REFERENCE CASES FOR USE IN THE CEMENTITIOUS BARRIERS PARTNERSHIP PROJECT

Cementitious Barriers Partnership

August 2010

CBP-TR-2010-006, Rev. 0

REFERENCE CASES FOR USE IN THE CEMENTITIOUS BARRIERS PARTNERSHIP PROJECT

Cementitious Barriers Partnership

August 2010

CBP-TR-2010-006, Rev. 0

ACKNOWLEDGEMENTS

This report was prepared for the United States Department of Energy in part under Contract No. DE-AC09-08SR22470 and is an account of work performed in part under that contract. Reference herein to any specific commercial product, process, or service by trademark, name, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring of same by Savannah River Nuclear Solutions or by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. The authors would like to acknowledge the contributions of Elmer Wilhite of Savannah River National Laboratory, David Kosson of Vanderbilt University and CRESP, Jake Philip of the U.S. Nuclear Regulatory Commission, and Ed Garboczi of the National Institute of Standards and Technology for contributions to the document. They would also like to acknowledge the contributions of Media Services of Savannah River Nuclear Solutions and Savannah River National Laboratory personnel for editing and assistance with production of the document.

and

This report is based on work supported by the U. S. Department of Energy, under Cooperative Agreement Number DE-FC01-06EW07053 entitled 'The Consortium for Risk Evaluation with Stakeholder Participation III' awarded to Vanderbilt University. The opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily represent the views of the U.S. Department of Energy or Vanderbilt University.

DISCLAIMER

Printed in the United States of America

United States Department of Energy
Office of Environmental Management
Washington, DC

This document is available on the U.S. DOE Information Bridge and on the CBP website: http://cementbarriers.org/
An electronic copy of this document is also available through links on the following websites: http://srnl.doe.gov/ and http://cementbarriers.org/

FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc. The Nuclear Regulatory Commission (NRC) is providing support under a Memorandum of Understanding. The National Institute of Standards and Technology (NIST) is providing research under an Interagency Agreement. Neither the NRC nor NIST are signatories to the CRADA.

The periods of cementitious performance being evaluated are up to or longer than 100 years for operating facilities and longer than 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

Christine A. Langton, PhD
Savannah River National Laboratory

David S. Kosson, PhD
Vanderbilt University / CRESP

CONTENTS

CONTENTS Continued

LIST OF FIGURES

REFERENCE CASES FOR USE IN THE CEMENTITIOUS BARRIERS PARTNERSHIP PROJECT

Christine A Langton
Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

David S. Kosson and Andrew C. Garrabrants
Vanderbilt University, Department of Civil and Environmental Engineering
Consortium for Risk Evaluation with Stakeholder Participation III
Nashville, TN 37235

ABSTRACT

The Cementitious Barriers Partnership Project (CBP) is a multi-disciplinary, multi-institution cross cutting collaborative effort supported by the US Department of Energy (DOE) to develop a reasonable and credible set of tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. The period of performance is >100 years for operating facilities and > 1000 years for waste management. The CBP has defined a set of reference cases to provide the following functions: (i) a common set of system configurations to illustrate the methods and tools developed by the CBP, (ii) a common basis for evaluating methodology for uncertainty characterization, (iii) a common set of cases to develop a complete set of parameter and changes in parameters as a function of time and changing conditions, (iv) a basis for experiments and model validation, and (v) a basis for improving conceptual models and reducing model uncertainties. These reference cases include the following two reference disposal units and a reference storage unit: (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank), and (iii) a spent nuclear fuel basin during operation. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Examples of concretes, grout fills and a cementitious waste form are identified for the relevant reference case configurations.

1.0 INTRODUCTION

The Cementitious Barriers Partnership (CBP) Project is a multidisciplinary effort supported by the US DOE to develop a set of tools to improve prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and > 1000 years for waste management) [1]. The CPB partners, in addition to the US DOE, are the U.S. Nuclear regulatory Agency (NRC), the National Institute of Standards and Technology (NIST), the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with

Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO, Technologies, Inc.

The project is focused on reducing uncertainties associated with current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will support long-term performance predictions and performance-based decision making and are applicable to several of the strategic initiatives in the U. S. Department of Energy (DOE) Environmental Management Engineering & Technology Roadmap [2].

Performance assessments (PAs) for low-level waste facilities consist of 1) ground water flow and contaminant transport models, 2) air and radon transport pathway models, 3) inadvertent intruder analyses, and 4) all path ways human health risk analyses. The CBP project is focused on understanding and predicting the physical (hydraulic), chemical (contaminant retention and matrix evolution) and mechanical (structural) performance of cementitious barriers including waste zones for the subsurface flow and contaminant transport modeling. The set of simulation tools and data developed by this project will be applicable to near surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools will also support analysis of chemical degradation of concrete used in nuclear facilities containment structures (spent fuel pools, dry spent fuel storage units, and recycling facilities, e.g., fuel fabrication, separations processes).

Three prototype reference systems/configurations described in this paper were defined to capture the essential features of the various types of engineered cementitious barriers. The reference cases are intended to provide:

- Full descriptions of the engineered structures that are sufficient to support Performance Assessment (PA) modeling;

- Simplified descriptions for 1- and 2-D analyses with representative materials and interfaces that will be used to evaluate time and spatially dependent evolution of performance in response to dynamic boundary conditions;

- Material descriptions and boundary conditions for experimental programs designed to support property-based chemical and physical constitutive models (non spatially dependent);

- Focused experimental programs that will be designed to reduce uncertainties associated with assumptions about material performance in interfacial regions between the waste, engineered materials, and environmental media.

2.0 REFERENCE CASES

Key information required as inputs for defining systems and scenarios for PA modeling includes:

- Geometry
- Initial conditions
- Boundary conditions (e.g., fluxes, concentrations, etc.)
- Material properties that control matrix durability and contaminant leaching including:

    a. Physical
    b. Hydraulic
    c. Structural
    d. Chemical
    e. Mineralogical

In addition, meaningful temporal and spatial scales must be selected to best address the modeling needs.

Key outputs required for cementitious barrier performance modeling include:

- Moisture and gas flow and constituent (contaminant) transport (leaching) function of time and spatial relationships,
- Changes in the physical / hydraulic properties of the barrier and waste as a function of time and spatial relationships.

2.1 Reference Case Geometry

Actual structures, engineered barriers, process equipment, and waste packages, etc. are three dimensional (3-D) and typically geometrically complex. For computational convenience, most low-level waste PAs reduce the 3-D complexities to 2-D cross sections that are considered to be reasonable approximations sufficient for addressing the geometrical issues. When cementitious barriers are present, 1-D approximations must be applied with caution and are rarely adequate due to the contrast in the hydraulic conductivities between the barrier and environmental media and/or waste zone.

The proposed CBP progression for the reference cases is illustrated in Figures 1 and 2. Mechanistic understanding will be obtained initially from 1-D phenomenological modeling and supporting experiments as shown in Figure 1. This information will be used as input to multi-dimensional PA flow and transport models, which are schematically illustrated in Figure 2, or in 1-D relative uncertainty analyses, such as those obtained with the Goldsim environmental transport modeling. The process for incorporating the phenomenological information into the multi-dimensional PA codes will be via algorithms developed from the 1-D experimental and associated modeling effort.

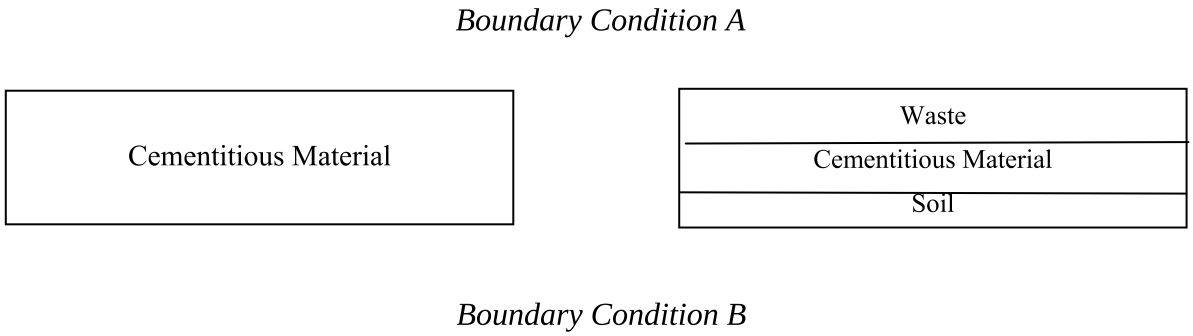


Figure 1. Examples of a One-Dimensional Reference Case Configuration for Evaluating Chemical and Physical Phenomena and Mechanisms.

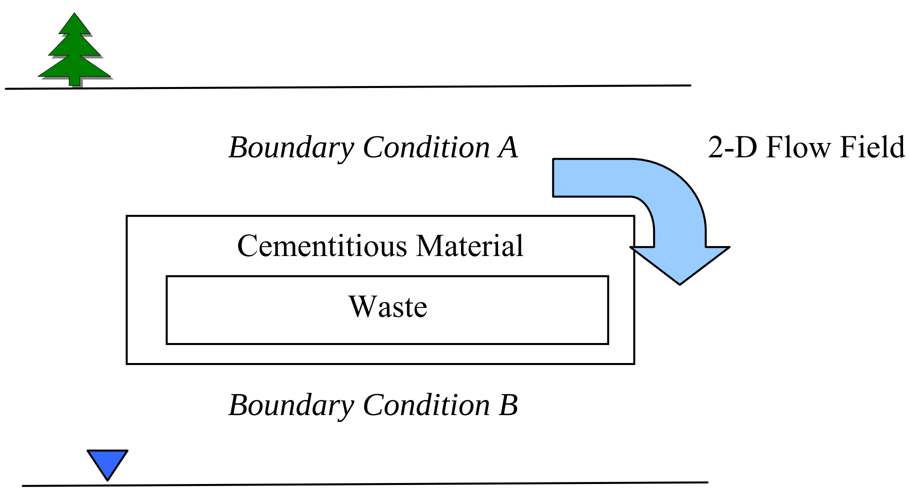


Figure 2. Example of a Two-Dimensional Reference Case Configuration that Incorporates a Flow Field for PA Calculations.

2.2 Reference Case Initial and Boundary Conditions

Initial conditions typically defined in PAs that are important to the performance of disposal units, including engineered cementitious barriers are:

- Waste inventory and characteristics

  - Radioactive and chemical species of interest

- Influxes of water, gas, and chemical species at the system boundaries (fluxes across material interfaces)

  - Water (% saturation, pH, Eh, dissolved O_2 and CO_2)
  - Air (% O_2, CO_2, H_2O – relative humidity)
  - Corrodent chemicals such as Cl^-, SO_4^{2-}, alkalis, organic and inorganic acids

- Infiltration rates and flow along material interfaces (flow fields)

- Temperature and temperature cycling

- Structural condition

  - Initial cracks from thermal stresses and drying shrinkage stresses
  - Structure penetrations, construction joints, and other construction details
  - Steel reinforcements (rebar and other)

- Episodic events such as seismic events and structural settlement or failure.

The CBP effort will focus primarily on the consequences of the influxes and fluxes across material interfaces and through materials of moisture, gas, and chemical species on the cementitious barrier materials as functions of long-term exposure. Temperature and temperature cycling will also be considered. The radioactive species of interest for the CBP reference cases are primarily Cs^+, Sr^{2+}, and the long lived mobile isotopes, Tc-99, I-129, C-14 and selected actinides, such as U and Pu or suitable surrogates. Degradation of structural penetrations, e.g., construction joints and other construction details will not be included in the mechanistic or phenomenological investigations except for the potential to provide fast pathways.

2.3 Reference Case Time Periods

Time periods over which performance predictions are required are 100 years for storage structures and 1000 to 10,000 years for disposal units. Consequently, the phenomenological models will be run to estimate corresponding time periods. Laboratory experiments for mechanistic or validation studies are not expected to exceed a 5-year time period. If specific data are required for older (aged) materials (5-50+ years) cores from existing structures will be collected and analyzed.

2.4 Reference Case Outputs

The parameters required for PA modeling are the reference case outputs for the CBP experimental and phenomenological modeling efforts. These parameters are typically chemical, hydraulic, and physical properties of the engineered barrier materials and of the barriers themselves and evolution of the properties as a function of time, influx of chemicals and physical conditions that modify the properties. Examples of important properties for cementitious barriers include: bulk composition, mineralogy, hydraulic conductivity, solubilities and diffusivities of the matrix phases and contaminant species (leaching properties), porosity and pore size distribution, moisture retention curves (function of pore size distribution and pore structure), bulk density and particle density.

2.5 Reference Case Cementitious Materials

Three types of cementitious materials were selected as reference cases. Each of the reference case materials have been used as barriers in actual waste disposal units. These materials are listed below:

- Reinforced Concrete (carbon steel rebar with three inch cover)
    - Type I/II Binary Blend (portland cement + blast furnace slag binder)
    - Type I/II Ternary Blend (portland cement + blast furnace slag + Class F fly ash binder)
    - Type V Sulfate Resistant Quaternary Blend (portland cement + slag + Class F fly ash + silica fume binder)
- Flowable, Stable (zero-bleed) Infill/Back Fill Grout
    - Three chemically reducing ternary blends
        - High water to cementitious material ratio
        - Medium water to cementitious material ratio
        - Low water to cementitious material ratio with 3/8 inch stone and sand
    - Non reducing binary blend
        - Low water to cementitious material ratio with 3/8 inch stone and sand
        - Salt waste form.

