes govern the 1) influx of reactive gases [i.e., oxygen (O_2), carbon dioxide (CO_2), water vapor (H_2O)] into the waste form, 2) influx of external water chemistry, 3) access of liquid- and gas-phase components to reactive surfaces, and 4) conveyance of dissolved contaminants out of the waste form.

An important issue is the characterization and modeling of Cast Stone cracks and fractures. In contrast to the low permeability of the intact Cast Stone matrix, cracks and fractures can provide the principal flow paths through the waste form, if present. Flow modeling techniques to address the presence of fractures range from the specification of discrete fracture geometry using Navier-Stokes equations to treatment as equivalent porous media based on Darcy’s Law requiring hydraulic conductivities for fractures and matrix.

4.2.1 Fluid and Flow Properties and Conditions

In general, the principal fluid properties are density, dynamic viscosity, surface tension, and compressibility. Note that significant compositional effects on the fluid properties must be addressed by an equation of state compositional model. Liquids are generally assumed to be incompressible fluids and gases are assumed to be compressible fluids. Liquids are only compressible when they are highly pressurized, and the compressibility of gases may be disregarded whenever the change in pressure is very small.

The principal flow-modeling parameters for the waste form are the absolute permeability, porosity, and saturation functions. Saturation and relative permeability are functions of the capillary pressure, which is the difference between the gas-phase and liquid-phase pressures. Standard saturation functions include the van Genuchten and Brooks-Corey functions, which have fitting parameters. The initial and boundary conditions for liquid and gas phases include pressure, saturation, and source/sink terms.

4.2.2 Transport Properties and Conditions

The principal physical transport properties required to model release from the Cast Stone and surrounding "waste package" components are the porosity, bulk density, tortuosity, molecular diffusion coefficients (including COC-specific values), and dispersivities. An important distinction that should be investigated is the fraction of Cast Stone porosity participating in transport and the fraction that is not (i.e., porosity from disconnected pores). The transport porosity is further divided into fractions for advective and diffusive transport, for diffusion only, and controlled by the electrical double layer.

Depending on the operational mode, STOMP uses different equations of state (e.g., Redlich and Kwong 1949; Peng and Robinson 1976) to determine phase partitioning of components. Effective diffusion coefficients for a variably saturated porous medium can be defined in various ways, such as:

$$D_{i,\gamma}^{eff} = D_{i,\gamma}^{mol}\left(\frac{\theta_{\gamma}^{a}}{\emptyset^{b}}\right) \qquad \text{Eq. 2}$$

where i = chemical component (e.g.,, O_2 or CO_2)
γ = fluid phase (gas or aqueous)
a and b = empirical parameters
θ = volumetric water content
ϕ = porosity.

Millington and Quirk (1960) used empirical parameters a = 2 and b = 2/3, while Millington and Quirk (1961) used a = 10/3 and b = 2. Moldrup et al. (2000) evaluated several data sets for gas diffusion in repacked soils, and determined that overall, the data were best represented using a = 2.5 and b = 1. Other expressions for effective diffusion coefficients that include residual water content or irreducible saturation terms have also been proposed (Olesen et al. 1996).

4.2.3 Reaction Parameters and Conditions

The lumped-parameter partitioning models require COC-specific K_ds with COC initial and boundary concentrations. For the mechanistic multicomponent reaction process modeling, the requirements include reaction stoichiometry, thermodynamic stability constants, rate law parameters, and initial and boundary conditions. Thermodynamic databases cover most of the reactions and thermodynamics. Reaction rates and adsorption/desorption reactions are typically situation-specific and empirically determined.

4.3 Measures of Release (IAEA, 2002)

To evaluate contaminant release rates and mechanisms, the following parameters need to be experimentally determined. Various types of experiments, ranging from laboratory- to field-scale, can be employed. Data obtained during the retrieval of waste packages from field experiments, as well as natural analogue studies, can also be useful in understanding release mechanisms.

4.3.1 Leaching Rate

The release of radionuclides from the waste package is often expressed in the form of the Incremental Fractional Release (IFR) or Cumulative Fractional Release (CFR). The IFR is the amount of contaminant released between experimental measurements normalized to the initial inventory of the contaminant in the waste form. The fractional leaching rate is the IFR divided by the time between measurements. The leaching rate is measured by standard leaching tests, such as ANS 16.1 or ISO 6961. The CFR is the ratio of the total amount released over all time up to the current sampling divided by the initial inventory in the waste form. The CFR is the sum of all IFRs, and is another measure of the capability of the waste form to retain contaminants. Fractional release rates can be translated into mass release rates using the radionuclide-specific inventory and surface area of the waste form.

4.3.2 Diffusion Coefficient

The migration of radionuclides from many waste forms is controlled by the diffusion process. Effective (empirical lumped-parameter) diffusion coefficients can be determined experimentally by means of measuring steady-state movement through porous samples, or by measuring diffusion into or out of a sample. For example, diffusion experiments with tritiated water either being used to prepare solid waste forms or for immersing a porous solid in a reservoir containing the tritiated water have been used to provide a conservative estimate for diffusion coefficients of other contaminants.

In developing an understanding of leach tests results, it is important to take into account the scale factor. The surface area-to-volume of the waste form has been found to be the appropriate scale factor for diffusion-controlled processes. The larger this ratio, the larger the IFR, if all other parameters are the same.

Field experiments often provide results that do not correspond directly to those obtained in the laboratory. This may be related to scale issues, as the field tests often use full-size waste forms. However, it is more likely to be due to the different and often-times varying environmental conditions in the field as compared to the more controlled conditions prescribed in standardized tests.

4.3.3 Distribution Coefficient (K_d)

Some COCs are sorbed on the waste form matrix, which delays their release. The distribution coefficient is a measure of the sorption selectivity of the material for a given COC. It is often experimentally determined from a mass balance of the amount of contaminant on the waste material divided by the concentration in the water contacting the solid at steady-state.

The distribution coefficient, K_d, is typically measured using steady-state, batch sorption methodology. More reactive (sorptive) COCs have higher distribution coefficients.

4.3.4 Dissolution Rate

The dissolution rate is an experimentally determined measure of the rate of reactions that dissolve the waste form minerals. Characterization involves the determination of the COC concentrations associated with the mineral phases of the waste.

4.3.5 Solubility Limit

The release rate of some contaminants is controlled by their solubility limits in the given aqueous environment. For example, some COCs will have low solubility in a cementitious environment. The determination of COC solubility must also take into account the fact that some COC mass may be bound to sorption sites on waste form/package minerals (e.g., waste form matrix, container corrosion products, and nearby backfill) as a function of the repository conditions (e.g., pH, Eh, water composition). Solubility can be determined experimentally or calculated using geochemical speciation codes, provided that the necessary thermodynamic stability constants are known for all relevant reactions.

Determining a solubility limit can be difficult. When using a geochemical speciation model to calculate solubility, uncertainty often exists as to whether the proper geochemical conditions are being modeled. When determining solubility limits experimentally, this is often analytically challenging due to low concentration levels and the possibility of sorption reactions confounding the experiment. Also, there can be uncertainty over the representativeness of the experimental conditions for the range of expected environmental conditions in the overall time history of the disposal unit. This is an important issue because solubility can change by orders of magnitude depending on chemical conditions.

5.0 Contaminant Release Data Test Methods

The general IDF Cast Stone PA strategy is heavily invested in the development of models that are capable of representing the processes, properties, and conditions controlling the release and transport of COCs for >10,000 years. In the context of near-surface disposal, the two major functions of the waste package are its physical durability and its leach resistance. An important part of the technical basis for understanding waste package performance is a robust testing program. In this approach, experimental studies are necessary and indispensable for characterizing COC behavior, waste form properties, and backfill conditions. This program may involve laboratory tests, field tests, and analogue studies. It is important for the tests/analogues to provide data that help in understanding the long-term behavior under the anticipated IDF disposal conditions. However, it is recognized that these studies cannot fully account for the evolving conditions that govern the release and transport of COCs over the operational length and time scales of the IDF. Consequently, another objective of the Cast Stone modeling strategy is for the mechanistic modeling to provide a critical link between the short-term understanding from laboratory and field tests, and the prediction of performance over repository time frames and scales. Characterization studies and experiments should therefore be carefully designed to permit the appropriate scaling in the models.

Waste package testing can have many objectives, including the screening of candidate Cast Stone liquid waste-dry blend recipes under a range of conditions, providing characterization data to determine fundamental mechanisms that control performance, demonstrating compliance with WAC, and verifying solidification process control. The type, quality, and quantity of data will be dependent on the objectives. From a safety assessment perspective, the main purpose of waste package testing is to demonstrate post-closure safety; hence, waste package data and testing should be focused on safety assessment needs (in particular, source term evaluation). Research investigations are used to evaluate the fundamental mechanisms for contaminant release.

Here we focus on test methods and approaches that may be applied for the assessment of waste package behavior and performance. It should be recognized, however, that some experimental testing protocols enforce predetermined process conceptualizations (e.g., measuring effective diffusion coefficients and K_ds) for situations that may be governed by other processes. Bondietti et al. (1979) point out that "although K_d values, which define the partitioning of the element between solid and solution, are convenient in chromatographic-type models of radionuclide migration through porous media, they do not necessarily reflect the nature of radionuclide-rock interactions. In fact, for many hydrolytic species including the reduced forms of Tc, Np, and Pu, their solubility-related characteristics may be more reflective of the true controls on maximum solution concentrations."

5.1 Effective Diffusion Coefficients

Cast Stone monoliths are generally subjected to EPA Method 1315 to estimate the effective diffusion coefficient of the target contaminants leaching out of the waste forms.

5.1.1 EPA Method 1315

The EPA Method 1315 (Mass Transfer Rates of Constituents in Monolith or Compacted Granular Materials) is a semi-dynamic leach experiment that consists of submerging a monolithic sample (with a fixed geometry) in a leachant (often DI water or synthesized vadose zone pore water) at a fixed liquid volume-to-solid surface area ratio, and sampling at fixed periods of time (EPA 2009). A schematic of this process is shown in Figure 5.1. The simulated vadose zone pore water is often used because it is more relevant to the long-term burial environment in the IDF subsurface. This method is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic or compacted granular material, under diffusion-controlled release conditions, as a function of leaching time.

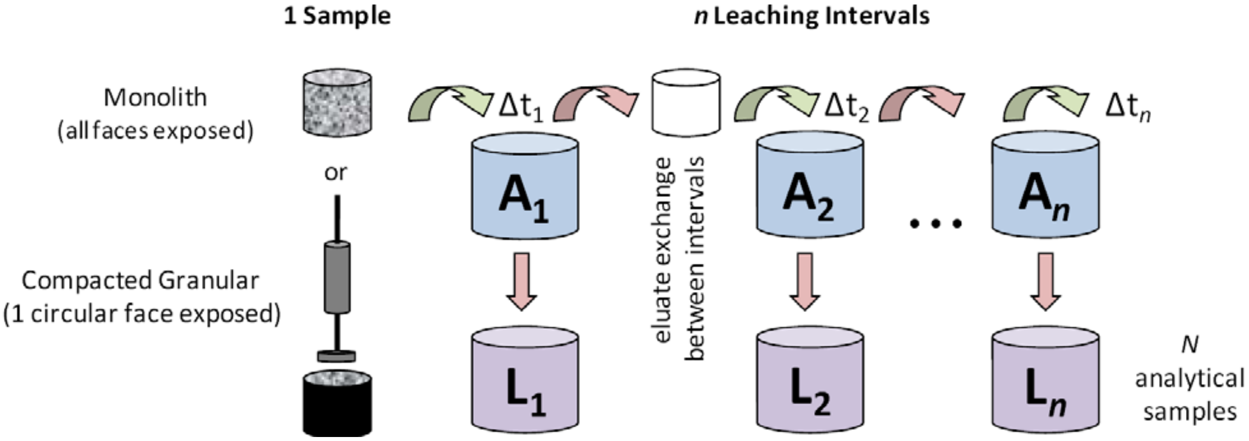


Figure 5.1. Schematic of 1315 Test Method (EPA 2013a)

The geometric surface area is used in this test method and calculated based on the cylindrical dimensions of the Cast Stone monolith, which in current testing are right cylinders with dimensions of 2-inch diameter by 4-inch height. The fixed liquid volume-to-solid surface area ratio is 9 ± 1 mL of leachant/cm^2 of solid sample geometric surface area. At each predetermined leaching interval, test vessel mass is recorded, and the leaching solution is changed. The cumulative leaching times at which solution exchanges are performed are: 0.08, 1, 2, 7, 14, 28, 42, 49, and 63 days, but for long-term PA reasons, leach testing is often continued well beyond 63 days. That is, the time period for leaching the monoliths may be extended out beyond 63 days to continue collecting long-term leaching data. Leachate samples collected during these intervals are used to measure pH; after filtration, the samples are used to measure the major cations, anions, alkalinity, and COCs.