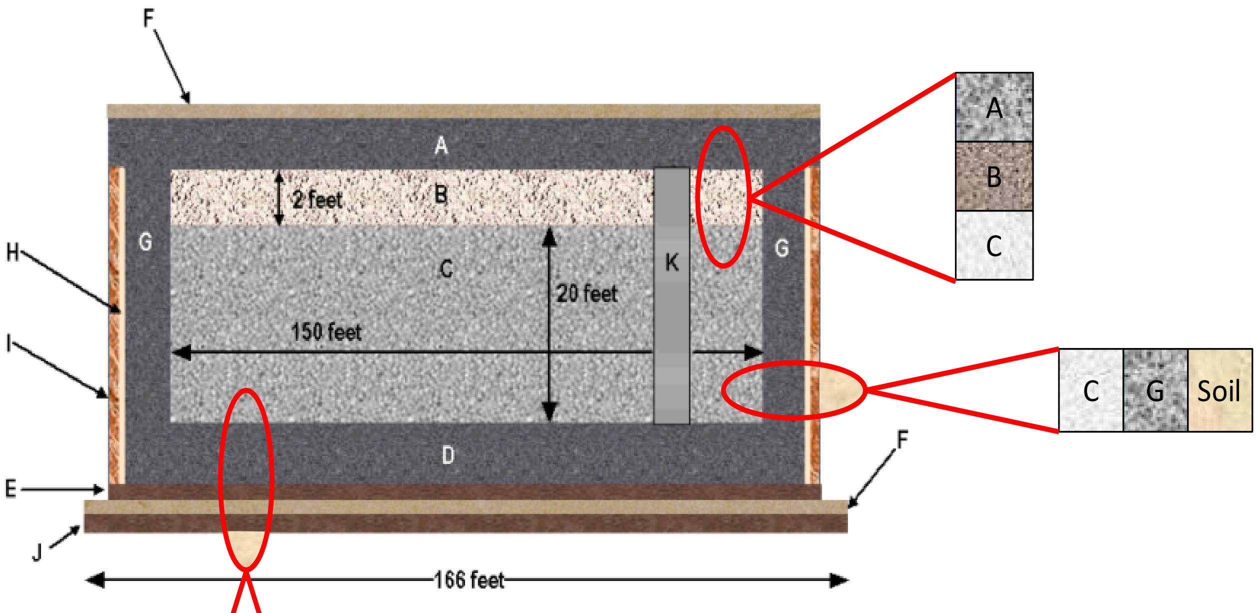
These materials are described in more detail in Tables 1 to 3, respectively.

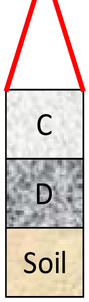
2.6 Reference Disposal and Storage Units

The CBP reference case materials have been used in actual low-level waste (LLW) disposal units in the DOE complex or in commercial nuclear industry process/storage units. Three reference case configurations are listed below:

a) Cementitious low-level salt waste form in a reinforced concrete disposal vault.
b) Reinforced concrete vault containing a carbon steel high-level waste tank filled with a chemically and structurally stabilizing cementitious grout and low-level waste residuals.
c) Reinforced concrete spent nuclear fuel basis with a stainless steel liner.

Schematic illustrations of the two disposal units and of the spent fuel basin are provided in Figures 3-5.





Key	*Material*	*Thickness (cm)*
A	*Reinforced Concrete for Resistance to Moderate Sulfate Exposure*	*20.5*
B	*Clean Fill Grout*	*61*
C	*Cementitious Salt Waste Form*	*610*
D	*Reinforced Concrete for Resistance to High Sulfate Exposure*	*20.5*
E	*Upper Mud Mat Concrete for Resistance to High Sulfate Exposure*	*10*
F	*Geotextile Material (HDPE / GCL)*	*0.76*
G	*Reinforced Concrete for Resistance to High Sulfate Exposure*	*20.5*
H	*Carbon Steel Wall Liner*	*0.047*
I	*Geotextile Material (HDPE)*	*0.254*
J	*Lower Mud Mat Concrete*	*10*
K	*Reinforced Concrete Column with Resistance to High Sulfate Exposure*	*35.6*

Figure 3. Schematic Illustration of a Reinforced Concrete Vault Containing a Cementitious Low Activity Waste Form. Examples of Multi-layer Material and Interfaces Relevant to 1-D Mechanistic Studies are Illustrated.

2.6.1 Cementitious Waste Form in Reinforced Concrete Vault

A brief description of the reference cementitious waste form disposed of in a concrete vault is provided below:

- Reinforced concrete vault filled with a monolithic cementitious low-level radioactive salt waste form. The concrete vault also contains carbon steel columns and trusses to support the roof. The vault is filled in layers typically 15 to 30 cm thick.

- A clean grout cap is placed between the final waste form layer and the top of the vault.

- Upon closure of the disposal facility, which will contain multiple vaults, soil backfill will be placed around vaults constructed on grade and a multi-layer cap will be constructed to limit infiltration. (New vault designs call for the vaults to be constructed below grade.)

- External boundary conditions for the at grade vaults prior to closure include: exposure of the concrete walls and roof to ambient air conditions, for example, free exchange of moisture and air with atmosphere, unsaturated concrete with intermittent wetting, and precipitation diverted away from waste form. The base slab will be exposed to unsaturated soil.

- Internal boundary conditions for the vault walls and base slab are a function of exposure to the salt waste form. The waste form is a highly alkaline material with a very high sulfate content and is therefore a potential source of chemicals that are known to degrade concrete.

- External boundary conditions for the concrete vault after closure include: contact with native soil (sand and clay) with very low, intermittent infiltration and unsaturated moisture content controlled by balance of capillary pressures and pore water-vapor equilibrium that is a function of pore space relative humidity.

- Internal boundary conditions for the vault walls and base slab are a function of exposure to the salt waste form (same as above).

  For this system, the CBP will conduct research to improve the understanding of degradation mechanisms and material evolution as a function of long times and develop algorithms that link degradation to changes in hydraulic properties of the cementitious barriers which can be used in the PA models.

2.6.2 Closed High-Level Waste Tank:

A brief description of the reference closed carbon steel high-level waste tank surrounded by a concrete vault and filled with a cementitious grout is provided below:

- Carbon steel liner (HLW tank) in a reinforced concrete vault will be filled with a cementitious grout to physically stabilize the structure and prevent collapse and to also chemically stabilize residual waste and contaminants. The annulus space between tank and concrete vault will also be filled with cementitious grout.
- One or more grout formulations will be used to fill the tank. A chemically reducing formulation (containing blast furnace slag) will be used for grout in contact with waste residuals.
- Tanks typically contain metal piping (e.g., cooling coils) and process equipment (e.g., pumps) which will also be filled with grout where practical.

- Closure includes backfill in some cases and coverage with multi-layer cap to limit infiltration.

- Each engineered barrier has a unique set of boundary conditions. For example, the external boundary conditions for the concrete vault are determined by the surrounding soil with a low, intermittent infiltration and unsaturated moisture content controlled by the balance of capillary pressures and pore water-vapor equilibrium and atmospheric exchange by gas diffusion. For the purposes of estimating the consequences over long performance times, the interfaces between the annulus grout and steel tank and the fill grout and the steel piping in the tank will be assumed to be similar to the interfaces between the reinforcing steel in the vault concrete and the concrete itself.

For this system, the CBP will conduct research to improve the understanding of degradation mechanisms and material evolution as a function of soil saturation, episodic events that may create fast pathways, i.e., cracking and its effect on hydraulic and leaching performance.

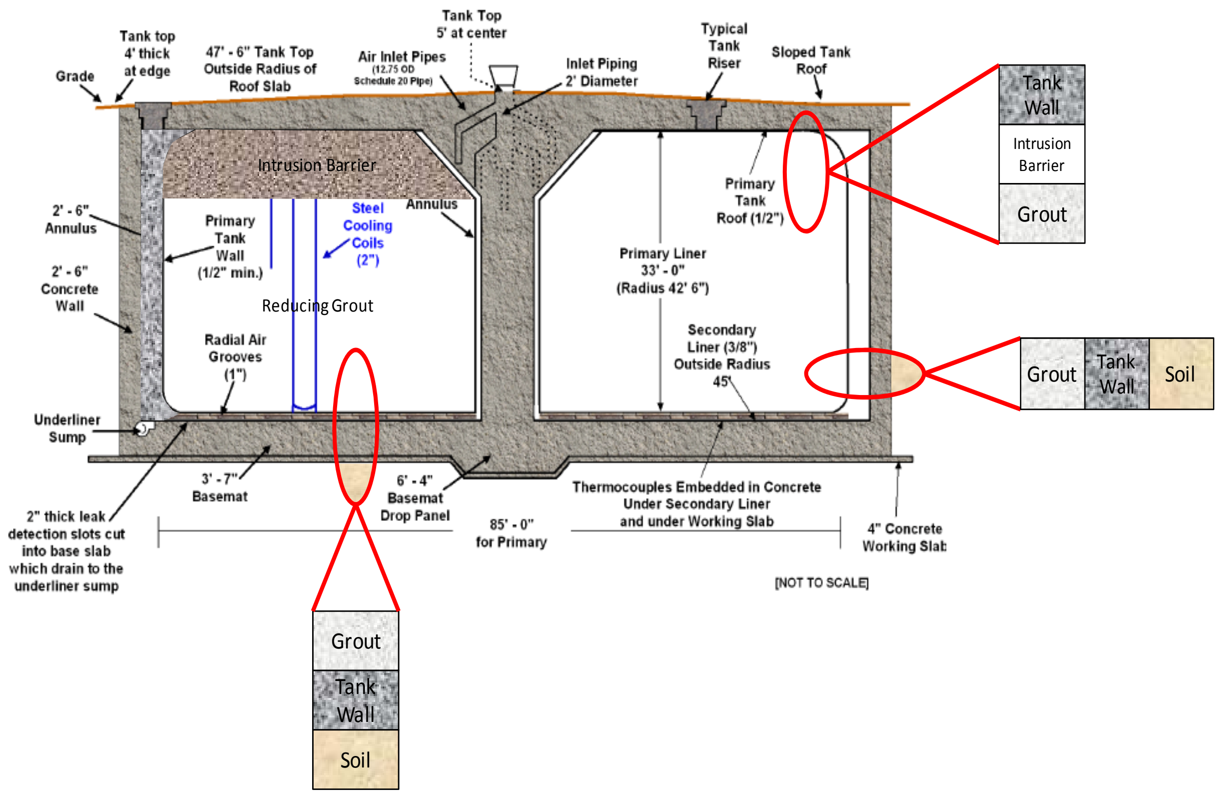


Figure 4. Schematic Illustration of a Closed High-level Waste Tank (Carbon Steel Tank in a Reinforced Concrete Vault) Containing a Cementitious Grout Fill. Examples of Multi-layer Material and Interfaces Relevant to 1-D Mechanistic Studies are Illustrated.

2.6.3 Spent Fuel Basin

A brief description of the reference case for a stainless steel-lined spent fuel basin is provided below:

- Below grade stainless steel-lined, reinforced concrete basin filled with borated water that results in approximately 6 m (20 ft) of hydraulic head on the basin.
- Internal boundary conditions for the reinforced concrete include complete saturation (water) of concrete pores with water containing borate.
- External boundary conditions include contact with saturated soil.

For this system, the development of through wall cracks due to initial conditions, construction joint failure, or post construction settlement and the resulting impact on flow and transport are of primary interest.

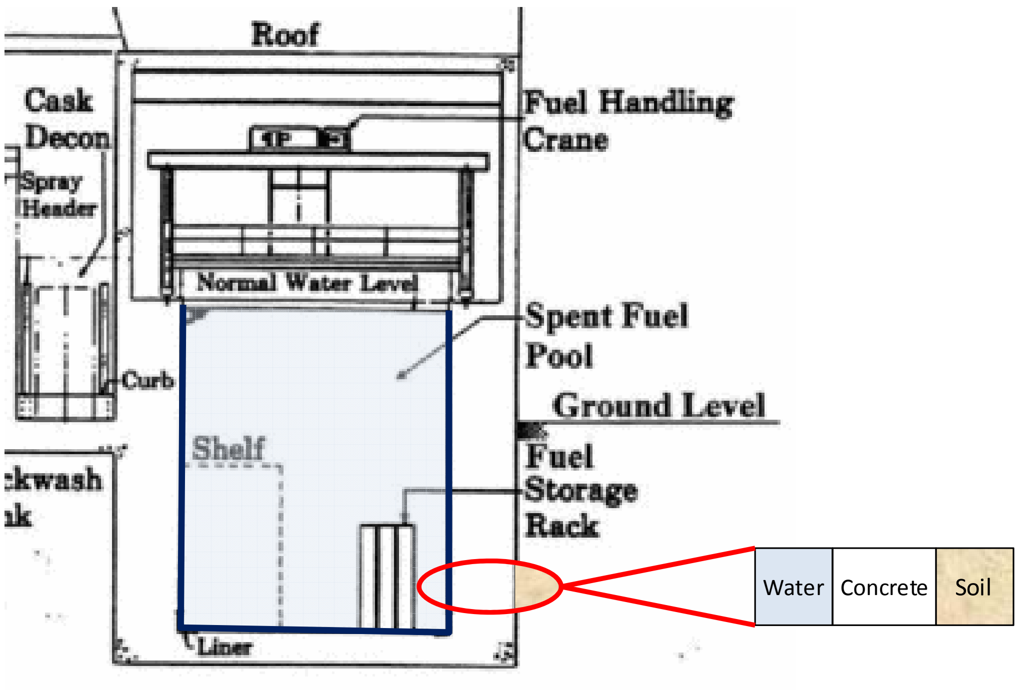


Figure 5. Schematic Dagram of Spent Fuel Pool During Operations. Examples of Multi-layer Material and Interfaces Relevant to 1-D Mechanistic Studies are Illustrated [7]

3.0 BOUNDARY CONDITIONS AND INTERFACES

The processes at interfaces between adjacent materials with different properties are of great significance, as reactions may occur that can have both beneficial as well as detrimental effects. This to a large extent relates to the gradients in different constituents and properties between the adjacent matrices. When there is a gradient between two matrices, diffusion will proceed to reduce the gradient. For this process to occur a transport medium is necessary. Gas phase transport is important for some species, but reaction of gas with dry solid is usually very slow. However, the combination of gas phase diffusion of reactive species (CO_2 and O_2) in a moist environment is a condition that will speed up chemical reactions. The degree of relative saturation has an important impact on transport. Three regimes can be described: (i) a continuous gas phase and discontinuous liquid phase where only gas phase diffusion occurs; (ii) both liquid and gas phases are continuous and diffusion occurs in both phases; and (iii) a continuous liquid phase is present and the gas phase is discontinuous and only liquid phase diffusion occurs.

The most common gradients are pH gradients, redox gradients, salt gradients and, obviously, the gradients of radionuclide concentrations within the cement stabilized grout. The reactions at interfaces are quite complex, as over a relatively small distance very substantial changes in solubility controlling conditions occur. Understanding these processes is helpful to decide whether such reactive zones play an active role in the transport of substances across an interface.

3.1 Cementitious Waste – Concrete

The interface boundary between cement stabilized waste and concrete is characterized by a gradient in soluble salts and depending on the nature of the cement used a redox gradient. Different pore structures amongst the two materials also can result in capillary suction from one to the other material across the interface. In the grout substances may be present that can have a detrimental effect on concrete (like sulfates) or chlorides. If there is a void between concrete and grout, then the carbonation/oxidation will proceed faster in the grout than in the concrete. The rate of front movement is of great relevance for the mobility of different elements.

3.2 Concrete – Soil

The interface between concrete and clay barrier and/or soil is characterized by a large pH gradient. The consequences are remineralization reactions, which depending on the nature of the soil can have surface effects on the concrete. Organic matter from soil interacts with the concrete and can potentially mobilize constituents. As long as the monolithic product remains intact the affected layer is generally limited. Concrete exposed to a moist soil atmosphere will carbonate faster then when exposed to the atmosphere, as the CO_2 concentration in the soil gas phase is generally higher than the CO_2 level in the atmosphere. This has to do with the degradation of organic matter continuously taking place in soil. Concrete exposed to environmental conditions is only slowly carbonated, unlike the much more porous Roman cements used to construct aquaducts. The ancient pozzolans (TRAS) used have a rather high porosity, which allows carbonation to penetrate deeper. Lumps of Roman cement tested for trace element behavior were found to be fully carbonated to the core (depth of some 10 cm) in some 2000 years (ECRICEM II, 2008).

3.3 Additional barriers

Additional barriers between grout and surroundings may be steel linings or other additional barriers like High Density Polyethylene Liners. These will form an effective barrier, until the lining fails, which at a time scale of 1000's of years may happen. Corrosion of the barrier will be dependent on the interfacial chemistry. The modeling must assume failure at some point in time.

4.0 DISCUSSION AND CONCLUSIONS

Each reference case includes the physical geometry of the engineered system, materials of construction (including wastes and contaminants where applicable), and environmental interfaces. In addition, the description of each system includes a scenario which with multiple reference states over defined time intervals:

(i) Initial construction,
(ii) Operations
(iii) Closure (with maintenance) and
(iv) Closure (post-maintenance).

The close state may also have multiple evolutionary states, which include fast pathways or other features that will require consideration in the performance modeling.

Initial definition of the reference cases is focused on a single reference state, i.e., closure (post-maintenance) for waste management units, or operations for operating/storage units. For the purpose of developing algorithms that predict changes in parameters as a function of time and conditions, each reference case was selected to have a plausible system configuration and set of characteristics. However, the reference disposal units are not defined to represent a specific field case. This allows for development and testing over a range of field conditions that cover those encountered across the DOE complex.

Each reference case is a simplification of the actual expected disposal or storage unit and is a conceptual model of a unit. The definition of each reference case is expected to evolve over time as more knowledge is obtained and model uncertainties are addressed in addition to parameter and numerical uncertainties.

5.0 REFERENCES

1. C. A. Langton, et. al., 2008. "Partnership for the Development of Next Generation Simulation Tools to Evaluate Cementitious Barriers and Materials Used in Nuclear Applications" DOE Waste Management Symposium, February 2008, Phoenix, AZ.

2. U.S. Department of Energy Office of Environmental Management, September 2007, Technology Engineering Road Map: Reducing Technical Risk and Uncertainty in the EM Program, U.S. DOE, Washington DC, www.em.doe.gov.

3. K. L. Dixon, J. Harbour, and M. A. Phifer. 2008. "Hydraulic and Physical Properties of Saltstone Grouts and Vault Concretes," SRNL-STI-2008-00421, Revision 0, November 2008, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC 29808.

4. M. A. Phifer, M. R. Millings, and G. P. Flach, "Hydraulic Property Data Package for the E-Area and Z-Area Soils, Cementitious Materials, and Waste Zones," WSRC-STI-2006-00198, Revision 0, September 2006, Washington Savannah River Company, Savannah River Site, Aiken, SC 29808.

5. K. L. Dixon and M. A. Phifer, 2007. "Hydraulic and Physical Properties of Tank Grouts and Base Mat Surrogate Concrete for FTF Closure, WSRC-STI-2007-00369 Revision 0, October 2007, Washington Savannah River Company, Savannah River Site, Aiken, SC 29808.

6. K. L. Dixon and M. A. Phifer, 20007. "Cementitious Material Selection for the Future Component-In-Grout Waste Disposals," WSRC-STI-2007-00207, Revision 0, December 2007, Washington Savannah River Company, Savannah River Site, Aiken, SC 29808.

7. J. Philip, 2007. Personal Communication, US Nuclear Regulatory Commission.

8. D. I. Kaplan and J. M. Coates, 2007. "Partitioning of Dissolved Radionuclides to Concrete Under Scenarios Appropriate for Tank Closure Performance Assessments," WSRC-STI-2007-00640, Revision 0, December 21, 2007, Washington Savannah River Company, Savannah River Site, Aiken, SC 29808.

9. D. I. Kaplan, 2006. "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site," WSRC-TR-2006-00004, Revision 0. Fegruary 28, 2006, Washington Savannah River Company, Savannah River Site, Aiken, SC 29808.

10. D. I. Kaplan, K. Roberts, J. Coates, M. Siegfried, and S. Serkiz, "Saltstone and Concrete Interactions with Radionuclides: Sorption (Kd), Desorption, and Reductin Capacity Measurements," SRNS-STI-2008-00045, October 30, 2008, Savannah River Nuclear Solutions, Savannah River Site, Aiken, SC 29808.

11. Nichols, R. L., Looney, B. B., Flach, G. P., and Rossabi, J., 2000. "Recommendations for Phase II Vadose Zone Characterization and Monitoring at the E-Area Disposal "Slit" Trenches and Mega-Trench (U)," WSRC-TR-2000-00059, February 2000, Westinghouse Savannah River Company, Aiken, South Carolina.

6.0 ATTACHMENTS

6.1 ATTACHMENT A - REFERENCE CASE MATERIALS AND PHYSICAL PROPERTIES

Table A-1. Reference Case Binary, Ternary, and Quaternary Concrete Formulations [3, 4].

Ingredient	**Type I/II Binary Blend [3] (kg/m^3) *(lbs/yd^3)***	**Type I/II Ternary Blend [4] (kg/m^3) *(lbs/yd^3)***	**Type V Quaternary Blend [3] (kg/m^3) *(lbs/yd^3)***
Type I/II Cement (ASTM C 150)	239 *(419)*	71.3 *(120)*	0
Type V Cement (ASTM C 150)	0	0	133.5 *(225)*
Blast Furnace Slag (ASTM C 989)	158 *(278)*	163 *(275)*	178 *(300)*
Type F Fly Ash (ASTM C 618)	0	80.1 *(135)*	103.8 (175)
Silica Fume (ASTM C 1240)	0	0	29.7 *(50)*
Quartz Sand (ASTM C 33)	646 *(1133)*	756.7 *(1270)*	540.7 *(911)*
No. 67 Granite Aggregate (maximum ¾ in) (ASTM C 33)	1025 *(1798)*	1038.6 *(1750)*	1098 *(1850)*
Water (maximum)	152 *268 (32.1gallons)*	142.4 *240 (28.8 gallons)*	168.6 *284 (34 gallons)*
Water to Cementitious Material Ratio	0.385	0.38	0.38
Grace WRDA 35 (ml /100 kg cement + pozzolan) *(oz/cwt cement + pozzolans)*	32.6 *(5.0)*	32.6 *(5.0)*	32.6 *(5.0)*
Grace Darex II (ml /100 kg cement + pozzolan) *(oz/cwt cement + pozzolans)*	2.6-3.3 *(0.4-0.5)*	2.6-3.3 *(0.4-0.5)*	2.6-3.3 *(0.4-0.5)*
Grace Adva 380 (ml /100 kg cement + pozzolan) *(oz/cwt cement + pozzolan)*	19.6 - 26.1 *(3 - 4)*	19.6 - 26.1 *(3 - 4)*	19.6 - 26.1 *(3 - 4)*
Unit Weight (kg/m^3) *(lbs/yd^3)*	2220 *(3896)*	2156 *(3790)*	2162 *(3795)*
Compressive Strength at 28 Days (MPa) (psi)	27.6 *(4000)*	27.6 *(4000)*	34.5 *(5000)*

Table A-2. Reference Case Concretes Physical and Hydraulic Property Data [3, 4].

Property	**CBP Reference Type I/II Binary Blend [3] (kg/m³) *(lbs/yd³)***	**CBP Reference Type I/II Ternary Blend [4] (kg/m³) *(lbs/yd³)***	**CBP Reference Type V Quaternary Blend [3] (kg/m³) *(lbs/yd³)***
Compressive Strength (psi)			
28 Days	8725		7430
90 Days	9430		9280
Saturated Hydraulic Conductivity (cm/s) Samples Cured 28 Days (log average)	3.1E-10 Range 1.1E-10 to 2.1E-09		1.1E-10 Range 6.0E-11 to2.8E-10
Intrinsic Permeability (Darcy) Based on Properties of Tap Water (log average)	3.2E-08 Range 1.1E-08 to 2.2E-07		1.1E-08 Range 6.2E-09 to 2.9E-08
Dry Bulk Density (g/cm^3) 28 Days (arithmetic average)	2.24 Range 2.15 to 2.31		2.19 Range 2.16 to 2.21
Particle Density (g/cm^3) 28 Days (arithmetic average)	2.53 Range 2.44 to 2.58		2.48 Range 2.39 to 2.50
Porosity (volume fraction) 28 Days (arithmetic average)	0.11 Range 0.10 to 0.12		0.12 Range 0.08 to 0.13
Moisture Retention Curves Over Pressure Range 102 to 15,296 cm H_2O (0.1 to 15 bars)	Figure A-1		Figure A-2
Characterization Curves	Figure A-3		Figure A-4
Van Genuchten Transport Parameters			
θ_s (cm^3/cm^{-3})	0.121		0.124
θ_r (cm^3/cm^{-3})	0.115		0.119
α (1/cm)	0.054		0.006
n	1.27		1.65
m	0.2099		0.3951

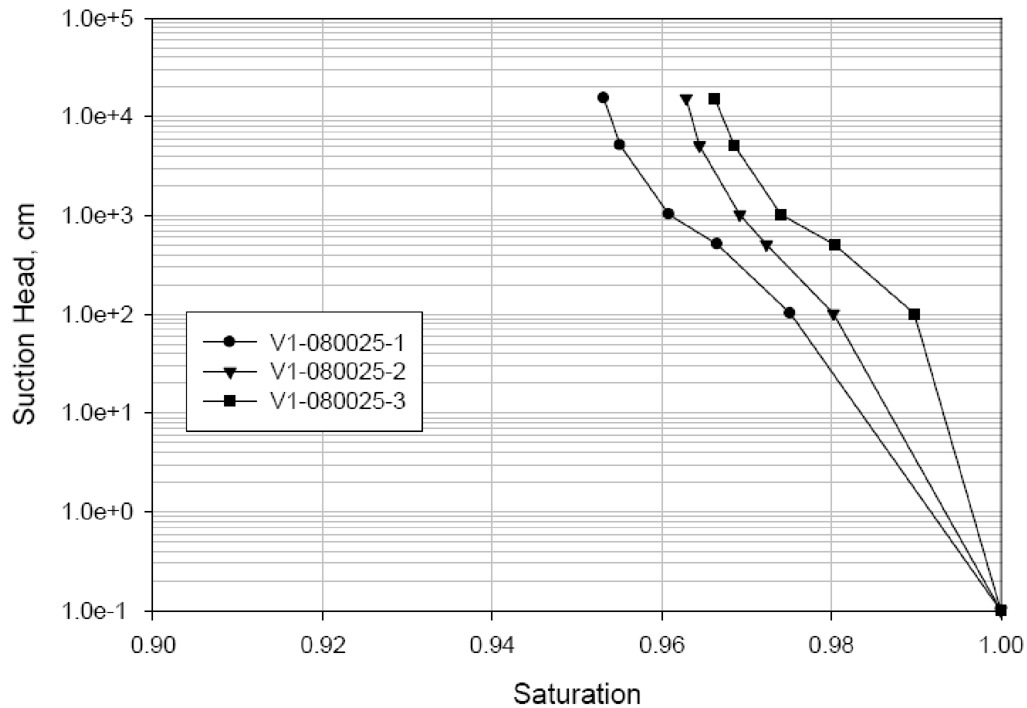


Figure A-1. Moisture retention curves for the 28 day binary concrete samples (Vault 1/4).