The observed effective diffusivity for each constituent is calculated using the analytical solution for Fick's 2nd Law using Eq. 3, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

$$D_i = \pi \left[\frac{M_{t_i}}{2\rho C_o \left(\sqrt{t_i} - \sqrt{t_{i-1}} \right)} \right]^2 \qquad \text{Eq. 3}$$

where
D_i = observed diffusivity of a specific constituent for leaching interval, *i* (m^2/s)
M_{ti} = mass released during leaching interval *i* (mg/m^2)
t_i = cumulative contact time after leaching interval, *i* (s)
t_{i-1} = cumulative contact time after leaching interval, *i-1* (s)
C_o = initial leachable content (mg/kg)
ρ = Cast Stone dry bulk density ($kg\text{-}dry/m^3$).

The mean observed diffusivity for each constituent can be determined by taking the average of the interval observed diffusivity with the standard deviation. If more than 20% of the mass of a given constituent of interest leaches from the cylindrical monoliths, effective diffusivity corrections (to account for depletion of the mass of the leaching constituent) recommended by the ANS16.1 protocol can be used.

This method is similar to ANSI/ANS16.1 (see ANS 1986) and ASTM C1308-08, but the leaching intervals are modified, and the process of mass transfer can be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling. Mattigod et al. (2011) have shown that these three monolith leach test methods yield the same effective diffusion coefficient over time periods of 91 days for Cast Stone monoliths containing several secondary waste simulants.

5.2 Liquid-Solid Partitioning as a Function of pH

5.2.1 EPA Method 1313

Cast Stone specimens are often subjected to EPA Method 1313 to determine the liquid-solid partitioning of the target contaminants as a function of pH. EPA Method 1313 (Liquid-Solid Partitioning as a Function of Extract pH) is a static test method in which a set of parallel extraction experiments are conducted in dilute acid- or base-laden DI water at fixed pH values (pH range from 4 to 12) and a fixed liquid-to-solid ratio (10 mL/g) (EPA 2009a). Prior to initiating the static test, a series of pre-titrations are conducted at a fixed liquid-to-solid ratio (10 mL/g) using <0.3-mm sized crushed material. After a 24-hour period of mixing in the absence of acid or base additions, the sample slurry is centrifuged, and the supernatant is removed and used to determine the equilibrated pH. Since the measured pH values of the leachate solutions for Cast Stone are normally high (pH ~12 to 13), a pre-titration was developed based upon dilute HNO_3 additions to decrease the pH from 12 to lower targeted values after 24 hours of equilibration. Analytical-grade HNO_3 is used to prepare a solution of 2N HNO_3 for these experiments. Based upon the pre-titration results, test samples are prepared by mixing 10 g of <0.3-mm sized material with a predetermined amount of 2N HNO_3, and bringing the samples to volume with DI water. All samples are then placed on a platform shaker and allowed to mix at room temperature (23 ± 2 °C) for 24 hours. After mixing, the extractant vessels are centrifuged (minimum at 4000 ± 100 RPM) for 10 ± 2 minutes, and the decanted clear supernatant (~5 mL) is used to measure the solution pH, electrical conductivity, and redox potential. The remaining solution is then filtered using a 0.45-µm polypropylene membrane syringe filter and submitted for additional chemical analyses (Pierce et al. 2010b).

5.3 Intrinsic Permeability or Saturated Hydraulic Conductivity

Several methods have been reported for measuring the intrinsic permeability or saturated hydraulic conductivity of concretes (Rockhold et al. 1993; Phifer 2014; Jones & Grasley 2009). The three methods are: hollow flow-through, hollow dynamic pressurization, and flexible wall permeameter. One of these methods will be used to measure hydraulic conductivity of cured Cast Stone based on which method is expected to yield the most accurate hydraulic conductivity given the expected range of values.

5.3.1 Hollow Flow-Through Test

The hollow flow-through test (see Figure 5.2) for measuring hydraulic conductivity or permeability involves using a material specimen of cylindrical shape with an axial hole down the center of the specimen. The hollow cylinder is subjected to a hydrostatic fluid pressure on the outer radial face, while the inner radial face is subjected to a much lower pressure (roughly atmospheric pressure). The result of the pressure gradient is that fluid flows through the pore structure from the outer face to the inner axial hole. The rate of pore fluid flux into the center hole is measured, and once steady-state is achieved, is utilized to determine the permeability of the sample. The ends of the hollow cylinder are sealed to prevent moisture intrusion. The radial flow-through test allows for much higher pressure gradients to be applied without the risk of damage (Jones & Grasley 2009).

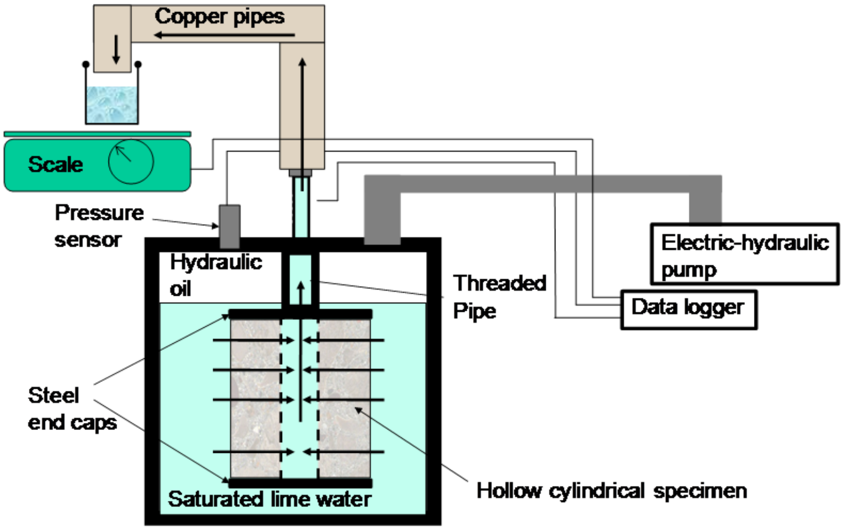


Figure 5.2. The Radial Flow-Through (RFT) Apparatus that Pressurizes the Outer Surface of a Sample and Monitors the Fluid Volume that Flows Through as a Function of Time

The flow can be measured either by a float attached to an LVDT (linear variable differential transformer) (Figure 5.2), or by measuring the rate of the mass of water flowing out using a weighing scale. The choice of fluid to use in the test can influence the measured permeability. It is recommended that a solution that closely simulates Cast Stone pore water be used to minimize reactions such as solid-phase dissolution or precipitation. For a hollow cylinder with a constant pressure, P_{out}, applied to the outer radial surface and negligible pressure applied to the inner radial surface, the hydraulic conductivity can be obtained as:

$$k = \frac{q\eta_L \ln[R_0 / R_i]}{2P_{out}\pi h} \qquad \text{Eq. 4}$$

where R_0 = the outer radius of the hollow cylinder
R_i = the inner radius of the hollow cylinder
h = the height of the hollow cylinder
q_r = the radial component of the flow rate (dimensions of volume/time)
η_L = the pore fluid viscosity.

The fluid flow rate, q_r, is determined by fitting the slope of the steady-state outflow volume through the center of the hollow cylinder as a function of time.

5.3.2 Hollow Dynamic Pressurization Test

The hollow dynamic pressurization test is based on the principles of poromechanics (Figure 5.3). A fluid- (e.g., water) saturated porous, hollow cylinder specimen is subjected to a sudden increase in fluid pressure at both the inner and outer radial surfaces. The immediate response to this increase in boundary pressure is a volumetric contraction of the cylinder. However, the cylinder will quickly begin to re-expand because the pore fluid pressure within the core of the sample is low in comparison to the boundary fluid pressure. This pressure gradient causes fluid to flow from the radial surfaces into the specimen, which causes the internal pore fluid pressure to increase, and thus the specimen to re-expand. The rate of re-expansion is directly dependent on the rate of fluid flow within the pore network, and is thus directly related to the material permeability. By fitting the re-expansion, one can determine the permeability of the specimen being tested. The permeability is calculated as (Jones & Grasley 2009):

$$k = \frac{\eta_L (R_0 - R_i)^2}{\tau}\left(\frac{\beta b^2}{K_p} + \frac{1}{M}\right) \qquad \text{Eq. 5}$$

where β = material property
b = Biot coefficient
M = Biot modulus
K_p = the bulk modulus of the porous body
τ = the sole fit parameter.

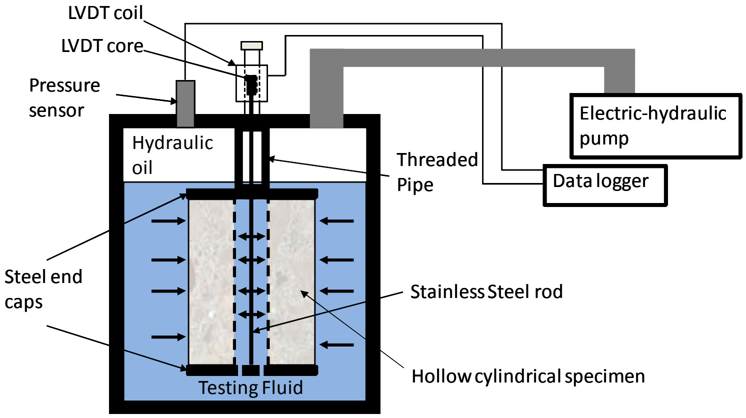


Figure 5.3. The Hollow Dynamic Pressurization (HDP) Apparatus where the Specimen is Pressurized from Both the Inner and Outer Surfaces

5.3.3 Flexible Wall Permeameter (ASTM D5084)

Based on the application of the Darcy flow equation to a sample of uniform cross-sectional area, ASTM D5084, *Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a* Flexible *Wall Permeameter* (ASTM D5084-10), is the standard test method currently used by the industry for the determination of laboratory hydraulic conductivity. ASTM D5084 generally consists of two different methods—falling-head and constant-head. In the constant-head method, the hydraulic conductivity (*k*) is calculated as follows:

$$k = \frac{\Delta Q \cdot L}{A \cdot \Delta h \cdot \Delta t} \qquad \text{Eq. 6}$$

where ΔQ = the quantity of flow for a given time interval Δt
L = the length of the sample
A = is the cross-sectional area of sample
Δh = the average head loss across the sample, i.e., constant hydraulic head difference.

To prevent undue influence of large aggregates on saturated hydraulic conductivity results, ASTM D5084 requires that the sample diameter and height each be at least six times greater than the largest particle size within the sample. For Cast Stone waste forms, no aggregate is added such that the largest particles in the dry blend are likely fine-sand sized.

With the help of a modified constant-head method, Rockhold et al. (1993) measured saturated hydraulic conductivity (k) values on concrete and grout samples using the Ruska permeameter, which is a constant-head device that confines small samples under relatively high pressures. The hydraulic conductivity was calculated using Eq. 6, in which the Δh equals the difference between the applied pressure and atmospheric pressure.

Yu et al. (1993) reported constant-head method-measured k values on SRS E-Area vault concrete. The saturated hydraulic conductivity testing of their cementitious samples was conducted on samples pressure-saturated for a week with either tap water or a brine solution. After saturation, the samples were mounted in an epoxy coating to prevent bypass flow. It is assumed that the samples were mounted in a horizontal orientation. Either tap water or the brine solution was injected into the sample at a constant upstream pressure of 50 psi, and the flow rate out of the sample was measured until the flow rate essentially obtained a steady-state.

Dixon and Phifer (2010) reported saturated hydraulic conductivity measurements on SRS E-Area vault concrete using the falling-head method; they obtained results with poor accuracy. The test was conducted on 5.7-inch diameter by 5-inch tall cores using ASTM D5084 method F (constant volume-falling-head (by mercury), rising tailwater elevation). The test was conducted at gradients less than 22.5 over time periods of less than 3 days, which resulted in a total outflow that was significantly less than 1 mL.

5.3.4 Drying Laboratory Test

The drying laboratory test is a modification of ASTM C1585-13, *Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes* (ASTM C1585-13). The drying laboratory test consists of periodically weighing initially saturated samples as they are dried under constant relative humidity (50%) and temperature (23 °C) conditions. The test involves exposing two series of initially saturated samples (10 mm and 50 mm thickness) to a constant 50% RH. The 10-mm series test is used to determine the equilibrium water content at the tested relative humidity, while the 50-mm series test is directly used to estimate the intrinsic permeability. The mass of the samples is monitored for the duration of the test. When equilibrium is reached for the 10-mm series, the test is terminated. According to the drying test method, equilibrium of 10-mm-thick specimens is considered to be reached when four successive mass changes determined at intervals of seven days exhibit less than 0.5% of the cumulative mass loss. The mass loss of the 50-mm series is then analyzed with the moisture transport model developed by SIMCO Technologies to yield the intrinsic permeability (Phifer 2014). Briefly, the test was performed in a climate chamber. The test specimens were saturated before being tested. The round side surface of each specimen was sealed with epoxy, while the two flat surfaces remained uncoated (see Figure 5.4).). The specimens were weighed periodically during testing. The cumulative mass loss was determined and plotted against test duration. Permeability was then analyzed through simulations based on the recorded mass loss in the 50-mm-thick specimens, equilibrium water content, and other material parameters such as tortuosity, porosity, and isotherms. The STADIUM® MTC laboratory module uses the moisture transport model in STADIUM® to analyze the drying laboratory test results. The moisture transport model accounts for both liquid and vapor transport out of the sample. This is a much more sensitive method than the ASTM D5084 Flexible Wall Permeameter method (ASTM D5084-10).