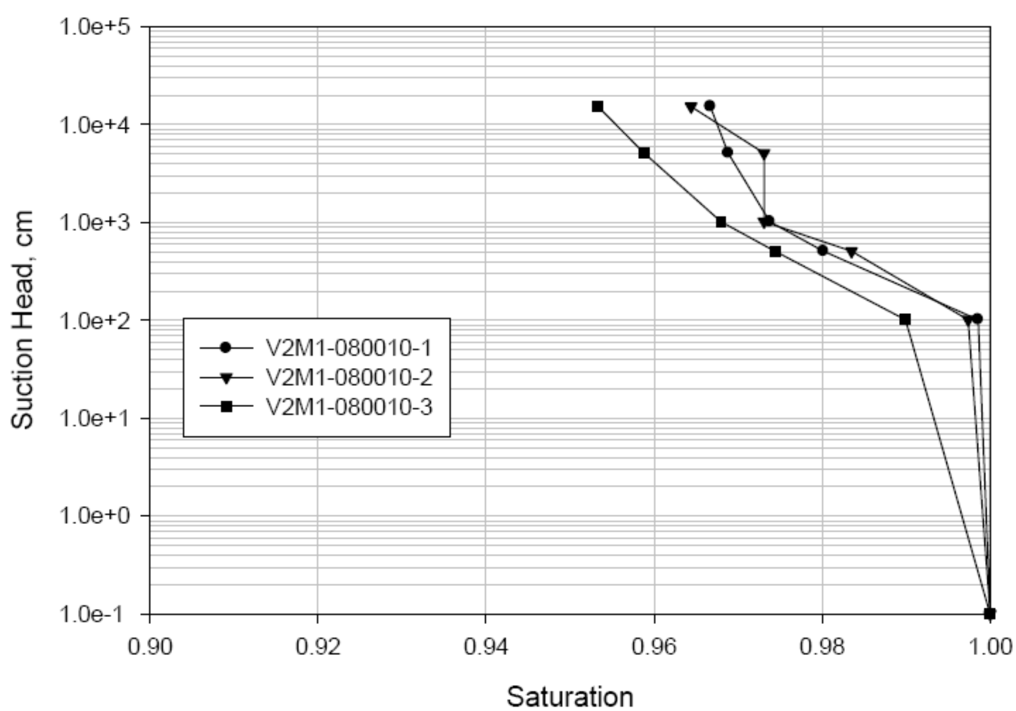


Figure A-2. Moisture retention curves for the 28 day quaternary concrete samples (Vault 2).

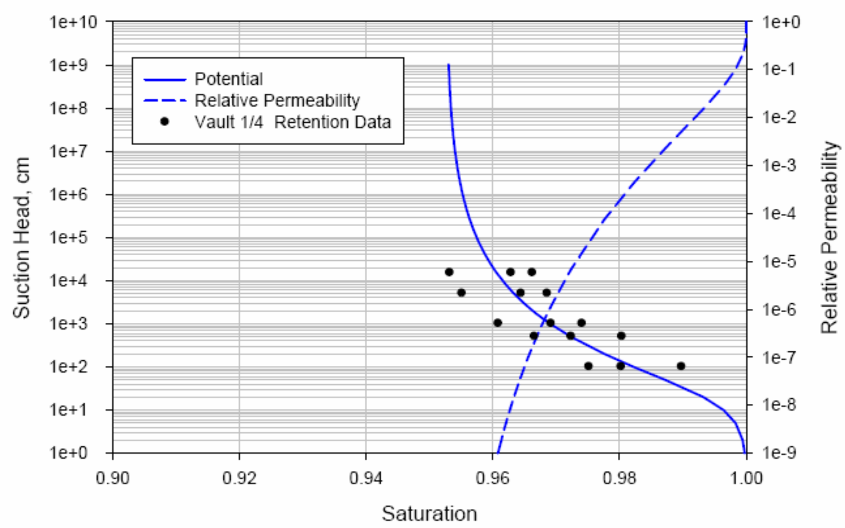


Figure A-3. Characteristic Curves for Binary Concrete based on 28 day curing.

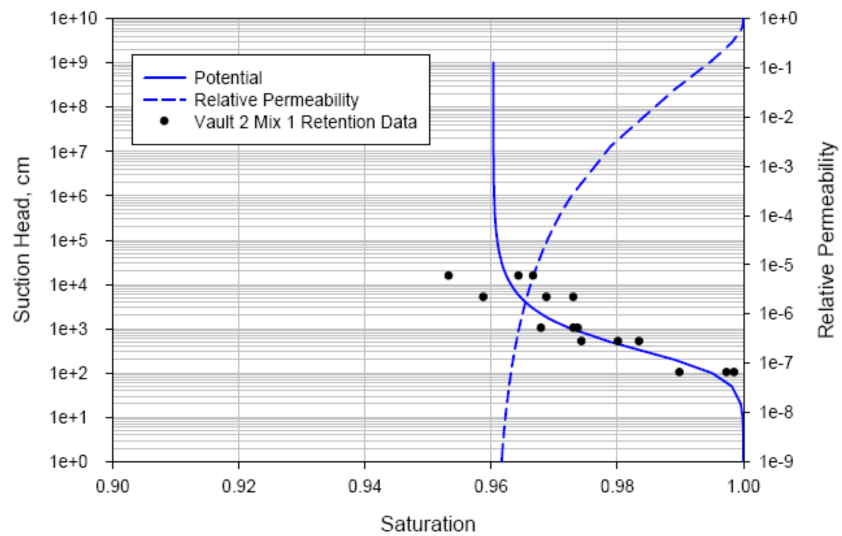


Figure A-4. Characteristic Curves for Quaternary Concrete based on 28 day curing.

6.2 ATTACHMENT B - REFERENCE CASE FILL MATERIALS AND PHYSICAL PROPERTIES

Table B-1. Reference Case Fill Grout Formulations.

Ingredient	**Type I/II Ternary Blend [5] (kg/m^3) *(lbs/yd^3)***	**Type I/II Ternary Blend 2 [5] (kg/m^3) *(lb/yd^3)***	**Type I/II Ternary Blend 3 [5] (kg/m^3) *(lbs/yd^3)***	**Type I/II Binary Blend [6] (kg/m^3) *(lbs/yd^3)***
Type I/II Cement (ASTM C 150)	44.5 *(75)*	109.8 *(185)*	109.8 *(185)*	267 *(450)*
Grade 100 Blast Furnace Slag (ASTM C 989)	124.6 *(210)*	154.3 *(260)*	154.3 *(260)*	0
Type F Fly Ash (ASTM C 618)	222.6 *(375)*	344.2 *(580)*	504.5 *(850)*	267 *(450)*
Quartz Sand (ASTM C 33)	1365 (2300)	1118.7 *(1885)*	559.1 *(942)*	746.6 *(1258)*
No. 8 Granite Aggregate (maximum 3/8 in) (ASTM C 33)	0	0	561.5 *(946)*	741.9 *(1250)*
Water (maximum) (kg/m^3) *(lbs/yd^3)*	297 *501 (60 gallons)*	297 *501 (60 gallons)*	302 *509 (61 gallons)*	207.7 *350 (42 gallons)*
Water to Cementitious Material Ratio	0.76	0.49	0.39	0.39
Viscosity Modifier (Welan Gum) Kelco-Crete ($grams/m^3$) *($grams/yd^3$)*	360 *(275)*	283 *(216)*	283 *(216)*	0
High Range Water Reducer (HRWR) (L/m^3) *($fl\ oz/yd^3$)*	3.48 90*	2.88 54**	2.88 54***	2.88 – 2.707 54-70
Sodium Thiosulfate (optional)	1.25 *(2.1)*	1.25 *(2.1)*	1.25 *(2.1)*	0
Set Regulator (W. R. Grace Recover *($fl\ oz/yd^3$)*	as needed	as needed	as needed	as needed
Unit Weight (kg/m^3) *(lbs/yd^3)*	1972 (3461)	1952 *(3426)*	2104 *(3692)*	2141 *(3758)*
Compressive strength at 28 Days MPa *(psi)*	27.6 *(4000)*	27.6 *(4000)*	34.5 *(5000)*	27.6 *(4000)*

* W. R. Grace Adva flow ** Sika ViscoCrete 2100 *** W. R. Grace Advaflex

Table B-2. Physical and Hydraulic Property Data for Reference Case Flowable Fill Grout Formulations [5, 6].

Property	**Type I/II Ternary Blend [5] (kg/m^3) *(lbs/yd^3)***	**Type I/II Ternary Blend 2 [5] (kg/m^3) *(lb/yd^3)***	**Type I/II Ternary Blend 3 [5] (kg/m^3) *(lbs/yd^3)***	**Type I/II Binary Blend [6] (kg/m^3) *(lbs/yd^3)***
Compressive Strength (psi)				
28 Days Average of 2 Samples	1,710 Range 1,660 to 1,760	3,550 Range 3,500 to 3,610	2,885 Range 2,280 to 3,490	4,680 Range 4,420 to 4,830
90 Days	2,275 Range 2,250 to 2,300	*5,295* Range 5,160 to 5,430	4,840 Range 4,600 to 5,080	1,640 Range 7,520 to 7,700
180 Days	2,410	NA	NA	NA
Saturated Hydraulic Conductivity (cm/s) Samples Cured 28 Days (arithmetic average)	3.6E-08 Range 1.0E-08 to 8.5E-08	8.9E-09 Range 8.2E-09 to 9.5E-09	6.6E-09 Range 5.5E-09 to 8.1E-09	3.6E-08 Range 1.5 E-08 to 7.2E-08
Intrinsic Permeability (darcy) Based on Properties of Tap Water (log average)				
Dry Bulk Density (g/cm^3) 28 Days (arithmetic ave.)	1.81 Range 1.80 to 1.86	1.86 Range 1.84 to 1.88	1.96 Range 1.92 to 2.06	2.01 Range 1.99 to 2.04
Particle Density (g/cm^3) 28 Days (arithmetic ave.)				
Porosity (volume fraction) 28 Days Water Exchangeable Porosity (arithmetic ave.)	0.266 Range 0.219 to 0.278	0.220 Range 0.190 to 0.250	0.209 Range 0.186 to 0.225	0.167 Range 0.137 to 0.216
Moisture Retention Curves Over Pressure Range 102 to 15,296 cm H_2O (0.1 to 15 bars)			Figure B-4	
Characteristic Curves	Figure B-1	Figure B-2	Figure B-3	
Van Genuchten Transport Parameters				
θ_s (cm^3/cm^{-3})				
θ_r (cm^3/cm^{-3})				
α (1/cm)				
n				
m				

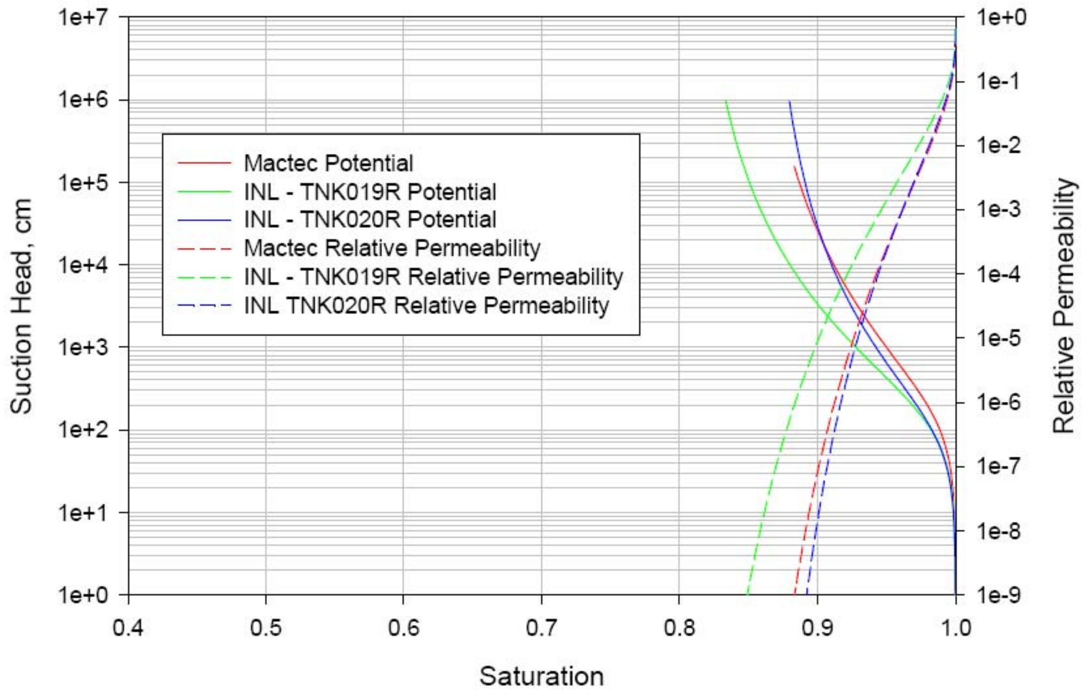


Figure B-1. Comparison of characteristic curves for Type I/II Ternary Blend Reducing Grout using measurements from various sources [5].

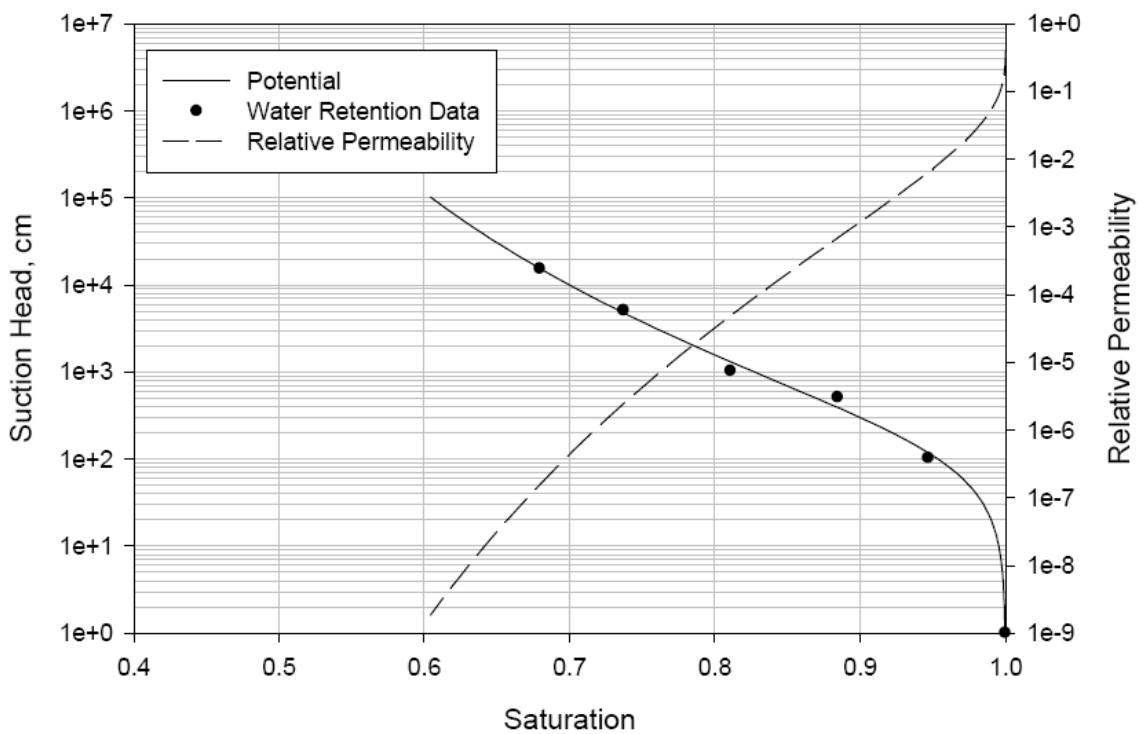


Figure B-2. Characteristic curves for Type I/II Ternary Blend 2 Reducing Grout [5].