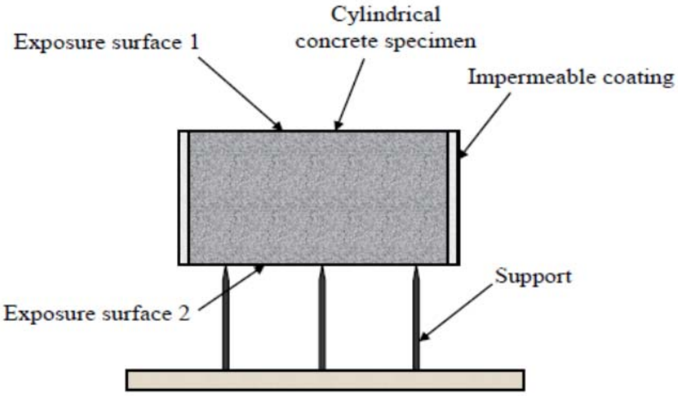


Figure 5.4. Drying Test Setup

5.4 Relative Permeability-Saturation-Capillary Pressure Relations

Cast Stone is expected to remain nearly fully water-saturated, owing to the small pore sizes and relatively high ionic strength of the pore water. However, plausible scenarios could develop that lead to partial desaturation of the Cast Stone (e.g., inadvertent intruder scenario with subsequent exposure of the Cast Stone to the atmosphere). Furthermore, the numerical simulators used for modeling fluid flow and contaminant transport in variably saturated porous media require parameters describing the relative permeability-saturation-capillary pressure (k-S-p) relations of the porous media. Therefore, methods are needed to estimate these constitutive relations for Cast Stone.

Multistep outflow experiments and inverse modeling are popular methods for estimating k-S-p relations for granular, unconsolidated porous media (Tuli et al. 2001). Figure 5.5 shows an experimental apparatus for these types of measurements that is housed in PNNL's Environmental Molecular Sciences Laboratory (EMSL).

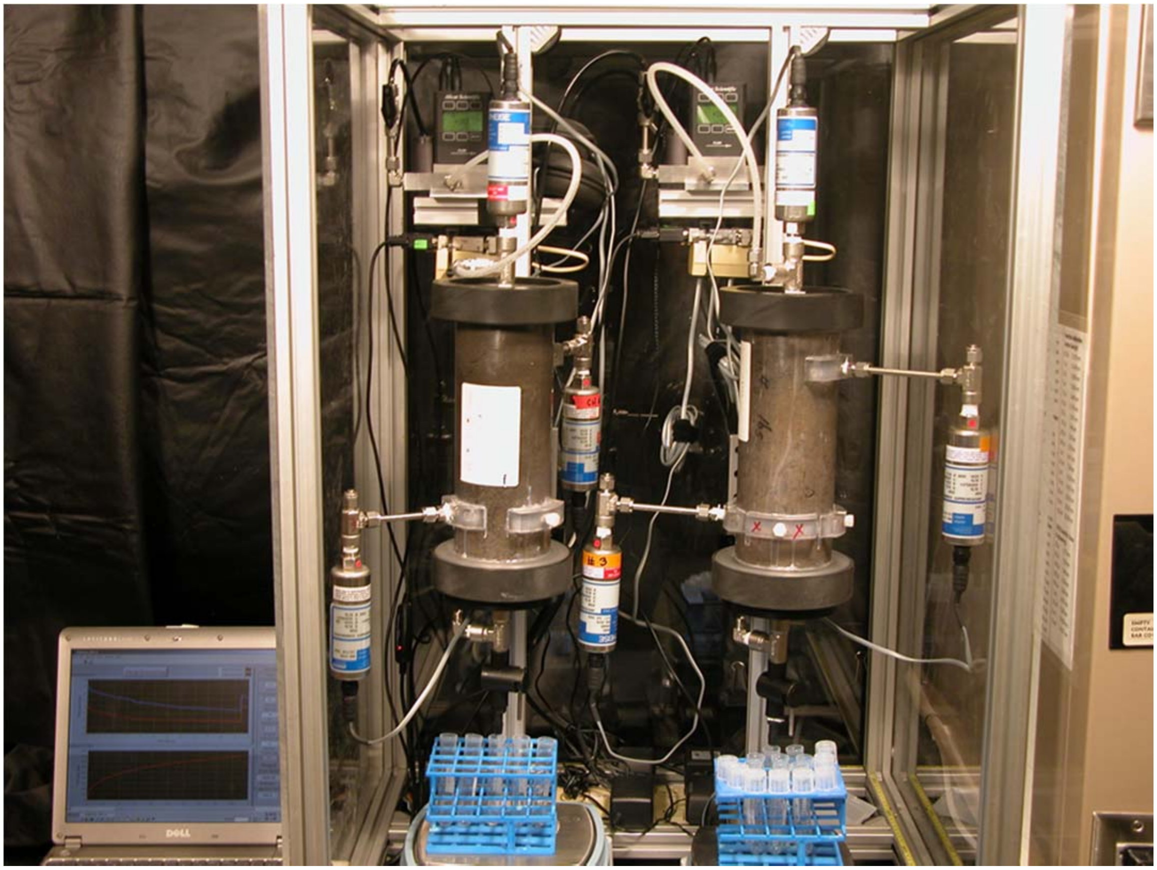


Figure 5.5. Apparatus for Automated, Laboratory Measurement of Sediment Hydraulic Properties (k-S-p relations) in EMSL (SFTEL)

However, the expected low intrinsic permeability and high air-entry pressure for concrete and grout suggest that alternative methods may be needed for the measurement of k-S-p relations for Cast Stone (Rockhold et al. 1993). In lieu of direct measurements, relative permeabilities can be estimated from S-p data and theoretical relative permeability models (Burdine 1956; Mualem 1976). Rockhold et al. (1993) measured S-p relations for concrete and grout using a vapor equilibrium method with a commercially available water activity meter (Decagon Devices, Inc., Pullman, WA). Relative permeability or unsaturated hydraulic conductivity was then calculated using the Mualem (1976) model.

5.5 Porosity and Dry Bulk Density

The porosity and dry bulk density of the cured grout monoliths is usually determined using ASTM C642-13, *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete* (ASTM C642-13). This test method consists of weighing the specimen following four successive sample treatment procedures as described below:

1. Oven dry mass (A) — Dry the Cast Stone specimen in an oven at a temperature of 110 ± 5 °C for not less than 24 h, followed by cooling it in dry air (preferably in a desiccator) to a temperature of 20-25 °C and determine the mass. Then return the dried specimen to the oven and dry it a second time. The specimen mass should be comparatively dry after the first oven-drying step, and if the

second mass determination closely agrees with the first, consider it dry. If the difference between values obtained from two successive drying steps exceeds 0.5 % of the lesser value, return the specimen to the oven for an additional 24-h drying period, and repeat the procedure until the difference between any two successive values is less than 0.5 % of the lowest value obtained.

2. Saturated mass after immersion (B) — Immerse the dried specimen in water at approximately 21 °C for not less than 48 h until two successive values of mass of the surface-dried sample at intervals of 24 h show an increase in mass of less than 0.5 % of the larger value.
3. Saturated mass after boiling (C) — Place the specimen, processed as described in Step 2, in a suitable receptacle, covered with tap water, and boil for 5 h. Allow it to cool by natural loss of heat for not less than 14 h to a final temperature of 20-25 °C. Remove the surface moisture with a towel and determine the mass of the specimen.
4. Immersed apparent mass (D) — Suspend the specimen, after immersion and boiling, by a wire and determine the apparent mass in water.

With the help of above-determined specimen masses, the dry bulk density (g_1) and porosity will be calculated using the follow suite of equations:

$$\text{Dry bulk density } (g_1) = [A/(C\text{-}D)]*\rho \qquad \text{Eq. 7}$$
$$\text{Apparent density } (g_2) = [A/(A\text{-}D)]*\rho$$
$$\text{Porosity} = (g_2\text{-}g_1)/g_2$$

where ρ is the density of water.

5.6 Particle Density

Particle density can be measured using ASTM D854-14, *Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer* (ASTM D854-14).

The ASTM D854-14 Method B (for oven-dry specimens) is used to determine particle density. Briefly, the Cast Stone specimen is dried to a constant mass in an oven maintained at 110 ± 5 °C. Any clods of Cast Stone are broken up using a mortar and pestle. The dried crushed Cast Stone solids is then spooned into the pycnometer, and water added until the water level is between 1⁄3 and 1⁄2 of the depth of the main body of the pycnometer. The water is agitated until a slurry is formed. The entrapped air in the slurry is removed using either heat (boiling) or vacuum. Then, the pycnometer is filled with water up to desired volume, and the total mass of pycnometer, crushed Cast Stone, and water is recorded. The dry Cast Stone weight in the pycnometer is determined by transferring the Cast Stone slurry to the tare or pan, drying the specimen to a constant mass in an oven maintained at 110 ± 5 °C, and cooling it in a desiccator.

The specific gravity, G_t, of the Cast Stone solids at the test temperature is calculated as follows:

$$G_t = \rho_s/\rho_{w,t} = M_s/(M_{pw,t}-(M_{pws,t}-M_s)) \qquad \text{Eq. 8}$$

where
ρ_s = the density of the Cast Stone solids
$\rho_{w,t}$ = the density of water at the test temperature
M_s = the mass of the oven-dry Cast Stone solids
$M_{\rho ws,t}$ = the summed mass of pycnometer, water, and Cast Stone solids at the test temperature
$M_{\rho w,t}$ = the summed mass of the pycnometer and water at the test temperature.

5.7 Solubility of Tc Phases Under Reducing Conditions

The experimental methods from Kaplan et al. (2012) and Cantrell and Williams (2012) could be used to measure the solubility of Tc phases under reducing conditions. In addition, the involved Tc solid phase could be evaluated through thermodynamic calculations.

During batch experiments measuring technetium sorption by cementitious materials under reducing conditions, based on the observations of different K_d values and similar aqueous phases concentrations for similar cementitious solid, Kaplan et al. (2012) found that the aqueous-phase concentrations of ^{99}Tc in the batch suspension were controlled by the solubility of a ^{99}Tc(IV-)--bearing phase. In their batch experiment, for the samples Vault 2, TR547, and TR545 (with different sorption capacity), it appears that a relatively constant ^{99}Tc concentration was obtained between the 154- and 319-day sampling events, suggesting equilibrium with respect to ^{99}Tc partitioning had been reached. The aqueous ^{99}Tc concentrations of these cementitious materials appears to level off, and the samples initially receiving 2.5 and 10.0 ppb total ^{99}Tc spiking also appeared to converge on single concentrations, resulting in a ^{99}Tc(IV)−bearing phase solubility values of about 10^{-9} M to 10^{-8} M in a pH of ~11.8 and Eh -0.44 V. Therefore, the solubility of ^{99}Tc phases under varied geochemical conditions could be determined through K_d measurements with a series of initial spiking Tc concentration levels under reducing conditions.