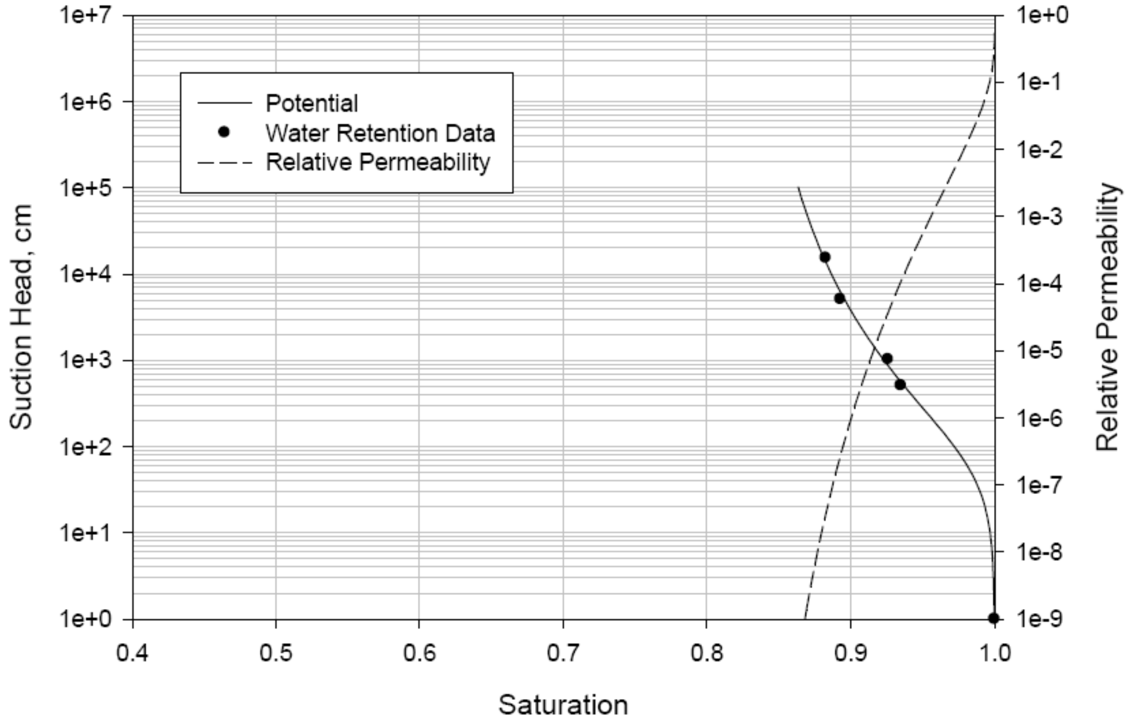


Figure B-3. Characteristic curves for Type I/II Ternary Blend 3 Reducing Grout [5].

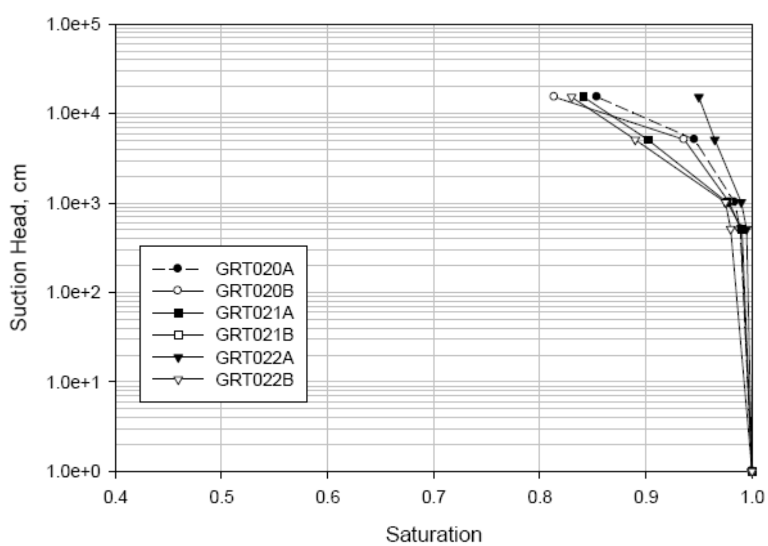


Figure B-4. Characteristic curves for Type I/II Ternary Blend 3 Reducing Grout [5].

6.3 ATTACHMENT C - REFERENCE CASE SALT WASTEFORM AND PHYSICAL PROPERTIES

The reference case salt waste form is prepared from a premix of cementitious reagents and a low-level radioactive solution containing dissolved sodium salts. The formulation for the premix is provided in Table 3. The formulation for a typical DOE salt waste solution stabilized with the reference premix is provided in Table 4.

Table C-1. Reference Case Blended Premix Reagents for DOE Salt Waste Forms [3].

Ingredient	Wt. %
Type I/II Cement (ASTM C 150)	10
Grade 100 Blast Furnace Slag (ASTM C 989)	45
Type F Fly Ash (ASTM C 618)	45

Table C-2. Reference Case Non Radioactive Salt Waste Solution [3].

Ingredient	Molarity (Moles/Liter)	Mass (g/Liter H_2O)
Sodium Hydroxide, NaOH (50% by weight solution)	2.866	229.28
Sodium Nitrate, $NaNO_3$	1.973	167.66
Sodium Nitrite, $NaNO_2$	0.485	33.43
Sodium Carbonate, Na_2CO_3	0.118	12.46
Aluminum Nitrate Nona-hydrate, $Al(NO_3)_3 \cdot 9H_2O$	0.114	42.90
Sodium Sulfate, NA_2SO_4	0.055	7.84
Sodium Phosphate $Na_3PO_4 \cdot 12H_2O$	0.007	2.76
Density (g/ml)	1.248	
Dynamic Viscosity (cP)	2.78	
Wt.% Water	71.12	
Wt. % Solids	28.88	
Wt. % Salt in Wet Waste Form with a Water to Premix Ratio of 0.60	13.0	

Table C-3. Physical and Hydraulic Properties for Reference Case Salt Waste Form [3].

Property	**Cement-Based Salt Waste Form [3]**	
Compressive Strength (psi)		
28 Days	1,213 Range 1,200 to 1,230	
90 Days	1,467 Range 1,450 to 1,480	
Saturated Hydraulic Conductivity (cm/s) Samples Cured 28 Days (log average)	6.0E-09 (1.5E-09)	
Intrinsic Permeability (Darcy) Based on Properties of Tap Water (log average)		
Dry Bulk Density (g/cm^3) 28 Days (arithmetic average)	1.01	
Particle Density (g/cm^3) 28 Days (arithmetic average)	2.42	
Porosity (volume fraction) 28 Days (arithmetic average)	0.58	
Moisture Retention Curves Over Pressure Range 102 to 15,296 cm H_2O (0.1 to 15 bars)	Figure C-2 Figure C-3	
Characteristic Curves	Figure C-1	
Van Genuchten Transport Parameters		
θ_s (cm^3/cm^{-3})	0.580	
θ_r (cm^3/cm^{-3})	0.572	
α (1/cm)	0.1550	
n	1.30	
m	0.2308	

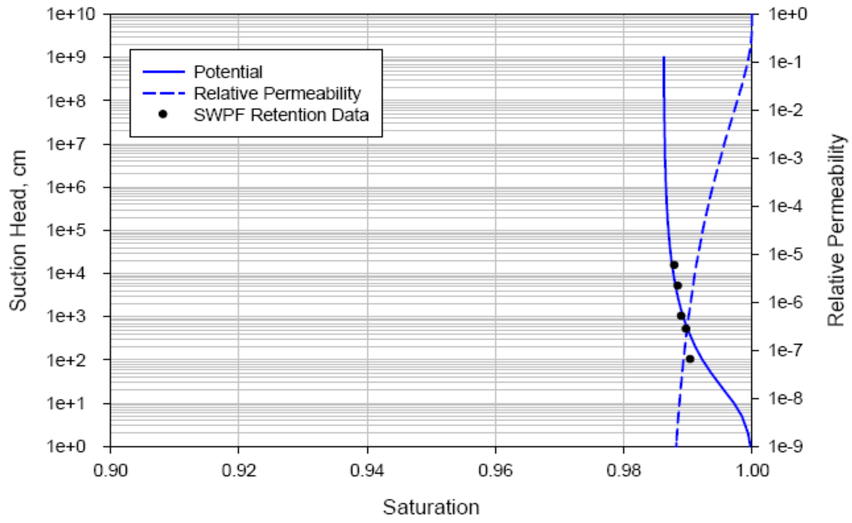


Figure C-1. Characteristic Curves for the SWPF Saltstone (using 28 and 90 day retention data).

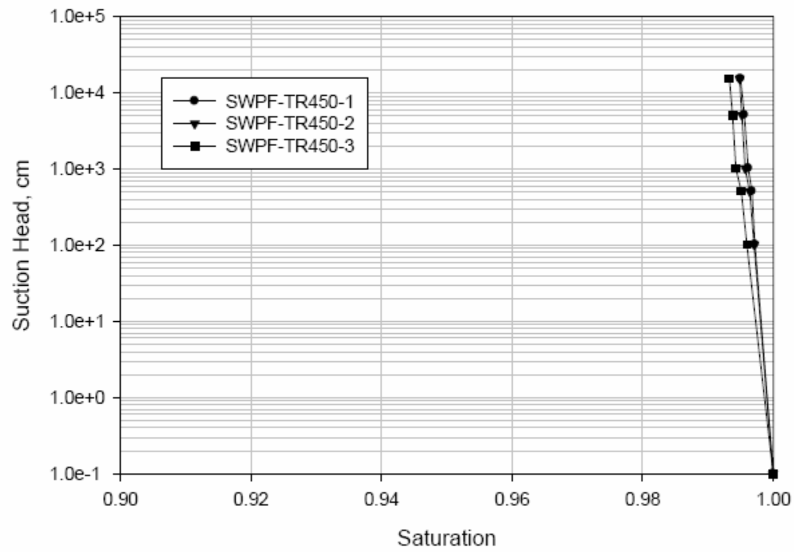


Figure C-2. Moisture retention curves for the 28 day SWPF saltstone samples.

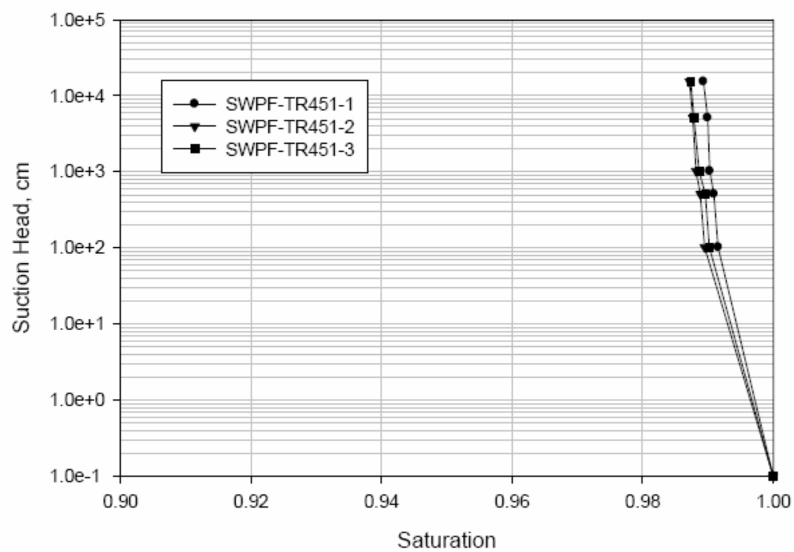


Figure C-3. Moisture retention curves for the 90 day SWPF saltstone samples.

6.4 ATTACHMENT D - CONTAMINANT K_d DATA FOR REFERENCE CASE ORDINARY (OXIDIZED) PORTLAND CEMENTITIOUS MATERIALS

Table D-1. K_d values for selected radionuclides for new and aged ordinary portland cement (oxidized) concrete used in the SRS PAs [8].

Contaminant	Stage 1 New Concrete (pore solution pH ~12.4 in equilibrium with $Ca(OH)_2$)	Stage 2 Partially Aged Concrete (pore solution pH ~10.5 in equilibrium with calcium silicate, aluminate hydrates)	Stage 3 Aged Concrete (pore solution in equilibrium with $CaCO_3$)
AM(III)			
Cd(II)			
Ce(III)			
Co(II)	1000	1000	500
Cs(I)	2	4	2
Hg(I)			
I(I)	8	20	0
Np(V)			
Pa(V)			
Pu(IV/V)	5000	5000	500
Sn(IV)	4000	4000	2000
Sr(II)	1	1	0.8
Tc(VII)	0	0	0
U(VI)	1000	1000	70
Y(III)			

Table D-2. K_d values for selected radionuclides for new and aged ordinary portland cement(oxidizing) concrete used in the SRS PAs [9].