Cantrell and Williams (2012) reported a ^{99}Tc phase solubility with a saltstone (similar but not identical in composition to TR547) through a flow cell leaching test in an anaerobic chamber by observing the effluent ^{99}Tc concentrations. They determined that the solid phase was $TcO_2{\bullet}2H_2O$ through thermodynamic calculations, and also noted that its solubility decreased significantly as the pH of the system decreased. The flow cell leaching test is a system where a solution contacts the Tc-loaded samples at a known flow rate and constant temperature. Briefly, in their experimental setup, each batch (approximately 1 kg) of the crushed <2 mm ^{99}Tc-loaded saltstone material was loaded into a heavy-walled 1-L Teflon® pressure vessel (Savillex, Eden Prairie, Minnesota), and the vessel reactors were filled with 0.005 M $Ca(OH)_2$ leachant solution. The reactors were then placed into a chamber containing a very-low-oxygen atmosphere (~26 ppm). Nitrogen was used to maintain a slight positive pressure in the chamber. In their experiment, after the initial 14 days continuously flow leaching stage, where the effluent Tc concentration decreased significantly to a tailing stage, static leaching conditions were employed with only periodic temporary flow during sampling events. During the sampling events, leachant solution was pumped into the reactor at a low flow rate to displace the required volume of effluent solution needed for the desired analytical measurements. Fresh leachant (0.005 M $Ca(OH)_2$) was pumped into the top of the reactor at approximately 3 mL/minute, while the effluent was collected from near the bottom of the reactor. This reactor configuration was designed to maximize the redox buffer capacity of the saltstone in contact with the leachant solution and thereby minimize any impact of oxygen contamination. Effluent lines exited the chamber and passed through flow cells prior to sample collection. The flow cells were sealed around probes that measured redox potential during sample collection without exposure to ambient atmospheric conditions. After the effluent exited the flow cells for Eh measurements, samples were collected for pH, alkalinity, major cations, anions, technetium, sulfide, and ferrous iron. Effluent samples were collected under anoxic conditions periodically for 84 days, and the concentration of Tc, as well as other leached elements, was plotted against reaction times. The saturation indices of various Tc phases under reducing conditions were determined by geochemical modeling. Li and Kaplan (2012) did the thermodynamic calculation on the solubility of three Tc dioxide phases (TcO_2-c, $TcO_2 \cdot 1.6H_2O$, and $TcO_2 \cdot 2H_2O$) using Geochemist's Workbench (GWB) and various thermodynamic datasets. They found that the solubility of hydrated $TcO_2 \cdot xH_2O$ (likely $TcO_2 \cdot 1.6H_2O$) limited the Tc concentration in reducing saltstone leachates as long as the Eh remained < -0.38 V. However, as the Eh increased just above -0.35 V, the highly soluble Tc(VII) species, TcO_4^-, became the dominant species due to the re-oxidation of Tc(IV) in the aqueous and solid phases. Under the more oxidized environmental conditions, the TcO_4^- concentration increased dramatically to the millimolar level. The influence of pH on Tc phase solubility was evaluated because it is used to define the "age of the saltstone" in the PA. Saltstone pore water is initially at pH 12, then as it ages, the evolving mineral assemblage of the saltstone buffers its pore-water pH to ~10.5. After extensive weathering, saltstone is expected to degrade, and eventually its pore water will take on the pH of the background SRS sediment at pH ~5.5. Under reducing conditions (Eh < -0.38 V), the calculated Tc phases solubility decreased as the pH decreased. For example, when pH changed from 12.7 to 10.5 (the approximate pH decrease between the young and moderately-aged saltstone stages used in the PA), the solubility of $TcO_2 \cdot 1.6H_2O$ significantly decreased from 6.3×10^{-7} M to 5.2×10^{-9} M.

5.8 Desorption K_d Values

The methods of Estes et al. (2012) and Almond et al. (2012) could be used to measure desorption K_d values for the grout waste form.

Sorption/desorption K_d, a commonly used model to describe the equilibrium distribution of the radionuclides between the solid and aqueous phases, is frequently used in contaminant transport modeling to describe the sorption capacity of the material for given COCs. The sorption/desorption K_d for a given radionuclide from the grout waste form (e.g., Cast Stone) is typically measured using steady-state batch methods based on mass balances of the amount of COCs on the waste material divided by the concentration in water at steady-state, as shown below:

$$K_d = \frac{(C_i - C_f)\times V}{C_f \times m_{solids}} \qquad \text{Eq. 9}$$

where C_i = the initial aqueous activity of each radionuclide
C_f = the final equilibrium activity of each radionuclide
V = volume of liquid in the final equilibrated suspension
m_{solids} = the solids mass of the grout waste.

Although there is no "Standard K_d Measurement Methodology" established, similar methods on COCs K_d measurement from waste forms have been used among the current research communities. Below is an example of a batch sorption/desorption experiment conducted by Estes et al. (2012).

All sorption batch experiments were performed in an anaerobic glovebag (with approximately 0.1% H_2/99.9% N_2), in which the oxidation/reduction potential and pH were monitored. A ^{99}Tc working solution was prepared by diluting a stock solution of ^{99}Tc(VII) (Isotope Products, Valencia, CA) in distilled-deionized (DDI) water. Based on the detected aqueous concentration in the DDI water solution, it is reasonable to assume that the Tc existed as Tc(VII). The reduced Tc(IV) oxidation state would have a very low solubility under these conditions. A 1.0-g aliquot of solid was added to the batch tube, followed by 40 mL of calcite-saturated solution (generally, calcite solution was used with totally weathered grout, where a slime solution was used for freshly cured grout). The resulting solutions were then spiked with ^{99}Tc(VII) to the target initial concentrations (2.5 ppb or 10 ppb) and shaken end-over-end. The point at which the ^{99}Tc(VII) amendment was made was considered time zero. These spike concentrations were close to actual concentration measured in actual samples recovered from the SRS Facility. A set of no-solids control batch tubes at the target initial concentrations were also prepared. At 1, 4, 8, 19, 56, 154, and 319 days after spiking with ^{99}Tc, approximately 2 mL of each suspension was recovered. Care was taken to remove a homogeneous suspension sample to prevent changing the aqueous-to-solid ratio in the sample, which was accomplished by pipetting the 2-mL aliquot while the suspension was being mixed. The 2-mL aliquot was passed through a 200-nm PTFE filter and the soluble ^{99}Tc concentration was determined using ICP-MS. The Eh and pH of the remaining suspensions were measured and recorded at each sampling interval. After the sorption step, the samples were removed from the glovebag and immediately diluted with a saturated calcite solution that had been pre-equilibrated with the respective cementitious material. These diluents were prepared by suspending each of the respective cementitious materials at 25 g/L in a saturated calcite solution, initially prepared in DDI water. The solids were removed by filtration using a 0.45-µm nylon syringe filter, and the supernatant was used as the diluent. This was done to buffer the aqueous-phase pH of the diluent to the expected pH of the suspension, as the waste form has a strong pH buffering capacity and will change the pH of DDI water or saturated calcite. This pre-equilibration step prevented the large pH shift that could impact the sorption behavior. All preparation was done on the bench top under oxic conditions. After all sampling events during the sorption step, there was approximately 15 mL remaining in each reactor. Therefore, 20 mL of the pre-equilibrated solution for each solid was added to reach a total volume of approximately 35 mL in each reactor. This was necessary to have sufficient volume for the desorption step. During the desorption period, samples were removed after 1, 7, and 20 days, and the aqueous ^{99}Tc concentration was determined as discussed above.

Two notes should be considered in K_d measurements. First, as described in Section 3.1.2.1, K_d is element-dependent, and differs as the system redox and pH conditions change over time. It is clear that multiple sorption K_d measurement should be conducted to reflect the varied geochemical conditions (such as pH and redox conditions) during the aging of the waste forms. For example, Almond and Kaplan (2011) measured desorption K_d values from a Vault 4 saltstone sample in calcite-saturated solutions in a glovebag maintained at trace levels of 30 to 60 ppm $O_{2\,(gas)}$. They also conducted an identical desorption test outside the glovebag with air sparged into the bottom of the suspension, maintaining the aqueous system at ~8 ppm O_2. They reported the Tc K_d of 12 mg/L and 139 mL/g, respectively, under the oxidizing and the reducing conditions. Second, batch sorption/desorption equilibrium time setup is critical for obtaining reliable K_d results. Varied equilibrium time could be used among samples with different grain sizes due to kinetic reasons. The equilibrium time could be determined by a pre-test.

5.9 Reductive Capacity Measurement

In the Cast Stone waste form, ferrous iron and sulfide (S^{2-}) ions in BFS are considered the major reductants capable of reducing Tc from Tc(VII) to Tc(IV) (Atkins and Glasser 1992). Dissolution of BFS at alkaline pH releases sulfide species into the cement pore fluid, predominantly as S^{2-} and possibly with a small contribution from SO_3 and S_2O_3 (Atkins and Glasser 1992), which impose a strong reduction potential in Cast Stone. Therefore, measuring the reductive capacity of Cast Stone, as well as the dry ingredients and simulants used to make Cast Stone, is needed to understand the Tc release for the long-term performance of the Cast Stone in the subsurface environment. In addition, the reductive capacity of Cast Stone after leaching could also be determined and compared to unleached Cast Stone to estimate the change of reductive capacity in the Cast Stone between the unleached and leached states (Um et al. 2013).

Two different measurement techniques have been used to determine the reductive capacity in anthropogenic or natural materials (Angus and Glasser 1985; Lee and Batchelor 2003). The reductive capacity is determined as the amount of an oxidant that can be reduced when sufficient time is given for the reaction to proceed to its maximum extent (Lee and Batchelor 2003). The reductive capacity measurements are based on the difference between the oxidizing equivalent in a Ce(IV) or Cr(VI) solution and the reducing equivalent of Fe(II) needed to neutralize excess Ce(IV) or Cr(VI) after a reaction with the specimen. Um et al. (2013) used both methods to measure the reductive capacity of Cast Stone as described below in the following subsections.

5.9.1 Ce(IV) Method

The Ce(IV) stock solution [$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$] was prepared in 10% H_2SO_4 with a concentration of 30–60 mM, depending on the reductive capacity of the specimen. Approximately 0.5 g of crushed Cast Stone, dry ingredient, or liquid simulant was mixed with 15 mL of the Ce(IV) stock solution in a 20-mL quartz vial. Immediately after mixing, the vial was tightly closed and placed on a platform shaker. The sample was reacted at room temperature for seven days. After seven days reacting, the supernatant solution was filtered through a 0.45-µm syringe filter and 0.05 mL of ferroin solution [0.025 M Fe (o--phenanthroline)$_3$ $^{2+}$] was added to 5 mL of the filtrate. The final solution was titrated using 20 mM ammonium ferrous sulfate prepared in a 4% H_2SO_4 solution until the solution developed and retained a lilac color. The reductive capacity was calculated by determining the difference between the oxidizing equivalent in a Ce(IV) solution [meq Ce(IV)] and the reducing equivalent of Fe(II) needed to neutralize excess Ce(IV) after reaction with the sample [meq Fe(II)]. The final reductive capacity per gram of sample was determined by dividing the reductive capacity (meq) by the mass of the sample (g) (Um et al. 2013).

5.9.2 Cr(VI) Method

The Cr(VI) stock solution (30–50 mM K_2CrO_4) was prepared in a 10 mM $NaHCO_3$ solution. The Cr(VI) solution was purged with N_2 gas for one hour and was moved into an anoxic chamber (Coy Laboratory Products, Inc.) containing a mixed-gas atmosphere (4% H_2 and 96% N_2). Approximately 0.5 g of solid powdered Cast Stone, dry ingredient, or liquid simulant sample was placed in a 20-mL quartz vial, and then the vial was introduced into the anoxic chamber. The sample vials and Cr(VI) stock solution were kept in the anoxic chamber for two days with lids off to remove atmospheric air present in the sample vials and Cr(VI) stock solution before use. After the 2-day air-purging period in the H_2/N_2 atmosphere, 10 mL of the Cr(VI) stock solution was added into the sample vial, and the pH of the suspension was adjusted to 7 ± 1 by adding a few drops of 1 M NaOH or 1 M H_2SO_4 solution. After closing the vials tightly, the vials were moved from the anoxic chamber to a platform shaker, and the samples were reacted at room temperature for seven days. After the 7-day reaction, the vials were moved to the anoxic chamber again, and 0.142 g of sodium sulfate was added into the vials. The vials were removed from the anoxic chamber and placed on the platform shaker for one more day in order to remove any potentially adsorbed Cr(VI) from the materials before the final supernatant was filtered through a 0.45-µm syringe filter. An amount of 1 mL of the filtrate was mixed with 1 mL of 10% H_2SO_4 solution (1:1 ratio in 3.3 volume), and 0.05 mL of ferroin solution was added. The solution was titrated with 20 mM ammonium ferrous sulfate solution prepared in 4% H_2SO_4 solution until the solution became and remained lilac in color. The final reductive capacity per gram of sample was determined by dividing the reducing equivalent (meq) by the mass of the sample (g) (Um et al. 2013).

6.0 References

40 CFR Part 268. 2010. “Land Disposal Restrictions.” *Code of Federal Regulations*, U.S. Environmental Protection Agency, Washington, DC.

Almond PM and DI Kaplan. 2011. *Distribution Coefficients (Kd) Generated from a Core Sample Collected from the Saltstone Disposal Facility*, SRNL-STI-2010-00667, Savannah River National Laboratory, Aiken, SC.

Almond PM, DI Kaplan, and EP Shine. 2012. *Variability of Kd Values in Cementitious Materials and Sediments*, SRNL-STI-2011-00672, Savannah River National Laboratory, Aiken, SC.

Angus MJ and FP Glasser. 1985. “The Chemical Environment in Cement Matrices.” Materials Research Society Symposium Proceedings 50:547–556.

ANSI/ANS—American National Standards Institute/American Nuclear Society. 2003. *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure.* ANSI/ANS-16.1, La Grange Park, Illinois.

ASTM C1308-08. *Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms.* ASTM International, West Conshohocken, PA.

ASTM C1663-09. *Standard Test Method for Measuring Waste Glass or Glass Ceramic Durability by Vapor Hydration Test*. ASTM International, West Conshohocken, PA.