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement [(b)] 3rd Stage (pH ~5.5)		
	Conser-vative	"Best"	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
							cement is highly reversible when Cl is added to aqueous phase, suggesting it adsorbed and was not precipitated (*3*). Increasing pH, decreased I^- sorption (*3;* therefore Stage 3 *Kd* values will be slightly greater than other stages). Iodide sorption on CSH varies with its C/S ratio, increasing towards high C/S ratios (*3*). Decreased *Kd* values in "Young Concrete" because of high concentration of aqueous salts. In 1st Stage *Kd* values were decreased because high ionic strength likely resulted in anion exchange (desorption).
Inorganic C [(c)]	14	20	7	10	0	0	^{14}C chemistry is very complicated and is not well characterized by the *Kd* construct. It is influenced by carbon dioxide gas/water/solid phase equilibrium, isotopic exchange, adsorption, precipitation, and coprecipitation. To be conservative the role of gas phase and isotopic exchange (two very important processes for removing ^{14}C from groundwater) will not be considered. Inorganic C exists as an anion, CO_3^{2-} (*1*). Subsurface C chemistry in a cementitious environment is discussed by Dayal (7, 8) and how it has been applied to the SRS by Kaplan (*9*).
Ac, Am, Bk, Cf, Cm, Eu, Gd, Sm	2500	5000	2500	5000	360	500	Trivalent cation *Kd* values for concrete exceed those for sediments (3). Am *Kd* > 10,000 mL/g (*10*). Am *Kd* value was 12,000 mL/g based on diffusion tests in cement (*11*). Am *Kd* values ranged from 2,500 to 35,000 mL/g for 7 fresh concrete blends (*1, 6*). Am *Kd* for 65-yr old concrete sample = 10,000 mL/g (1, 6). Fresh cement Am *Kd* = 2000 for 24-h contact time (*12*). Eu *Kd* = 2,400 mL/g for 24-h contact time (*12*). Very large *Kd* values may reflect precipitation reaction that occurred during the adsorption measurements.
Co, Ni	500	1000	500	1000	360	500	Three studies were found that included adsorption data for Ni onto cement/concrete. Hietanen et al (*15*) reported *Kd* values that ranged from 500 to 3000 mL/g, Kato and Yanase (*12*) reported a Ni *Kd* value of 1500 mL/g, and Pilkington and Stone (*16*) reported *Kd* values that ranged from 500 to 3000 mL/g.
Ra, Ba	70	100	70	100	50	70	Bayliss et al. (*11*) and Berry et al. (*13*) measured Ra *Kd* values onto ordinary Portland cement and as a function of Ra concentration. They reported *Kd* that ranged from 50 to 530 mL/g.
Sr	0.2	1	0.5	1	0.2	0.8	Jakubick et al. (*14*) reported Sr *Kd* values of 0.8 to 1.6 mL/g for high density and normal density concretes, and 1.3 to 3 mL/g for the same concretes, but in lower ionic strength solutions. Ewart et al. *(14)* reported *Kd* values between 1 and 4 mL/g. Kato and Yanase reported a Sr *Kd* value of 56 mL/g for an experiment involving 24 h contact time, dried cement powder, pH 11

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement [(b)] 3rd Stage (pH ~5.5)		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser -vative**	**"Best"**	**Comments/References[(a)]**
							cement equilibrated water. We elected to disregard this value because it is an order-of-magnitude greater than those reported by other researchers and the nature of the solid phase was not clearly described by the author. In 1st Stage *Kd* values were decreased because high ionic strength likely results in competitive exchange (desorption).
Sn	2000	4000	2000	4000	1000	2000	Sn exists in cementitious environments in the +4 state (*17*) and as such readily hydrolyses. Using sulfate resistant Portand cement, Sn *Kd* values were >30,000 mL/g; this likely reflected some precipitation (*17*).
Cs, Fr	1	2	2	4	1	2	Cs *Kd* values in hardened HTS cement discs, pH 13.3 were close to 3 mL/g (*15*). Wieland and Van Loon (*17*) reviewed Cs *Kd* values onto various cementitious materials and they had a very narrow range: from 0.2 to 5.0 mL/g. In 1st Stage *Kd* values were decreased because high ionic strength likely results in competitive exchange (desorption). This has been shown experimentally (*17*).
Nb	500	1000	500	1000	360	500	Krupka and Serne (*18*) review Nb *Kd* values and concluded that there was a great deal of variability related in Nb sorption data to cementitious materials. They reported *Kd* ranges of 11 to 69,000 mL/g (from studies that had problems with the blanks, *i.e.*, the blanks indicated Nb sorbed to the glassware). We defer to their best values (1000 mL/g) and add conservatism to these values.
Np, Pa	1000	2000	1000	2000	140	200	These radionuclides are assumed to exist in the +5 oxidation state. Np sorption test to 7 different 65-yr old cements using cement pore water reached steady state after 30 days, *Kd* values ranged from 1500 to 9500 mL/g (*1, 6*). As is the case with all large *Kd* values, these values may reflect some precipitation occurring during the adsorption measurement.
Se, Te	100	300	210	300	110	150	Twenty-seven cementitious formulations (varying water/solid, silica fume %, and clay concentration) were used to measure selenate (SeO_3^{2-}) *Kd* values from an alkaline solution (Johnson et al. 2000). *Kd* values ranged from 250 to 930 mL/g. Sorption was irreversible. At high selenate (SeO_4^{2-}) concentrations, sorption to ettringite, monosulfate, calcium-silicate-hydrate (all mineral constituents of concrete) resulted in selenate substitutes for sulfate (*23*). Selenite *Kd* values measured in sulfate resistant Portland cement ranged from 30 to 100 mL/g (Wieland and Van Loon 2003). It is not clear why these latter *Kd* values were so much lower than those reported by Johnson et al (2000). This variability in results requires that conservative

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement [(b)] 3rd Stage (pH ~5.5)		
	Conser-vative	"Best"	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
							values in table be lowered.
Pb, Po	250	500	250	500	180	250	Soft divalent cations: Bayliss et al. (1988) conducted a series of sorption experiments with Pb and crushed sulfate resisting Portland cement and ordinary Portland cement/blast furnace slag pastes with an Eh of +50 to -500 mV. The main findings were that sorption was concentration and cement composition dependent. Data strongly suggested solubility controls on Pb aqueous concentrations. "Best" estimates taken from (*19*).
Pu(III/IV), Pu(V/VI), Pu(combo) Th, Zr	1000	5000	1000	5000	250	500	Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu *Kd* values than those that did not contain BFS. High *Kd* values are attributed more to low solubility of Pu in high pH systems, than to adsorption/absorption processes. Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, Th-*Kd* values were 2,500 to 5,500 mL/g (*1, 6*). Th- *Kd* values were consistently less than Am *Kd* values, greater than U- *Kd* values, and very similar to Np and Pu *Kd* values (*1, 6*). Pu- *Kd* values ranged from 1,000 to 12,000 mL/g (*1, 6*). Using a sulfate resistant Portland cement, Th *Kd* values were measured to be 100,000 mL/g (*17*).
U	500	1000	500	1000	50	70	U(VI)- *Kd* values for 7 types of cement were 350 to 13,000 mL/g; median = 1400 mL/g (*1,6*).

(a) References: (*1*) = Allard et al. 1984; (*2*) = Sarott et al. 1992 ; (*3*) = Atkins and Glasser 1992 ; (*4*) = Brodda 1988 ; (*5*) = Macias et al. 1997; (*6*) = Hoglund et al. 1985 ; (*7*) = Dayal and Reardon 1992; (*8*) = Dayal et al. 1989; (*9*) = Kaplan 2005; (*10*) = Ewart et al. 1988; (*11*) = Bayliss et al. 1991; (*12*) = Kato and Yanase 1993; (*14*) = Ewart et al. 1986; (*15*) = Sarott et al. 1992; (*16*) = Pilkington and Stone 1990; (*17*) = Wieland and Van Loon 2003; (*18*) = Krupka and Serne 1998; (*19*) = Bradbury and Sarott 1995; (*20*) = Tits et al. 2003; (*21*) = Krupka et al. 2004; (*22*) = Johnson et al. 2000; (*23*) = Baur and Johnson 2003.

(b) The age of each of the stages is facility specific because it depends on the amount of water that passes through the cementitious material (see Section 4.2.4).

(c) Inorganic carbon geochemistry is very complicated. The use of only the *Kd* value without the associated solubility value in a cementitious environment will greatly overestimate the true mobility of C through this environment.

6.5 ATTACHMENT E - CONTAMINANT K_d DATA FOR REFERENCE CASE CHEMICALLY REDUCED CEMENTITIOUS MATERIALS

Table E-1. Summary of K_d values for selected radionuclides for new and aged chemically reduced concrete used in the SRS PAs [10].

Contaminant	Stage 1 New Concrete (pore solution pH ~12.4 in equilibrium with $Ca(OH)_2$)	Stage 2 Partially Aged Concrete (pore solution pH ~10.5 in equilibrium with calcium silicate, aluminate hydrates	Stage 3 Aged Concrete (pore solution in equilibrium with $CaCO_3$)
Sn	5,000	5,000	2,000
Am	5,000	5,000	1,000
Ce	5,000	5,000	1,000
Y	5,000	5,000	1,000
Cd	5,000	5,000	1,000
Co	5,000	5,000	1,000
Hg	1,000	1,000	300
Sr	0.5 - 3.0	0.5 - 3.0	20
U	2,500	2,500	2,500
Cs	0 - 2	0 - 2	10
Np (V)	2,000 4,000 recommended	3,000 4,000 recommended	200 - 300 3,000 recommended
Pa(V)	5,000	5,000	500
Pu	5,000 10,000 recommended	5,000 10,000 recommended	500 10,000 recommended
I	5-9	5-9	0
Tc(VII)	5,000	5,000	5,000
Se	300	300	300

Table E-2. K_d values for selected radionuclides for new and aged chemically reduced concrete used in the SRS PAs [9].

Table 14. Distribution coefficients (*Kd* values, mL/g): Reducing Cementitious Solids

Radio-nuclide	Young Cement (pH ~12.5)		Moderately-aged Cement (pH ~10.5)		Aged Cement (pH ~5.5)		Comments/References[(a)]
	Conser-vative	"Best"	Conser-vative	"Best"	Conser-vative	"Best"	
^{3}H, Cl, Kr, Rn, Sr, Ra, Zr, Th, Nb, Sn, I, Cs, Ac, Am, Cf, Cm, Eu, Po, Se, C, Co, Ni, Pb, Bk, Sm, Fr, Gd, At, Ar, Te, Ba, Np, Pa, Pu, Rb, Pu(IV), Pu(V), Pu(combo)	(Same values as reported in Table 13 for Oxidizing Cementitious Solids)						Concrete containing reducing agents (blast furnace slag, BFS) did not have greater **Pu**, **Np**, or **Pa** *Kd* values than those that did not contain BFS (*1, 2, 3*).
Tc, Re	2500	5000	2500	5000	2500	5000	$Tc^{VII}O_4^-$ gets reduced to Tc^{4+}, which like other tetravalent cations sorbs strongly to surfaces. "Best" values taken from Bradbury and Sarott (1995).
U	2500	5000	2500	5000	2500	5000	UO_2^{2+} gets reduced to U^{4+}, which like other tetravalent cations sorbs strongly to surfaces. "Best" Values taken from Bradbury and Sarott (1995).

[(a)] References: (*1*) = Wieland and Van Loon 2003; (*2*) = Krupka and Serne 1998; (*3*) = Bradbury and Sarott 1995.

6.6 ATTACHMENT F - CONTAMINANT SOLUBILITY DATA FOR ORDINARY PORTLAND (OXIDIZING) REFERENCE

Table F-1. Radionuclide solubility data for ordinary portland cement (oxidized) young, moderately aged and aged concrete [9]

Table 11. Apparent solubility concentration limits (mol/L or M) for Oxidizing Cementitious Solids

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement(b) 3rd Stage (pH ~5.5)		
	Conser-vative	"Best"	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References(a)
^{3}H, Cl, Tc, Re, Kr, Rn, Ar, Nb, Se, Te, I, At, Cs, Fr, Rb	NA	NA	NA	NA	NA	NA	No solubility constrains are assumed to exist with these radionuclides. Ochs et al. (*15*) reported that SeO_4^{2-} may substitute for sulfate in ettringite, but more recent reports (*3*) indicate that this substitution on ettringite is quantitatively unimportant. Johnson et al. (2000) has also recently conducted some Se partitioning research with various cements.
C	$5x10^{-5}$	10^{-6}	$5x\ 10^{-3}$	10^{-4}	$5x\ 10^{-3}$	10^{-4}	^{14}C chemistry is influenced by carbon dioxide gas/water/solid phase equilibrium, isotopic exchange, adsorption, precipitation, aqueous chemistry, and coprecipitation. To be conservative the role of gas phase and isotopic exchange (two very important processes for removing ^{14}C from groundwater) will not be considered. For young concrete, assumed that portlandite controls Ca to 10^{-3} M and CO_3^{2-} to 10^{-6} M (*1*). Ca concentrations are set by the solubility of calcite to "fix" the carbonate concentration. For moderately aged cement the Ca is controlled at 10^{-2} M by some undefined reactions (*1*). Subsurface C chemistry in a cementitious environment is discussed by Dayal (*16, 17*) and modeling gaseous C-14 in cementitious environments in the SRS subsurface has been discussed by Kaplan (*18*).
Ac, Am, Bk, Cf, Cm, Eu, Gd, Sm	$5x\ 10^{-10}$	10^{-11}	$5x\ 10^{-7}$	10^{-8}	$5x\ 10^{-6}$	10^{-7}	All +3 oxidation state: Young Concrete: Am solubility in concrete rinsate at pH 12 = 8e-11 M, at pH 13 = 1e-11 to 7e-12 M Am (*2*). Solid phase controlling solubility assumed to be $Am(OH)_3$ or $Am(OH)CO_3$ (*2,4*); Using a variety of cements and contact times of 100 days under oxidizing conditions measured Am solubility average was 1e-11 M (*5*). Experiments with sulfate resistant Portland cement consistently had Eu concentrations <1e-11 M. Time-resolved laser fluorescence spectroscopy (TRLFS) showed that Eu was incorporated within CSH and another fraction had properties suggesting it was within a structure like $Eu(OH)_3$ (*11*). Similarly, Cm was shown to be incorporated into the structure of calcium-silicate-hydrate (CSH) gels (*6*). Moderately Aged Concrete: Am solubility in concrete rinsate (no solid phase) at pH 10 to 11 was 1e-8 to 1.5e-10 M Am (*2*).