ASTM D5084-10. *Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter.* ASTM International, West Conshohocken, PA.

ASTM C1585-13. *Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes*. ASTM International, West Conshohocken, PA.

ASTM C642-13. *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete*. ASTM International, West Conshohocken, PA.

ASTM D854-14. *Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer.* , ASTM International, West Conshohocken, PA.

Atkins M, AN Beckley, and FP Glasser. 1988. “Influence of Cement on the Near-Field Environment and Its Specific Interactions with Uranium and Iodine.” *Radiochem. Acta* **44-5**:255-261.

Atkins M and FP Glasser. 1992. “Application of portland cement-based materials to radioactive waste immobilization.” *Waste Management* 12:105–131.

Bacon DH, MD White, and BP McGrail. 2000. *Subsurface Transport Over Reactive Multiphases (STORM): A General, Coupled, Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator*, Version 2, User’s Guide. PNNL-13108, Pacific Northwest National Laboratory, Richland, WA.

Bacon DH and BP McGrail. 2001. *Waste Form Release Calculations for the 2001 Immobilized Low-Activity Waste Performance Assessment*. PNNL-13369, Pacific Northwest National Laboratory, Richland, WA.

Bacon DH, MD White, and BP McGrail. 2004. *Subsurface Transport Over Reactive Multiphases (STORM): A Parallel, Coupled, Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator*, Version 3.0, User's Guide. PNNL-14783, Pacific Northwest National Laboratory, Richland, WA.

Bacon DH and BP McGrail. 2005. *Waste Form Release Calculations for the 2005 Integrated Disposal Facility Performance Assessment*. PNNL-15198, Pacific Northwest National Laboratory, Richland, WA.

Blanc P, A Lassin, P Piantone, M Azaroual, N Jacquemet, A Fabbri, and EC Gaucher. 2012. Thermoddem: A Geochemical Database Focused on Low Temperature Water/Rock Interactions and Waste Materials, App. Geochem. 27(10):2107-2116.

Bondietti EA and CW Francis. 1979. Geologic Migration Potentials of Technetium-99 and Neptunium-237, Science, Vol. 203, 30:1337-1340.

Bradbury MH and F Sarott. 1995. Sorption Database for the Cementitious Near-Field of a L/ILW Repository for Performance Assessment, PIT-MISC-0075, ISSN 1019-0643, Paul Scherrer Institut, Switzerland.

Brown KG, J Arnold, S Sarkar, G Flach, H van der Sloot, JCL Meeussen and DS Kosson. 2013. Modeling Carbonation of High-Level Waste Tank Integrity and Closure, In *EPJ Web of Conferences* (Vol. 56, p. 05003), EDP Sciences.

Burbank DA. 2005. *Waste Acceptance Criteria for the Immobilized Low-Activity Waste Disposal Facility*. RPP-8402 Rev. 1, CH2M HILL Hanford Group, Inc., Richland, Washington.

Burdine NT. 1953. "Relative Permeability Calculation from Size Distribution Data." *Trans. AIME* 198:71-78.

Bye GC. 1983. Portland Cement: Composition, Production and Properties. Pergamon Press, NY.

Cantrell KJ and JH Westsik, Jr. 2011. *Secondary Waste Form Down Selection Data Package – Ceramicrete*. PNNL-20681, Pacific Northwest National Laboratory, Richland, WA.

Cantrell KJ and BD Williams. 2012. *Equilibrium Solubility Model for Technetium Release from Saltstone Based on Anoxic Single-Pass Flow through Experiments*. PNNL-21723, Pacific Northwest National Laboratory, Richland, WA.

Cantrell KJ and BD Williams. 2013. "Solubility Control of Technetium Release from Saltstone by $Tc0_2$•xH_2O." Journal of Nuclear Materials 437(1-3):424-431. doi:10.1016/j.jnucmat.2013.02.049

Cary JW and SA Taylor. 1964. The Dynamics of Soil Water, Part II – Temperature and Solute Effects. pp. 245-253.

CBP. 2009. *Review of Mechanistic Understanding and Modeling and Uncertainty Analysis Methods for Predicting Cementitious Barrier Performance - Cementitious Barriers Partnership*. CBP-TR-2009-002, Rev. 0. U. S. Department of Energy, Office of Environmental Management, Washington, D.C.

Chamberlain B, N Chiesl, J Day, L Dowd, B Overocker, D Pape, M Petrus, M Swanson, and J Toles. 1995. "Concrete A Material For The New Stone Age." Material Science and Technology, University of Illinois Urbana-Champaign.

CHPRC. 2013. *Groundwater Monitoring Plan for the Liquid Effluent Retention Facility*, DOE/RL-2013-46, CH2M HILL Plateau Remediation Company, Richland, WA.

Cooke GA and LL Lockrem. 2005. *Effluent Treatment Facility Waste Stream Stabilization Testing*, RPP-RPT-26851, CH2M Hill Hanford Group, Inc. Richland, WA.

Cooke GA, LL Lockrem, M Avila, and RA Westberg. 2006. *Effluent Treatment Facility Waste Stream Monolith Testing Phase II*, RPP-RPT-31077, CH2M Hill Hanford Group, Richland, WA.

Coumes CCD, S Courtois, S Peysson, J Ambroise, and J Pera. 2009. Calcium sulfoaluminate cement blended with OPC: A potential binder to encapsulate low-level radioactive slurries of complex chemistry. Cement and Concrete Research 39 (2009) 740–747.

Crank J. 1986. "Mathematics of Diffusion." Oxford University Press, London.

Davis J.A., Meece, D.E., Kohler, M., Curtis, G.P., 2004. Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments. Geochimica Et Cosmochimica Acta 68 (18), 3621–3641.

Denham, M. 2008. *Thermodynamic and Mass Balance Analysis of Expansive Phase Precipitation in Saltstone*, WSRC-STI-2008-00236, Savannah River National Laboratory, Aiken, SC.

De Windt, L. and P. Devillers. 2010. Modeling the degradation of Portland cement pastes by biogenic organic acids. Cement And Concrete Research 40(8): 1165-1174.

De Windt, L., F. Marsal, E. Tinseau, D. Pellegrini. 2008. Reactive transport modeling of geochemical interactions at a concrete/argillite interface, Tournemire site (France), Physics And Chemistry Of The Earth 33: S295-S305.

Dijkstra JJ, HA van der Sloot, and RNJ Comans. 2002, "Process identification and model development of contaminant transport in MSWI bottom ash" Waste Management, vol. 22, no. 5, pp. 531-541.

Dixon KL and Phifer MA. 2010. Hydraulic and Physical Property Data for E-Area Test Wall Concrete from MACTEC Testing Laboratory, SRNL-6200-2009-00035, Savannah River National Laboratory, Aiken, South Carolina. August 18, 2010.

DOE. 1988. Radioactive Waste Management, DOE Order 5820.2A. US Department of Energy, Washington, D.C.

DOE. 1998. Radioactive Waste Management, DOE Order 435.1. US Department of Energy, Washington, D.C.

DOE. 2000. Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant, US Department of Energy, Office of River Protection, Richland, WA.

DOE. 2001. Final Review Team Report for the March 2001 Revision of the Hanford Immobilized Low-Activity Waste Performance Assessment, US Department of Energy, Richland, WA.

DOE. 2003. *Environmental Impact Statement for Retrieval, Treatment, and Disposal of Tank Waste and Closure of Single-Shell Tanks at the Hanford Site, Richland, WA: Waste Treatment and Supplemental Technology Data Package.* DOE/ORP-2003-07, Rev. 0, Office of River Protection, Richland, Washington.

DOE. 2005. *Technical Guidance Document for Tank Closure Impact Statement Vadose Zone and Groundwater Revised Analyses*.

DOE-OS-2013-10-15-01, Low Level Waste Disposal Facility Federal Review Group Review Report on the Savannah River Site Salt Waste Disposal Special Analysis to the 2009 Performance Assessment, U.S. Department of Energy, Washington DC, October 15, 2013.

Durner W. 1994. Hydraulic conductivity estimation for soils with heterogeneous pore structure. Water Resour. Res. 30:211-233.

Dzombak DA and F Morel. 1990. Surface complexation modeling: hydrous ferric oxide, *Wiley-Interscience.*

Eary LE and D Rai. 1988. "Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion." Environmental Science & Technology 22(8): 972-977.

EPA—U.S. Environmental Protection Agency. 2013a. *Method 1315 – Mass Transfer Rates of Constituents in Monoliths or Compacted Granular Materials Using a Semi-dynamic Tank Leaching Test.*

EPA—U.S. Environmental Protection Agency. 2013b. *Method 1313 – Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure*

Estes SL, DI Kaplan, and BA Powell. 2012. *Technetium Sorption by Cementitious Materials Under Reducing Conditions*, SRNL-STI-2012-00596, Savannah River National Laboratory, Aiken, SC.

Estes SL, Y Arai, DI Kaplan, and BA Powell. 2013. *Technetium Sorption by Cementitious Materials Under Reducing Conditions*, SRNL-STI-2011-00716, Revision 1, Savannah River National Laboratory, Aiken, SC.

Fakcharoenphol P, B Kurtoglu, H Kazemi, S Charoenwongsa, and Y-S Wu. 2014. The effect of osmotic potential on improved oil recovery from fractured shale formations. SPE-198998-MS, Society of Petroleum Engineers.

Flach GP and FG Smith III. 2013. Degradation of Cementitious Materials Associated with Saltstone Disposal Units, SRNL-STI-2013-00118, Rev. 1. Savannah River National Laboratory, Aiken, SC.

Flach GP, JM Jordan, and T Whitside. 2009. Numerical Flow and Transport Simulations Supporting the Saltstone Disposal Facility Performance Assessment, SRNL-STI-2009-00115, Rev. 0. Savannah River National Laboratory, Aiken, SC.

Flury M and TF Gimmi. 2002. *Solute Diffusion*. In Methods of Soil Analysis, Part 4 - Physical Methods. JH Dane and GC Topp (eds.) Soil Science Society of America Book Series, Number 5, Soil Science Society of America, Madison, Wisconsin.

Freedman VL, DH Bacon, KP Saripalli, and PD Meyer. 2004. “A film depositional model of permeability for mineral reactions in unsaturated media.” *Vadose Zone Journal* (3):1414-1424.

Freedman VL, KP Saripalli, and PD Meyer. 2003. “Influence of mineral precipitation and dissolution on hydrologic properties of porous media in static and dynamic systems.” *Applied Geochemistry* 18:589-606.

Garrabrants AC and Kosson DS. 2005, ‘Leaching processes and evaluation tests for inorganic constituent release from cement-based matrices’, in Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes, Spence, RD and Shi, C (eds), CRC Press, Boca Raton, pp. 229-280.

Gaucher EC and P Blanc. 2006. Cement/clay interactions - A review: Experiments, natural analogues, and modeling. Waste Management **26**(7), 776-788.

Gerke HH and MTh van Genuchten. 1996. “Macroscopic representation of structural geometry for simulating water and solute movement in dual-porosity media.” *Adv. Water Resour*. 19:343-357.

Gerke HH and MTh van Genuchten. 1993a. “A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media.” *Water Resour. Res*. 29:305-31.9

Gerke HH, and MTh van Genuchten. 1993b. “Evaluation of a first-order water transfer term for variably saturated dual-porosity flow models.” *Water Resour. Res*. 29:1225-1238.

Gong W, W Lutze, and IL Pegg. 2011. *DuraLith Alkali-Aluminosilicate Geopolymer Waste Form Testing for Hanford Secondary Waste*, VSL-10R2140-1 Rev 1, Vitreous State Laboratory, The Catholic University of America, Washington, DC.

Gupta SK, CR Cole, CT Kincaid, and AM Monti. 1987. *Coupled Fluid, Energy, and Solute Transport (CFEST) Model: Formulation and User's Manual*, BMI/ONWI-660, Battelle Memorial Institute, Columbus, Ohio.

Hirshfelder JO, CF Curtiss, and RB Bird. 1964. Molecular theory of gases and liquids. Wiley, New York.

Huyakorn PS and S Panday. 1999. VAM3DF - Variably Saturated Analysis Model in Three Dimensions for the Data Fusion System: Documentation and User's Guide, Version 2.0, HydroGeoLogic, Inc., Herndon, Virginia.

IAEA. 2002. *Long term behaviour of low and intermediate level waste packages under repository conditions.* IAEA-TECDOC-1397.

IAEA. 2013. The Use of Numerical Models in Support of Site Characterization and Performance Assessment Studies of Geological Repositories, IAEA TECDOC 1717. International Atomic Energy Agency, Vienna, Austria.

Jacques D, J Perko, SC Seetharam, and D Mallants. 2014. A cement degradation model for evaluating the evolution of retardation factors in radionuclide leaching models, Applied Geochemistry 49 (2014) 143–158.