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement[(b)] 3rd Stage (pH ~5.5)		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References[(a)]**
Co,Ni	5x 10^{-6}	10^{-7}	5x 10^{-6}	10^{-7}	5x 10^{-5}	10^{-6}	Solid phase assumed to control solubility is $Co(OH)_2$ (*5, 6*). Experiments with sulfate resistant Portland cement had Co solubility values of 5e-8 and 2e-7 M at pH 13.3 (*6*). The solubility of $Co(OH)_2$ was calculated to be 6.5e-5 M (*6*). Calculated values are considered less reliable than experimental values. Experiments and calculations have also been done with aged cement end members under alkaline cement conditions (*2, 4, 7*). Several experiments show solubility controls (*6, 2, 4, 7*). Solubility controls of Ni are shown by (*8, 9, 10*). Ni concentrations consistently in range of 5e-8 to 2e-7 M regardless of the solid/liquid ratio (*6*).
Np, Pa	5x 10^{-7}	10^{-8}	5x 10^{-7}	10^{-8}	5x 10^{-6}	10^{-7}	Oxidation state of radionuclides is +5. Assume that NpO_2^+ and PaO_2^+ is the controlling solid. There is empirical data in Ewart et al. (*2*) that predicts much lower concentrations than thermodynamic predictions (*2,4,7*). Allard et al. (1984) added Np(V) to a variety of cements & measured solubility after 100 days of 4e-9 M. Solubility of Np(IV) is ~1e-8 M for pH 9.75 through pH 12.6 (*3*). Thus, according to Allard et al. (1984) and Ewart et al (1992) solubility of Np is about the same in concrete whether it is in +4 or +5 state.
Ra	5x 10^{-5}	10^{-6}	5x 10^{-5}	10^{-6}	5x 10^{-5}	10^{-6}	$RaSO_4$ is the controlling solid (*1, 14*). Bayliss et al. (1989) found no precipitation for Ra at • 1e-7 M in concrete leachate. When appropriate, such as in the Salstone Facility, it may be necessary to use sulfate controlling solubility phases, *i.e.,* $BaSO_4$ and $SrSO_4$.
Sr, Ba	5x 10^{-4}	10^{-5}	5x 10^{-4}	10^{-5}	NA	NA	$SrCO_3$ is solubility controlling phase. However, Sr may coprecipitate as $(Ca,Sr)CO_3$ which has an even lower solubility value (*12*). But solubility controls are only important at pH <11, *i.e.*, in the absence of $Ca(OH)_2$ and high ratios of calcium-silicate-hydrate gel (*12*). Therefore, coprecipitation is unlikely in the paste matrix, but may occur at the cement/leachate interface. For this reason Atkins and Glasser (*12*) recommend a minimum Sr solubility of ~2e-5 M. This solubility value is likely to decrease even further if coprecipitation occurs (*13*). No solubility data is provided for "Aged Cement in the 3rd Stage" because it is believed that it will likely not precipitate in this stage.
Pb, Po, Pu(V/VI) Pu(III/IV), Pu(combo)	5x 10^{-7}	10^{-8}	5x 10^{-7}	10^{-8}	5x 10^{-6}	10^{-7}	Assumed solubility controlling phase are hydroxide/hydrous oxides for Th, Zr, Pu and hydroxycarbonates for Pb. The following is from (*2*) and was conducted by adding Th(IV) to water equilibrated with concrete and pH adjusted: solubility ranged from 1e-8 M to 4e-9 M as pH increased

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement[b] 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References[a]**
Th, Zr, Sn							from 8.3 to 12.9. In essence, the solubility didn't change for Th. Sn exists in the tetravalent state, (Sn(IV), under the cementitious conditions and readily hydrolyses in the pH range >8. It sorbed to the same extent as Th(IV) to sulfate resistant Portland cement (*2*). Calculations of Pb, Pu, Th, and Zr solubility under cementitious conditions have been conducted (*4, 7*).
U(VI)	$5x\ 10^{-6}$	10^{-7}	$5x\ 10^{-6}$	10^{-7}	$5x\ 10^{-5}$	10^{-6}	Solubility controlling phases are likely U(VI) hydrous oxide [schoepite] and uranophase [calcium U(VI) silicate] (*4, 7*). Brady and Kozak (*7*) calculated a solubility of 1e-8 M U(VI).

[a] References: (*1*) = Krupka et al. 2004; (*2*) = Ewart et al. 1992; (*3*) = Baur and Johnson 2003; (*4*) = Brady and Kozak 1995; (*5*) Allard et al. 1984; (*6*) = Wieland & Van Loon 2003; (*7*) = Krupka and Serne 1998; (8) = Hietanen et al. 1984; (*9*) = Pilkington and Stone 1990; (*10*) = Atkins et al. 1993; (*11*) = Pointeau et al. 2001; (*12*) = Atkins and Glasser 1992; (*13*) = Smith and Walton 1991; (*14*) = Bayliss et al. 1989; (*15*) = Oches et al. 2002; (*16*) = Dayal and Reardon 1992; (*17*) = Dayal et al. 1989; (*18*) = Kaplan 2005.

[b] Making the same assumptions about the solid phase changes in the cementitious materials as Bradbury and Sarott (1995) and as described in Section 4.2, the solubility concentration limits values in the Aged Concrete (3rd Stage) were set to an order of magnitude higher (more soluble) than those in the Moderately Aged Concrete (2nd Stage). This same approach to assigning solubility concentration limits values to the 3rd Stage was used by Bradbury and Sarott (1995).

6.7 ATTACHMENT G - CONTAMINANT SOLUBILITY DATA FOR CHEMICALLY RECUCING REFERENCE CASE CEMENTITIOUS MATERIALS

Table G-1. Radionuclide solubility data for reduced young, moderately aged and aged concrete [9].

Table 12. Apparent solubility concentration limits (mol/L or M) for Reducing Cementitious Solids

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement[(b)] 3rd Stage (pH ~5.5)		
	Conser-vative	"Best"	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
^{3}H, Cl, Kr, Rn, Sr, Ra, Zr, Th, Nb, Sn, I, Cs, Ac, Am, Cf, Cm, Eu, Po, Se, C, Co,Ni, Pb, Bk, Sm, Fr, Gd, At, Ar, Te, Ba,	These radionuclides are assumed to have the same apparent solubility values as for the Oxidizing Cementitious Solids (Table 11).						The solubility of a number of other metals would likely be further lowered in a concrete that contains blast furnace slag (BFS) because BFS greatly increases the concentration of sulfides (S^{2-}) in the porewater (*1*). Sulfide concentrations in BFS concrete porewater have been measured as high as 1100 mg/L (*1*). However, there hasn't been any experimental or theoretical work to substantiate the assertion that metal sulfides form and lower the solution concentrations of metals in this group below concentrations presented in Table 11.
Tc(IV), Re (IV)	10^{-9}	10^{-10}	10^{-9}	10^{-10}	10^{-9}	10^{-10}	Bayliss et al. (*2*) adsorbed Tc onto Portland cement or concrete in an anoxic glove box with 0.05 M dithionite in 1.5 M NaCl for 28 days in 50:1 water:crushed cement: *Kd* = 5000 mL/g and measured Tc solution concentration was 1e-11 M. Assuming Tc_2S_7 as the solubility controlling phase, MMES (1992; Appendix D) calculated that reducing grout used in the SRS saltstone program would maintain Tc at a concentration of 1.4e-20 M (2.4e-8 pCi/L). Allard (*4*) calculated that reducing concrete would maintain Tc at a concentration <1e-10 M. It is assumed that the SRS cementitious materials containing blast furnace slag remain reducing throughout all three stages.
Np(IV), Pa(IV)	$5x\ 10^{-5}$	10^{-6}	$5x\ 10^{-5}$	10^{-6}	$5x\ 10^{-4}$	10^{-5}	Under reducing conditions, both Np and Pa are reduced from +5 to +4. In the tetravalent form they would be expected to sorb very strongly or be insolble. Assume that metal hydroxide is the controlling solid. The empirical laboratory data generated by Ewart et al. (1992) is much lower than thermodynamic predictions (*2,4,7*). Berry et al. 1988 reported that Pa sorbed very strongly, but due to experimental problems (sorption to glassware and filters) was unable to come up with reliable cement sorption values. It is assumed that the cementitious materials remain reducing throughout all three stages.
Pu(III/IV)	$5x\ 10^{-9}$	10^{-10}	$5x\ 10^{-9}$	10^{-10}	$5x\ 10^{-8}$	10^{-9}	Pu(IV) solubility measured by adding Pu(IV) spike into concrete rinsate under reducing conditions without solid phase and adjusting pH: from 9 to 11 the solubility was 1e-10 to 5e-11; essentially not changing (*8*). Assumed $Pu(OH)_4$ controlled solubility. Based on thermodynamic calculations,

Radio-nuclide	Young Cement 1st Stage (pH ~12.5)		Moderately-aged Cement, 2nd Stage (pH ~10.5)		Aged Cement[b] 3rd Stage (pH ~5.5)		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References[a]**
							solubility limits under reducing cementitious conditions were estimated to be less than 10^{-9} to 10^{-10} M Pu (*9*). It is assumed that the cementitious materials remain reducing throughout all three stages.
Pu(combo)	5x 10^{-9}	10^{-10}	5x 10^{-9}	10^{-10}	5x 10^{-8}	10^{-9}	Pu(combo) is a single geochemical parameter for Pu taking into account its many oxidation states. For this system, all Pu is assumed to exist in the +4 oxidation state.
U	5x 10^{-5}	10^{-6}	5x 10^{-6}	10^{-7}	5x 10^{-6}	10^{-7}	U(IV) solubility measured by adding U(IV) spike into concrete rinsate under reducing conditions without solid phase and adjusting pH: from 5 to 13 the solubility was 8e-7 to 2e-7; essentially not changing over that entire pH range (*8*). This wide pH range suggests that the solubility concentration limits does not change as a function of cement Stage. Assumed UO_2(crystal) and UO_2(amorph) were the solubility controlling phases. Based on thermodynamic calculations, solubility limits of U under reducing cementitious conditions were estimated to be less than 10^{-9} to 10^{-10} M U(IV) (*9*). It is assumed that the cementitious materials remain reducing throughout all three stages.

[a] References: (*1*) = Angus and Glasser 1985; (*2*) = Bayliss et al. 1991; (*3*) = MMES 1992; (*4*) = Allard 1984; (*5*) = Bajt et al. 1993; (*6*) = Macias et al. 1997; (*7*) = Rai and Szelmeczka 1990; (*8*) = Ewart et al. 1992; (*9*) = Brady and Kozak 1995.

[b] Discussion of the age of each of the stages is facility specific because it depends on the amount of water that passes through the cementitious material (see Section 4.2.4).

6.8 ATTACHMENT H - DISTRIBUTION COEFFICIENTS FOR SOIL

Table H-1. Typical SRS Soil Physical Properties [4,11].

Material	Saturated Hydraulic Conductivity			Typical Water Content [1]		Bulk Properties			
	K_h (cm/s)	K_v (cm/s)	k_h/k_v	Saturation	Volumetric Water Content	Saturated Effective Diffusion Coefficient, D_e (cm^2/s)	Total Porosity (%)	Dry Bulk Density (g/cm^3)	Particle Density (g/cm^3)
Sand (<25% Mud)	5.0E-04	2.8E-04	1.8	0.665 to 0.708	0.253 to 0.269	8.0E-06	38	1.65	2.66
Clay-Sand (25-50% Mud)	8.3E-05	2.1E-05	4.0	0.843 to 0.874	0.312 to 0.323	5.3E-06	37	1.68	2.67
Clay (>50% Mud)	2.0E-06	9.5E-07	2.1	0.920 to 0.934	0.396 to 0.402	4.0E-06	43	1.52	2.67

1 The typical matrix potential (pore pressure) of vadose zone soils at SRS ranges from -125 to -175 cm-H_20 (Nichols et al. 2000); the range of saturation and volumetric water content provided is based upon the characteristic curves produced by Phifer et al. 2006 and the typical range of vadose zone soil matrix potential from Nichols et al. 2000.