Jaynes DB and AS Rogowski. 1983. Applicability of Fick's Law to Gas Diffusion. Soil Sci. Soc. Am. J. 47:425-430.

Jones CA and ZC Grasley. 2009. Correlation of radial flow-through and hollow cylinder dynamic pressurization test for measuring permeability. Journal of Materials in Civil Engineering, 21, 594-600.

Kaplan DI, KE Parker, and IV Kutynakov. 1998. Radionuclide Distribution Coefficients of Sediments Collected from Borehole 299-E17-21: Final Report for Subtask 1a . PNNL-11966, Pacific Northwest National Laboratory, Richland, WA.

Kaplan DI, RJ Serne, KE Parker, and IV Kutnyakov. 2000. "Iodide sorption to subsurface sediments and illitic minerals." Environmental Science and Technology 34(3):399-405.

Kaplan DI and JM Coates. 2007. Partitioning of Dissolved Radionuclides to Concrete Under Scenarios Appropriate for Tank Closure Performance Assessments. WSRC-STI-2007-00640, Savannah River Site, Aiken, SC.

Kaplan DI, K Roberts, JM Coates, M Siegfried, and S Serkiz. 2008. Saltstone and Concrete Interactions with Radionuclides: Sorption (K_d), Desorption, and Reduction Capacity Measurements. SRNS-STI-2008-00045, Savannah River Site, Aiken, SC.

Kaplan DI and L Dien. 2012. Solubility of Technetium Dioxides (TcO_2-c,$TcO_2 \bullet 1.6H_2O$ and $TcO_2 \bullet 2H_2O$) in Reducing Cementitious Material Leachates: A Thermodynamic Calculation, SRNL-STI-2012-00769, Rev. 1, Savannah River Site, Aiken, SC.

Kemper WD. 1961. Movement of water as affected by free energy and pressure gradient. II. Experimental analysis of porous systems in which free energy and pressure gradients act in opposite directions. Soil Sci. Soc. Am Proc. 25(4): 260-265.

Krupka KM, RJ Serne, and DI Kaplan. 2004. *Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility Performance Assessment (IDF PA)*, PNNL-13037, Rev. 2, Pacific Northwest National Laboratory, Richland, Washington.

Lagerblad B. 2001. “Leaching Performance of Concrete Based on Studies of Samples From Old Concrete Constructions.” TR–01–27. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company. 2001.

Langton CA. 2014. SRNL-STI-2014-00399_Technetium Oxidation in Slag-based Sodium Salt Waste Forms_Rev 0. Savannah River National Laboratory, Aiken, SC.

Lasaga AC. 1998. Kinetic Theory in the Earth Sciences, ISBN: 9780691607719, Princeton Legacy Library.

Lee WJ and Batchelor B. 2003. “Reductive capacity of natural reductants.” *Environmental Science & Technology* 37:535–541.

Li D and DI Kaplan. 2012. *Solubility of Technetium Dioxides (TcO2-c, TcO2·a.6 H2O and TcO2·2H2O) in Reducing Cementitious Material Leachates: A thermodynamic Calculation*, SRNL-STI-2012-00769, Savannah River National Laboratory, Aiken, SC.

Lichtner PC and Q Kang. 2007. Upscaling pore-scale reactive transport equations using a multiscale continuum formulation. Water Resour. Res. 43(12):W12S15 1-W12S15.19.

Lide DR (ed.). 1996, Handbook of Chemistry and Physics. 77th Ed., CRC Press, Boca Raton, Florida.

Lockrem LL. 2005a. *Hanford Containerized Cast Stone Facility Task 1 – Process Testing and Development Final Report*, RPP-RPT-26742 Revision 0, CH2M Hill Hanford Group, Inc., Richland, WA.

Lockrem LL. 2005b. *Cast Stone Technology for Treatment and Disposal of Iodine-Rich Caustic Waste Demonstration - Final Report*, RPP-RPT-26725, CH2M HILL Hanford Group, Inc., Richland, WA.

Lothenbach B, T Matschei, G Möschner, and FP Glasser. 2008. "Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement", Cement and Concrete Research, vol. 38, no. 1, pp. 1-18.

Lukens WW, JJ Bucher, DK Shuh, and NM Edelstein. 2005. "Evolution of Technetium Speciation in Reducing Grout." Environmental Science & Technology 39(20):8064–8070.

Mann FM. 1996. *INTEG: A Program to Calculate Groundwater Contamination and Human Doses*, WHC-SD-WM-RPT-219, Westinghouse Hanford Company, Richland, WA.

Mann FM. 1997. Statements of Work for FY 1998 to 2003 for the Hanford Low-Level Tank Waste Performance Assessment Project. HNF-SD-WM-PAP-062, Rev. 2, Richland, WA.

Mann FM and RJ Puigh II. 2001. *Data Packages for the Hanford Immobilized Low-Activity Tank Waste Performance Assessment: 2001 Version*, HNF-5636 Rev 2, prepared by Fluor Federal Services for Fluor Daniel Hanford Company, Richland, WA.

Mann FM, KC Burgard, WR Root, RP Puigh, SH Finfrock, R Khaleel, DH Bacon, EJ Freeman, BP McGrail, SK Wurstner, and PE LaMont. 2001. *Hanford Immobilization Low-Activity Tank Waste Performance Assessment: 2001 Version*. DOE/ORP-2000-24, US Department of Energy, Office of River Protection, Richland, WA.

Mann FM, CR Eiholzer, AH Lu, PD Rittmann, NW Kline, Y Chen, and BP McGrail. 1996. Hanford Low-Level Tank Waste Interim Performance Assessment. WHC-EP-0884, Rev. 0, Richland, WA.

Mann FM, CR Eiholzer, AH Lu, PD Rittmann, NW Kline, Y Chen, and BP McGrail. 1997. Hanford Low-Level Tank Waste Interim Performance Assessment. HNF-EP-0884, Rev. 1, Richland, WA.

Mann FM, CR Eiholzer, AH Lu, PD Rittmann, NW Kline, Y Chen, and BP McGrail. 1998. Hanford Low-Activity Tank Waste Performance Assessment. DOE/RL-97-69, Rev. 0, Richland, WA.

Mann FM, RJ Puigh, SH Finfrock, R Khaleel, MI Wood. 2003a, Integrated Disposal Facility Risk Assessment. RPP-15834, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, WA.

Mann FM, RJ Puigh, R Khaleel, S Finfrock, BP McGrail, DH Bacon, and RJ Serne. 2003b. *Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies*. RPP-17675, Revision 0, CH2M Hill Hanford Group Inc., Richland, WA.

Marine IW and SJ Fritz. 1981. Osmotic model to explain anomalous hydraulic heads. Water Resour. Res. 17(1):73-82.

Massman J and DF Farrier. 1992. "Effects of Atmospheric Pressures on Gas Transport in the Vadose Zone." *Water Resources Research* 28:777-791

Matschei T, B Lothenbach, and FP Glasser. 2007. "Thermodynamic Properties of Portland Cement Hydrates in the System CaO-Al2O3-SiO2-CaSO4-CaCO3-H2O", Cement and Concrete Research, vol. 37, pp. 1379-1410.

Mattigod SV and JH Westsik, Jr. 2011. *Secondary Waste Form Down-Selection Data Package—DuraLith*. PNNL-20718, Pacific Northwest National Laboratory, Richland, WA.

Mattigod SV, GA Whyatt, RJ Serne, PF Martin, KE Schwab, and MI Wood. 2001. Diffusion and Leaching of Selected Radionuclides (Iodine-129, Technetium-99, and Uranium) Through Category 3 Waste Encasement Concrete and Soil Fill Material. PNNL-13639. Pacific Northwest National Laboratory, Richland, Washington.

Mattigod SV, JH Westsik, Jr, CW Chung, MJ Lindberg, and KE Parker. 2011. *Waste Acceptance Testing of Secondary Waste Forms: Cast Stone, Ceramicrete and DuraLith*. PNNL-20632, Pacific Northwest National Laboratory, Richland, WA

May TH, PD Gehner, G Stegen, J Hyman, A Pajunen, R Sexton, and A Ramsey. 2009. *Secondary Waste – ETF Pre-Conceptual Engineering Study*, RPP-RPT-43588, Washington River Protection Solutions, Richland, WA.

McCarthy JF. 1995. Comparison of fast algorithms for estimating large-scale permeabilities of heterogeneous porous media. Transport in Porous Media. 19(2):123-137.

McGrail BP, WL Ebert, DH Bacon, DM Strachan. 1998. A Strategy to Conduct an Analysis of the Long-term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford. PNNL-11834, Richland, WA.

McGrail BP, DH Bacon, WL Ebert, and KP Saripalli. 2000. A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford. PNNL-11834 Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

McGrail BP, DH Bacon, RJ Serne, and EM Pierce. 2003. A Strategy to Assess Performance of Selected Low-Activity Waste Forms in an Integrated Disposal Facility, PNNL-14362, Pacific Northwest National Laboratory, Richland, WA.

McGrail BP, JP Icenhower, PF Martin, HT Schaef, MJ O'Hara, EA Rodriguez, and JL Steele. 2001. Waste Form Release Data Package for the 2001 Immobilized Low-Activity Waste Performance Assessment. PNNL-13043 Rev. 2, Pacific Northwest National Laboratory, Richland, WA.

McKoy ML and WN Sams. 1997. Tight Gas Reservoir Simulation: Modeling Discrete Irregular Strata-Bound Fracture Networks and Network Flow, Including Dynamic Recharge from the Matrix. Reference document supplied with FracGen and NFflow codes.

Millington RJ and JM Quirk. 1960. Transport in Porous Media. p. 97-106. In FA Van Beren et a. (ed.) Trans. 7th Int. Congr. Soil Sic. Vol. 1, Madison, WI, Elsevier, Amsterdam.

Millington RJ and JM Quirk. 1961. Permeability of porous solids. Trans. Faraday Soc. 57:1200-1207.

ML100820097, Request for Additional Information on the 2009 Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site, U.S. Nuclear Regulatory Commission, Washington DC, March 31, 2010.

ML103400571, Second Request for Additional Information on the 2009 Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site, Docket Number PROJ0734, U.S. Nuclear Regulatory Commission, Washington DC, December 15, 2010.

ML120650576, Satorious, M. to Gilbertson, M., Letter of Concern (Type IV) Regarding U.S. Department of Energy Disposal Activities at the Savannah River Site Saltstone Disposal Facility, U.S. Nuclear Regulatory Commission, Washington DC, April 30, 2012.

NDAA_3116, Public Law 108-375, Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005, Section 3116, Defense Site Acceleration Completion, October 28, 2004.

Moldrup P, T Olesen, J Gamst, P. Schjønning, T Yamaguchi, and DE Rolston. 2000. Predicting the gas diffusion coefficient in repacked soil: Water-induced linear reduction model. Soil Sci. Soc. Am. J. 64:1588-1594.

Mualem Y. 1976. "A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media." *Water Resources Research* 12:513-522.

Neeway JJ, EM Pierce, VL Freedman, JV Ryan, and N Qafoku. 2014a. *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford* . PNNL-23503; RPT-66309-001 Rev. 0, Pacific Northwest National Laboratory, Richland, WA

Neeway JJ, N Qafoku, RJ Serne, AR Lawter, JR Stephenson, WW Lukens, and JH Westsik, Jr. 2014b. Evaluation of Technetium Getters to Improve the Performance of Cast Stone . PNNL-23667, Pacific Northwest National Laboratory, Richland, WA.

Nobel PS. 1991. Physicochemical and Environmental Plant Physiology. Academic Press, Inc., San Diego, CA.

Ojovan, M.I., Varlackova, G.A., Golubeva, Z.I., Burlaka, O.N. (2011) Long-term field and laboratory leaching tests of cemented radioactive wastes, Journal of Hazardous Materials, 187 (1-3), pp. 296-302

Olesen T, P Moldrup, K Henriksen, and LW Petersen. 1996. Modeling diffusion and reaction in soils: IV. New models for predicting ion diffusivity. Soil Sci. 161:633-645.

Pabalan RT, FP Glasser, DA Pickett, GR Walter, S Biswas, MR Juckett, LM Sabido, JL Myers. 2009. Review Of Literature And Assessment Of Factors Relevant To Performance Of Grouted Systems For Radioactive Waste Disposal. CNWRA 2009-001. Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas.

Papadakis VG, CG Vayenas, MN Fardis. 1991. Experimental Investigation and Mathematical Modeling of the Concrete Carbonation Problem, Chemical Engineering Science, 46(5/6):1333-1338.

Peng DY and DB Robinson. 1976. A new two-constant equation of state. Industrial and Engineering Chemistry: Fundamentals 15:59-64.

Perko J, KU Mayer, G Kosakowski, L De Windt, J Govaerts, D Jacques, D Su, JCL Meeussen. 2015. Decalcification of cracked cement structures. Computational Geosciences, in press.

Peters RR and EA Klavetter. 1988. A continuum model for water movement in an unsaturated fractured rock mass. Water Resour. Res. 24(3):416-430.

Phifer MA. 2014. *E-Area Vault Concrete Material Property and Vault Durability/Degradation Projection Recommendations*, SRNL-STI-2013-00706, Savannah River National Laboratory, Aiken, SC.

Pierce EM, SV Mattigod, JH Westsik, Jr, RJ Serne, JP Icenhower, RD Scheele, W Um, and N Qafoku. 2010a. *Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams*. PNNL-19122, Pacific Northwest National Laboratory, Richland, Washington.

Pierce EM, KJ Cantrell, JH Westsik, Jr., KE Parker, W Um, MM Valenta, and RJ Serne. 2010b. *Secondary Waste Form Screening Test Results – Cast Stone and Alkali Alumino-Silicate Geopolymer*. PNNL-19505, Pacific Northwest National Laboratory, Richland, Washington.

Pierce EM, BP McGrail, EA Rodriguez, HT Schaef, KP Saripalli, RJ Serne, PF Martin, SR Baum, KN Geiszler, LR Reed, WJ Shaw. 2004. Waste Form Release Data Package for the 2005 Integrated Disposal Facility Performance Assessment. PNNL-14805, Pacific Northwest National Laboratory, Richland, WA.

Pitzer KS. 1987. A Thermodynamic Model for Aqueous Solutions of Liquid-Like density. In Thermodynamic Modeling of Geologic Materials: Minerals, Fluids and Melts. ISE Carmichael and HP Eugster (eds.). Reviews of Mineralogy 17, American Mineralogy Society, Washington, D.C., pp. 97-142.

Poling BE, JM Prausnitz, and JP O' Connell. 2001. The Properties of Gases and Liquids. 5th ed. McGraw-Hill, New York. Pruess K, PC Lichtner, CI Steefel, MD White, and SB Yabusaki. 2000. Simulation studies of unsaturated flow at Hanford tanks., EOS Trans. AGU, 81(48), Fall Meet. Suppl. Abstract H52D-05.

Qafoku N, JJ Neeway, AR Lawter, TG Levitskaia, RJ Serne, JH Westsik, Jr, and MMV Snyder. 2014. Technetium and Iodine Getters to Improve Cast Stone Performance . PNNL-23282, Pacific Northwest National Laboratory, Richland, WA.

Ramallo de Goldschmidt TR. 2004. Low And Intermediate Level Waste Package Assessment Under Interim Storage And Final Disposal Conditions, p.33 In Long term behaviour of low and intermediate level waste packages under repository conditions. IAEA-TECDOC-1397.

Rassat SD, LA Mahoney, RL Russell, SA Bryan, and RL Sell. 2003. *Cold Dissolved Saltcake Simulant Development, Preparation, and Analysis*. PNNL-14194, Rev 1, Pacific Northwest National Laboratory, Richland, Washington.

Raymond RE, RW Powell, DW Hamilton, WA Kitchen, BM Mauss, and TM Brouns. 2004. "Initial Selection of Supplemental Treatment Technologies for Hanford's Low-Activity Tank Waste" in *WM'04 Conference*, Phoenix, AZ.

Redlich O and JNS Kwong. 1949. On the thermodynamics of solutions. Chem. Rev. 44(1):233-244

Richards LA. 1931. Capillary conduction of liquids through porous mediums, Physics, 1.

Robinson BA. 1989. A fracture network model for water flow and solute transport. Los Alamos National Laboratory, New Mexico. Report No. LA-UR-89-11.

Rockhold ML, MJ Fayer, and PR Heller. 1993. *Physical and Hydraulic Properties of Sediments and Engineered Materials Associated with Grouted Double-Shell Tank Waste Disposal at Hanford*. PNL-8813, Pacific Northwest Laboratory, Richland, Washington.

Rockhold ML, RR Yarwood, and JS Selker. 2004. "Coupled Microbial and Transport Processes in Soils." *Vadose Zone Journal* 3:368-383.

Rockhold ML, ZF Zhang, PD Meyer, and JN Thomle. 2014. *Physical, Hydraulic, and Transport Properties of Sediments and Engineered Materials Associated with Hanford Immobilized Low-Activity Waste.* PNNL-xxxxx (in review), RPT-66309-004, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Rowat JR. 2004. Solidification of low level radioactive waste at AECL's Chalk River laboratories. P.65 IN Long term behaviour of low and intermediate level waste packages under repository conditions. IAEA-TECDOC-1397.

Santos MN. 2004. Behavior Of Concrete Container Ce-2 A Under Disposal Conditions. P. 189 IN Long term behaviour of low and intermediate level waste packages under repository conditions. IAEA-TECDOC-1397.

Seitz RR, KG Brown, GA Taylor, and DW Esh. 2009. *Overview of the U. S. Department of Energy and Nuclear Regulatory Commission Performance Assessment Approaches*, CBP-TR-2009-001,

Serne RJ, RO Lokken, and LJ Criscenti. 1992. "Characterization of Grouted LLW to Support Performance Assessment." *Waste Management* **12**:271-287.

Serne RJ and JH Westsik, Jr. 2011. Data Package for Secondary Waste Form Down-Selection—Cast Stone. PNNL-20706, Pacific Northwest National Laboratory, Richland, WA.

Šimůnek J, NJ Jarvis, MTh van Genuchten, and A Gärdenäs. 2003. Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. J Hydrology 272:14-35.

Singh D, R Ganga, J Gaviria, and Y Ysufoglu. 2011. *Secondary Waste Form Testing Ceramicrete Phosphate Bonded Ceramics*. ANL-11/16, Argonne National Laboratory, Argonne, Illinois.

Smith DK, TP Rose, ML Davisson, GB Hudson, S Niemeyer, and AE Moeller. 1998. Volatile and Fluid Transport in Deep, Arid Soils, UCRL-ID-129653, Lawrence Livermore National Laboratory, Livermore, CA.

Sobolev IA, AS Barinov, MI Ozhovan, NV Ozhjovan, IV Startceva, GN Tchuikova, ZI Golubeva, and AV Timopheeva. 2004. Long term tests of low and intermediate level waste packages under field and experimental repository conditions, p. 169 IN Long term behaviour of low and intermediate level waste packages under repository conditions. IAEA-TECDOC-1397.

SRR-CWDA-2010-00033, Comment Response Matrix for NRC Requests for Additional Information (RAIs) on the Saltstone Disposal Facility Performance Assessment (SRR-CWDA-2009-00017, Revision 0, dated October 29, 2009), Savannah River Site, Aiken, SC, Rev. 1, July 23, 2010.

SRR-CWDA-2011-00044, Comment Response Matrix for Nuclear Regulatory Commission RAI-2009-02 Second Request for Additional Information (RAI) on the Saltstone Disposal Facility Performance Assessment (SRR-CWDA-2009-00017, Revision 0, dated October 29, 2009), Savannah River Site, Aiken, SC, Rev. 1, August 25, 2011.

SRR-CWDA-2012-00103, Sensitivity Analysis for Disposal Operations into Saltstone Disposal Facility Vault 1, Vault 4, and SDUs 2, 3 and 5, Savannah River Site, Aiken, SC, Rev. 1, July 2012.

SRR-CWDA-2014-00006, FY2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site, Savannah River Site, Aiken, SC, Rev. 2, September 2014.

Steefel CI, CAJ Appelo, G Hammond, O Kolditz, V Lagneau, PC Lichtner, KU Mayer, H Meussen, S Molins, DL Parkhurst, H Shao, EL Sonnenthal, N Spycher, J Van der Lee, SB Yabusaki, and G-T Yeh. 2014. Subsurface environmental simulation benchmarks: Formulation and code descriptions. Comput. Geosci., DOI: 10.1007/s10596-014-9443-x.

Tartakovsky AM, DM Tartakovsky, TD Scheibe, and P Meakin. 2008. Hybrid simulations of reaction-diffusion systems in porous media. SIAM J. Sci. Comput. 30(6):2799-2816.

TRW. 2000. Total System Performance Assessment for the Site Recommendation, TDR-WIS-PA-000001 REV 00 ICN 01, Las Vegas, NV.

Tuli A, MA Denton, JW Hopmans, T Harter, and JL MacIntyre. 2001. Multi-Step Outflow Experiment: From Soil Preparation to Parameter Estimation. Report 100037, University of California, Dept. of Land, Air, and Water Resources, Davis, California.

Um W, RJ Serne, and KM Krupka. 2004. "Linearity and Reversibility of Iodide Adsorption on Sediments from Hanford, Washington Under Water Saturated Conditions." Water Research 38(8):2009-2016.

Um W, H-S Chang, JP Icenhower, WW Lukens, RJ Serne, NP Qafoku, JH Westsik, Jr, EC Buck, and SC Smith. 2011a. Immobilization of 99-Technetium (VII) by Fe(II)-Goethite and Limited Reoxidation, Environ. Sci. Technol. 2011, 45, 4904–4913.

Um W, RJ Serne, MM Valenta, KE Parker, C-W Chung, G Wang, JS Yang, KJ Cantrell, MH Engelhard, and JH Westsik, Jr. 2011b. Radionuclide Retention Mechanisms in Secondary Waste-Form Testing: Phase II, PNNL-20753, Pacific Northwest National Laboratory, Richland, WA.

Um W, HB Jung, G Wang, JH Westsik, Jr, and RA Peterson. 2013. Characterization of technetium speciation in Cast Stone. PNNL-22977, Pacific Northwest National Laboratory, Richland, WA.

van der Sloot HA. 2000. “Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling”, Cement and Concrete Research, vol. 30, no. 7, pp. 1079-1096.Viani, BE, Torretto, PC & Matzen, SL 1997, Radionuclide Transport through Engineered Barrier System Alteration Products, UCRL-ID-129281, Lawrence Livermore National Laboratory.

WDPD-12-49, Disposal Authorization Statement for the Savannah River Site Saltstone Disposal Facility, United States Department of Energy, Washington, DC, Rev. 1, May 22, 2012.

Westsik JH, Jr, GF Piepel, MJ Lindberg, PG Heasler, TM Mercier, RL Russell, A Cozzi, WE Daniel, Jr, RE Eibling, EK Hansen, MM Reigel, and DJ Swanberg. 2013. *Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests*. PNNL-22747, Pacific Northwest National Laboratory, Richland, WA.,

Weisbrod N, MR Niemet, and JS Selker. 2002. Imbibition of saline solutions into dry and prewetted porous media. Adv. Water Resour. 25:841-855.

Weisbrod N, MR Niemet, T McGinnis, and JS Selker. 2003. Water vapor transport in the vicinity of imbibing saline plumes: Homogeneous and layered unsaturated porous media. 39(16), 1145, doi:10.1029/2002WR001539.

Weisbrod N, T McGinnis, ML Rockhold, MR Niemet, and JS Selker. 2009. Effective Darcy-scale contact angles in porous media imbibing solutions of various surface tensions. Water Resour. Res. 45, W00D39, doi:10.1029/2008WR006957.

Whitaker S. 1986. Transient diffusion, adsorption, and reaction in a porous catalyst. Chem. Eng. Sci. 41:3015-3022.

White MD and M Oostrom. 2006. STOMP: Subsurface Transport Over Multiple Phases, Version 4.0, User's Guide. PNNL-15782, Pacific Northwest National Laboratory, Richland, WA.

Whiting, D. and A.L. Walitt. 1988. Permeability of Concrete, American Concrete Institute, Detroit, MI.

Winter, NP. 2012. Understanding Cement, WHD Microanalysis Consultants Ltd.

Wieland, E. and L.R. Van Loon. 2002. Cementitious Near-Field Sorption Data Base for Performance Assessment of an ILW Repository in Opalinus Clay. NAGRA NTB 02-20, NAGRA, Hardstrasse 73, CH-5430 Wettingen/Switzerland.

Xu C, DI Kaplan, S Zhang, M Athon, YF Ho, YF Ho, HP Li, CM Yeager, KA Schwehr, R Grandbois, D Wellman, and PH Santschi. 2014. Radioiodine sorption/desorption and speciation transformation by subsurface sediments from the Hanford Site. Journal of Environmental Radioactivity 139:43-55.

Yu, A. D., Langton, C. A., and Serrato, M. G. 1993. Physical Properties Measurement Program (U), WSRC-RP-93-894, Westinghouse Savannah River Company, Aiken, South Carolina. June 30, 1993.