Table H-2. Soil Kds

Radio-nuclide	Sandy Sediment		Clayey Sediment		
	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
					In this study, Np *Kd* values for a soil (pH = 5.1, cation exchange capacity = 2.5 meq/100 g, 3.6% silt, 0.5% clay, $CaCO_3$ = <0.2 mg/kg) were 0.25 and 0.16 mL/g . This sediment is lower in clay content and pH than our assumed typical sediments for the "Sandy Sediment" or "Clayey Sediment". Therefore higher values were chosen herein. Np will exist primarily as NpO_2^+ (*21*). It has been shown that Np: 1) sorbs moderately to iron oxides and clays, 2) does not compete favorably with dissolved Ca or other divalent ions, 3) sorption is strongly pH dependent, and 4) does not readily convert to Np(IV) under ambient groundwater conditions (*21*). Due to lack of experimental data, extra conservatism is included in "Conservative" estimates.
Pu(V/VI)	11	16	2500	5000	A great deal of Pu sorption studies has recently been completed by SRNL and Clemson University (*10–19; 26, 27*). In these papers the conceptual model for how Pu subsurface transport of Pu is believed to occur at SRS is described. These studies include batch equilibrium, kinetic, and 11 year field lysimeter studies containing sources of Pu of known oxidation state. Wet chemistry and spectroscopic methods (X-ray Absorption Spectroscopy) were conducted to determine Pu oxidation state on aqueous and solid phase samples. Briefly, the dominant Pu oxidation state in the aqueous phase was shown to be Pu(V) and on the solid phase Pu(IV), irrespective of what was the starting Pu oxidation of the solid or aqueous phases. (Note: Although most of Pu in the aqueous phase consist of Pu(V), only trace concentrations of Pu exist in the aqueous phase compared to the solid phase, which is primarily Pu(IV).) After 11 yr, Pu(IV) moved only a couple centimeters in the field, with >95% remaining within 2 cm of the source material (*10, 15*). Sediment Pu concentration profiles were modeled using *Kd* sorption terms for a Pu(III/IV) and Pu(V/VI) and kinetic terms to describe the oxidation of Pu(III/IV) to Pu(V/VI) and a reduction term to describe the opposite reaction. Irrespective of what oxidation state Pu is added to SRS sediment, it quickly (within a day) is converted to Pu(IV) sorbed onto sediment (*15*). Most recently, aqueous Pu concentrations appear to be more controlled by solubility constraints than by adsorption (*19*). Powell et al. (2002) measured Pu(V) sorption to 4 end-member (extreme geological types) SRS sediments, two of which would be appropriate for consideration here, the "Subsurface Sandy" and "Subsurface Clayey" sediments. Sorption values in the "Subsurface Sandy" most representative of Pu(V) (*i.e.,* before all of the Pu was reduced to Pu(IV)) may be those measured after "1-day contact time": at pH 5.3 the *Kd* was 9 mL/g, at pH 5.72, the *Kd* was 20 mL/g, at pH 5.94, the *Kd* was 30 mL/g and at pH 5.90, the *Kd* was 60 mL/g. The following are taken from the "33-day contact" Subsurface Sandy sediment and likely are more representative of Pu(IV) in the system: pH5.41/*Kd* 4900, and pH 5.62/*Kd* 3100. Similarly, for the Subsurface Clayey sediment after 1 day contact (*Kd* units mL/g): pH 4.81/*Kd* 2100, pH 5.82/*Kd* 6600, and pH 5.98/*Kd* 9000. For the "33-day contact" Subsurface Clayey sediment: pH5.32/*Kd* 10,000, and pH5.68/*Kd* 4700. It was shown through speciation studies that during the 33 days of time that the Pu(V) had in fact reduced to Pu(IV). Thus, the *Kd* value in this case is not the true exchange

Radio-nuclide	Sandy Sediment		Clayey Sediment		
	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
					Pu(V) *Kd* value and it is clear that Pu(V) is unstable in the SRS subsurface. If the presence of both Pu(IV) and Pu(V) are not included in the transport model, it is more accurate to assume that all the Pu exists as Pu(IV) since >97% of the Pu exists as Pu(IV) (*19*). Prout's (1958) frequently referenced research with Pu is purposely not applied here because of compromised experimental procedures. Furthermore, emphasis of the selection of data was placed on the most recent data, where controls of the Pu speciation were monitored and attempts were made to understand the differences between the sorption behavior of the various Pu oxidation states.
Pu(III/IV)	200	300	3000	6000	Powell et al. (2002) using a subsurface SRS sandy sediment and adding Pu(IV), reported a *Kd* of 220 at pH 4.5 and 390 mL/g at pH 5.85. Using a SRS subsurface clay sediment and adding Pu(IV), they report *Kd* values of 2100 mL/g at pH 4.81, 6600 mL/g at pH 5.82, and 9000 mL/g at pH 5.98. The "typical" sediment is assumed to have a pH of 5.5. (Also, see the Comments/References for Pu(V) in this table).
Pu(combo)	180	270	2950	5900	Pu is a single geochemical parameter for Pu. It is a hybrid value of 90% of the Pu(III/IV) and 10% Pu(V/VI) measured Kd values. Kaplan et al. (2004), in a laboratory experiment showed that after 50-hr that 99% of the Pu added as Pu(V) had converted to Pu(IV) in the sediment/water system. Demirkanli et at (2006) using computer simulation of a lysimeter study reported that during a 24 yr simulation that 99.99% of the Pu existed as Pu(III/IV). But reported that the the short periods of time that Pu existed in the oxidized form, it moved appreciably faster than Pu in the reduced form, Pu(III/IV), but clearly much slower than Pu(V/VI).
Th, Zr	75	900	100	2000	<u>Tetravalent Cations</u>: Kaplan and Serkiz (2004) reported that SRS sandy sediment had a Zr(IV) *Kd* = 991 ± 352 mL/g at pH 5.3; SRS clayey sediment had a Zr(IV) *Kd* = 1969 ± 561 mL/g at pH 5.3 (*1*). Kaplan and Serkiz (2004) reported that SRS sandy sediment had a Th(IV) *Kd* = 245 ± 0 mL/g (the standard error is in fact zero) at pH 5.3; SRS clayey sediment Th(IV) *Kd* = 99 ± 48 mL/g at pH 5.3 (*1*). The latter Th(IV) data appears suspect in that greater sorption to sand than clay is inconsistent with basic principles of surface chemistry. This latter value will drive the uncertainty high and the "Conservative" estimates low. Thibault et al. (1990) in their *Kd* compilation of sorption values from throughout the world provide a very wide range of Th *Kd* values, with almost all values being >10,000 mL/g, however, a few values were as low as 35 mL/g.
Pb, Po, Sn	500	2000	2500	5000	<u>Divalent Soft Metals</u>: Bibler and Marson (1992) reported that Pb *Kd* values for a SRS burial ground sediment (TF1, 40-60 mesh) was generally >10,000 mL/g, a second burial ground sediment (TF2 40-60 mesh) was 63 to 925 mL/g, and a sediment from near the ETF (40-60 mesh) facility had Pb *Kd* values generally >2,000,000 mL/g. It appears quite likely that all these experiments were conducted at concentrations above the solubility of Pb, and thus reflect precipitation more than adsorption; the experiments were conducted at an initial Pb concentration of 5 mg/L Pb^{2+}. Furthermore, the <40-mesh fraction of the sediment was not included in these experiments, thus greater sorption would likely have been measured with the entire sediment. In a

Radio-nuclide	Sandy Sediment		Clayey Sediment		
	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
					compilation put together for groundwater modelers throughout the world, the estimated range of *Kd* values for sediments with a pH of 4 to 6.3 was 940 to 8,650 mL/g. Finally, these elements tend to have low solubility values. Solubility limits can easily be exceeded by these elements. Therefore it is especially important to consider using solubility constraints rather than *Kd* values when concentrations are slightly elevated for these elements.
Sr, Ra, Ba	4	5	12	17	Alkaline Earth Elements (Group IIA): Kaplan and Serkiz (2004) reported that SRS sandy sediment Sr *Kd* = 5 ± 1 mL/g at pH 5.3; SRS clayey sediment Sr *Kd* = 17 ± 0 mL/g at pH 5.3. Hoeffner (1985) reported SRS sandy sediment (9% clay) Sr *Kd* = 3 mL/g, pH ~4.7; SRS clayey sediment (23% clay) Sr *Kd* = 9 mL/g, pH ~4.7; very strong pH effect on Sr *Kd* values on SRS sediments: for sandy sediment (9% clay) between pH 2 to 4.8 (background) *Kd* slightly increased from 4 to 19, then increased sharply from pH 4.8 to 6.0-7.0, where the *Kd* became 2000 mL/g, then the *Kd* decreased gradually to 100 mL/g as the pH increased to pH 11 (*2*). Prout's work (1958) with Sr is purposely not applied here because of compromised experimental procedures. Sr sorption is almost entirely by cation exchange (*25*), and as such, is readily reversible upon changes in groundwater chemistry. Estimates in look-up table reflect this weak-sorption mechanism.
Se, Te	800	1000	800	1000	Selenate (SeO_4^{2-}) sorbs strongly to SRS sediments between the pH values of 3.9 and 6.7 (*24*). With 0 mg/L C from fulvic acid added to SRS groundwater, selenate *Kd* values for a clayey subsurface SRS sediment were 1041±0.7 mL/g at pH 3.9; 1041± 0.4 mL/g at pH 5.3, and 1041±0.3 mL/g at pH 6.7 (*24*). The authors remarked that there appeared to be an upper sorption limit reached yielded such similar *Kd* values as a function of pH. Under similar experimental conditions but using a subsurface sandy sediment, selenate *Kd* values were 1041± 0 mL/g at pH 3.9, 1311± 384 mL/g at pH 5.3, and 601± 65 mL/g at pH 6.7 (*24*). The sandy sediment, but not the clayey sediment, showed the characteristic decrease in *Kd* values as the pH increased. Troubling, is that the sandy sediment also had larger *Kd* values than the clayey sediment.
Tc, Re	0.05	0.1	0.1	0.2	TcO_4^- exists in oxidized systems, including vadose zone. Hoeffner (1985) reported correlation between clay content in SRS sediments and Tc *Kd*: <10% clay *Kd*=0.17 mL/g, ~10% clay *Kd* = 0.14 mL/g, ~10% clay *Kd* = 0.23 mL/g, 11% clay *Kd*=0.10 mL/g, 30% clay *Kd*=0.33 mL/g, 43% clay *Kd*=1.31 mL/g, 45% clay *Kd* = 1.16 mL/g. Kaplan (2005) reported TcO_4^- sorption to an SRS sediment occurred only when the pH was <4.3; the *Kd* values to this sandy subsurface sediment increased from 0 at pH 4.3 to ~0.11 at pH 3.7. Sorption studies with ReO_4^- to a clayey subsurface SRS sediment in SRS groundwater as a function of pH all had a *Kd* of ~0 mL/g: -0.6 ± 0.6 mL/g at pH 3.9; -0.3 ± 0.1 mL/g at pH5.3; -0.1 ± 0.3mL/g at pH 6.7(*24*). Similar studies conducted with sandy subsurface SRS sediment also showed no sorption between the pH of 3.9 and 6.7: *Kd* = -0.4 ± 0.3mL/g at pH 3.9, *Kd* = -0.2 ± 0.4mL/g at pH5.3, and *Kd* = 0 ± 0.2mL/g at pH 6.7 (*24*). The variability in these latter studies was quite high due to the limited number of replicates, two. However, they indicate that Tc or Re sorption is either non-existent or very limited to SRS

Radio-nuclide	Sandy Sediment		Clayey Sediment		
	Conser-vative	"Best"	Conser-vative	"Best"	Comments/References[(a)]
					sediments.
U	100	200	150	300	Johnson (1995) and Serkiz and Johnson (1994) conducted several field studies and laboratory studies to determine the processes controlling U sorption to SRS sediments. A portion of this work involved the collection of paired sediment-pore water samples from F-Area, within a U contaminated plume. Using the sequential extraction data (as defined by the sum of the concentrations of the first 6 extraction steps divided by the porewater U concentration in a saturated paste extract; see Johnson 1995): at pH 4.7 the *Kd* was 87 mL/g, at pH 4.75 the *Kd* was 100 mL/g, at pH 5.05 the *Kd* was 37 mL/g, and at pH 5.12 the Kd was 93 mL/g. The lack of trend with pH can be attributed to the fact that this was field data and reflects several different sediments. In an (ad)sorption test to a sandy subsurface F-Area sediment as a function of pH, at pH 4.82, 4.87, 5.01, and 5.04, the *Kd* values were 116, 153, 198, and 238 mL/g. At pH 5.5, the assumed background pH, the *Kd* is likely going to be greater than 238 mL/g (the Kd at pH 5.04) or 100 mL/g (the *Kd* measured at pH 4.75). Using all the U in the solid phase to calculate in situ *Kd* values resulted in *Kd* values that were 2000 to 10,000 mL/g (Serkiz and Johnson (1994; see Figure 4-12). This will clearly overestimate *Kd* values appropriate for use in reactive transport modeling. They reported *Kd* values of (presented as sample ID/pH/*Kd* (mL/g)): A-52/pH5.47/*Kd* 2,200, C-32/pH5.53/*Kd* >6300, C-42/pH5.27/*Kd* >14,000, F-42/pH5.2/*Kd* 34,000, F-52/pH5.91/*Kd* 5500, F-53/pH5.63/ *Kd* 27,000. The data across the entire pH range of 3.0 to 6.8 suggest that U was solubility controlled in this field site. Additional work needs to be conducted to further understand this process to permit inclusion of solubility constraints, if appropriate, into PA modeling. Additional U sorption mechanistic experiments have been conducted with SRS sediments (*8*, *9*). Bibler and Marson (1992) U sorption data could not be used for this review because it was conducted at pH 3.

[(a)] References: (*1*) = Kaplan and Serkiz 2004 ; (*2*) = Hoeffner 1985; (*3*) = Oblath et al. 1983; (*4*) = Prout 1958 ; (*5*) = Kaplan 2003 ; (*6*) = Rai and Serne 1978 ; (*7*) = Bibler and Marson 1992 ; (*8*) = Johnson 1995; (*9*) = Bertsch et al. 1994 ; (*10*) = Kaplan et al. 2006a (*11*) = Powell et al. 2005 (*12*) = Serkiz et al. 2005 (*13*) = Powell et al. 2004 (*14*) = Kaplan et al. 2004 ; (*15*) =Fjeld et al. 2004 ; (*16*) = Powell et al. 2006; (*17*) = Kaplan et al. 2001; (*18*) = Kaplan and Wilhite 2001; (*19*) = Kaplan et al. 2006b; (*20*) = Sheppard et al. 1979; (*21*) = EPA 2004; (*22*) = Findley 1998; (*23*) = Goto 2001; (*24*) = Kaplan and Serkiz (2006); (*25*) = EPA 1999; (*26*) = Kaplan et al. 2001; (*27*) = Kaplan et al. 2004.

U.S. DEPARTMENT OF ENERGY

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

CRESP

VANDERBILT UNIVERSITY

UNITED STATES NUCLEAR REGULATORY COMMISSION

NIST
National Institute of Standards and Technology

ECN

SIMCO
Technologies inc.