Appendix A

Disposal System Description

Appendix A

Disposal System Description

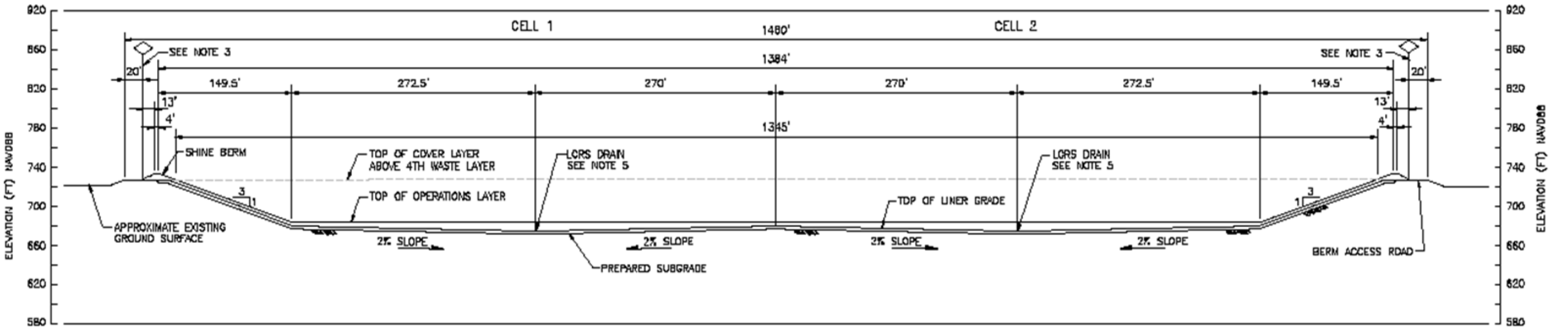
Plans call for the IDF system to include a protective surface barrier with design elements to minimize root intrusion, animal intrusion, and water infiltration. The site is not near any existing or past waste disposal sites. A conceptual design has been described by Mann et al. (2003) and is shown in Figure A.1 and Figure A.2. The use of silt-loam soils, when combined with a representative community of shrub-steppe vegetation, has been shown to cause most precipitation falling on the region to be lost through evapotranspiration. Consequently, the disposal facility is to be located in relatively dry, unsaturated soil, and PA models must be applicable to the specific physics and chemistry of this type of system.

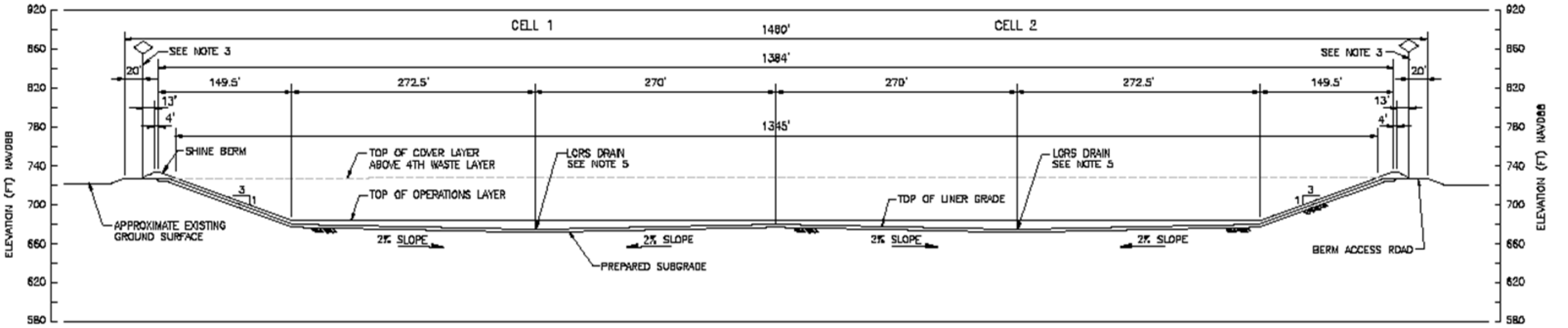
An important input for reactive transport modeling is water flow. Water flow in the near-surface unsaturated zone is transient due to infrequent precipitation events. Transient water flow begins when water enters at the ground surface and infiltrates downward into the soil column. At some point along the column depth, the transient effects will dampen out, and the downward-flowing water will reach a steady infiltration rate. Thus, the unsaturated zone essentially comprises two regions—one where water flow is transient and one where water flow is stable until it reaches the aquifer. The IDF will be situated in the region of steady flow. However, plans call for a protective surface barrier to be engineered to minimize water infiltration.

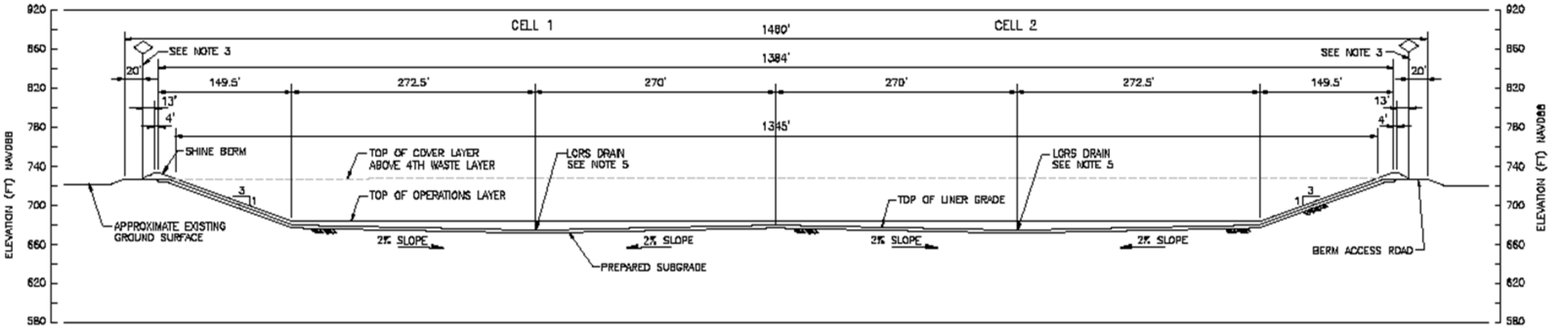
ILAW glass canisters produced at WTP are to be right circular cylinders (1.22 m diameter by 2.29 m tall), made of 304 L stainless steel and at least 85% filled with LAW glass (2 m high). These waste packages are stacked, at a maximum, 4 layers high in the IDF trench, corresponding to a maximum glass height of 8 meters. The remaining fill material into the trench is assumed to be backfill soil. Each cell in the IDF trench consists of a contiguous group of waste packages in a given layer.

Backfilled soil is included around and on top of the waste containers in the facility. The soil was included in these concepts 1) for structural support, 2) to wick moisture away from the waste containers, and 3) to provide radiation shielding for the facility workers. The waste packages are to be located approximately 15 m below the top of the surface barrier. At this depth, the ambient temperature is approximately 15 °C, and temperature fluctuations are less than 2 °C.

East – West Cross-Section







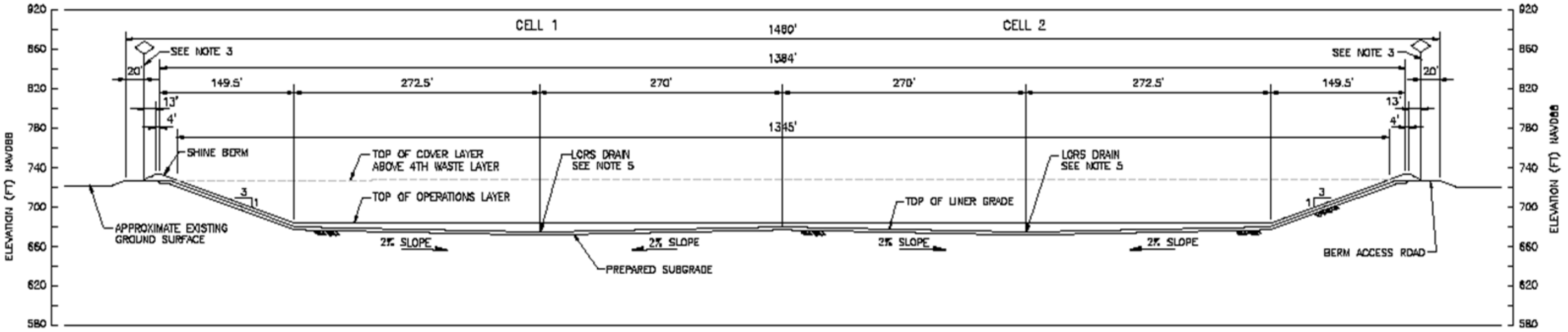
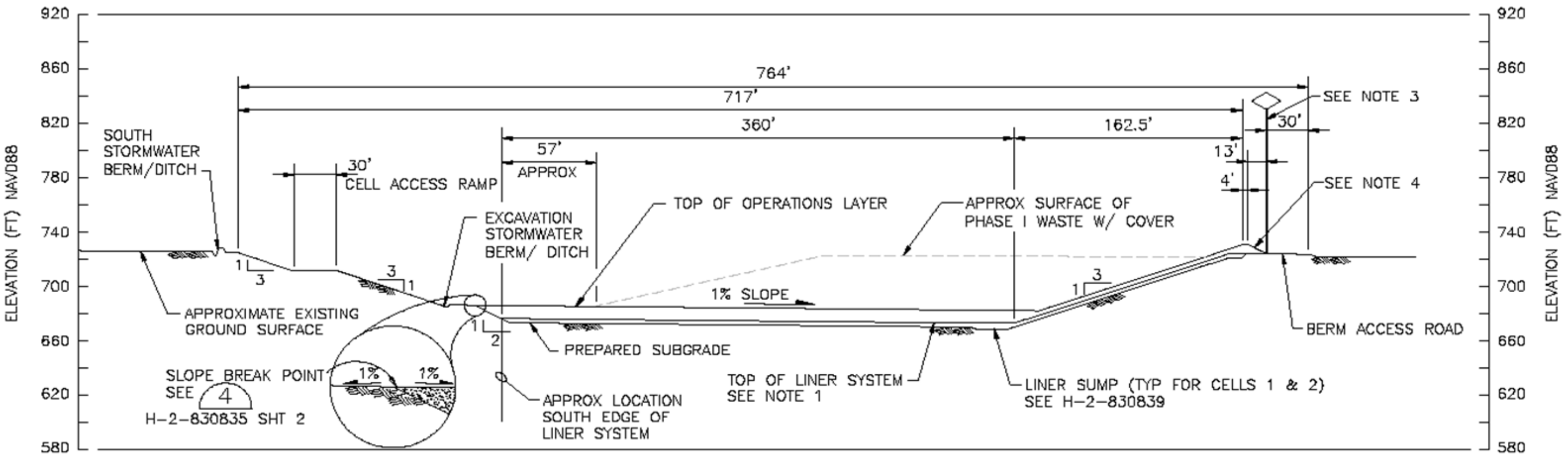


Figure A.1. IDF Trench Conceptual Model – West Cross-Section

-Section



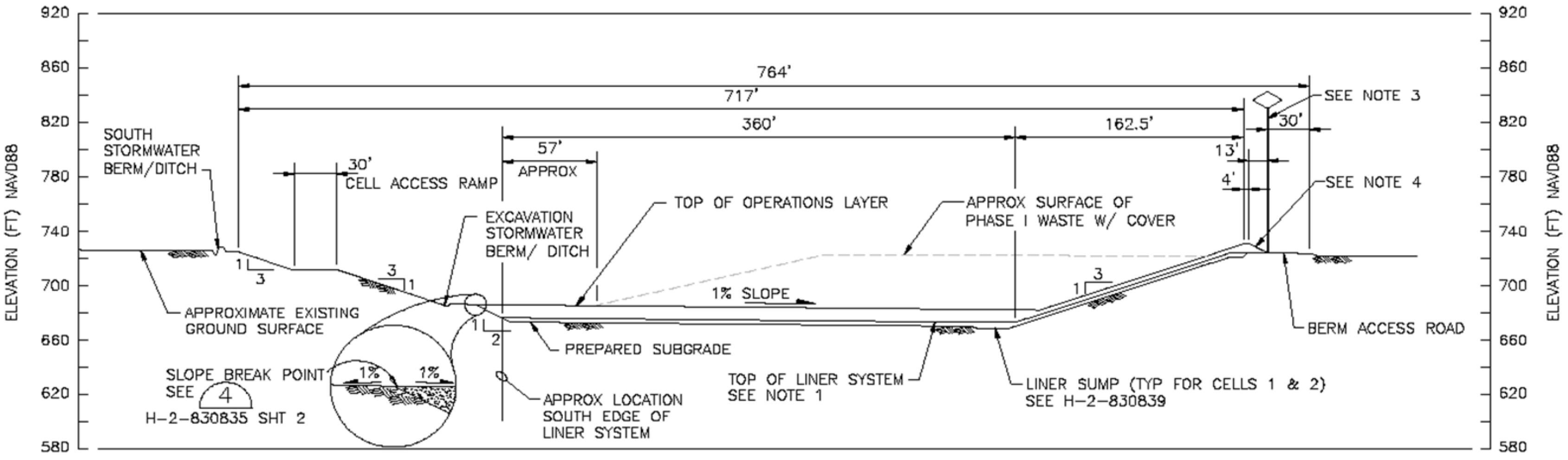


Figure A.2. IDF Trench Conceptual Model – South Cross-Section

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